

→ Solid state (दोम अवस्था): →

- The substances which have definite shape and volume are called solid.
- Solids differ from liquid and gas with respect to hardness, density, melting point, boiling point, lustre, electrical conductivity and thermal conductivity.

→ Types of solids: →

① Amorphous solids (अक्रिस्टलीय दोम): →

- Greek "amorphous" → no form
- An amorphous solid consist of particles of irregular shape.
- The arrangement of constituent particles (atoms, molecules or ions) in amorphous solid is only short range order.
- In short range order, a regular and periodically repeating pattern is observed over short distances only. such portions are scattered and in between the arrangement is disordered.
- The structure of amorphous solids is similar to that of liquid.
- Amorphous solids become soft over a range of temp. and can be moulded and converted into various shapes.



- Amorphous solids become crystalline at some temp.
 - Amorphous solids have a tendency to flow (very slow) like liquids. Therefore these are called pseudo solids (दृग्म द्रव) or super cooled liquids. (अतिशीत द्रव).
 - Amorphous solids are isotropic (अभेदीय) in nature.
- e.g.:- Glass, rubber, plastic, quartz glass, amorphous silicon etc.

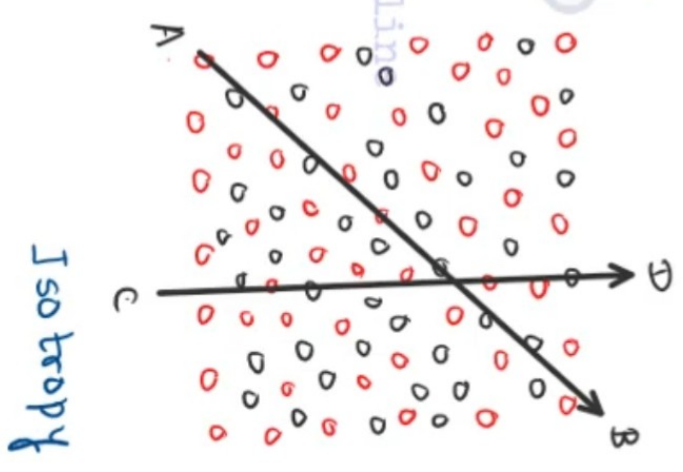
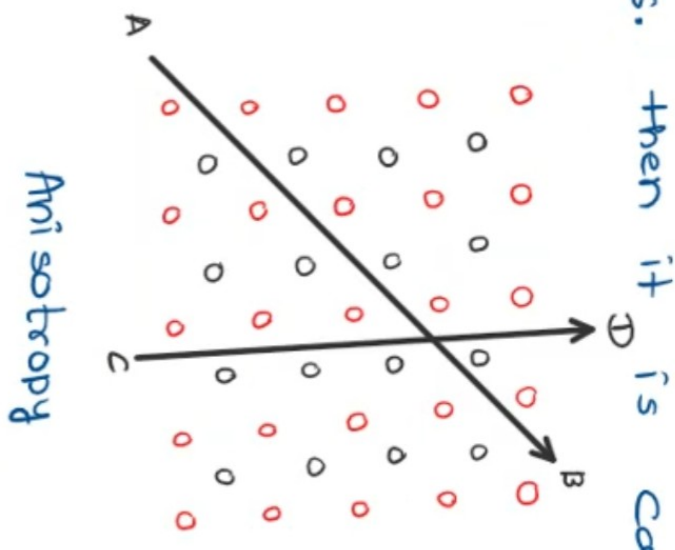
② Crystalline solids (क्रिस्टलीय द्रव) :->

- A crystalline solid consists of large no. of small crystals.
 - Crystals having a definite geometrical shape and the arrangement of constituent particles is ordered.
 - The arrangement of constituent particles in crystalline solids is very long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the crystal.
 - Crystalline solids have sharp melting points.
 - Crystalline solids are anisotropic (अभेदीय) in nature.
- e.g.:- Crystalline NaCl and quartz.

→ Isotropy and Anisotropy :->

- When physical properties like electrical cond., thermal cond., mechanical strength, refractive index etc. of the substance are same in all direction are same, then the substance are said to be isotropic and this property is called isotropy.

- When physical properties of the substance are different in different directions. then it is called anisotropy.



- Differences b/w crystalline and amorphous solids:->

Property

1. Shape
2. m.p.

- Geometrical shape
- sharp m.p.

Crystalline solids

3. Cleavage property

- when cut with a sharp tool, they split into two pieces and the newly generated surfaces are plain and smooth

4. Heat of fusion

- definite heat of fusion

5. Anisotropy nature

- Anisotropic in nature

6. order in arrangement of constituent particles

- Long range order

Amorphous solids

- Irregular shape

- Soften over a range of temp.

- when cut with a sharp tool, they cut into two pieces with irregular surface.

- do not have definite heat of fusion.

- Isotropic in nature

- Short range order.

→ Classification of crystalline solids →

- on the basis of nature of intermolecular forces -

① Molecular solids →

- The constituent particles of molecular solids are molecules.

② Non-polar molecular solids →

- In these solids, the atoms or molecules are held by weak dispersion forces or London forces.

- These solids are soft and non-conductors of electricity.

- These solids have low m.p. and are in liquid state or gaseous state at room temp and pressure.

e.g. Ar, He, H₂, Cl₂, I₂, Solid CO₂ (dry ice), ice etc.

③ Polar Molecular solids →

- In these solids, the molecules are held by relatively stronger dipole-dipole interaction.

- These solids are soft and non-conductors of electricity.

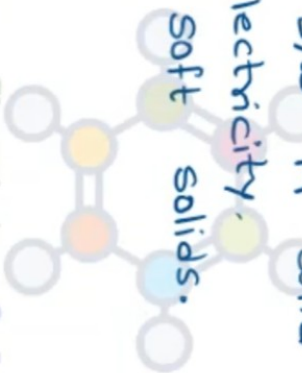
- These solids have higher m.p. than non-polar molecular solids and most of these are gaseous or liquids under room temp. and pressure.
e.g. solid SO_2 , Solid NH_3 etc.

③ Hydrogen bonded molecular solids :->

- In these solids, the molecules are held by strong hydrogen bond and contain polar covalent bonds b/w H and F, O, or N atoms.
- These are non-conductor of electricity.
- These are volatile liquids or soft solids.
e.g. H_2O (ice) etc.

② Ionic solids :->

- The constituent particles of ionic solids are ions (cation and anion)
- Cations and anions are bound by strong electrostatic force.
- Ionic solids are hard and brittle
- These solids have high m.p.
- These are non-conductor of electricity in solid state but conduct electricity in molten state or in aqueous sol.

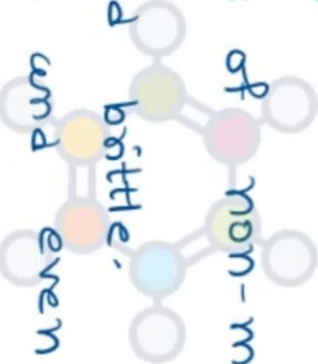


③ Metallic solids :->

- Metals are collection of +ve ions surrounded by sea of free e^-
- These are good conductor of electricity.
- show metallic lustre and colour.
- highly malleable and ductile.

④ Covalent or Network solids :->

- These are crystalline solids of non-metals bonded through covalent bond.
 - These solids are hard and brittle.
 - These solids have high m.p. and even decompose before melting.
- e.g. Diamond, Graphite, silicon carbide etc.



Symmetry in crystal system :->

- Three main symmetry in crystal system are as follows:-

- ① Plane of symmetry (सममिति तल)
- ② Axis of symmetry (सममिति अक्ष)
- ③ Centre of symmetry (सममिति केन्द्र)

① Plane of symmetry :->

- plane of symmetry is an imaginary plane which can divide a crystal in to two parts such that one is the exact mirror image of each other.



Learn Chemistry Online



Rectangular plane of symmetry

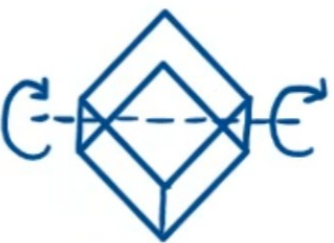
Diagonal plane of symmetry

Fig:- plane of symmetry in cubic crystal

② Axis of symmetry \Rightarrow

- An axis of symmetry is a line about which the crystal may be rotated such that it presents the same appearance more than once during the complete revolution.
- Two fold axis or diad axis \Rightarrow when similar appearance repeated after 180° angle
- Three fold axis or triad axis \Rightarrow when similar appearance repeated after 120° angle.
- four fold axis or tetrad axis \Rightarrow when similar appearance repeated after 90° angle.
- six fold axis or hexad axis \Rightarrow when similar appearance repeated after 60° angle.
- n-fold axis \Rightarrow if the similar appearance of a crystal is repeated on rotation through an angle of $\frac{360^\circ}{n}$, around an imaginary axis, then the axis is called n-fold axis.

Learn Chemistry Online



Two fold axis



Three fold axis



four fold axis



six fold axis

③ Centre of symmetry:->

- Centre of symmetry of a crystal is such a point that any line drawn through it intersects the surface of the crystal at equal distance in both direction
- * any crystal may have any number of planes or axes of symmetry but it has only one centre of symmetry.

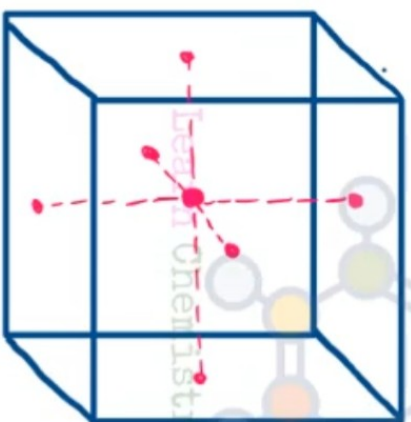


fig:- centre of symmetry in cubic crystal

→ Elements of symmetry of a crystal :->

- The total no. of planes, axes and centre of symmetries possess by a crystal is termed as elements of symmetry.

Example :- cubic crystal of NaCl has 23 elements of symmetry.

① Plane of symmetry

① Rectangular plane of symmetry :- 3

② Diagonal plane of symmetry :- 6

② Axis of symmetry

① four fold axis - 3

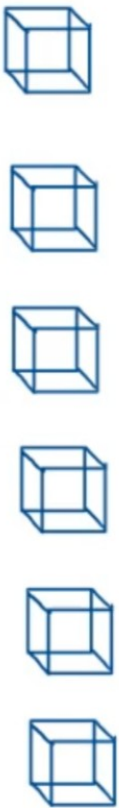
② three fold axis - 4

③ two fold axis - 6

③ Centre of symmetry

① Centre of symmetry - 1

Total ⇒ 9 + 13 + 1 = 23



(includes 2 faces)

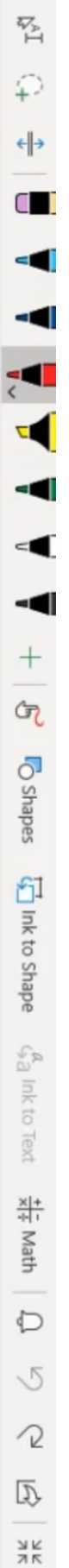


(includes 2 corners)



(includes 2 edges)

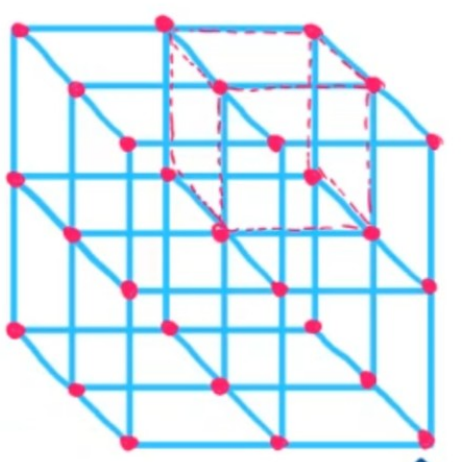




→ Space lattice and unit cell:->

→ Space lattice or Crystal lattice (त्रिदिम आकार या क्रिस्टल आकार):->

- A regular three dimensional arrangement of points or particles in space is called space lattice or crystal lattice.
- Each point in a lattice is called lattice point or lattice site.
- Each point in a crystal lattice represents one constituent particle which may be an atom, an ion or a molecule.



← lattice point

a molecule.

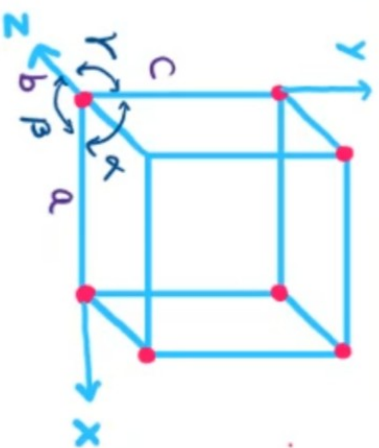
Learn Chemistry Online

Fig:- space lattice or Crystal lattice



Fig:- unit cell

→ Unit cell:-> A unit cell is the smallest repeating unit in space lattice which when repeated over and over again results in a crystal of the given substance.



- The three edges of a unit cell are represented by a, b and c. These edges may or may not be perpendicular
- The angles b/w the edge pairs are represented by α, β and γ.
- Knowing the unit cell dimensions, the theoretical density (ρ) of a crystal can be calculated from the relation

$$\rho = \frac{nM}{(N_A V)}$$

Where n = no. of molecules / atom / ions

M = Molar mass

V = Vol. of unit cell

→ Bravais lattice :->

- In 1848, Auguste Bravais showed that there can be only 14 different ways in which similar points can be arranged in three dimensional space.
- The crystals belonging to the cubic system have three kinds of Bravais lattices depending upon the shape of unit cell.

① Simple or primitive cubic lattice :->

- In this cubic lattice, points are only at the corners of unit cell.
- total no. of atoms in simple cubic lattice $\Rightarrow 1$



each corner atom is

shared b/w 8 cubic lattice



simple cubic
lattice

Calculation:-

$$\begin{aligned} \text{Total no. of atoms in primitive cubic lattice} &= 8 \text{ (at corners)} \times \frac{1}{8} \\ &= 1 \end{aligned}$$

2) The Face centered Cubic lattice :->

- In this cubic lattice, the points are at the corners as well as at the centre of each of the six faces of the cube.
- Total no. of atoms in face centered cubic lattice $\rightarrow 4$

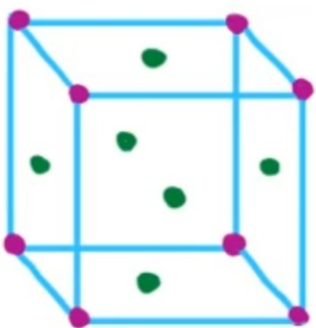
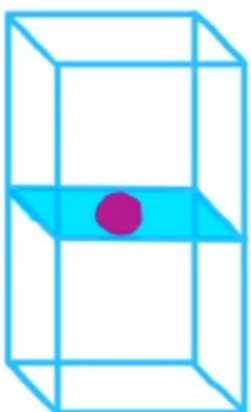


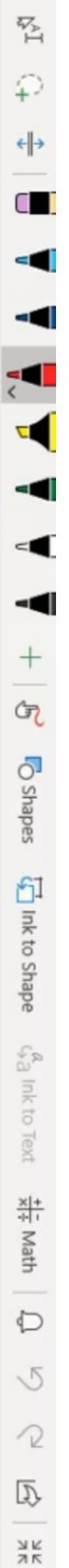
fig: Face centered cubic lattice

fig:- an atom at face is shared
b/w two cubic latticeCalculation

$$(i) 8 \text{ (at corners)} \frac{1}{8} = 1$$

$$(ii) 6 \text{ (at faces)} \frac{1}{2} = 3$$

$$\text{Total atoms} \quad \underline{\quad 4 \quad}$$



③ Body centered cubic lattice :->

- In this cubic lattice, points are at the corners as well as in the body centre of each cube.
- Total no. of atoms in body centered cubic lattice = 2

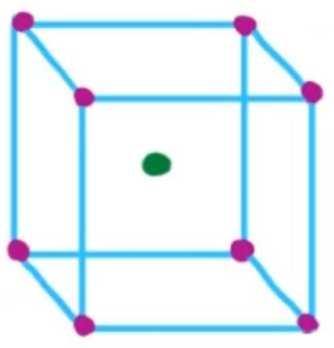
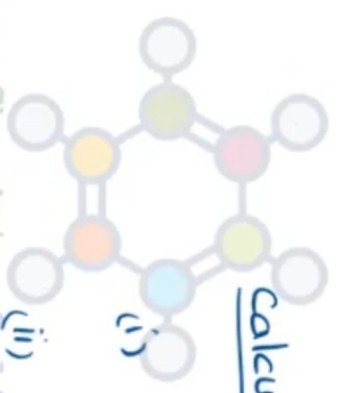


Fig:- Body centered cubic lattice

Learn Chemistry Online



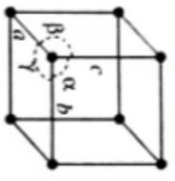
Calculation

(i) $8 \text{ (at corners)} \times \frac{1}{8} = 1$

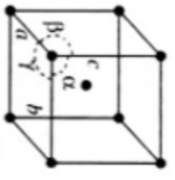
(ii) $1 \text{ (Body center)} = 1$

Total atoms 2

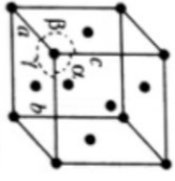
→ 14 Bravais Lattice



Simple or Primitive (P)

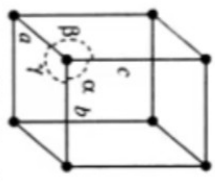


Body-centred (I)

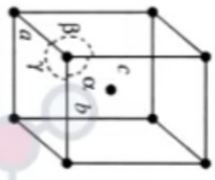


Face-centred (F)

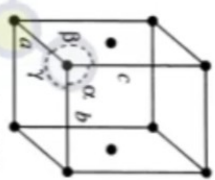
Cubic Space Lattices



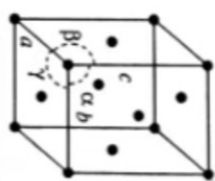
Simple or Primitive (P)



Body-centred (I)

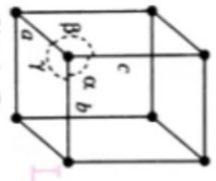


End-centred (C)



Face-centred (F)

Orthorhombic Space Lattices



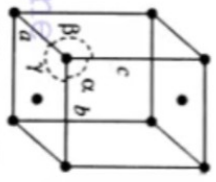
Simple (P)



Body-centred (I)

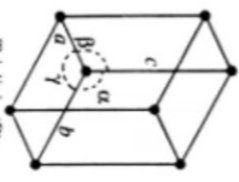


Simple (P)

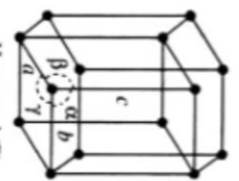


End-centred (C)

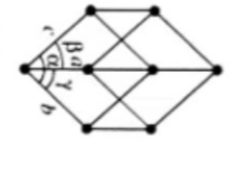
Tetragonal and Monoclinic Space Lattices



Triclinic (P)



Hexagonal (P)



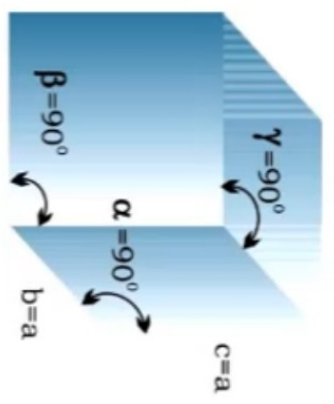
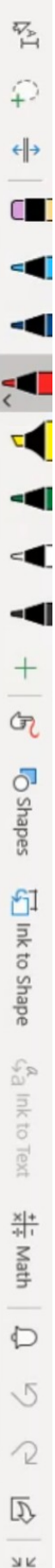
Rhombohedral or Trigonal (P)

Triclinic, Hexagonal and Rhombohedral Space Lattices

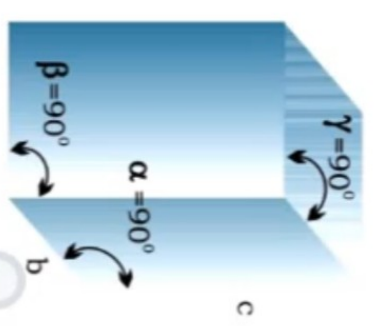
→ Seven crystal system:->

→ 32 point group and 14 space lattice are divided into seven crystal system

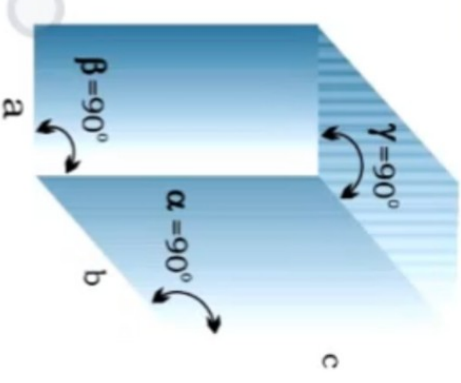
Crystal System	Bravais Lattices	Minimum symmetry Elements	Parameters of Unit Cell	
			Cell Dimensions	Interfacial Angles
1. Cubic	Primitive, Face-centred, Body-centred = 3	Four 3-fold axes : Three 4-fold axes	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
2. Orthorhombic	Primitive, Face-centred, Body-centred, End-centred = 4	Three mutually perpendicular 2-fold axes	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
3. Tetragonal	Primitive, Body-centred = 2	One 4-fold axis	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
4. Monoclinic	Primitive, End-centred = 2	One 2-fold axis	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
5. Triclinic	Primitive = 1	One 1-fold axis	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
6. Hexagonal	Primitive = 1	One 6-fold axis	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
7. Rhombohedral or Trigonal	Primitive = 1	One 3-fold axis	$a = b = c$	$\alpha = \gamma = \beta \neq 90^\circ$



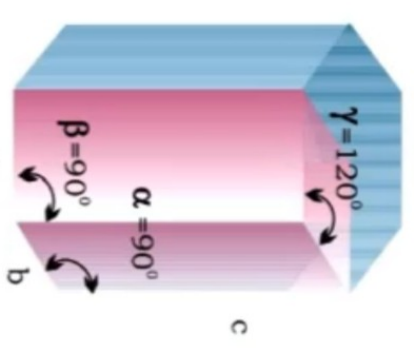
Cubic
(घनीय)



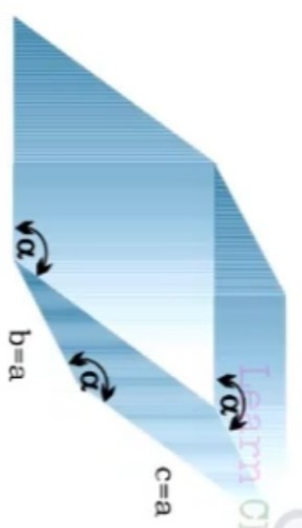
Tetragonal
(द्विसमलंबाक्ष)



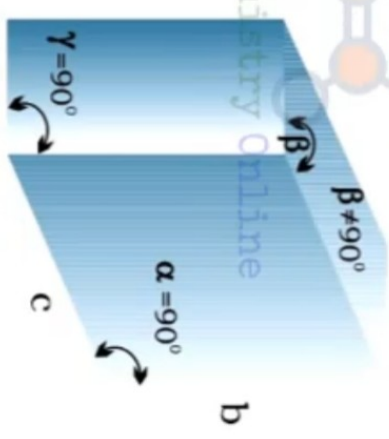
Orthorhombic
(त्रिसमलंबाक्ष)



Hexagonal
(षट्कोणीय)



Rhombohedral
(त्रिसमन्ताक्ष या त्रिकोणी)



Monoclinic
(एकमताक्ष)



Triclinic
(त्रिनताक्ष)

→ Laus of crystallography (क्रिस्टल विज्ञान के नियम) :->

- ① Law of constancy of interfacial angles (अन्तराकलक कोणों की स्थिरता का नियम)
- ② Law of Rational Indices (परिमेय सूचकांक/घातांक नियम)
- ③ Law of constancy of symmetry (सममिति स्थिरता का नियम)

① Law of constancy of interfacial angles :-> Steno, 1669

- This is also called First law of crystallography

- According to this law, "the angles between the corresponding faces of a crystal of the substance are always the same irrespective of the method of preparation or source of the crystal."

Learn Chemistry Online

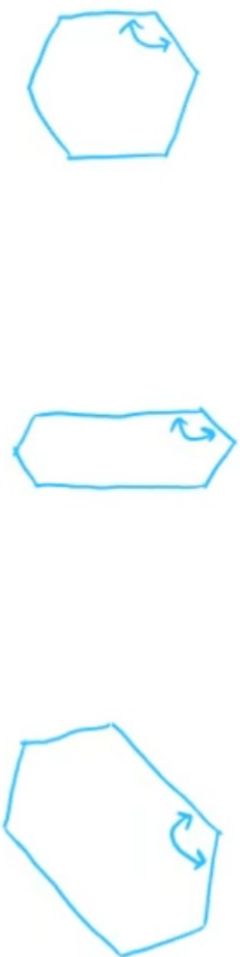


Fig:- Interfacial angles of crystal.

② Law of Rational Indices:->

- According to this law, intercepts of any face of a crystal along the crystallographic axes are either equal to the unit intercept (a, b, c) or some simple whole no. multiples of them.
- e.g. $na, n'b, n''c$ etc. where n, n', n'' etc are whole no.
- three crystallographic axis $\rightarrow OX, OY$ and OZ
- let ABC be a unit plane. The unit intercepts will then be a, b and c.
- According to above law, the intercepts of any face such as KLM, or n the same three axes will be simple whole no. multiples of a, b and c respectively

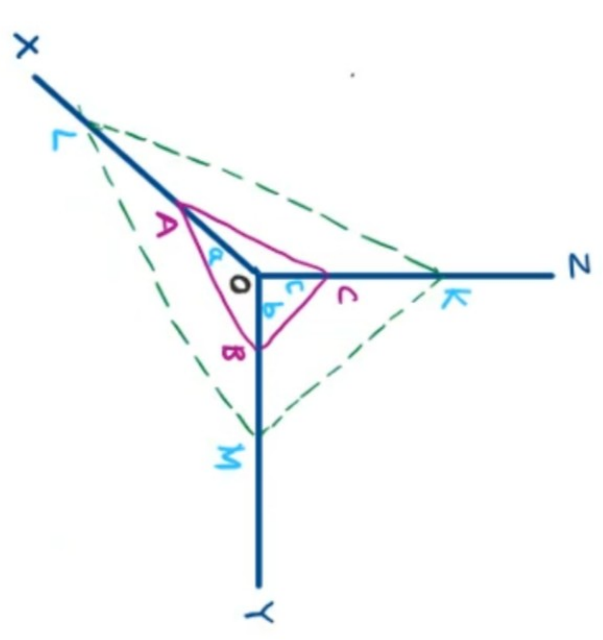
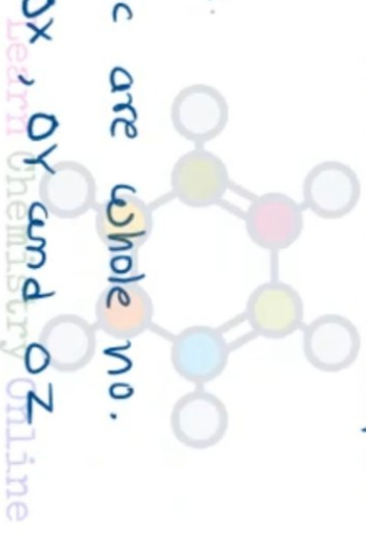


Fig:- crystallographic axes and law of rational indices.

→ Miller Indices:->

- Miller indices are a set of integers (h, k, l) which are used to describe a given plane in a crystal.
- The miller indices of a face of crystal are inversely proportional to the intercepts of that face on various axes.

→ Determination of Miller indices:->

- ① Prepare a three column table with the unit cell axes at the top of the columns.
- ② Enter in each column the intercept (expressed as a multiple of a, b and c) of the plane with these axes.
- ③ Invert all numbers
- ④ Clear fraction to obtain h, k and l

Example:- Calculate the miller indices of crystal planes which cut through the crystal axes at

(i) $2a, 3b, c$

(ii) $2a, -3b, -3c$

Solution (i) $2a, 3b, c$.

$a \quad b \quad c$

Intercept

Reciprocals

Clear fraction

Hence the miller indices are

(ii) $2a, -3b, -3c$

$a \quad b \quad c$

Intercept

Reciprocals

Clear fraction.

Hence the miller indices are

Learn Chemistry



→ Interplanar spacing in a crystal system:->

- Interplanar distance (d_{hkl}) in a crystal is given by -

$$\frac{1}{(d_{hkl})^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

where h, k, l → miller indices

a, b, c → cell dimensions

For a cubic system $a = b = c$ So that

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

For a tetragonal system. $a = b \neq c$

$$\frac{1}{(d_{hkl})^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2}$$

For orthorhombic system $a \neq b \neq c$

$$\frac{1}{(hkl)^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

③ The law of constancy of symmetry :->

- Any crystal has 3 elements of symmetry

- ① plane of symmetry (सममिति तल)
- ② Axis of symmetry (सममिति अक्ष)
- ③ Centre of symmetry (सममिति केन्द्र)

- for more detail, please see :- symmetry in crystal system (क्रिस्टल तंत्र में सममिति)



Chemistry Online

→ X-Ray Diffraction (एक्स रे विवर्तन) :->

- The German physicist "Laue" in 1913, suggested the possibility of diffraction of X-rays by crystals. because the wavelength of X-ray was of about same order as the interatomic distance in a crystal.

- W.H. Bragg used this technique for NaCl crystal. This observation has proved that X-Ray diffraction technique is highly useful in determining structures and dimensions of crystals as well as in the study of a no. of properties of X-Ray themselves.

→ The Bragg equation :->

- According to Bragg, unlike reflection of ordinary light, the reflection of X-Ray can take place only at certain angles which are determined by the wave length of X-Ray and the distance b/w the planes in the crystal.

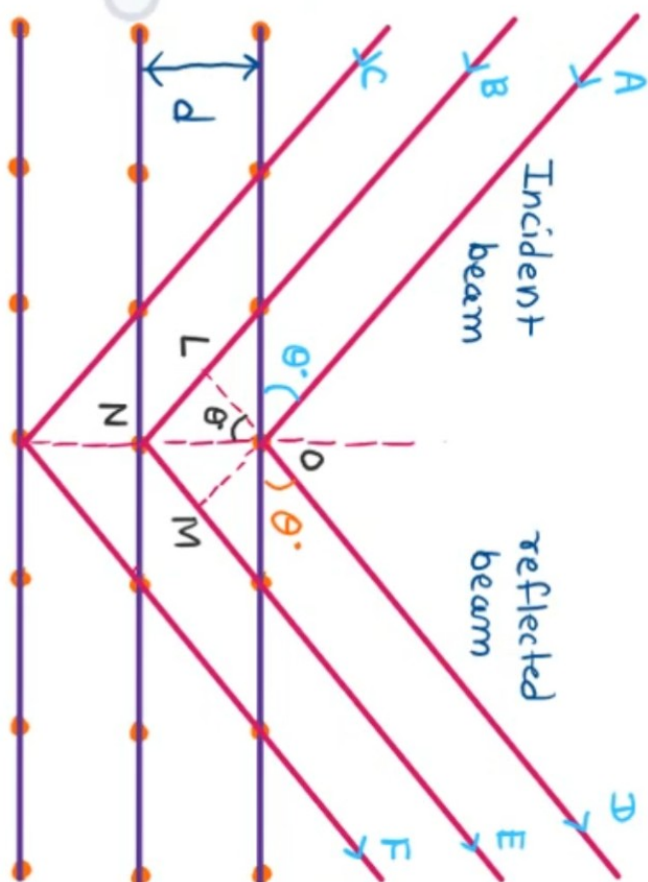
- The fundamental equation which give a simple relationship b/w wave length of X-Ray, the interplaner distance in the crystal and angle of reflection is known as the Bragg equation.



→ Derivation of Bragg equation:→

- Consider fig.
- The distance b/w parallel plane in the crystal structure = d
- Suppose a beam of X-Ray falls on the crystal at glancing angle θ° and reflected from the upper plane at the same angle θ° . while others will be absorbed and get reflected from the successive layers.
- The waves reflected by different layers planes will be in phase with one another only when the difference in path length is an integral number of wave length.

Learn Chemistry Online fig:- X-Ray reflection from crystal



$$\text{path difference} = n\lambda$$

$$\text{where } n = 1, 2, 3, 4, \dots$$

To determine the path difference of X-Ray AOD and BNE, draw perpendiculars OL and OM to the incident and reflected beams.

the path difference is equal to LN + NM

In ΔOLN

$$\sin \theta = \frac{LN}{ON}$$

In ΔOMN

$$\sin \theta = \frac{NM}{ON}$$

Since $ON = d$

then $\sin \theta = \frac{LN}{d}$ or $d \sin \theta = LN$ and $\sin \theta = \frac{NM}{d}$ or $d \sin \theta = NM$

therefore path difference $LN + NM = 2d \sin \theta$

or $n\lambda = 2d \sin \theta$ \therefore path difference = $n\lambda$

This is called Bragg equation. knowing θ , n and λ , d can be calculated.

Learn Chemistry Online

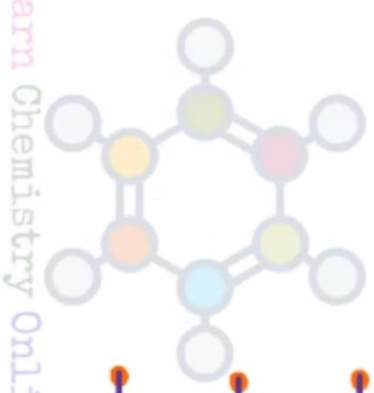
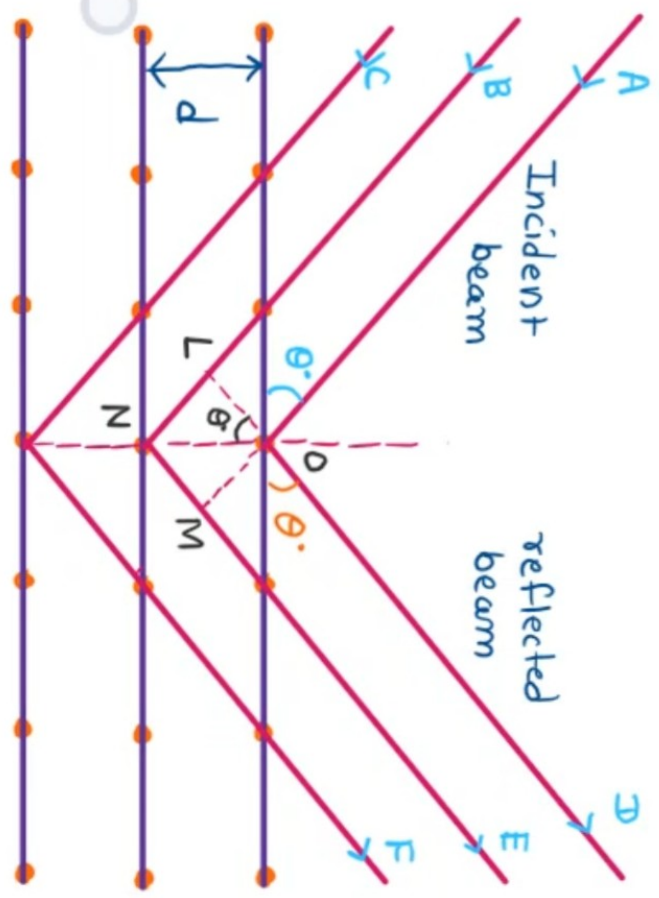


Fig:- X-Ray reflection from crystal



→ Determination of crystal structure →

① Laue's method →

- In this method, a sample of crystal is mounted on a stand with crystal axis perpendicular to x ray beam.
- A beam of x-ray after passing from slits is allowed to fall upon the crystal.
- After diffraction, x-ray falls on photographic plate which records the intensities and positions of diffracted rays.
- The Bragg eq. is used to find interplanar distances.
- This method is very useful to find out symmetry of constituent particles with the help of photographic plate.
- This method is not useful to find unknown lattice parameters because wave length cannot be identified using specific spot in the photographic plate.

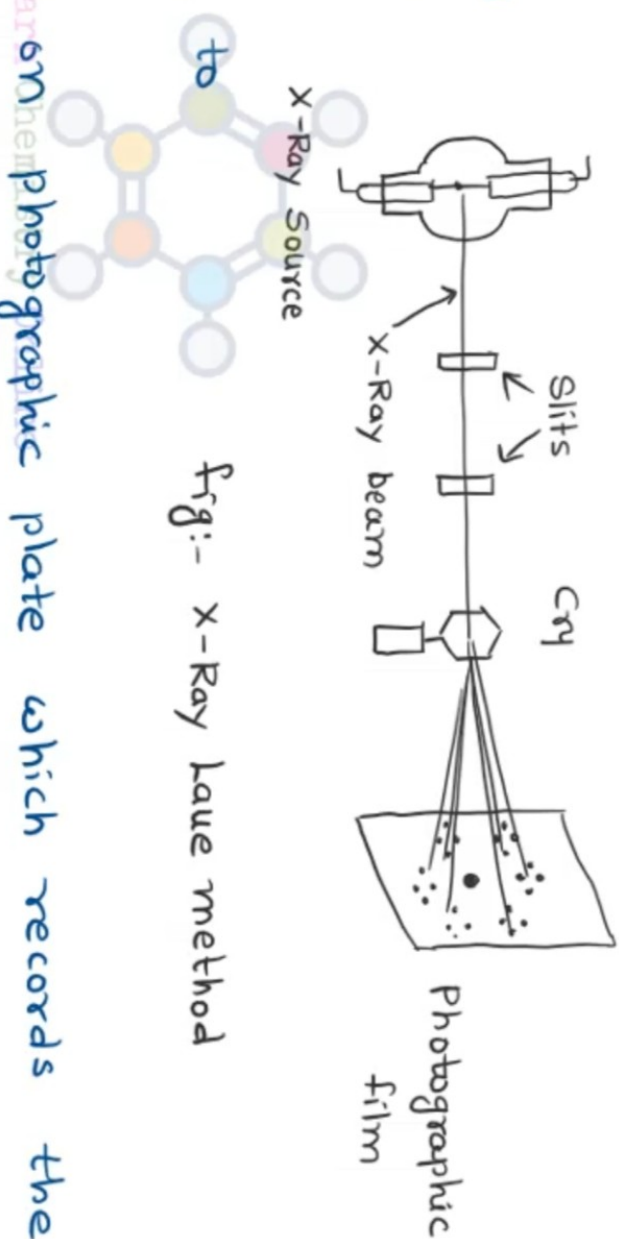


Fig:- X-Ray Laue method

② Powder method :->

- Also called Debye - Scherrer method.
- The powder method is widely used particularly for crystal with simple structure.
- The powder consist of many small crystal which are oriented in all possible directions. as a result x-ray are scattered from all sets of planes.
- In this method , powder sample is kept in the thin glass cylinder. and narrow beam of x-ray is allowed to fall on the powder.
- The diffracted x-ray strike a strip of photographic film arranged in the form of a circular arc.
- In this method , rotation of sample is not necessary because the powder sample already contain microcrystals arranged in all possible directions.
- Bragg equation is used for calculation.

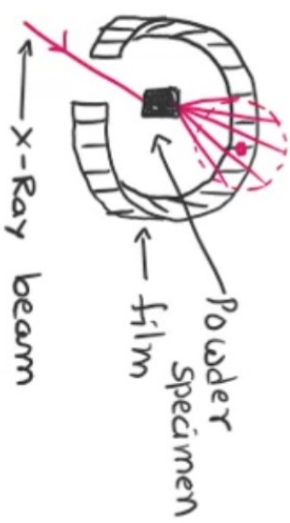


Fig:- The powder method