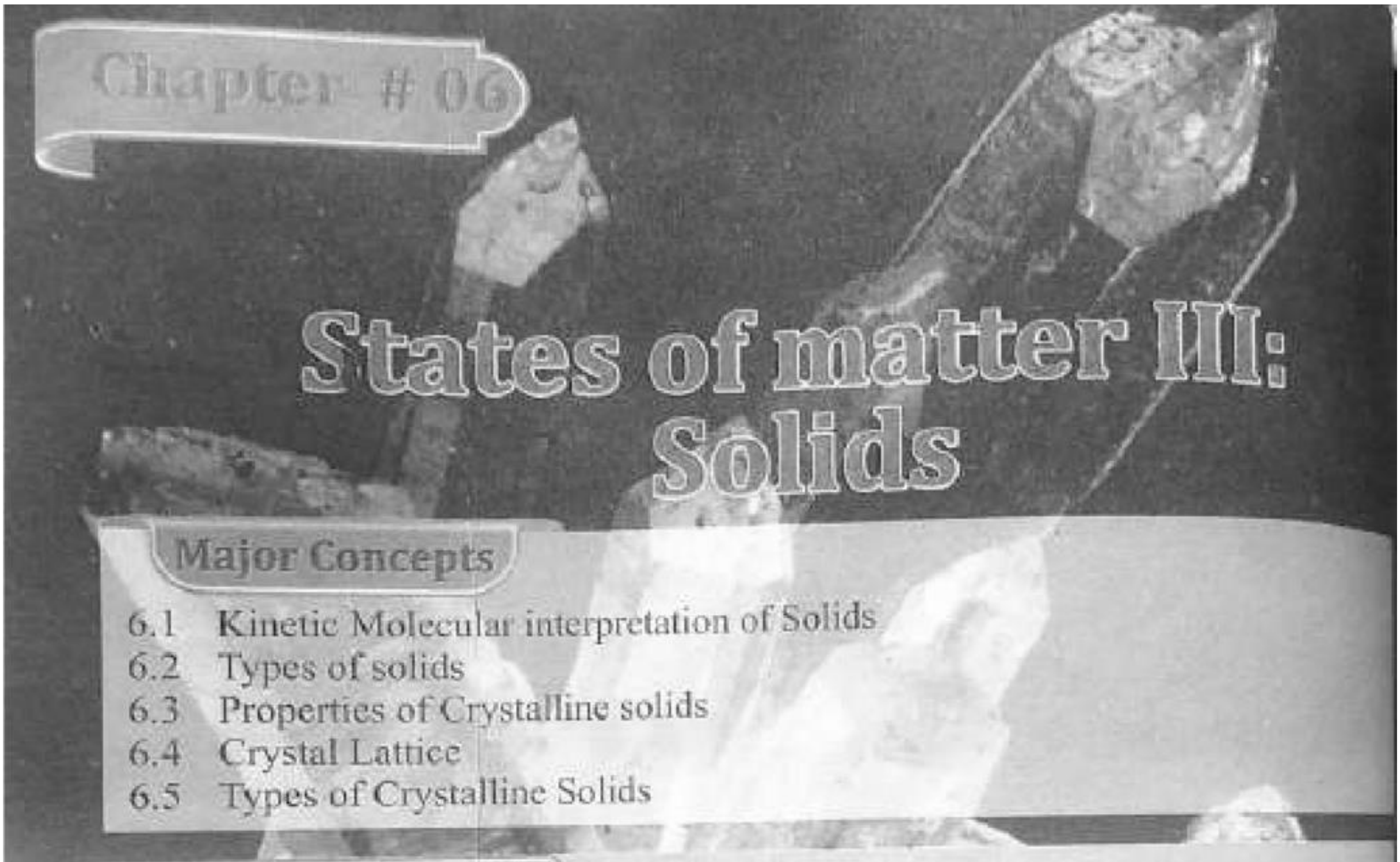


## Chapter # 06

# States of matter III: Solids

### Major Concepts

6.1 Kinetic Molecular interpretation of Solids
6.2 Types of solids
6.3 Properties of Crystalline solids
6.4 Crystal Lattice
6.5 Types of Crystalline Solids

### Learning Outcomes

The students will be able to:

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

## Introduction

Solid is the physical state of matter which has definite shape and volume and is rigid and hard. If we look around us we will find lot of substances in the solid state rather than in liquid and gaseous state. The clothes we wear, the paper we write on, the books we read, the television we watch, the radio we listen, the gold used in jewelry, the plastic used in making water bottles, utensils, water pipes, rain coats, surgical gloves, toys and purses, the refrigerator used to preserve foods, the cars and buses we travel in, the trees that bear fruits are all important solids. The solid state of mater is the growing area of chemistry because it relates to the development of interesting new materials. In this chapter we will discuss the properties, structures and types of solids.

## 6.1 Kinetic Molecular Interpretation of Solids

The key points of kinetic molecular theory are given below:

i) The particles (atom, ions or molecules) of solids are very close to each other and they are tightly packed and more ordered than liquids and are much more ordered than gases. For that reason, solids are slightly denser than liquids and much denser than gases. However, water is an exception to this rule i.e. the ice, the solid form of water, has lower density than liquid water. The spaces between solid particles are smaller than both of the liquids and gases.

ii) The solids are generally less compressible than liquids and are considered as incompressible. The solids such as foam, wood and cork give the impression of being compressible but they are actually not. They have spaces filled with airs. By applying pressure, the spaces are compressed but not the solid matter in the foam, wood or cork.

iii) The temperature or pressure change has a very little influence on the volume of solids.

iv) The attractive forces in solids are much more effective than gases and liquids. Because of this, solids have lower melting and boiling points than gases and liquids.

v) The solid particles have low kinetic energy than liquids and gases. Kinetic energy is directly proportional to the temperature of solids. Their kinetic energy decreases by decreasing temperature and increases by increasing temperature. All the substances are converted into solids if cooled sufficiently.

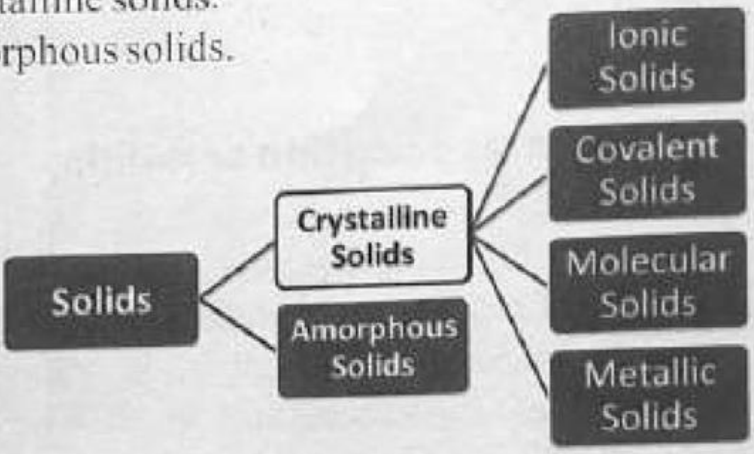
vi) The solid particles are locked in place that are why their molecules can't slip and slide over one another. They are, therefore, unable to flow (i.e. they are rigid), and hence retain their shapes and volume without a vessel. Solid particles usually have only vibrational motions.

vii) Solids particles do not diffuse into other solids readily. The diffusion in sol occurs but extremely slowly. If a lead plate and a gold plate are placed in clo contact for a several months, a few atoms of lead will diffuse into gold and vi versa. This observation is evidence that diffusion does occur in solids but at a v slow rate.

## 6.2 Types of Solids

There are two types of solids on the basis of arrangement of particles.

i) Crystalline solids.
ii) Amorphous solids.



### 6.2.1 Crystalline Solids

The solids which have repetitive three dimensional arrangements of particles called crystalline solids. They are also called true solids. A crystalline sol composed of one or more crystals that are fused together. Each particle occup fixed position in the crystal. Because of ordered arrangement of par crystalline solids usually have flat faces which construct specific angles with another. The regular arrangement of particles in crystals also produces li regular shaped beautiful crystals. The beautiful crystals of diamond, quartz (S sucrose and table salt are the examples of crystalline solids. Other examples of solids are alum, urea, $KNO_3$ and $CuSO_4$.

### 6.2.2 Amorphous or Non-crystalline Solids

The solids which have non-repetitive three dimensional arrangements of p are called amorphous solids or pseudo solids. The term *amorphous* is a Greek w which means *shapeless*. These solids do not have the orderly arrangem particles like that in crystalline solids. The structures of these solids are simi the structures of liquids but their particles do not have freedom of motio liquids. The elasticity of rubber and twisting of plastic reveals that the partic amorphous solids do not have fixed positions as in crystalline solids. structural point of view, the amorphous solids are considered as the inter between the liquid and solid states. Therefore, amorphous solids are sometimes called super-cooled liquids. The well-known examples of amorphous solids are glass, rubber, plastic, cement, ceramics and concrete.

Many crystalline solid can be changed into amorphous solids by melting them and then cooling the molten mass rapidly. In this way particles do not find time for orderly arrangement. Amorphous solids are hard and elastic like crystalline solids. They do not have definite melting points. These amorphous solids may have orderly arrangement of particles in small regions. These solids which are partly crystalline and partly amorphous are called crystallites.

Table 6.1: Difference between Crystalline and Amorphous Solids

| Crystalline Solids | Amorphous Solids |
|---|---|
| They have definite geometrical shapes. | They do not have definite geometrical shapes. |
| The fragments of shattered crystalline solids have definite geometrical shapes. | The fragments of shattered amorphous solids cannot have definite geometrical shapes. |
| They have regular intermolecular forces throughout. | They have irregular intermolecular forces throughout. |
| They have sharp and distinct melting points. | They do not have sharp and distinct melting points. |
| These solids are formed due to slow ooling of liquid. | These solids are formed due to sudden cooling of liquid. |
| hey are anisotropic i.e. they have ifferent physical properties such as lectrical conductivity, in different rections. | They are isotropic i.e. they have same physical properties in different directions. |
| hese solids are symmetrical i.e. their pearance do not change when they are ated by 360° along its axis. | These solids are not symmetrical. |
| amples are:<br>NaCl, copper sulphate ($CuSO_4$), sugar, iamond etc. | Examples are:<br>Glass, Plastic, Rubber, coke etc. |

## ociety, Technology and Science

**ecific Uses of Solids in our Daily Life:**

oth kinds of solids (crystalline and amorphous) play an important role and have ecific uses in our daily life. Table salt (NaCl), the crystalline solid, is used to flavour ode; diamond, the crystalline solid, is used to engrave stones and metals; NaF, a ystalline solid, is added to tooth pastes to prevent tooth decay; silver and gold are

precious crystalline solids and are used in ornaments and jewelry; **iron**, a crystalline solid, is used as structural material and is an essential ingredient in our diet.
On the other hand the rubber, an amorphous solid, is used in tires and rubber balls; **plastic**, an amorphous solid, has many industrial and commercial uses and is used in the manufacture of CDs, DVDs, footwear and fluid containers such as milk or oil; and **glass**, an amorphous solid, is used to make tumbler, mirrors, dishes, eye glasses, windows and for laboratory equipment such as beaker, test tube, reagent bottle. Amorphous semiconductors are used in solar cells, laser printers, flat-panel television and monitor screens.

## 6.3 Properties of Crystalline Solids

### 6.3.1 Symmetry

The concept of symmetry is very useful in describing the shapes of crystals. We easily recognize an object if we know the symmetry of that object. A crystal has a number of surfaces (faces), edges, and the interfacial angles (the angles between the faces). When a crystal is rotated along its axis by $360^\circ$, the faces, angles and edges are repeated consistently. The repetition of faces, angles and edges, when a crystal is rotated by 360° along its axis is called symmetry. Various types of symmetrical elements are:

i) Centre of symmetry
ii) Plane of symmetry
iii) Axis of symmetry

### 6.3.2 Geometric Shape

Crystalline solids have definite geometrical shapes. This is due to the orderly arrangement of their atoms, ions or molecules. The orderly arrangement of atoms, molecules or ions is due to strong attractive forces between their particles. Their interfacial angles and distances are same in spite of the method or conditions of preparation. Even the fragments of finely divided crystalline solid have definite geometric shapes that display their internal structure.

### 6.3.3 Melting point

The temperature at which the change from solid to liquid occurs is known as the melting point of solid. At melting point, the particles of liquid and solid have same average kinetic energies. Crystalline solids have definite melting points. At melting point, the temperature is reached at which the kinetic energies of the particles of the crystalline solids are enough to overcome the attractive forces holding them together and the particles get free of their fixed positions in the solid. The crystalline solids can be identified from their definite melting points. On the other hand, the amorphous solids have no definite melting points. Because the amorphous solids not have orderly arrangement of particles and the particles are not constantly changing their positions. These solids have the ability to flow over a range of temperature. For example, when a glass is heated, first it softens and then starts flowing without undergoing abrupt or sharp change from solid to liquid. Hence amorphous solids are regarded as super cooled liquids.

## 6.3.4 Cleavage Plane

The breaking of bigger crystals into smaller identical crystals by applying pressure is called cleavage. Crystalline solids are broken down through particular planes (directions or sides). These planes are called cleavage planes. A crystal can easily be broken in one direction and not in any other direction. For example, a mica crystal contains infinite layers of $SiO_4^{4-}$ sheets. The sheets have weak attractive forces and are easily separated parallel to the layers only.

## 6.3.5 Habit of Crystal

A shape in which a crystal usually grows (prepares) is called habit of crystal. For example, NaCl has cubic habit, white tin has tetragonal habit, and graphite has hexagonal habit.

## 6.3.6 Crystal Growth

Crystals are usually grown (prepared) by slow cooling of liquid or saturated solution under certain conditions. Outer appearance (shape) of crystals depends upon the method of preparation and conditions (temperature, pressure, concentration) under which it is prepared. For example, NaCl always crystallizes in cubic shape, if conditions are not changed. Different crystals of the same substance may sometimes appear to be different from outside due to different rate of growth by different faces but their interfacial angles are always the same.The change in appearance is because of the presence of impurity in the solution or due to change in conditions. For example, the habit of NaCl is cubic but in the presence of 10% urea as impurity, its habit is octahedral. It is called change of habit.

## 6.3.7 Anisotropy

The physical properties of crystals depend upon directions. They can vary from direction to direction. These properties are called anisotropic properties and the process is called anisotropy. A substance which has this property is called anisotrope. The physical properties such as thermal expansion, electrical conductivity, cleavage, and refractive index are anisotropic properties. For example, graphite is an isotrope, the conduction of heat and electricity, in graphite, is different in different directions. It conducts electricity parallel to the plane of layers but is a poor conductor perpendicular to the layers.

### 6.3.8 Isomorphism

The process in which two or more different elements or compounds exist in same crystalline shape is called isomorphism and compounds are known as isomorphs of each other. The isomorphs have following properties:

i) They have same ratio of atoms.

ii) Their physical and chemical properties are different.

Table 6.2: Isomorphs and their crystalline forms with atomic ratios

| Isomorphs | Crystalline Form | Atomic Ratio |
|---|---|---|
| NaCl, MgO | Cubic | 1:1 |
| $NaNO_3$, $CaCO_3$ | Trigonal | 1:1:3 |
| $ZnSO_4$, $NiSO_4$ | Orthorhombic | 1:1:4 |
| $Ag_2SO_4$, $Na_2SO_4$ | Hexagonal | 2:1:4 |
| Diamond, iron | Cubic | 1:1 |
| Graphite, zinc | Hexagonal | 1:1 |

In table 6.2, NaCl and MgO are two different compounds and have same shape i.e. cubic shape, hence called isomorphs.

### 6.3.9 Polymorphism

The process in which same compound is present in more than one crystalline forms is called polymorphism and different crystalline forms of same compound are called polymorphs. The polymorphs have following properties:

i) They have same chemical properties but different physical properties. The difference in physical properties is due to different structural arrangement of particles in space.

ii) They belong to same compound.

In table 6.3, calcium carbonate, the same compound is present in two crystalline forms i.e. trigonal and orthorhombic forms. These crystalline forms of same compound are called polymorphs.

Table 6.3: Polymorphs and their crystalline forms

| Polymorphs | Crystalline Forms |
|---|---|
| $AgNO_3$ | Trigonal,<br>Orthorhombic |
| $CaCO_3$ | Trigonal (calcite)<br>Orthorhombic (aragonite) |
| $KNO_3$ | Trigonal,<br>Orthorhombic |

### 6.3.10 Allotropy

The process in which an element is present in more than one crystalline forms is called allotropy and different forms of the element are called allotropes or allotropes forms. Allotropes have same chemical properties but different physical properties due to different arrangement of atoms. The common elements that show allotropy are: carbon, tin, sulphur, and oxygen. Their allotropic forms are given in the table.

In table 6.4, carbon has two different crystalline forms (cubic and hexagonal). These different crystalline forms of the same element (carbon) are called allotropic forms.

Table 6.4: Allotropes and their Crystalline Forms

| Allotropes | Crystalline Forms |
|---|---|
| Carbon | Diamond (cubic)<br>Graphite (hexagonal) |
| Tin | Grey tin (cubic)<br>White tin (tetragonal)<br>Rhombic tin (orthorhombic) |
| Suphur | Rhombic sulphur<br>Monoclinic sulphur<br>Plastic sulphur (amorphous form) |
| Oxygen | Dioxygen ($O_2$)<br>Ozone ($O_3$) |

**Keep in Mind**

The allotropy is for elements and the polymorphism is for compounds.

### 3.11 Transition Temperature

The arrangement of particles of a substance can also be changed with the change temperature and a new allotrope of an element or a new polymorph of a compound is formed.

The temperature at which two crystalline forms of same substance exist in equilibrium with each other is called transition temperature.

Above and below this temperature only one crystalline form of a substance exists. For example, the transition temperature of $KNO_3$ is 128.5 ℃, at which both the forms of this compound exist in equilibrium with each other. Above this temperature (128.5℃) $KNO_3$ exists in orthorhombic form and below this temperature, it exists in rhombohedral form.

$$\underset{\text{(Rhombohedral)}}{KNO_3} \quad \overset{128.5^\circ C}{\rightleftarrows} \quad \underset{\text{(Orthorhombic)}}{KNO_3}$$

The transition temperature of sulphure is 95.5℃. Above transition temperature, suphur exists in monoclinic form and below this temperature, it exists rhombic form.

$$\underset{\text{(Rhombic)}}{S_8} \quad \overset{95.5^\circ C}{\rightleftarrows} \quad \underset{\text{(Monoclinic)}}{S_8}$$

Transition temperature is always less than melting point of substance.

## 6.4 Crystal Lattice and the Unit Cell

The crystals are regular shaped solid particles with flat shiny faces and have th dimensional ordered arrangements of particles. The ordered structure of a crysta described in terms of a crystal lattice. A crystal lattice is a three dimensio structure of points that designates the positions of particles (ato molecules, or ions) in a crystal. Crystal lattice is also known as space lattice. A crystal lattice is not an actual object but it is a structure or pattern. The crystal structure depends on the nature and the size of the particles that are involved. The particles that make up the pattern are different in different type of crystals. A crystal is made up of atoms, ions or molecules. These particles are located at particular positions and are represented by points and these points are joined together by lines. This type of structure is known as crystal lattice.

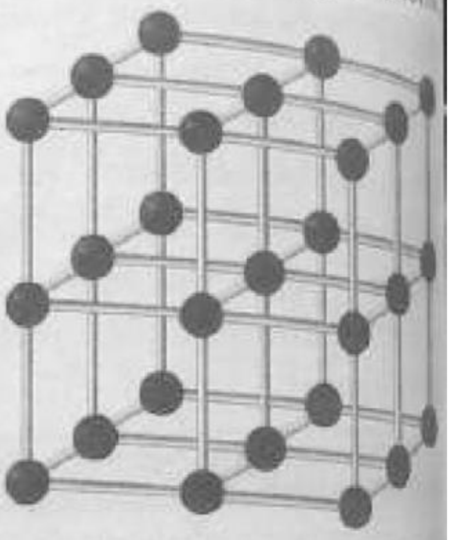


Figure 6.1:
Crystal Lattice Consists of 8 Unit Ce

### 6.4.1 Unit Cell

The smallest part of crystal lattice showing all the properties of crystal pattern is called unit cell. The crystal lattice is the building block of unit cells. The unit cells repeat in all directions in a perfectly regular way and build up the whole crystal. A unit cell gives complete information about crystal structure. It will be easy to know the exact arrangement of particles in a whole crystal, if we know its arrangement in a unit ce Unit cell has definite shape and definite number of particles. These particles a arranged in three dimensions.

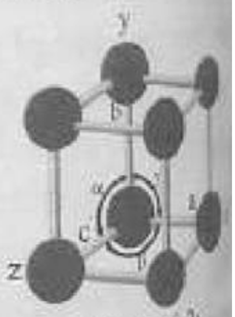


Figure 6.2:
A single unit ce

### Representation of a Unit Cell

Shape of unit cell depends upon the length of three sides (a, b, and c) and ang between these sides (α, β and γ). In common practice, side 'a' is along x-axis, sid is along y-axis and side 'c' is along z-axis.

The angle "α" is between sides 'b' and 'c'.

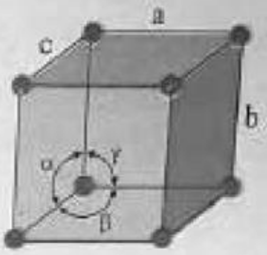
The angle "β" is between sides 'c' and 'a'.

The angle "γ" is between sides 'a' and 'b'.

These six parameters of unit cell are called unit cell **dimensions** or crystallographic elements. Unit cell of CsCl is cubic, in which a = b = c and $\alpha=\beta=\gamma=90°$.

## Seven Crystal Systems OR Crystals and their Classifications

A crystal system can be identified by the dimensions of its unit cell along its three axes a,b,c and three angles α, β and γ. The seven crystal systems are described below:



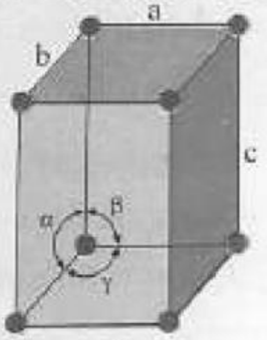
### Cubic System

In cubic system, all the three axes are of equal lengths and all angles are of 90°.

$a=b=c$ and $\alpha=\beta=\gamma=90°$

Example are: NaCl, diamond, iron (Fe), copper (Cu), CsCl

Cubic unit cells are of three types and they are simple cubic, body-centered cubic, or face-centered cubic. They have a total of one, two, or four particles, respectively.

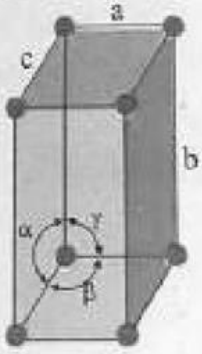


### Tetragonal System

In this system, two axes are of equal lengths and the third one is different. It may either be shorter or larger than the other two. All the angles are of 90°.

$a=b\neq c$ and $\alpha=\beta=\gamma=90°$

Example are: $SnO_2$, $MnO_2$, white tin (Sn), $NH_4Br$



### Orthorhombic System

All the lengths are unequal and all the angles are of 90°.

$a\neq b\neq c$ and $\alpha=\beta=\gamma=90°$

Examples are: $FeSO_4.7H_2O$, $ZnSO_4.7H_2O$, $KNO_3$, $I_2$, Rhombic sulfur

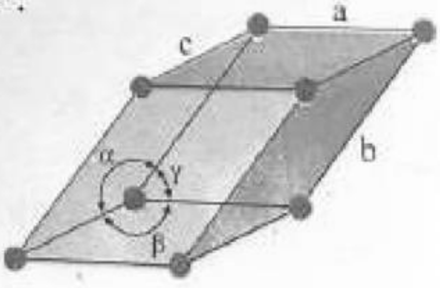
### Trigonal or Rhombohedral System

All the lengths are equal but none of the angle is of 90°.

hey lie between 90° and 120°.

$=b=c$ and $\alpha=\beta=\gamma\neq>90°$ and $<120°$

xample are: $NaNO_3$, $KNO_3$, Bi, $Al_2O_3$



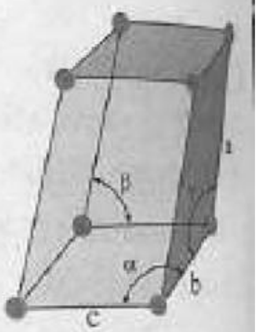
### Hexagonal System

Two axes (a and b) are of equal lengths and third (c) is different in length. Two angles are of 90° but third angle is of 120°.

$a = b \neq c$ and $\alpha = \beta = 90°, \gamma = 120°$

Examples are: ZnO, CdS, graphite

### Monoclinic System

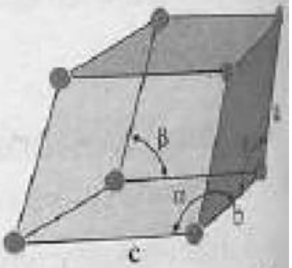


All the lengths are unequal. Two angles of 90° and third one is greater than 90°.

$a \neq b \neq c$ and $\alpha = \beta = 90°, \gamma = > 90°$

Examples are: $C_{12}H_{22}O_{11}$, $Na_2CO_3.10H_2O$, $Na_2B_4O_7.10H_2O$

### Triclinic System



All the lengths and angles are unequal.

$a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$

Examples are: $CuSO_4.5H_2O$, $K_2Cr_2O_7$, $H_3BO_3$ (Boric acid)

The unit cells of the seven different crystal systems are summarized in table 6.5.

Table 6.5: Seven Crystal System

| Crystal System | Axes | Angles | Examples |
|---|---|---|---|
| Cubic | $a = b = c$ | $\propto = \beta = \gamma = 90°$ | NaCl, NaBr, diamond, gold |
| Tetragonal | $a = b \neq c$ | $\propto = \beta = \gamma = 90°$ | $MnO_2$, $NH_4Br$, white tin (S |
| Orthorhombic | $a \neq b \neq c$ | $\propto = \beta = \gamma = 90°$ | $BaSO_4$, $CaCO_3$ (aragonite), rhombic sulphur, iodine |
| Monoclinic | $a \neq b \neq c$ | $\propto = \beta = 90°, \gamma \neq 90°$ | Sugar, borax, $PbCrO_4$, monoclinic sulphur |
| Hexagonal | $a = b \neq c$ | $\propto = \beta = 90°, \gamma = 120°$ | Ice, $NaNO_3$, CdS, graphite, zinc |
| Trigonal | $a = b = c$ | $\propto = \beta = \gamma \neq 90°$ | $NaNO_3$, $CaCO_3$ (calcite), HgS (cinnabar), bismuth |
| Triclinic | $a \neq b \neq c$ | $\propto \neq \beta \neq \gamma \neq 90°$ | $K_2Cr_2O_7$, $CuSO_4.5H_2O$, $H_3BO_3$ |

### 6.4.2 Shape of NaCl Crystal

The structure of sodium chloride, is one of the most common ionic crystal lattice. It has face-centered cubic arrangement in the octahedral structure. In the structure, each sodium ion, $Na^+$, is surrounded by six chloride ions, $Cl^-$, and each $Cl^-$ ion is surrounded by six $Na^+$ ions. Hence, the coordination number of each ion is 6. The distance between two adjacent ions of different kinds is 2.815A°.

Chloride ion is bigger in size than sodium ion. The larger chloride ions occupy corners and faces of an octahedron whereas, the smaller sodium ions fit into the cavities (holes) between the adjacent anions. The unit cell of NaCl is repeated in the several directions where we can see six chloride ions around some of the other sodium ions.

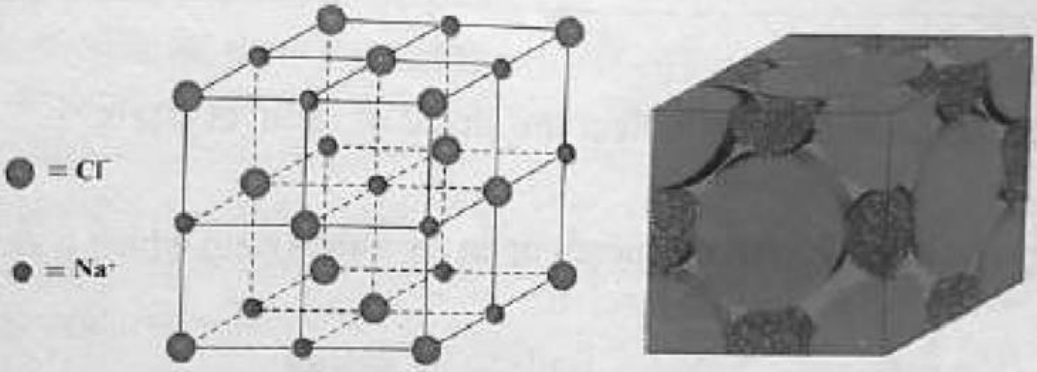


Figure 6.3: Representation of the unit cell of NaCl

The formula of an ionic compound is derived from the unit cell structure. The formula of NaCl is obtained by counting the number of sodium ions and chloride ions present in its unit cell. There are eight chloride ions at each corner of the unit cell. Each $Cl^-$ ion is shared among eight unit cells, hence each contributes one eighth of $Cl^-$ ion to the unit cell. There are six chloride ions in the center of each face. Each $Cl^-$ ion is shared among two unit cells, so each contributes one half of $Cl^-$ ion to the unit cell. The total number of $Cl^-$ ions within the unit cell is calculated as:

$$\frac{1}{8}\ Cl^-\text{ per corner} \times 8\text{ corners} = 1\ Cl^-$$

$$\frac{1}{2}\ Cl^-\text{ per face} \times 6\text{ faces} = 3\ Cl^-$$

Total number of $Cl^-$ ions in a unit cell = 4 $Cl^-$ ions

There is one complete $Na^+$ ion in the center of the unit cell. There are 12 $Na^+$ ions at the midpoints of edges of the unit cell. Each $Na^+$ is shared among four unit cells, hence, each contributes one fourth of $Na^+$ ion to the unit cell. Thus the total number of $Na^+$ ions within the unit cell is calculated as:

$\frac{1}{4}$ $Na^+$ per edge × 12 edges $= 3Na^+$

1 $Na^+$ per center × 1 center $= 1Na^+$

Total number of $Na^+$ ions in a unit cell = $4Na^+$ ions

Thus, the unit cell of NaCl has four $Na^+$ and four $Cl^-$ ions, in the ratio of 1:1 as required by its chemical formula.

**Keep in Mind**

NaCl crystallizes in face centered cubic shape while CsCl crystallizes in simple cub shape. The different arrangement of CsCl is due to larger size of cesium ion a compared to sodium ion.

### 6.4.3 Factors Affecting the Shape of Ionic Crystals

There are three factors that affect the shape of ionic crystals.

**(i) Radius Ratio:**

The shape of an ionic crystal depends upon the radius ratio which is defined as th ratio of radius of cation to that of anion.

$$\text{Radius Ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}}$$

The effect of radius ratio in determining the shape of an ionic crystal known as radius ratio effect. The range of radius ratio may be expressed as limit radius ratio.

Table 6.6: Limiting Radius Ratio and Shape of Ionic Crystals

| Limiting Radius Ratio | Shape | Example |
|---|---|---|
| <0.155 | Linear | $CaF_2$ |
| 0.155-0.225 | Planar triangular | $B_2O_3$ |
| 0.225-0.414 | Tetrahedral | ZnS |
| 0.414-0.732 | Octahedral | NaCl |
| 0.732-1.000 | Body centred cubic | CsCl |

The shape of NaCl is Octahedral and that of CsCl is body centred cu because their radius ratio values are different.

**(ii) Electrostatic Forces of Attractions:**

Ionic crystals are held together by strong electrostatic forces of attractions betw cations and anions. Example: sodium chloride, NaCl. These forces give a ve defined geometric shape to ionic crystals.

**(iii) Poor Conductivity:**

Ionic crystals do not conduct electricity in solid state because their ions are fixed in positions and are unable to move. Hence, the shape of ionic crystals remains as such. They can only conduct electricity when their ions are free to move i.e. they conduct electricity when dissolved in water or melted.

## 6.4.4 Lattice Energy

The amount of heat needed to break one mole of ionic crystal into its gaseous ions is called lattice energy.

It has positive value. It is expressed in kJ mol$^{-1}$.

$$K^+_{(g)} + Cl^-_{(g)} \longrightarrow KCl_{(s)} \qquad \Delta H^o = -715\ kJ/mol$$

Ionic crystals are composed of ions. These ions are located at fixed positions. A definite amount of energy is needed to remove these ions from their fixed positions, called lattice energy. It can also be defined as:

The amount of energy released when gaseous ions of opposite charges are combined to form one mole of crystalline ionic compound is called lattice energy.

It has negative value.

$$KCl_{(s)} \longrightarrow K^+_{(g)} + Cl^-_{(g)} \qquad \Delta H^o = +715\ kJ/mol$$

The magnitude of lattice energy depends on ionic size, ionic charge and arrangement of ions in the solid. The lattice energy decreases by increasing the size of either cation or anion and increases by increasing the ionic charge.

**Effect of Ionic Radius**

The smaller the ionic radius, the shorter the distance among the ions, and the stronger the attractive forces among ions. As a result of this, the ions come close to each other and their packing become tight. From top to bottom in a group of periodic table, the ionic radius increases, hence, the lattice energies of their compounds decrease.

i) The lattice energies for those compounds, which have same anion but different cations, decrease with the increase in the size of cations.

ii) The lattice energies for those compounds, which have same cation but different anions, decrease with the increase in the size of anions.

Table 6.7: Lattice energies of compounds having same anions

| Name | Formulas | Lattice Energies (kJmol$^{-1}$) |
|---|---|---|
| Lithium chloride | LiCl | 845 |
| Sodium chloride | NaCl | 787 |
| Potassium cholride | KCl | 715 |

The larger the lattice energy, the more stable the ionic compound and the more tightly held the ions. The solid with higher lattice energy has higher melting point than one with smaller lattice energy.

Table 6.8: Lattice Energies of Compounds having same Cations

| Name | Formulas | Lattice Energies ($kJmol^{-1}$) |
|---|---|---|
| Sodium fluoride | NaF | 923 |
| Sodium chloride | NaCl | 787 |
| Sodium bromide | NaBr | 747 |
| Sodium iodide | NaI | 704 |

### Effect of Ionic Charge

The higher the ionic charges, the greater the force of attraction between oppositely charged ions, so the lattice energy has high value for more highly charged ions.

If we compare lithium fluoride with magnesium oxide, then we find that, they have cations (the radius of $Li^+$ is 76 pm and that of $Mg^{2+}$ is 72 pm) and anions (the radius of $F^-$ is 133 pm and that of $O^{2-}$ is 140 pm) of about equal radii. But lattice energy of MgO ($4050kJmol^{-1}$) is about four times greater than that of LiF ($1050kJmol^{-1}$). This fourfold increase in the lattice energies of CaO is due to the fourfold increase in the product of charges on $Mg^{2+}$ and $O^{2-}$ ions.

Table 6.9: Lattice Energies of Compounds having different Cations or Anions

| Name | Formulas | Lattice Energies ($kJmol^{-1}$) |
|---|---|---|
| Lithium fluoride | LiF | 1050 |
| Magnesium chloride | $MgCl_2$ | 2527 |
| Magnesium oxide | MgO | 405 |
| Calcium oxide | CaO | 3424 |

The lattice energy is directly proportional to the product of charges of cations and anions and inversely proportional to the sum of their radii.

$$\text{Lattice energy } (\Delta H^{o}_{\text{lattice}}) \propto \frac{\text{charge of cation} \times \text{charge of anion}}{\text{cation radius} + \text{anion radius}}$$

## 6.5 Types of Crystalline Solids

The structure and properties of crystalline solids such as melting point, boiling point, hardness, and density depend upon types of particles in the crystalline solids and types of chemical bonding present between their particles. There are four types of crystalline solids on the basis of types of chemical bonding present in them and they are ionic solids, covalent solids, metallic solids and molecular solids.

**Keep in mind**

The internal forces of attractions that hold the solid particles together determine many of the properties of solid. For example, copper is a good conductor of electricity while diamond is an isulator although they both are atomic solids. The difference in the properties between these two substances is because of differences in the chemical bonding present in them.

## .5.1 Ionic Solids

he solids in which ions are held together by ionic bonds are called ionic solids. These ions are held together by electrostatic forces of attractions. Examples of such olids are NaCl, KCl, KBr, CsCl, and $CaF_2$. The ionic solids are generally formed hen alkali metals (group IA metals) and alkaline earth metals (group IIA metals) ombine with chalcogens (group VIA non-metals), halogens (group VIIA non-etals), and non-metallic polyatomic ions.

### roperties

The ions in ionic compounds are held together by strong attractive forces; erefore, they are hard and have generally higher melting and boiling points than olecular compounds. They can also have low volatility. The higher the melting dboiling points the stable the ionic compound.

They are highly brittle. For example, the ionic solids are broken into small eces when we struck them by a hammer, the ions are driven down a layer and the me charge ions come next to each other and because of this the same charge ions pel each other that split the solid.

They have definite geometric shapes; and have high density due to close cking of ions.

They do not conduct electricity in solid state because their ions are fixed in sition and are unable to move. When they are melted or dissolved in water, the s set free and move freely through the solution or liquid, hence the liquid or the lution conducts electricity readily.

They are frequently soluble in polar solvents like water. The ions of ionic solids parate from each other when dissolved in water and are surrounded by water lecules. Some ionic compounds are not dissolved in water, because the attractive ces between the ions and water molecules are not enough to overcome the actions between the ions.

They show the process of isomorphism and polymorphism.

They have formula mass but no molecular mass, because they do not exist in cular forms.

**Conceptual Check Point:**

Ionic crystalline solids are brittle but not malleable, why?

### 6.5.2 Covalent Solids

The solids in which atoms are held together by covalent bonds are called covalent solids. Examples include diamond, graphite, quartz ($SiO_2$, found in some kinds of sand) and Silicon carbide ($SiC$, a common abrasive used in sand paper).

Covalent solids are of two types:

i) When covalent bonds give huge molecule like diamond, $SiC$, $AlN$ etc.

ii) When atoms combine to give separate layers of atoms like Graphite, Cadmium iodide ($CdI_2$), Boron nitride ($BN$) etc.

#### Properties

i) They are usually very hard and have very high melting and boiling points due to strong attractive forces between covalently bonded atoms.

ii) They are insoluble in polar solvents like water.

iii) They are poor conductors of heat and electricity in either the solid or liquid state. This is due to absence of ions but some of them, such as silicon, are semi-conductors.

iv) Their chemical reactions are very slow.

**Conceptual Check Point:**

The chemical reactions of ionic solids are faster than covalent solids, why?

### 6.5.3 Metallic Solids

The solids in which atoms are held together by metallic bonds are called metallic solids. Examples include copper, silver, gold, iron etc.

Many theories have been proposed to explain the metallic bond, but here we will discuss only the electron gas theory.

#### Electron Gas Theory

According to this theory, the valence electrons in metals are free to move from one part of the crystal to the other. These free electrons do not belong to any particular atom.

These electrons produce negative atmosphere (sea) around metal positive ions. This

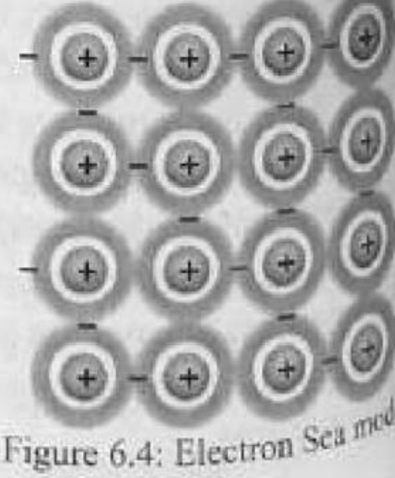


Figure 6.4: Electron Sea model

atmosphere of electrons is called Electron Sea or pool or gas. The force of attraction which holds metal positive ions and Electron Sea together is called metallic bond. This theory explains the following properties of metallic solids.

## Properties of Metallic Solids

i) They are good conductors of heat and electricity because electrons are free to move and carry kinetic energy through the solid.

ii) Most of the metallic solids have lustrous (shining) surface. This is because when light falls on the surface of metals. The electrons are jumped from lower energy level to higher energy level. When the electrons come back from higher energy level to lower energy level, they emit energy in the form of light at the frequency similar to the absorbed frequency. This reflected light is responsible for the lustrous surfaces of metals.

iii) Metallic solids have variable melting points. Some metals have low and the others have very high melting and boiling points. For example, mercury (mp= –38.72°C), gallium (mp = 29.93°C) and francium (mp = 27.00°C) have quite low melting points and on the other hand chromium (mp = 1877.00°C), molybdenum (mp = 2617.00°C), and tungsten (mp = 3427.00°C) have quite high melting points. This is because the charge density of mercury, gallium, and francium is low and they are weakly attracted to the electron sea and the charge density of chromium, molybdenum, and tungsten is high and they are strongly attracted to the electron sea.

iv) They are malleable and ductile. The ability of a substance to be hammered or eaten in thin sheets is called malleability while the ability of a substance to be rawn or pulled into thin wires is called ductility. That is why most of the metallic lids are easy to form into desired shapes.

) They are insoluble in all common solvents.

**Conceptual Check Point:**

**he metallic solids (metals) usually dent rather than shatter when we struck them by a mmer, why?**

## ructure of Metals

pure metal is a crystalline solid in which metal atoms are closely packed in a stal lattice (metallic lattice). A metal may be regarded as an assembly of positive s usually considered as spheres, which are packed together to fill space as mpletely as possible.

To understand the close packing of atoms in metal structures, let us consider structure of balls. If a number of solid spheres (or metallic balls) are packed in a box as shown in figure 6.5, when the box is well shaken, the balls will rearrange as shown in figure 6.6. The rearrangement of balls in figure 6.6 is more stable and more closely packed than figure 6.5.

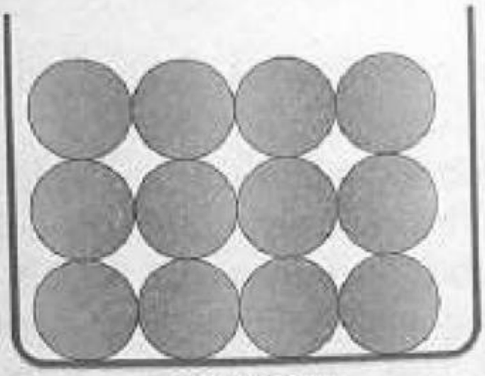


Figure 6.5

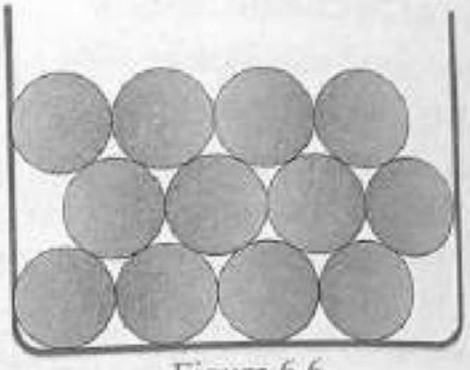


Figure 6.6

Metals have three major types of crystal structures:

i) Face centered cubic structure ii) Body centered cubic structure.

iii) Hexagonal close packing structure.

## I) Face Centered Cubic (FCC) Structure

There are eight atoms at each corner of the unit cell. Each atom is shared by eight unit cells. Hence each atom contributes one eig to the unit cell. There are six atoms in the center of each face and each atom is shar by two unit cells. So each atom contributes one half to the unit cell. The total numbe of atoms per unit cell is ( $\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 1 + 3 = 4$ ) four.

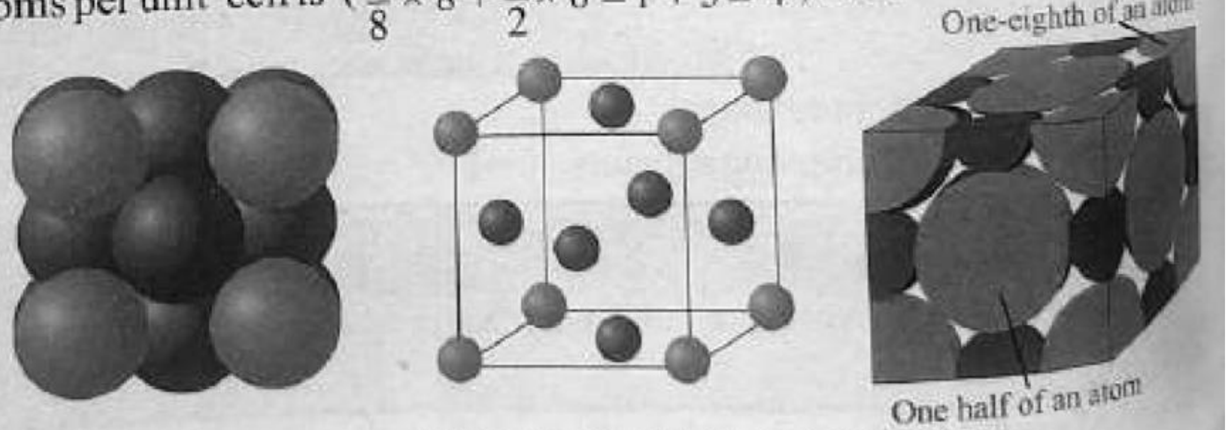


Figure 6.7: Face centered cubic structure

Every atom in the crystal is bonded with twelve neighbours and coordination number is 12. In this case 74% of the available volume is occupi the spheres. Examples are Ag, Au, Ca, Co, Cu, and Ni.

## ii) Body Centered Cubic (BCC) Structures

In body centered-cubic structures, there is one eighth of an atom at each co the unit cell and only one atom at the center of unit cell. The total number of atoms per unit cell is ($\frac{1}{8}\times8+1\times1=1+1=2$) two.

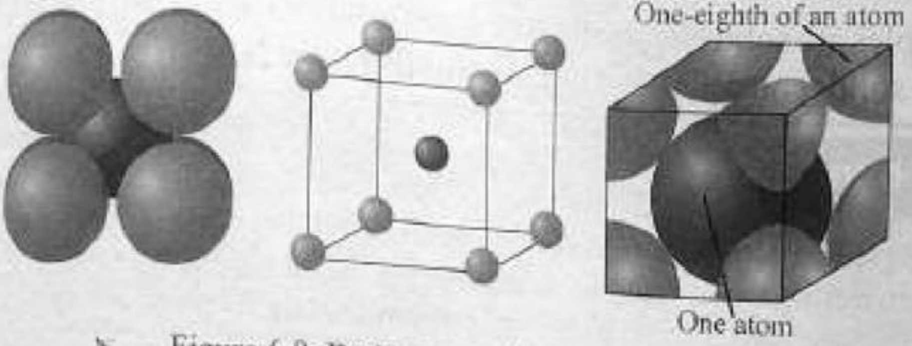


Figure 6.8: Body centered cubic structure

The coordination number is 8. In this case only 68% of the available volume is occupied by the spheres. Examples are Li, Na and K.

### iii) Hexagonal Close Packing Structure (HCP)

Let us consider, the atoms of metals are arranged in the form of layers. In HCP, the top and bottom layers have seven atoms where six atoms arrange themselves in the shape of a hexagon and a seventh atom sit in the middle of the hexagon. The atoms of the top layer (third layer) are exactly above the bottom layer (first layer). The middle layer has three spherical atoms. The spherical atoms of the fourth layer are exactly above the middle (second) layer and so on.

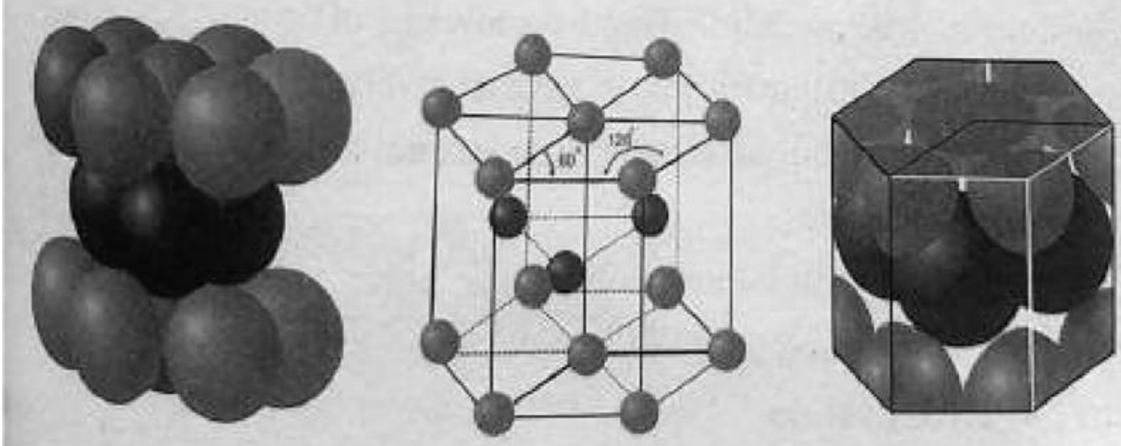


Figure 6.9: Hexagonal close packing structure

The packing efficiency is 74%. Every atom is bonded with twelve neighbours and the coordination number is 12. For example, Ba, Ca, Mg and Zn are crystallizes in HCP.

## 6.5.4 Molecular Solids

The solids in which atoms or molecules are held together by intermolecular forc are called molecular solids.

Examples are solid $NH_3$, solid $SO_2$, Ice, solid $CO_2$ (dry ice), $I_2$ etc. These solids consist of two types of molecular solids.

**Keep In mind**

Both covalent solids and molecular solids contain covalent bonds. The covalent bond are not broken during the melting of molecular solid. The higher the melting points o molecular solids the stronger the intermolecular attractive forces.

i) The molecular solids which have dipole-dipole forces and hydrogen bondin between their molecules are called polar molecular solids. Examples of such soli are ice, sugar, solid HF etc.

ii) The molecular solids in which molecules are held together by Londo dispersion forces only are called non-polar molecular solids. Examples of suc solids are $I_2$, $S_8$, $P_4$, solid $CO_2$ (dry ice), the solids of group VIIIA(1 elements such as neon etc.

## Properties

i) They are soft and can be compressed easily. This is due to weak forces o attractions among the molecules.

ii) They have low to moderately low melting and boiling points. Most of the molecular solids melt below 200°C. They have low heat of fusion.

iii) They are volatile in nature and hence, have relatively high vapour pressure.

iv) They are poor conductors of electricity and are not malleable.

v) They have low densities.

vi) Polar molecular crystals are soluble in polar solvents and non-p molecular crystals are soluble in non-polar solvents.

## Structure of Ice Crystals

The familiar example of molecular solids is ice. The structure of Ice is just like th of diamond. The ice has regular hexagonal rings in which water molecules are h together by hydrogen bonds. The water molecules in the structure of ice arra themselves in a regular manner in such a way that empty spaces are produ Hence, ice occupies 10% more space than liquid water and its density decrea This means that there are fewer molecules, and hence less mass, given volume of solid (ice) than in the same volume of liquid water. Water has unusually high heat of fusion due to presence of strong hydrogen bonding among its molecules. The large amount of heat is released in the process of freezing (The conversion of water into ice) which is used to save crops from freezing by spraying them with liquid water. Because of this reason citrus fruit growers spray their trees with water on cold nights to protect the tree from frost damage. When water freezes on the surface of leaves it gives off energy which is enough to save the tree from freezing. The heat of fusion of water is the highest of all molecular solids except ammonia.

Table 6.10: Comparison of the Properties of Ionic, Covalent, Molecular and Metallic Solids

| Type of Solid | Force of Attraction | General Properties | Examples |
|---|---|---|---|
| **Ionic** | Electrostatic Force of attraction | Hard, brittle, high melting point (400 to 3000°C), poor conductor of heat and electricity | NaCl, $K_2SO_4$, LiF, $CaCO_3$ |
| **Covalent** | Covalent bond | Very Hard, high melting point (1200 to 4000°C), poor conductor of heat and electricity | Diamond, Silica ($SiO_2$), Silicon, carbide (SiC) |
| **Molecular** | Dipole-dipole forces,<br>Hydrogen bonds,<br>London forces | Soft, low to moderate melting point (-272 to 400°C), poor conductor of heat and electricity | Sucrose, ice, solid $CO_2$, solid benzene |
| **Metallic** | Metallic bond | Variable hardness form soft to very hard, low to high melting point (-39 to 3400°C), good conductor of heat and electricity, malleable and ductile | Gold, iron, copper, sodium etc. All metallic elements. |

## Interesting Information:

When an apple is kept in the freezer, it freezes; the water within a cell expands and disrupts the cells, the same as water freezing within the pipe bursts the pipe. When the vegetables or foods with high water content like spinach freezes, it will be damaged when you unfreeze it.

## Conceptual Check Point:

Why the most of the organisms do not survive freezing?

## Summary of Facts and Concepts

- Solid is the physical state of matter and has definite shape and volume. Th particles are closely packed and locked at their position and are unable move. Their particles have to and fro motions.
- Solids are either crystalline or amorphous. Crystalline solids have order arrangement of particles where amorphous solids lack internal order.
- Crystalline solids have high melting and boiling points, low compressibili very low vapour pressure, and almost no diffusion.
- The particles in crystalline solids are arranged in a three dimensional lattic structure. A crystal lattice consists of a repeating pattern of unit cells.
- Unit cell is the basic repeating structural unit of crystal lattice that displays the properties of crystal pattern. All of the unit cells in the crystalline soli have alike arrangement of particles.
- Crystalline solids are classified into seven different types of lattice types. ray diffraction is one of the most important methods which are used determine the structures of crystalline solids.
- Crystalline solids can be further divided into four types as ionic, covale metallic, and molecular solids depending upon the arrangement of partic and forces of attractions among their particles. For example, ionic solids hard, covalent solids are very hard, molecular solids are soft and meta solids have variable hardness. Hardness, melting point, and electri conductivity are related to the structure of solids.
- Ionic solids are those whose components are ions that are held together ionic bonds such as $NH_4Cl$ and potash alum.
- Covalent solids are those whose components are atoms that are held toge by covalent bonds into giant three dimensional arrays such as diamond graphite.
- Metallic solids are those whose components are metal atoms that are together by metallic bonds into large arrays of atoms such as copper and g
- Molecular solids are those whose components are simple molecules th held together by dipole-dipole forces when the molecules are polar such and sucrose (sugar) and by London forces when the molecules are non such as dry ice (solid $CO_2$) and iodine.
- In a crystalline solid each sphere is surrounded by a certain number of sp The numbers of spheres that would found in the vicinity of each sp known as coordination number.

## Questions and Problems

Q.1. Four answers are given for each question. Select the correct one.

i) Crystalline solids are also called

(a) True solids (b) pseudo solids

(c) glasses (d) amorphous solids

ii) Which of the following is amorphous solid?

(a) Sucrose (b) NaCl

(c) rubber (d) SiC

iii) Solid is made up of

(a) Atoms (b) ions

(c) molecules (d) all of them

iv) The process in which same compound is present in more than one crystalline forms is called:

(a) Allotropy (b) anisotropy

(c) isomorphism (d) polymorphism

v) Isomorphs have

(a) same physical properties (b) different physical properties

(c) same chemical properties (d) different ratio of atoms

vi) Solids that can be drawn into thin wires are called

(a) Ductile (b) malleable

(c) brittle (d) flexible

vii) Which one of the following has the highest value of lattice energy

(a) NaI (b) NaBr

(c) NaCl (d) NaF

viii) Which one of the following is a polar molecular solid?

(a) Dry ice (b) ice

(c) phosphorus (d) sulphur

ix) In cubic system, the angles

(a) $\alpha \neq \beta \neq \gamma \neq 90^\circ$ (b) $\alpha = \beta = \gamma \neq 90^\circ$

(c) $\alpha = \beta = \gamma = 90^\circ$ (d) $\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$

x) Which of the following is **NOT** the property of solid?

(a) the definite melting point

(b) the high density

(c) the extremely low rate of diffusion

(d) the high expansion on heating

Q.2. Fill in the blanks with suitable words given in the brackets.

i) The word amorphous means ________. (motionless/shapeless)

ii) Cleavage is an ________ property. (isotropic/anisotropic)

iii) Sugar crystallizes in ________ shape. (cubic/monoclinic)

iv) All the lengths are ________ in rhombohedral system (equal/unequal)

v) Crystalline solids have ordered ________ dimensional arrangement of particles. (one/three)

vi) The orderly arrangement of particles in crystalline solids is ________ in different direction. (same/different)

vii) The cubic crystals of sodium chloride change to needle like if 10% ________ is added to the solution as impurity. (urea/lime)

viii) In ________ solids, the atoms in the lattice are displaced easily with respect to each other. (ionic/metallic)

ix) In ________ solids, the electrons are localized in the bonds. (metallic/covalent)

x) Wax is the example of ________ solid. (crystalline/amorphous)

Q.3. Label the following statements as True or False:

i) Solids particles have low kinetic energy as compared to liquids.

ii) Heat is absorbed when a liquid is changed to solid.

iii) Plastic is the example of crystalline solid.

iv) Crystalline solids can be divided into seven crystal systems.

v) Six parameters of unit cell are called crystallographic elements.

vi) The branch of science in which we study about crystals is called crystallography.

vii) The particles in solids have translational motion.

viii) Transition temperature is for compounds only.

ix) At melting point the solid and liquid phases exist in equilibrium.

x) The molecular solids are good conductors of electricity in the molten state.

Q.4: What are solids? How kinetic molecular theory explains the behaviour of solids?

Q.5: Define crystalline and amorphous solids. How does a crystalline solid differ from an amorphous solid? Give examples of each.

Q.6: Explain the following properties of crystalline solids and give examples in each case.

i) Geometrical shape
ii) Melting point
iii) Cleavage planes
iv) Habit of crystal
v) Crystal growth
vi) Anisotropy
vii) Symmetry
viii) Isomorphism
ix) Polymorphism
x) Allotropy
xi) Transition temperature

Q.7: What is the difference between (a) isomorphism and polymorphism, (b)allotropy and polymorphism?

Q.8: What do the terms amorphous, isomorphism and polymorphism mean?

Q.9: What is a unit cell? Explain the significance of the unit cell to the shape of the crystal using NaCl as an example.

Q.10: Describe various types of crystal systems and draw the shapes of the unit cells of various crystal systems?

Q.11: Define and explain lattice energy by giving examples.

Q.12: Give examples of some crystalline and amorphous solids that are used in your community.

Q.13: Discuss the electron sea model. How the electron sea model accounts for the high electrical conductivity, thermal conductivity and lustrous surfaces of metals?

Q.14: What are ionic solids? What types of attractive forces exist among these solids? Discuss their properties. What do you think are they water soluble or not?

Q.15: What are covalent solids? Discuss their properties.

Q.16: What are metallic solids? Give the characteristic properties of metallic solids.

Q.17: What are molecular solids? Give their properties.

Q.18: Explain why ionic solids are generally harder than molecular solids?

Q.19: Why the ceramic bowl breaks and aluminum bowl do not breaks when dropped onto the concrete floor?

Q.20: Explain the density and high heat of fusion of ice.

Q.21: What kind of solid displays each of these sets of properties?

(a) Non-crystalline and melts over a wide range of temperature.
(b) Insoluble in water and conducts electricity in the solid state.

(c) Do not conduct electricity in solid state but are good conductors in solution form and in molten state.

(d) Soft and melts easily and the solid does not conduct electricity.

Q.22: Outer appearance of both the crystals looks similar but melting point of sucrose (186°C) is many times lower than sodium chloride (801°C), why?

Q.23: What types of attractive forces are there between the particles of?

(a) covalent solids

(b) ionic solids

(c) metallic solids

(d) molecular solids

Q.24: Classify each of the following substances as conductor, semiconductor and non-conductor:

(a) Germanium (b) sulphur (c) silver

Q.25: Define coordination number. What is the coordination number of each atom in face centered cubic structure, body centered cubic structure and hexagonal close packing structure?

Q.26: Explain the following with reasons:

(a) Solids have very low vapour pressure than liquids.

(b) Amorphous solids are termed as "super cooled liquids".

(c) Crystalline solids have sharp and distinct melting points while morphous solids do not.

(d) Cleavage is an anisotropic property.

(e) Metallic solids are good conductors of electricity.

(f) Ionic crystals are shattered when struck by a hammer.