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	DHYSICAL CHENISTRY [THE SOLID STATE - B.Sc - II (HONS) 20/03/2021]		
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The Solid State:-				
Types of solid :- There are two types of solid.				
(1) Crystalline Solids.				
(2) Amorphous Solid.				
(1) Crystalline Solids:-				
Such a solid in which atoms or molecules or ions are regularly arranged in a				
definite pattern in a geometrical fashion is called crystalline solids.				
For ex:- NaCl, KCl, metals.				
All metals (Fe. Cu. Ag. etc). Nonmetals like S. P. I ₂ . ZnS Naphthalene.				
(2) Amorphous Solids:-				
Such a solid in which constituting unit are not regularly arranged are called				
Amorphous solid.				
For EX:- Rubber, Glass, Plastic.				
Difference between crystalline solids and Amorphous solids:-				
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First Law of crystallography:- We know that the shape and size of a crystal depends upon various factors such as.

1. Temperature.

2. Method of crystallisation.

3. Concentration of solution.

But the corresponding interfacial angle between two adjacent faces in all crystals of a substance always remain the same. This statement is known as first Law of crystallography.

Symmetry:- Symmetry is a property by virtue of which we say are substance is symmetrical to other.

The properties in comparison to which symmetry is considered are called elements of symmetry. In crystals there are following different elements of symmetry.

(1). Plane of symmetry:- It is a plane in the body along which of the body is divided in to two parts, one part is mirror - image of the other. A body can have general plane of symmetry.

(2). Axis of symmetry:- It is line in the body along which if the body is completely rotated (360°) then the same appearance comes more than once.

(3). Point of symmetry or centre of symmetry:-

If there is such a point on the body along which if two opposite lines are drawn so that they cut two equal faces and the two faces are at equal distance then we say that the body from the point has a centre of symmetry.

It should be noted that a body can have several planes of symmetry, several axis of symmetry but it can have only one point of symmetry. Lattice:- Regular arrangement of similar point is called lattice.

Point:- A point is taken for a particle which may consist of one or single atoms are molecules or ions.

	Lattice	
One dimensional	Two dimensional	Three dimension
Lattice	Lattice	Lattice

(1). One dimension Lattice:- If similar points are arranged in one dimension. It is called one dimensional lattice.

(2). Two dimension Lattice:- If similar point are arranged in a two dimensional plane. It is called as Two dimensional lattice.

(3). Three dimension Lattice:- If similar point are arranged regularly in a three dimensional space which represents how atoms or molecules or ions

are arranged in a crystal regularly, then we can say. It is a Three dimensional lattice or space lattice.

OR,

The regular geometrical arrangement of array of similar points is a three dimensional space which represents how atoms or molecules or ions are arranged in a crystal is called space lattice.

Unit cell:- The smallest repeating unit in space lattice. Which when repeated over and over again is a three dimensional space gives rise to the formation of a space lattice crystal is called as "Unit cell".

Ex:- Unit cell of NaCl crystal consist of 14Na⁺ and 13Cl⁻ ions in a face – centred cubic lattice.



Bravais Lattice:- Bravais in 1800 suggested that there are 14 different ways in which similar point in space can be arranged regularly and therefore 14 space lattice are possible. These 14 - space lattice are called Bravais lattice which are as follows.

(1). Triclinic (one):- Simple Triclinic.

 $a \neq b \neq c, \quad \stackrel{\alpha}{\longrightarrow} \neq \stackrel{\beta}{\longrightarrow} \neq \stackrel{\gamma}{\longrightarrow} \neq 90^{0}$ (2). Cubic Lattice (Three):- Simple cubic Lattice. $a = b = c \quad -- \text{ Body centred cubic Lattice.}$ $\stackrel{\alpha}{\longrightarrow} = \stackrel{\beta}{\longrightarrow} = \stackrel{\gamma}{\longrightarrow} = 90^{0} \quad -- \text{ Face centred cubic Lattice.}$ (3). Monoclinic (Two): $a \neq b \neq c \quad --- \text{ One simple monoclinic.}$

 $\alpha = \gamma = 90^{\circ}$ One end – centred monoclinic. $\beta \neq 90^0$. (4). Orthorhombic (Four): $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^{\circ}$ -- Simple orthohombic. -- Body centered. -- Face centered. -- End centered. (5). Tetragonal (Two):- $a = b \neq c$ $\alpha_{Aptu} = \beta_{Bes} = \gamma_{General} 90^{\circ}$ Primitive. Body centred. (6). Hexagonal Lone:---Primitive $a = b \neq c$ $\alpha_{\text{Meta}} = \beta_{\text{Met}} 90^{\circ}, \quad \gamma_{\text{Meta}} = 120^{\circ}.$ (7). Trigonal (One) or Rhombohedral:a = b = c $\alpha_{\text{Apha}} = \beta_{\text{Bra}} = \gamma_{\text{Gamma}} \neq 90^{\circ}$ Total Bravais Lattice = 14 These 14 Bravais Lattice have been grouped in to seven systeme called crystal systemes. Second Law of crystallography.

OR

Law of Rational Indices.

According to this Law, the intercepts of a crystal plane along three crystallographic axis are either equal to or whole number multiple of the unit intercepts.



Let us consider OA, OB and OC as intercepts of a axis and let the unit intercepts be OA', OB', and OC'. Then according to this Law.

 $OA = n_1 OA'$

 $OB = n_2 OB'$

$$OC = n_3 OC'$$

Where n_{1} , n_{2} , and n_{3} , are whole number.

Indexing of crystal planes:-

In order to sort on different crystal planes in a crystal following two methods of indexing were suggested.

(1). Weiss Indices:-

- (2). Miller Indices:-
- (1). Weiss Indices:- Weiss suggested following methods for determining.
- First of all we have intercept of the crystal plane along three axis, let then be OA, OB, and OC.
- Then unit intercept along three axis are taken. Let these are OA', OB', and OC'.
- Each intercept is divided by corresponding unit intercept such as.

OA/OA', OB/OB' , OC/OC' We shall get whole number. Ex:- Let us suppose OA/OA' = 2 OB/OB' = 3 OC/OC' = 4

• There will be 234 weiss Indices of the plane under consideration.

(2). Miller Indices:- Miller suggested more appropriate method of indexing the crystal plane called miller Indices, miller Indices of a plane is determine as follows.

• The intercepts of the crystal plane along three crystallographic axis are taken. Let then be OA, OB and OC.

• Now Let, us take unit intercepts. Let than be OA', OB', and OC'.



• Each intercept is divided by corresponding unit intercept as follows.

1	_1	1
OA,	<u>OB</u> ,	OC
ŌĂ	OB'	OC'

• Now, the whole number ratio of these quantities are taken.

Let these are --
$$\frac{1}{2}$$
, $2\frac{1}{3}$, $\frac{1}{4}$, = 6, 4, 3
Thus, have miller Indices is (6, 4, 3)
Or, $\frac{OA'}{OA}$; $\frac{OB'}{OB}$; $\frac{OC'}{OC}$ = $h: k: l.$

• Here, (h, k, l) will represent the miller Indices of the crystal plane (6, 4, 3). Determination of Effective number of Atoms or Molecules or Ions is a cubic Lattice structure:-

It is to be remembered total apparently present atoms or molecule or ions are not totally counted for that unit cell. Only a fraction of these will be effective for one unit cell and this will depend upon the position. Occupied on the lattice point. For a cubic cell following rules are used to calculate effective number of atoms-

- (1). An atom at the corner of a cube contributes 1/8th part to one unit cell.
- (2). An atom at the face of the unit cell contributes ½ part to one unit cell.
- (3). An atom at the edge of the cube contribute $\frac{1}{4}$ th part to one unit cell.
- (4). An atom as the centre contribute totally to the unit cell.

8 Na⁺ at the corners =
$$8 \times \frac{1}{8}$$
 = 1 Na⁺

6 Na⁺ at the wall =
$$6 \times \frac{1}{2} = 3$$
 Na⁺

Effective number of Na⁺ = 4 Na⁺

(1). In simple cubic Lattice:-Effective no. of atoms.



(1). The number of oppositely charged ions surrounding an ion in ionic crystal is called CO - ordination number of that ion.

Ex:- In NaCl crystal, each Cl⁻ ion is surrounded by 6Na⁺ ions and each Na⁺ ion is also surrounded by 6Cl⁻ ions and so Co- ordination number of both Na⁺ and Cl⁻ = 6.

(2). For AB type crystal NaCl, KCl Co- Ordination number of A = Co-Ordination number of B.

(3). For AB₂ type crystal (CaF₂) Co- Ordination number of A = $2 \times$ Co-Ordination of B.

(4). For AB₃ type crystal.

Co- Ordination number of A = $3 \times$ Co- ordination number of B.

The Co- ordination number determine the shape and structure of the crystal.

The value of radius ratio determines Co- Ordination number and thus shape and geometry of the crystal. This effect is called radius ratio effect. Illustration:- We can illustrate this fact by following example.

Let us suppose an ionic crystal in which Co- ordination number of cation = 3. It means a cation will be surrounded by 3 anion on the basis of shape and size of cations and anion we can have following three possible structure. 1st case:- Cation touches onion but anions do not torch each other.

:. Force of attraction > Force of repulsion.

It is stable case.

2nd case:- Cation touches all anion and also anions touches each other.



:. Force of attraction = Force of repulsion.

This is limiting case.

3rd case:- Anion touches each other but cation does not touch the anion.



:. Force of attraction < Force of repulsion.

It is unstable case.

Let us suppose in the limiting case of we find.

 $\frac{r+}{r-} = 0.155$

Then we can have following conclusions.

(1). If $\frac{r_+}{r_-} > 0.155$ it will represent so, in such case Co- Ordination number 3 is possible.

(2). If $\frac{r_+}{r_-}$ < 0.155 if represent unstable case & Co- Ordination number 3 is not possible.

Following is the chart of limiting radius ratio 2 Co- Ordination number.

Limiting radius Ratio	Co- Ordination number	Geometry of voids.
0.155 – 0.225	3	Triangular.
0.225 – 0.444	4	Tetrahedral.
0.414 - 0.732	4 or 6	Square planar or
		Octahedral
0.732 – 1	8	Cubic.

(Q). Prove that limiting radius ratio of octahedral solid is $0 \cdot 414$.

Ans:- Let us consider an octahedral solid in which each cation is surrounded by Σ – anions.

In limiting case each cation will touch all anions and all anion will touch each other.



Now, let us suppose centre of cation is 0 and centre of 4 anion are A, B, C, D as given in figure. 5th anion is above and 6th anion is below cation. These are not shown in figure.

Let us suppose radius of cation $=r_+$ Let us suppose radius of anion $=r_-$

Then, AB = BC = CD = 2r.
:. OA = OC =
$$r_{+} + r_{-}$$

:. AC = OA + OC = $2(r_{+} + r_{-})$
 \triangle ABC is right angle triangle.
AC² = AB² + BC²
Or, $\{2(r_{+} + r_{-})\}^{2} = (2r_{-})^{2} + (2r_{-})^{2}$
Or, $4(r_{+} + r_{-})^{2} = 4r^{2} + 4r^{2} = 8r_{-}$
Or, $(r_{+} + r_{-})^{2} = 2r^{2}$.
Or, $r_{+} + r_{-} = \sqrt{2r}$.
Or, $r_{+} + r_{-} = \sqrt{2r}$.
Or, $r_{+} = \sqrt{2r} - r_{-}$
Or, $r_{+} = \sqrt{2r} = -r_{-} = r_{-}(\sqrt{2}-1)$
 $= r(-1) 1 \cdot 414$
Or, $r_{+} = r_{-} \times 0 \cdot 414$
Or, $\frac{r_{+}}{r_{-}} = 0 \cdot 414$

(Q). Prove that for Co- Ordination number = 3limiting radius ratio = $0 \cdot 155$. Ans:-

A
A
A
B = BC = AC = 2r.
OA = OB = OC = (r_+ + r_-)
AD² = AB²-BD²
AD² = (2r_-)² - r² = 4r² - r² = 3r².
AD =
$$\sqrt{3}r$$
.
 $\frac{OA}{AD} = \frac{2}{3}$ (From geometry we know).
Or, $\frac{r_++r_-}{\sqrt{3r_-}} = \frac{2}{3} = \frac{2}{\sqrt{3}\cdot\sqrt{3}}$
Or, $\sqrt{3}$ (r_+ + r_-) = 2r.

Or, $\sqrt{3} r_{+} + \sqrt{3} r_{-} = 2r_{-}$ Or, $\sqrt{3} r_{+} = 2r_{-} - \sqrt{3} r_{-} = r_{-}(2 - \sqrt{3})$ Or, $\frac{r_{+}}{r} = \frac{2 - \sqrt{3}}{\sqrt{3}} = \frac{2\sqrt{3} - 3}{3} = \frac{2 \times 1 \cdot 732 - 3}{3}$ Or, $\frac{r_{+}}{r_{-}} = \frac{3 \cdot 464 - 3}{3} = \frac{r_{+}}{r_{-}} = \frac{0 \cdot 464}{3} = 0.155$.

Bragg's Equation:-

When X-rays are allowed to be incident of a crystal, they are diffracted. The diffraction of X-rays is rays – wise reflection.

Let us suppose wavelength of X-rays is λ and angle plane and X-rays incidence = θ , then the inter planar distance between two successive planes in crystals is given by the following equation.

 $n \cdot \lambda = 2dsin\theta$

This equation is called Bragg's equation.

n = 1, 2, 3, 4, 5...

d = Inter planar distance.



Derivation:- Let us suppose X-rays P, Q, R are incident is crystal plane at point O, M, N as shown in figure So, we get refection as P', Q', R'.

θ

$$< POX = \theta$$
 $\therefore < P'OX' =$

Draw,

OC and OD perpendicular Clearly $< COM = \theta$ Similar $< DOM = \theta$

In right angle triangle OCM :- $\sin\theta = \frac{CM}{OM} = \frac{CM}{d}$, $\therefore DM = dsin\theta$ $\therefore OM$ = Interplanar distances (d) In triangle OMD:- $\sin\theta = \frac{DM}{OM} = \frac{DM}{d}$, $\therefore DM = dsin\theta$ **→** (1) $CM + DM = 2dsin\theta$ Path different between two X-rays = CM + MD. We know that for X-rays to be is phase the path difference must be integral multiple of wavelength of the X-rays. Suppose wavelength is λ The path difference = $n \cdot \lambda$ When n = 1, 2, 3, ... $CM + MD = n\lambda$ (2) Or comparing equation (1) and (2) we get. $n\lambda = 2dsin\theta$ Separation between two parallel plane:-For cubic cell – $\mathsf{dhkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$ Where, dhkl = Spacing between two successive line. a = Unit cell length hkl = Miler indices Find out separation between two successive plane of 110 $d_{110} = \frac{a}{\sqrt{1+1+0}} = \frac{a}{\sqrt{2}}$ (111) Plane - $d_{111} = \frac{a}{\sqrt{1+1+1}} = \frac{a}{\sqrt{3}}$ (100) Plane--- $d_{100} = \frac{a}{1} = a$ Determination of unit cell length:-First of all we know that the type of crystal. EX:- NaCl, Fcc lattice $\therefore E \cdot A \cdot No = 4$ So, one unit cell has 4 – effective number of NaCl.

Suppose, unit cell length = a \therefore Volume of unit cell = a³ Wt. of one NaCl molecule = $\frac{58\cdot45}{(6\cdot022H0^{232})^2}$ \therefore Wt. of 4NaCl molecules = $\frac{4\times58\cdot45}{(6\cdot022\times10^{23})^2}$ Density = $\frac{Wt}{Volume}$ Density = $\frac{4\times58\cdot45}{(6\cdot022\times10^{23})}$ / a³

Types of crystal:- On the basic of nature of the species present on the lattice points is crystal, we classify them in to four types.

(1). Ionic crystal:- The lattice points are occupied by ions in ionic crystal. The ions are not free and So, the ionic solids are very hard.

There are following properties of ionic crystals:-

(i). Ionic crystal have high Milting point and Boiling point.

(ii). Ionic solid are soluble in water.

(iii). In solid state the ions are not free and hance ions are non-conductor of electricity and in liquid state ions are good conductor of electricity. For examples NaCl, KCl, CsCl

(a). Metallic crystal:- In metallic crystal the lattice points are occupied by metallic ions. For example:- All metals.

Electro sea model of metallic bonding Good conductor of heat and electricity.

(b). Non-polar molecular solid.

(2). Molecular crystal:- In molecular crystal the lattice points are occupied by molecules or atoms.

For example:- ICl, Ar, He, H₂, Cl₂.

There are following properties of molecular crystal :-

(i). Molecular crystal have low M.P and B.P.

(ii). They are bad conductor of electricity and soft.

(3). Covalent crystal or, Atomic solid:- The lattice points are occupied by atoms of non-metals.

For ex:- Diamond , Graphite.

Diamond:- C(6) 1s², 2s², 2p²

Ground state :- $1s^2$ $2s^2$ $2p^2$

- In diamond each C—atom is Sp³ hybridised.
- So, each C—atom is bonded covalently by other four C—atoms in a tetrahedral space.
- Thus, we get a three dimensional network of C—C bonds in diamond and So, huge amount of energy is released in the formation of enormous C—C bond in diamond \$ that is why it is the hardest species.
- No unpaired electron is left in any C—atom of diamond and So, it is a bad conductor of heat and electricity.



Graphite:-

Excited state:-

- Each atom is Sp² hybridised and there is left one π- electron of each C atom of graphite.
- Sp² hybridised each C—atom with other 3C-atoms in a triangular plane, and on each C-atom there is left one unpaired π -electron.
- Thus, we get layer lattice structure given below.
- In each larger it appears that enormous benzene ring are fused together.
- Layers are weak bonded with each other at a distance just equal to 3.50 A⁰



Graphite.

Crystal structure:-NaCl:-

- The radius ratio is $\frac{rNa+}{rCl-} = 0.593$.
- Therefore Co.no. = 6
- NaCl is AB type crystal and So,

Co.no. of Na⁺ = 6

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Co.no. of Cl⁻ = 6
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So, each Na⁺ is surrounded by 6 Cl⁻ ions each Cl⁻ ion is surrounded by 6Na⁺ ion in an octahedral space.

• So, we get a face centred cubic lattice as show below.



One unit cell of NaCl crystal centred 14Na⁺ and 13Cl⁻ EAN = 4 So, per unit cell there are 4NaCl molecules. $8Na^+$ at the corner $=8 \times \frac{1}{8} = 1$ $6Na^+$ at the wall $= \therefore 6 \times \frac{1}{2} = 3$ Total Na⁺ = 4 12Cl⁻ at the edge $= 12 \times \frac{1}{4} = 3Cl^-$ 1Cl⁻ at the centre $= 1Cl^- + 3Cl^- = 4Cl^-$. CsCl:-Radius ratio $= \frac{rCs+}{rCl-} = 0.921$ • Co.no. = 8

 So, each Cs⁺ ion is surrounded by 8Cl⁻ ion. Since it is AB type crystal 8 So, each Cl⁻ ion is also surrounded by 8Cs⁺. Thus, we get a body centred cubic lattice.





(b). Interstitial defect:-

- Atoms or molecules occupy interstitial site. It increases the density.
- These two defects are shown by only Non-ionic solid.



Ionic-solids show-

(i). Frenkel Defect or Dislocation Defect:-

- Cation shift from normal site to interstitial site.
- It does not change the density.
- It happens when there is large change in size of cations and anion.



Ex:- ZnS, AgCl, AgBr, and AgI, Small size of Zn²⁺ and Ag⁺ (ii). Schottky Defect:-

- Vacance defect in ionic solids.
- To maintain electrical neutrality no. of missing cations and anions are decreases.
- Density decreases.
- Cations and anions are almost similar sizes.
- Ex- NaCl, KCl, CsCl and AgBr.
- AgBr shows both Frenkel as well as Schottky defects.

In NaCl there are approximately 10⁶ Schottky pairs per cm³ at room

temperature. In 1cm³ there are about 10²² ions. Thus, there is one Schottky defect per 10¹⁶ ions ($\frac{10^{22}}{10^6} = 10^{16}$)



(2). Impurity Defects:-



- (i). NaCl + CsCl₂ (Impurity) Electrically neutral crystallisation is performed.
- (ii). CdCl₂ + AgCl.
- (3). Non-Stoichiometric Defect:-

A large number of non-stoichiometric inorganic solids are known which contain the constituent elements is non-stoichiometric ratio due to defect in the crystal structures.

Two types:-

(A). Metal excels Defect:-

(i). Metal excels defect due to anionic vacancies-



- Alkali halides (NaCl, KCl, etc) Show this type of defect.
- NaCl crystal is heated in the atmosphere of Na-vapour.
- At the surface of crystal Na-vapour reacts with Cl⁻ ion to from NaCl.
- So, one electron is liberated and takes the position of Cl⁻ ion (called Fcentre) (Farbenzenter meas colour).
- This excess electron shows colour by excitation when high falls.
- NaCl -- Yellow
- LiCl -- Pink
- KCl -- Violet

(ii). Metal excess defect due to the presence of extra cations at interstitial sites:-

• ZnO <u>Heated</u> $Zn^{2+} + \frac{1}{2}O_2 + 2e^{-}$

White

- Yellow
- ZnO in white is colour at room temperature.
- On heating it loses Oxygen and turns yellow.
- There is excess of Zn^{2+} and its formula becomes $Zn_{1+x}O$.
- The excess Zn²⁺ ions more to interstitial sites and the electrons to the neighbouring interstitial sites.

(b). Metal Deficiency Defect:-

- FeO is a typical example of this type.
- It is found with composition Fe_{0.95}O.
- In crystals of FeO some Fe²⁺ ions are missing and the loss of positive charge is compensated by Fe³⁺.

Electrical Properties:-

The conductivities of solid ranges from 10⁻²⁰ to 10⁷ ohm⁻¹m⁻¹.

On the basis of conductivities, there are three types of solids-

(a). Conductors:- Conductivities from 10^4 to 10^7 ohm⁻¹m⁻¹ good conductors – 10^7 ohm⁻¹m⁻¹.

(b). Insulators:- 10⁻²⁰ to 10⁻¹⁰ ohm⁻¹m⁻¹.

(c). Semiconductors:- 10^{-6} to 10^4 ohm⁻¹m⁻¹.
