Chapter 6:

States of Matter - III

Solid

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① **Introduction:**

Definition:-

The state of matter having a fixed shape and volume is called solid.

② **Kinetic Molecular Interpretation of solids:**

Kinetic Molecular Interpretation of solids consist of following points / postulates:

1. **Attractive Forces:**

As molecules of solids are close to each other, so there are strong attractive forces among them.

2. **Rigidity:**

Molecules of solids are close to each other and have intermolecular forces among them due to which they cannot move freely and hence solids are rigid in nature.

3. **High Density:**

Molecules of solids are close to each other and occupy small volume. As volume is inversely related to density $(d = \frac{m}{V})$, so solids have high density.

4. **Collision:**

As molecules of solids are packed closely and cannot move from one place to another, so they donot collide with each other.

5. **Kinetic Energy:**

As molecules of solids are close to each other and do not possess translational and rotational motion, they just vibrate about their mean position and due to this vibration, they have vibrational kinetic energy.

6. **Geometric Shape:**

In solids, the molecules or ions or atoms have orderly arrangement, so they possess a definite clear geometric shape.

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③

Properties of Solids:

Following are the properties of solids on the basis of Kinetic Molecular Theory:-

1. **Diffusion:**

Rate of diffusion depends upon speed of molecules. In solids, molecules are closely packed and have low speed, so diffusion is also minimum.

2. **Compression:**

i. The decrease in volume on increasing pressure is called compression.

ii. Co-efficient of compressibility is denoted by β.

iii. As solid molecules are close to each other, so their compression is negligible ([illegible]).

3. Expansion:

i. On heating, intermolecular forces decrease and hence molecules move apart i.e the volume increases. This is called as expansions.

ii. Co-efficient of expansion is given by α.

4. Motion of molecules:

Due to intermolecular forces, molecules are close to each other and have no translational and rotational motion. They just vibrate about a fixed position which is called as vibrational motion.

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5. Intermolecular forces:

There exist strong forces among the molecules of solids which are responsible to keep the molecules at a fixed position.

6. Kinetic Energy:

As molecules of solids are close to each other and do not possess translational and rotational motion, they just vibrate about their mean position and due to this vibration, they have vibrational kinetic energy.

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Types of Solids:

There are two types of solids

1) crystalline solid
2) amorphous solid

Differences in them are as follows.

	Crystalline Solid	Amorphous Solid
definition	Solids which have a definite regular shape are called crystalline.	Solids which do not have definite shape are amorphous.
example	$CuSO_4 . 5H_2O$, $Na_2SO_4 . 10H_2O$ } crystalline solids	glass, plastic, rubber, dust } amorphous solids
particles	Particles (atoms, ions etc) have proper arrangement.	Particles (atom, ions etc) donot have proper shape.
melting point	They have high melting point.	They have low melting point.
presence of water	Water molecules can be a part of crystal e.g. $CuSO_4 . 5H_2O$ etc.	Water molecules are not a part of amorphous solids.
colours of solids	Crystals may have colours due to water e.g. $CuSO_4 \cdot 5H_2O$ is blue	They can have different colours, due to paints or dyes.
effect of heat	On heating, molecules of crystalline solid do not start moving.	On heating, molecules of amorphous solids start moving.

⑤ **Properties of crystalline solids:**

Solids which have definite regular shape are called crystalline solids. Their properties are as follows:

1. **Geometrical shape:**

Molecules of crystalline solids have regular orderly arrangement and are fixed at their positions. So these solids have definite clear shape.

"e.g. NaCl is cubic in shape."

2. **Melting point:**

When a crystalline solid is heated, molecules get vibrational kinetic energy and translational kinetic energy. So they move away and thus solid is changed to liquid. The temperature at which solid is changed to liquid is called melting point. Crystalline solids have high melting point.

"e.g. melting point of NaCl is 801°C."

3. **Cleavage planes:**

On applying pressure, large crystals break into smaller crystals of same size and shape. This is called as cleavage. Planes along which crystals break are called cleavage planes.

"e.g. cleavage of $NaNO_3$ is parallel to surface"

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4. Habit of a crystal:

Definition:-

The shape of a crystal in which it usually grows is called habit of crystal.

Example:-

a) NaCl is a cubic crystal with six faces.

b) If 10% urea is added to aqueous solution of NaCl, octahedral crystals of NaCl are obtained.

5. Crystal Growth:

When heated solution of a substance is allowed to cool, crystal growth (formation) takes place.

Relation with crystal shape:-

The shape of a crystal depends on crystal growth i.e. how it is prepared and under what conditions.

Different shapes can be:-

* cube * flat plate * long needle etc.

Relation with crystal size:-

Crystal growth also affects crystal size.

* slow growth (low cooling) → big size
* fast growth (high cooling) → small size
* medium growth (room temperature cooling) → medium size

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6. Anisotropy

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Definition:

A substance which shows different intensity of properties in different directions is called anisotropic and this property is known as anisotropy.

NOTE: Refractive index, co-efficient of thermal expansion, electrical and thermal conductivities show different intensity in different directions.

Example:

① Mica can be cut parallel to surface but can't be cut in some other plane.

② Electricity passes through graphite only when it is parallel to layers of graphite and can't pass through some other planes.

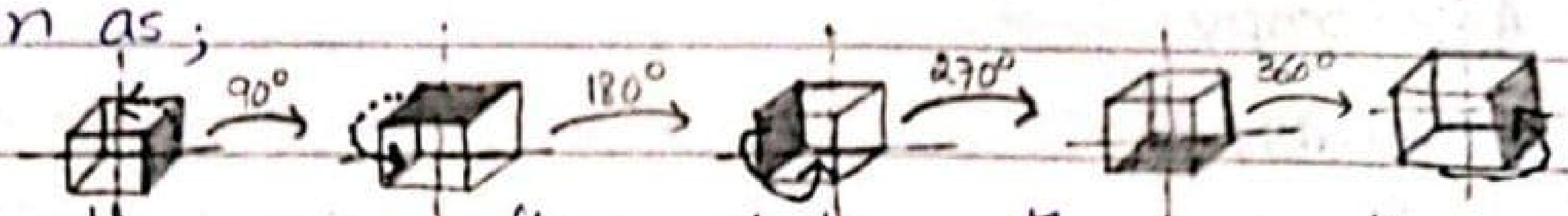
7. Symmetry

Definition:

When a crystalline solid is rotated to certain angles (90°, 180°, 360°), its corners or faces or edges are repeated. Property due which the solid can give same face on rotation is called symmetry.

Example:

Consider a cube rotated at an angle of 90°, 180° and 360°. Their rotation is shown as;



In all cases, after rotation, the overall structure of crystal is similar due to property of symmetry.

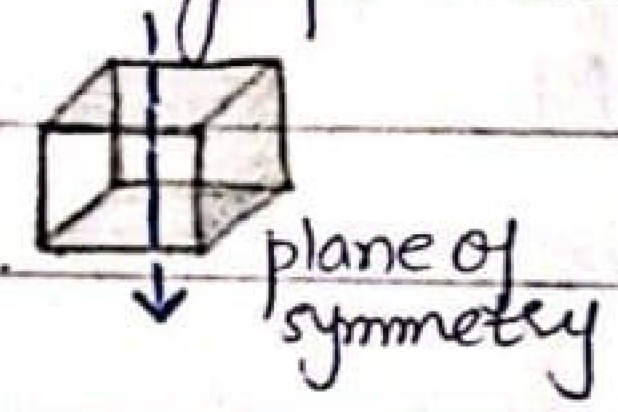
Four Fold Axis of Rotation:

An axis which contains four identical faces is called four fold axis of rotation.

Symmetry Operation:

Process in which crystal is brought back to its original position is called symmetry operation.

Plane of Symmetry:



An imaginary line which passes through the crystal and divides it into two halves is called plane of symmetry.

Types of Symmetry

A crystal can have four types of symmetry.

1. plane of symmetry
2. centre of symmetry
3. axis of symmetry
4. angle of symmetry

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8. Isomorphism

Definition:

If different crystalline solids have same shapes, they are isomorphs and this phenomenon is called as isomorphism.

Example:

Isomorphs have same atomic ratio and cystalline shape.

	names of isomorphs	shape	atomic ratio
1.	$ZnSO_4$ and $NiSO_4$	orthorombic	1:1:4
2.	Ag_2SO_4 and Na_2SO_4	hexagonal	2:1:4
3.	$CaCO_3$ and $NaNO_3$	rhombohedral	1:1:3

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9. Polymorphism

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Definition:

When a substance exists in more than one crystalline form, it is called polymorph and the phenomenon is called polymorphism.

Example:

① NaCl has two crystalline shapes;
→ cubic → octahedral

② $CaCO_3$ has also two crystalline shapes;
→ trigonal (when present as calcite)
→ or thorombic (when present as aragonite)

③ Two crystalline forms of HgI_2 are;
→ orthorhombic (yellow form)
→ tetragonal (red form)

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10. Allotropy

"Allos" means others while "tropia" means forms. So allotropes are defined as different crystalline forms of an element and this phenomenon is called allotropy.

Example:

Carbon has two allotropes.

* diamond (cubic)
* graphite (hexagonal)

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11. Transition Temperature

Definition:

The temperature at which more than one forms of a given substance exist in equilibrium is called as transition temperature.

When the temperature is increased or decreased than transition temperature, only one form can exist.

Temperature decrease ←	Transition Temperature	→ Temperature increase
only A can exist :	both A and B exist :	Only B exists

Example:

	Substance	Crystalline form	Transition temperature
①	tin (grey) tin (white)	• orthorhombic • tetragonal	18°C
②	sulphur	• monoclinic • orthorhombic	95.6°C
③	KNO_3	• orthorhombic • rhombohedral	128.5°C

⑥ <u>Allotropy :</u>

An element can exist in more than one crystalline forms called allotropes and the phenomenon is called allotropy.

OR

Ability of an element to exist in more than one crystalline forms is called allotropy.

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a) <u>Allotropes of oxygen:-</u>

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Oxygen has two allotropes.

① dioxygen (O_2)

② trioxygen or ozone (O_3)

<u>Formation</u>

i. When dioxygen (O_2) absorbs **142kgmol⁻** heat energy, it is converted to ozone (O_3)

$$3O_2 \xrightarrow{UV} 2O_3 \quad \Delta H = 142\,kgmol^{-}$$

ii. This reaction is powered by <u>UV light</u> i.e ultraviolet radiations.

iii. This process is <u>photochemical</u>.

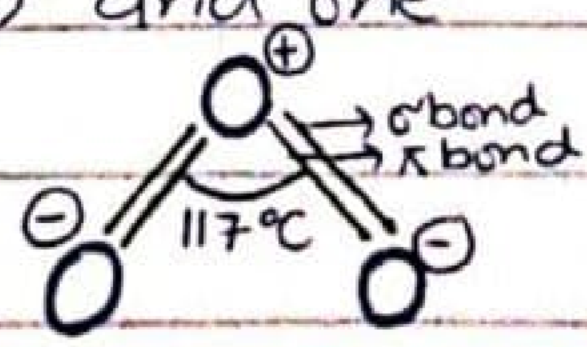
iv. It is called to be <u>monotropic</u> because it is spontaneous (خود بخود) and one directional.

v. The process is <u>irreversible</u>.

<u>Structure</u>

i. Oxygen molecule has one sigma (σ) and one pi (π) bond b/w atoms.

ii Angle b/w bonds of O_3 is **117°C**.



Characteristics of O_3

i. The maximum concentration of O_3 is **10 ppm** (parts per million).

ii. O_3 is present **24-30 km** above earth surface.

iii. It is mostly found in second layer of earth atmosphere i.e. **stratosphere**.

iv. It has a characteristic smell.

v. At a concentration above **1000 ppm**, it is harmful for health.

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b) Allotropes of sulphur :-

Sulphur has four allotropes.

① rhombic sulphur
② monoclinic sulphur
③ amorphous sulphur
④ plastic sulphur

Rhombic Sulphur :-

① It is also called **α-sulphur**.
② It is **yellow** in colour.
③ It is stable below **96°C**.
④ It is **crystalline** in nature.
⑤ It is made up of S_8 molecules.

Monoclinic Sulphur:-

1. It is also called **β-sulphur**.
2. It is a **crystalline** solid.
3. It is stable between **96°C** and **119°C**.
4. It is converted to rhombic sulphur at room temperature.

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Amorphous Sulphur:-

1. It is also called **σ-sulphur**.
2. It has **irregular crystalline** shape which is called as amorphous.
3. It is not found in free state.
4. It has **white** colour.
5. PREPARATION:-
   - → H_2S gas is passed through water for a long time.
   - → Saturated solution of H_2S is obtained.
   - → Solution is exposed to air.
   - → Amorphous sulphur is then produced.

$$2H_2S + O_2 \rightarrow 2H_2O + 2S \text{ (amorphous sulphur)}$$

Plastic Sulphur:-

1. When rhombic or yellow sulphur is heated to an extent (is) that it boils and poured into liquid water, it rolls and give yellow ribbons same as plastic material which is called plastic sulphur.
2. It is super cooled form of liquid.

③ It is not considered as true allotrope as it is soft and elastic.

④ It is insolube in H_2S.

⑦

CRYSTAL LATTICE

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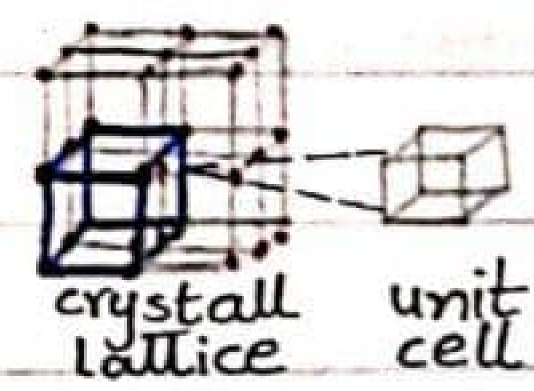
LATTICE:-

Arrangement or position of particles in a crystal is represented by lattice.

CRYSTAL LATTICE:-

Arrangement or position of particles in a crystal in three dimensions is called crystal lattice. **OR** If the lattice is drawn in three dimensions, it is called crystal lattice or space lattice.

UNIT CELL:-



Smallest unit / division of crystal that shows all the properties of its pattren / structure is called unit cell. **OR** Small blocks which repeat again and again to form a crystal lattice is called unit cell (as shown in figure above).

The crystal depends on;

→ shape of unit cell

→ contents of unit cell.

NOTE:

External structure of a crystal may be

different under different conditions e.g if crystal of NaCl is prepared from pure solution, it is cubic while if it is prepared from impure solution with urea as impurity, it is octahedral.

However, internal structure is same as unit cell of NaCl is same for both cube and octahedral shapes.

TYPES OF LATTICE.

A lattice can be of three types;

① one-dimensional lattice

② two-dimensional lattice

③ three-dimensional lattice.

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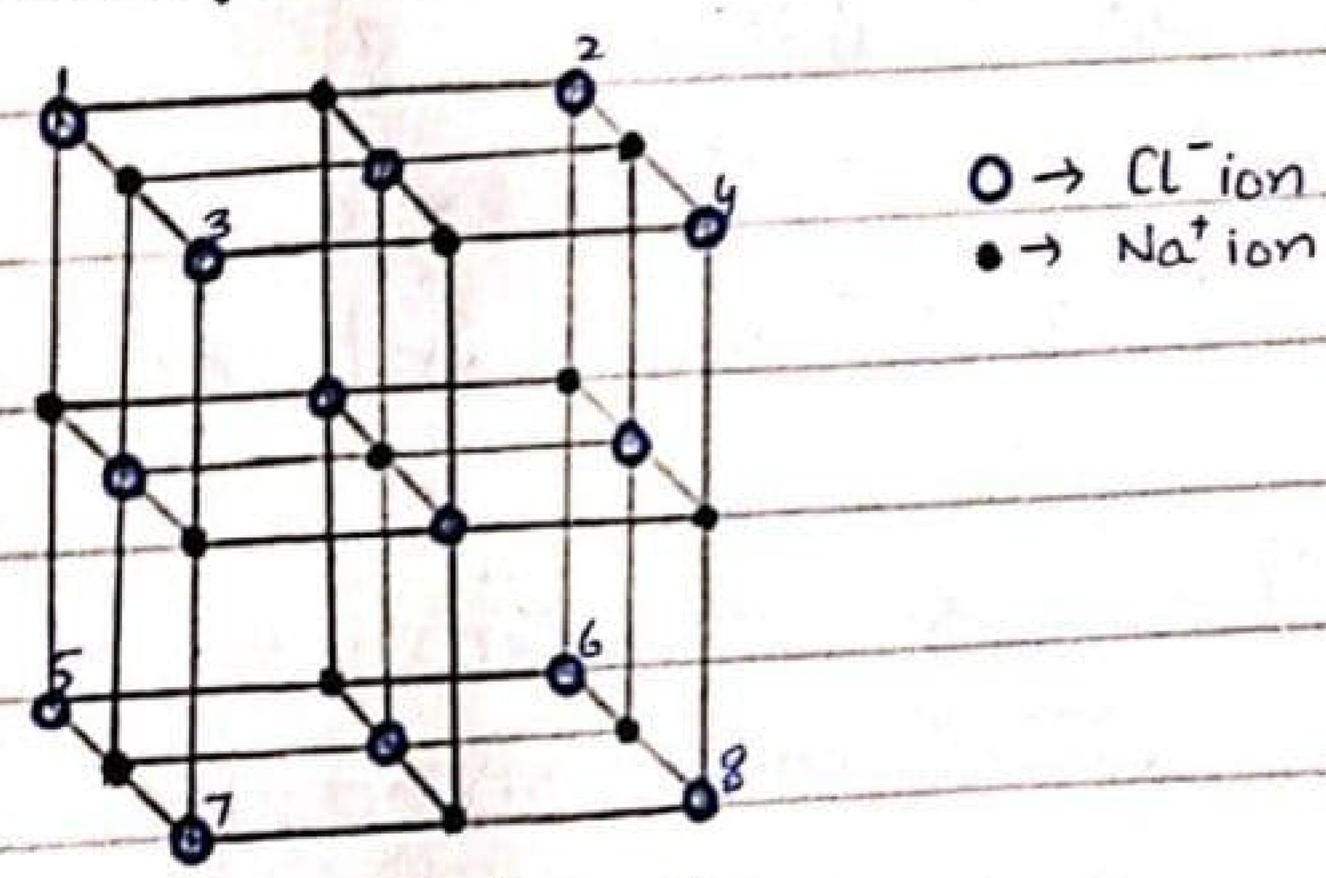
⑧ Unit Cell and Shape of NaCl



Structure of NaCl.

i. **Location of ions:**

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

ii. **Co-ordinate number:**

"The number of negative ion which contact a unit positive ion is called its co-ordinate number."

⇒ In NaCl, each Na^{+1} ion contacts with six (6) Cl^{-1} ions, so its co-ordinate number is 6. Similarly Cl^{-1} has co-ordinate number 6.

⇒ Distance between all Na^{+1} and Cl^{-1} ion is the same.

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iii. **No. of NaCl in each unit cell:**

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

There are 8 Cl^{-1} ions at each corner of cube, so each Cl^{-1} is shared among eight unit cells.

no. of unit cells = 8

" " Cl^{-} ions = 8

no. of Cl^{-1} in one unit cell = $\frac{8}{8}$ = 1

Each face shares with two unit cells.

Cl^{-1} at corner of octahedron = 6

no. of unit cell containing each face = 2

no. of Cl^{-} in unit cell = 6/2 = 3

Total number of Cl^{-} ion in each unit cell

= 1+3 = $4Cl^{-}$

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

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

No. of edges in cube = 12

No. of unit cells of Na^{+1} ions = 4

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

Na^{+1} present in centre = $1Na^{+1}$

Total no. of Na^{+1} ions = 3+1 = $4Na^{+}$ ions.

So each unit cell has $4Na^{+1}$ and $4Cl^{-1}$

hence $4Na^{+1} + 4Cl^{-1} = 4NaCl$

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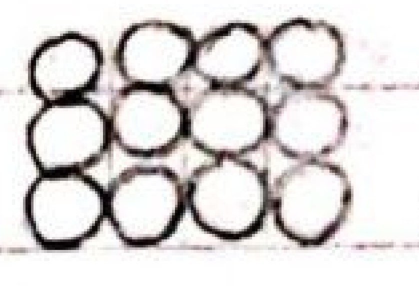
⑨ **Types of packing arrangements:**

There are two types of packings in metals;

1) close packing
2) Open packing

Open packing:

When metal atoms arrange loosely and their molecules have intermolecular distances, it is considered to be open packing.



open packing

Close packing:

Close packing is most efficient arrangement of spheres and all available spaces are filled. Each sphere touches six neighbouring spheres.

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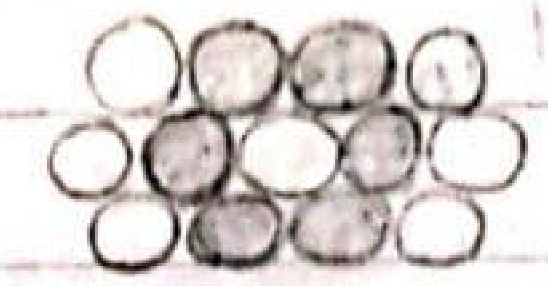
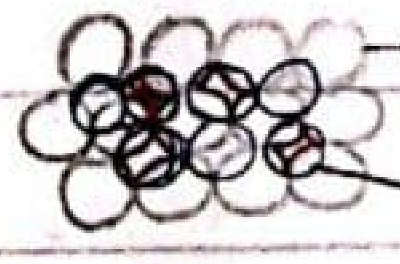


close packing

Types :

i) In close packing, when we place second layer of atoms on first, the spheres are always on holes of first layer.

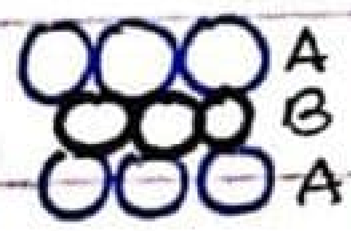
From figure,



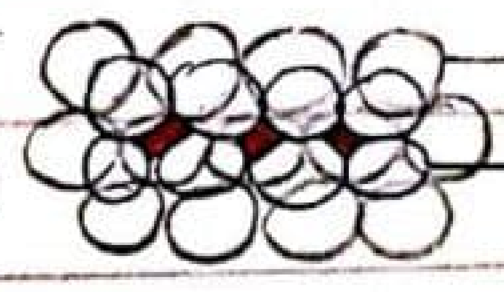
it is noticed that atoms of second layer are placed on holes of first layer (by red area).

ii) HCP (type-1 of close packing)

ii) If the holes of 2nd layer fall on sphere of first layer, they are the tetrahedral holes.



Notice that



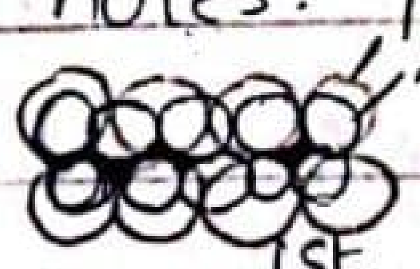
holes in 2nd layer are on atoms of first layer.

If a third layer is added above the tetrahedral holes, the third layers becomes same to first layer. This is called Hexagonal Close Paking (h.c.p). It is written as ABAB or 1212.

iii) CCP (type-2)

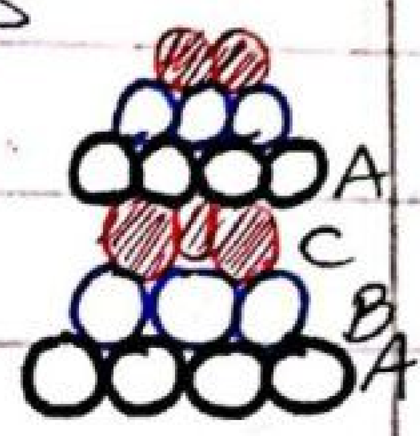
iii) If the holes of the second layer fall on holes of first layer, they are called octahedral holes.

Notice that



holes or voids of 2nd layer lie on 1st layer.

If third layer is added above octahedral holes, it does not matches the bottom 2 layers and remains as a separate layer. This is called Cubic Close Packing (c.c.p). It is written as ABCABC or 123123.



(10)

Factors that affect the shape of ionic solid

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

(i) **Electrostatic force of attraction:**

Ionic compounds have oppositely charged ions held by strong attractive forces to form a well-defined shape.

eg **NaCl** Sodium lose electron to form Na^{+1} which is gained by Cl_2 to form Cl^{-1}. Ions join by attractive forces.

$$Na^{+1} + Cl^{-1} \rightarrow NaCl \quad \Delta H = -787 \text{ kJ mol}^{-1}$$

This process release energy. In NaCl, each Cl^{-1} is surround by 6 Na^+ and each Na^+ is surrounded by 6 Cl^{-1} to give a cubic shape.

(ii) **Radius Ratio:**

"Ratio of radius of cation to radius of anion is called as radius ratio."

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Mathematically,

$$\text{radius ratio} = \frac{\text{radius of cation}}{\text{radius of anion}} = \frac{r^{+1}}{r^{-1}}$$

* **Application of radius ratio :-**

Radius ratio determines shape of solid.

1. if radius ratio is 0.732 and above, body is cubic
2. if r^+/r^- is 0.414 to 0.732, body is octahedral.
3. If r^+/r^- is 0.22 to 0.414, body is tetrahedral.
4. If r^+/r^- is 0.15 to 0.22, body is triangular.

* **Example :-**

name	r^+/r^-	shape
NaCl	0.522	octahedral / cubic
CsCl	0.93	body centred cubic
ZnS	0.40	tetrahedral

(iii) **Poor conductivity:**

In solid state, ions are closer and hence electricity is not conducted. When ionic solids are dissolved in water, they break down into cations (+) and anions (−). These ions then conduct current.

$$NaCl \xrightarrow{H_2O} Na^+ + Cl^-$$

(11)

Lattice Energy

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Definition:

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

$$Na^{+1}_{(g)} + Cl^{-1}_{(g)} \rightarrow NaCl_{(s)} \quad \Delta H = -787 kgmol^{-}$$

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

$$NaCl \rightarrow Na^{+1}_{(g)} + Cl^{-1}(g) \quad \Delta H = +787 kgmol^{-}$$

It is also called as crystal en

Factors:

It depends upon,

a) size of ions

Greater is the size of ions, they are bonded less tightly and lesser is lattice energy.

b) charge of ions

Lattice energy increases by increasing ionic charge.

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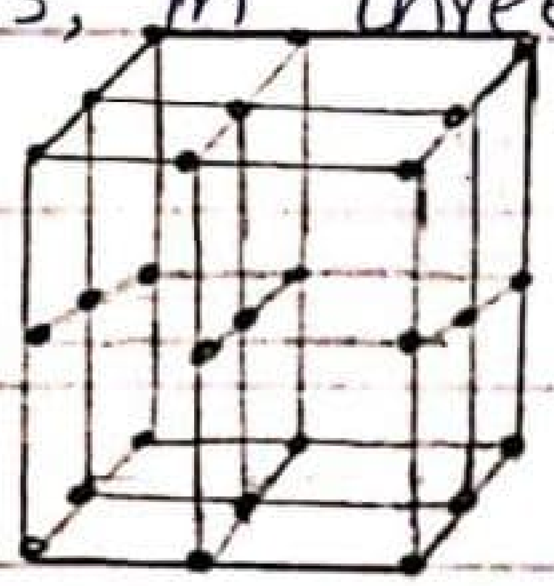
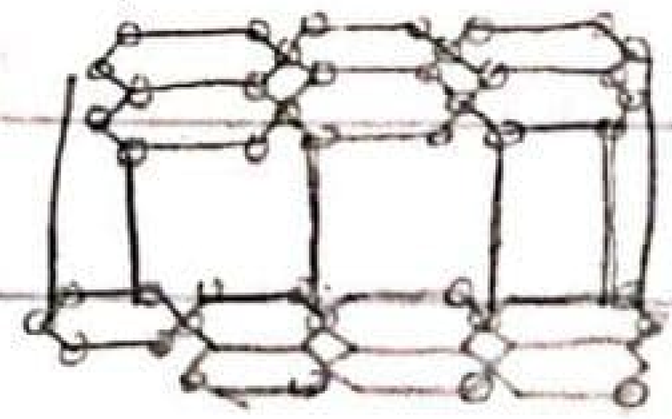
(12) Differentiate b/w ionic and covalent solids.

	Ionic Solids	Covalent Solids
(1)	When oppositely charged ions combine through ionic bond, ionic crystal is formed.	When atoms of same or different elements are held by network of covalent bonds, covalent solid is formed.
(2)	e.g. NaCl	e.g. diamond, SiC
(3)	They have definite shapes, in three dimensions.  NaCl (cubic)	They are arranged in separate layers  graphite
(4)	In solid state, they are non-conductors while in molten form, they conduct electricity.	They are bad conductors of electricity except graphite.
(5)	They are non-directional.	They are directional.
(6)	Their smallest particle is formula unit and not the molecules.	Their smallest particle is molecule.

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(13) Low Density and High Heat of Fusion of ice:

a) Low Density

When the water is cooled from 100°C to 4°C, its molecules come closer and density increase. But at 4°C, water show anamolous behaviour. It arranges itself into specific arrangement and volume increase by 9%. As $d = m/V$ so increase in volume decreases density of ice.

Application:

As mentioned above, density of ice is less than density of water, so ice floats on water surface. In countries where temperature of sea water in winter reduces to 0°C, the ice forms thick layer on surface of water and insulates the lower water so that aquatic life remains alive.

b) High Heat of Fusion

Definition:

Amount of heat required to convert one mole of solid into liquid is called molar heat of fusion.

$$H_2O_{(s)} \xrightarrow{\Delta} H_2O_{(l)} \qquad \Delta H_f = 6.02\ kJ\,mol^{-1}$$

Application:

Due to this property, ice is added to drinks to keep them cold. Each gram of ice absorbs 333 J to melt.

① If there is no ice in drink, then by absorbing 33.3 KJ of energy increases its temperature from 0° to 20°C.

② If there is ice in drink, then by absorbing 33.3 KJ of energy, it remains at 0°C but ice melts in the drink.

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⑭

Molecular and Metallic Solids

a) Molecular Solids

i. Definition:

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

ii. Force of attraction:

Forces found among molecules of molecular solids can be

→ dipole-dipole forces

→ Vander Wal's forces

iii. Examples:

Ice, sugar (polar molecules)

I_2, S_8, P_4, CO_2 (non-polar molecules)

iv. Properties:

1. By X-ray analysis, we find that molecules have regular arrangement.
2. Polar molecular solids have high M.P. and B.P. as compared to non-polar.

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 as they have weak attractive forces.
7. They are transparent to light.

b) Metallic Solids

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i. Definition

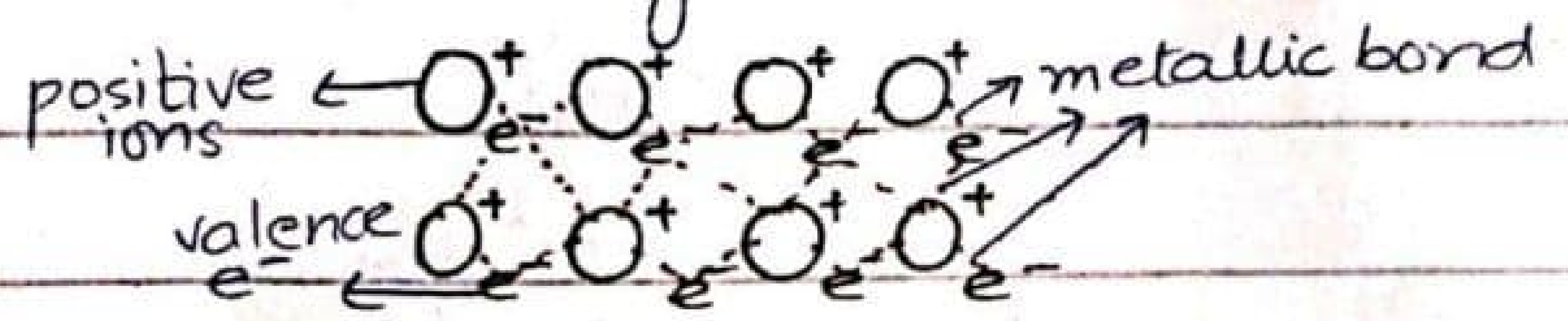
The crystalline solids in which metal atoms are held by metallic bonds is called metallic solids.

ii. Example

Na, Cu etc.

iii. Electron Gas / Sea Theory

Metals are good conductors as the valence electrons are loosely bound. These electrons move from one atom to other and hence conduct electricity.



Here the positive ions are surrounded by these valence electrons. It seems that positive charges are present in sea or gas of electrons. Such environment surrounding positive ions is electron gas or sea.

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iv. Forces responsible for metallic bonds

1) force of attraction b/w positive ions and electron gas.

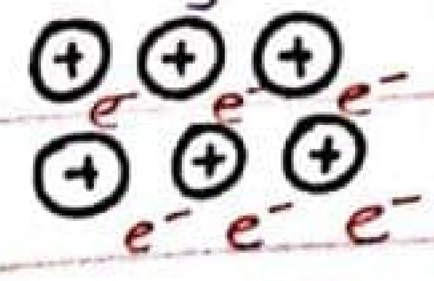
2) force of repulsion b/w positive ions

Both forces are equal but opposite so cancel effect of each other and metallic atom becomes neutral as a whole.

v. Properties

1. They are best conductor of heat and electricity.
2. They have lustrous (چمکدار) surfaces
3. They are malleable and ductile.
4. They have high melting points.

c) Comparison b/w molecular and metallic solids

	Molecular solids	Metallic solids
①	Types of solids in which molecules are held together by molecular interactions is molecular solid.	Solids in which metal atoms are held by metallic bonds are metallic solids.
②	e.g. ice	e.g. Na, Cu
③	Intermolecular forces may be dipole-dipole or London-dispersion forces.	In metallic solids, electron gas theory is involved. 
④	They are bad conductors of electricity as they donot	They are good conductors of electricity as they

	have free electrons.	have free electrons.
5	They are not malleable and ductile.	They are malleable and ductile.

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(15) **Hygroscopic Salts**

Definition:-

Salts which absorb moisture from soil are called as hygroscopic salts.

Example: $CaCl_2$

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HOD Chemistry
Askaria Colleges Rwp.

$CaCl_2$ is a hygroscopic salt. It absorbs water from atmosphere which becomes its part and is called water of crystallization. As $CaCl_2$ absorbs 2 water molecules at maximum, so hydrate will be $CaCl_2 . 2H_2O$. Presence of water increases mass of $CaCl_2$.

Q: How to get NaCl salt from saline solution?

1. Saline water has NaCl and impurities.
2. Firstly, the mixture (H_2O + NaCl + impurities) is allowed to freeze.
3. Impurities come up to surface in form of ice at 4°C.

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4. NaCl solution (pure) left now, can be
5. filtered to get NaCl.