CHEMISTRY-XII

CHAPTER-1 The Solid State

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Instructions:

- Go through the complete video for the complete lesson.
- Please click on the given icons in this slide for the videos and animations.
- Videos are provided as 2 parts.
- Students are requested to take class notes which is given in the following slides.
- Solid state animations and notes





CHAPTER-1 The Solid State



SOLIDS:

State of matter characterized by particles arranged such that their shape and <u>volume</u> are relatively stable. The constituents of a solid tend to be packed together much closer than the particles in a <u>gas</u> or <u>liquid</u>.

Examples: a brick, a penny, a piece of wood, a chunk of aluminum metal

Based on the nature of the order of arrangement of the constituent particles, solids are classified as follows

TYPES OF SOLIDS :

Amorphous Solids

Crystalline Solids

Differences between amorphous and crystalline solids are listed in the given table.

| | Amorphous solids | Crystalline solids | | |
|---|---|---|--|--|
| 1 | Have irregular shape | 1 Have definite characteristic geometrical shape | | |
| 2 | Have only short-range order in the arrangement of constituent particles | 2 Have long-range order in the arrangement of constituent particles | | |
| 3 | Gradually soften over a range of temperature | 3 Have sharp and characteristic melting point | | |
| 4 | Do not have definite heat of fusion | 4 Have definite and characteristic heat of fusion | | |

- 5 Isotropic in nature6 Pseudo solids or super-cooled liquids
- 5 Anisotropic in nature6 True solids



Classification of Crystalline Solids

- Molecular solids
 Ionic solids
 Metallic solids
- Covalent solids





2- Ionic solids

➤Constituent particles are ions

- ≻Hard but brittle
- ➤High melting point
- Attractive forces are Coulombic or electrostatic
- Example NaCl, MgO, ZnS

3- Metallic solids

In metallic solids, positive ions are surrounded and are held together in a sea of delocalized electrons.

Hard but malleable and ductile

- Fairly high melting point
- Particles are held by metallic bonding

≻Example – Fe, Cu, Mg

4- Covalent or network solids

Constituent particles are atoms
 Hard (except graphite, which is soft)
 Very high melting point and can decompose before melting
 Particles are held by covalent bonding
 Example – SiO₂ (quartz), SiC, diamond, graphite

Crystal Lattice

•Regular three-dimensional arrangement of points in space



There are 14 possible three-dimensional lattices, known as Bravais lattices.Characteristics of a crystal lattice:

•Each point in a lattice is called lattice point or lattice site.

•Each lattice point represents one constituent particle (atom, molecule or ion).

•Lattice points are joined by straight lines to bring out the geometry of the lattice

Unit Cell

•Smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice

Characterized by –
(i) Its dimensions along the three edges *a*, *b* and *c*(ii) Angles between the edges *α*, *β* and *γ*



The unit cells can be classified as follows:



Crystal Lattices and Unit Cells



The given table lists seven primitive unit cells and their possible variations as centered unit cells.

| Crystal Class | Axial Dist. | Axial Angles | Possible Types of Unit Cells | Examples |
|--------------------------------|-------------------|---|--|--|
| 1. Cubic | a = b = c | $\alpha = \beta = \gamma = 90^{\circ}$ | Primitive, body-centered, face-centered | KCl, NaCl |
| 2. Tetragonal | $a = b \neq c$ | $\alpha = \beta = \gamma = 90^{\circ}$ | Primitive, body-centered | SnO_2 , TiO_2 |
| 3. Orthorhombic | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90^{\circ}$ | Primitive, body-centered, face-centered, end- centered | KNO ₃ , BaSO ₄ |
| 4. Hexagonal | $a = b \neq c$ | $\alpha = \beta = 90^\circ; \gamma = 120^\circ$ | Primitive | Mg, Nzo |
| 5. Trigonal or Rhombohedral | a = b = c | $\alpha = \beta = \gamma \neq 90^{\circ}$ | Primitive | (CaCO ₃) Calcite, HgS (Cinnabar) |
| 6. Monoclinic | $a \neq b \neq c$ | $\alpha = \gamma =$ 90°; $\beta \neq$ 90° | Primitive and end-centred | Monoclinic sulphu Na ₂ SO ₄ .10H ₂ O |
| 7. Triclinic | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$ | Primitive | |

•Unit cells of 14 types Bravais lattices:

•Cubic lattices: All sides are of the same length, and the angles between the faces are 90° each



•Tetragonal lattices: One side is different in length from the other two, and the angles between the faces are 90° each



•Orthorhombic lattices: Unequal sides; angles between the faces are 90° each



Orthorhombic

•Monoclinic lattices: Unequal sides; two faces have angles not equal to 90°



•Hexagonal lattice:

One side is different in length from the other two, and the marked angles on two faces are 60°

•Rhombohedral lattice:

All sides are of equal length, and the marked angles on two faces are less than 90° •Triclinic lattice:

Unequal sides; unequal angles, with none equal to 90°



Calculation of number of atoms in a unit cell

The number of atoms in a unit cell can be calculated, by using the following approximations.

An atom at the corner is shared by 8 unit cells. Hence, an atom at the corner contributes 1/8 to the unit cell.

An atom at the face is shared by 2 unit cells. Hence, an atom at the face contributes 1/2 to the unit cell.

An atom within the body of a unit cell is shared by no other unit cell. Hence, an atom at the body contributes singly, i.e., 1 to the unit cell.

Primitive Cubic Unit Cell

Open structure for a primitive cubic unit cell is shown in the given figure.



Actual portions belonging to one unit cell are shown in the given figure.



Total number of atoms in one unit cell

= 8 corners
$$\times \frac{1}{8}$$
 per corner atom
= $8 \times \frac{1}{8}$
= 1

Body-Centered Cubic Unit Cell

Open structure for a body-centered cubic unit cell is shown in the given figure.



Actual portions belonging to one unit cell are shown in the given figure.



Total number of atoms in one unit cell

= 8 corners per corner atom
$$\times \frac{1}{8}$$
 + 1 body-centre atom

$$=8\times\frac{1}{8}+$$

= 2

Face-Centered Cubic Unit Cell

Open structure for a face-centered cubic unit cell is shown in given figure.



Actual portions of atoms belonging to one unit cell are shown in the given figure.



Total number of atoms in one unit cell

= 8 corner atoms $\times \frac{1}{8}$ atom per unit cell + 6 face-centred atoms $\times \frac{1}{2}$ atom per unit cell

$$=8\times\frac{1}{8}+6\times\frac{1}{2}$$
$$=4$$

Closed-Packed Structures

Coordination number

The number of nearest neighbors of an atom

Close-Packing in One dimension

•Only one way of arrangement, i.e., the particles are arranged in a row, touching each other



•Coordination number = 2



Close-Packing in Two Dimensions

Square close-packing in two dimensions

•AAA type arrangement



The particles in the second row are exactly above those in the first row. •Coordination number = 4

Hexagonal close-packing in two dimensions

•ABAB type arrangement



•The particles in the second row are fitted in the depressions of the first row. The particles in the third row are aligned with those in the first row.

•More efficient packing than square close-packing

•Coordination number = 6

Close-Packing in Three Dimensions

Three-dimensional close-packing is obtained by stacking two-dimensional layers (square close-packed or hexagonal close-packed) one above the other.

- •By stacking two-dimensional square close-packed layers
- •The particles in the second layer are exactly above those in the first layer.
- •AAA type pattern

•The lattice generated is simple cubic lattice, and its unit cell is primitive cubic unit cell.



•Coordination number = 6

Close-Packing in Three Dimensions

Three-dimensional close-packing is obtained by stacking two-dimensional layers (square close-packed or hexagonal close-packed) one above the other.

- •By stacking two-dimensional hexagonal close-packed layers
- •Placing the second layer over the first layer
- •The two layers are differently aligned.
- •Tetrahedral void is formed when a particle in the second layer is above a void of the first layer.
- •Octahedral void is formed when a void of the second layer is above the void of the first layer.



Here, T = Tetrahedral void, O = Octahedral void Number of octahedral voids = Number of close-packed particles Placing the third layer over the second layer: There are two ways –
Covering tetrahedral voids: ABAB ... pattern. The particles in the third layer are exactly aligned with those in the first layer. It results in a hexagonal close-packed (*hcp*) structure. Example: Arrangement of atoms in metals like Mg and Zn



➤ Covering octahedral voids: ABCABC ... octahedral voids. The particles in the third layer are not aligned either with those in the first layer or with those in the second layer, but with those in the fourth layer aligned with those in the first layer. This arrangement is called 'C' type. It results in cubic close-packed (*ccp*) or face-centered cubic (*fcc*) structure. Example: Arrangement of atoms in metals like Cu and Ag



Coordination number in both *hcp* ad *ccp* structures is 12.

Formula of a Compound and Number of Voids Filled

□Number of octahedral voids = Number of close-packed particles

- Number of tetrahedral voids = $2 \times$ Number of close-packed particles In ionic solids, the bigger ions (usually anions) form the close-packed structure and the smaller ions (usually cations) occupy the voids.
- If the latter ion is small enough, then it occupies the tetrahedral void, and if bigger, then it occupies the octahedral void.
- □Not all the voids are occupied. Only a fraction of the octahedral or tetrahedral voids are occupied.
- The fraction of the octahedral or tetrahedral voids that are occupied depends on the chemical formula of the compound.

Locating Tetrahedral Voids

•A unit cell of *ccp* or *fcc* lattice is divided into eight small cubes. Then, each small cube has 4 atoms at alternate corners. When these are joined to each other, a regular tetrahedron is formed.



•This implies that one tetrahedral void is present in each small cube. Therefore, a total of eight tetrahedral voids are present in one unit cell.

•Since each unit cell of *ccp* structure has 4 atoms, the number of tetrahedral voids is twice the number of atoms.

Locating Octahedral Voids

•When the six atoms of the face centers are joined, an octahedron is generated. This implies that the unit cell has one octahedral void at the body centre.



•Besides the body centre, there is one octahedral void at the centre of each of the 12 edges. But only $\frac{1}{4}^{\text{th}}$ Of each of these voids belongs to the unit cell.



Now, the total number of octahedral voids in a cubic loose-packed structure

$$=1+12\times\frac{1}{4}$$
$$=1+3$$

= 4

This means that in *ccp* structure, the number of octahedral voids is equal to the number of atoms in each unit

•hcp and ccp Structures

Let the edge length of the unit cell be 'a' and the length of the face diagonal AC be b.

From $\triangle ABC$, we have

 $AC^{2} = BC^{2} + AB^{2}$ $\Rightarrow b^{2} = a^{2} + a^{2}$ $\Rightarrow b^{2} = 2a^{2}$ $\Rightarrow b = \sqrt{2a}$



Let *r* be the radius of the atom. Now, from the figure, it can be observed that: $\Rightarrow \sqrt{2}a = 4r$ Now, volume of the cube, $a^3 = (2\sqrt{2}r)^3$ $\Rightarrow a = 2\sqrt{2}r$ We know that the number of atoms per unit cell is 4. So, volume of the occupied unit cell $= 4 \times \frac{4}{3}\pi r^3$

$$\therefore \text{ Packing efficiency} = \frac{\text{Volume occupied by four spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100 \%$$
$$= \frac{4 \times \frac{4}{3} \pi r^3}{\left(2\sqrt{2}r\right)^3} \times 100 \%$$
$$= \frac{\frac{16}{3} \pi r^3}{16\sqrt{2}r^3} \times 100 \%$$

= 74%

Thus, *ccp* and *hcp* structures have maximum packing efficiency.

Packing Efficiency

•Percentage of total space filled by particles

<u>Calculations of Packing Efficiency in Different Types of Structures</u> •<u>Simple cubic lattice</u>

In a simple cubic lattice, the particles are located only at the corners of the cube and touch each other along the edge.



Let the edge length of the cube be 'a' and the radius of each particle be r. Then, we can write:

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a = 2r
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Now, volume of the cubic unit cell = a^3
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$$=(2r)^{3}$$

 $= 8r^{3}$

The number of particles present per simple cubic unit cell is 1.

Therefore, volume of the occupied unit cell
$$=\frac{4}{3}\pi r^3$$

Hence, packing efficiency $=\frac{\text{Volume of one particle}}{\text{Volume of cubic unit cell}} \times 100\% = \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100\%$
 $=\frac{1}{6}\pi \times 100\%$
 $=\frac{1}{6} \times \frac{22}{7} \times 100\%$
 $=52.4\%$

Packing Efficiency & Calculations Involving Unit Cell Dimensions

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Calculations Involving Unit Cell Dimensions

In a cubic crystal, let a = Edge length of the unit cell d = Density of the solid substance M = Molar mass of the substanceThen, volume of the unit cell = a^3 Again, let z = Number of atoms present in one unit cell m = Mass of each atomNow, mass of the unit cell = Number of atoms in the unit cell × Mass of each atom $= z \times m$ But, mass of an atom, $= \frac{M}{N_A}$

Therefore, density of the unit cell,

 $d = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$ $\Rightarrow d = \frac{z \cdot m}{a^3}$ $\Rightarrow d = \frac{z \cdot M}{a^3 \cdot N_A}$

Imperfections in Solids

Defects

Irregularities or deviations from the ideal arrangement of constituent particles Two types:

Point defects – Irregularities in the arrangement of constituent particles around a point or an atom in a crystalline substance.

Line defects – Irregularities in the arrangement of constituent particles in entire rows of lattice points.

These irregularities are called crystal defects.

Types of Point Defects

Three types: ✓1- Stoichiometric defects

✓2- Impurity defect

✓ 3- Non-stoichiometric defects

✓1- Stoichiometric Defects

Do not disturb stoichiometry of the solid Also called intrinsic or thermodynamic defects

Two types – (i) Vacancy defect (ii) Interstitial defect

Imperfections in Solids

Stoichiometric Defects :-

1- Vacancy defect

- •When some of the lattice sites are vacant
- •Shown by non-ionic solids
- •Created when a substance is heated
- •Results in the decrease in density of the substance



2 - Interstitial defect

•Shown by non-ionic solids

•Created when some constituent particles (atoms or molecules) occupy an interstitial site of the crystal.



•Ionic solids show these two defects as *Frenkel* defect and *Schottky* defect.

Ionic solids show these two defects

•Frenkel defect

- •Shown by ionic solids containing large differences in the sizes of ions
- •Created when the smaller ion (usually cation) is dislocated from its normal site to an interstitial site
- •Creates a vacancy defect as well as an interstitial defect
- •Also known as dislocation defect
- •Ionic solids such as AgCl, AgBr, AgI and ZnS show this type of defect.



•Schottky defect

- •Basically a vacancy defect shown by ionic solids
- •An equal number of cations and anions are missing to maintain electrical neutrality
- •Results in the decrease in the density of the substance
- •Significant number of Schottky defect is present in ionic solids. For example, in NaCl, there are approximately 10⁶ Schottky pairs per cm³, at room temperature.
- •Shown by ionic substances containing similar-sized cations and anions; for example, NaCl, KCl CsCl, AgBr



✓ 3- Non-Stoichiometric Defects

•1- Metal excess defect

•Metal excess defect due to anionic vacancies:

•Alkali metals like NaCl and KCl show this type of defect.

•When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl- ions diffuse from the crystal to its surface and combine with Na atoms, forming NaCl. During this process, the Na atoms on the surface of the crystal lose electrons. These released electrons diffuse into the crystal and occupy the vacant anionic sites, creating F-centres.

•When the ionic sites of a crystal are occupied by unpaired electrons, the ionic sites are called F-centres.



Metal excess defect due to the presence of extra cations at interstitial sites:When white zinc oxide is heated, it loses oxygen and turns yellow.

$$ZnO \longrightarrow Zn^{2+} + \frac{1}{2}O_2 + 2e^{-1}$$

Then, zinc becomes excess in the crystal, leading the formula of the oxide to $Zn_{1+x}O$. The excess Zn^{2+} ions move to the interstitial sites, and the electrons move to the neighbouring interstitial sites.



✓ 3- Non-Stoichiometric Defects

•2- Metal deficiency defect

•Arises when a solid contains lesser number of cations compared to the stoichiometric proportion.

•For example, FeO is mostly found with a composition of $Fe_{0.95}O$. In crystals of FeO, some Fe_{2+} ions are missing, and the loss of positive charge is made up by the presence of the required number of Fe_{3+} ions.



Electrical Properties



Conduction of Electricity in Metals

•Metals conduct electricity in molten state.

•The conductivity of metals depends upon the number of valence electrons.

•In metals, the valence shell is partially filled, so this valence band overlaps with a higher energy unoccupied conduction band so that electrons can flow easily under an applied electric field.

•In the case of insulators, the gap between filled valence shell and the next higher unoccupied band is large so that electrons cannot jump from the valence band to the conduction band.

Conduction of Electricity in Semiconductors

The gap between the valence band and conduction band is so small that some electrons may jump to the conduction band.



CB: Conduction band VB: Valence band

Electrical conductivity of semiconductors increases with increase in temperature.
Substances like Si, Ge show this type of behaviour, and are called intrinsic semiconductors.

 Doping – Process of adding an appropriate amount of suitable impurity to increase conductivity

 Doping is done with either electron-rich or electron-deficient impurity as compared to the intrinsic semiconductor Si or Ge.

Electrical Properties

There are two types of semiconductors:

<u>n – type semiconductor</u>

<u>p – type semiconductor</u>

1-n – type semiconductor

•Conductivity increases due to negatively charged electrons

•Generated due to the doping of the crystal of a group 14 element such as Si or Ge, with a group 15 element such as P or As



<u>2- p – type semiconductor</u>

•Conductivity increases as a result of electron hole

•Generated due to the doping of the crystal of a group 14 element such as Si or Ge, with a group 13 element such as B, Al or Ga



Perfect crystal

p - type

Applications of n – type and p – type semiconductors

•In making a diode, which is used as a rectifier

- •In making transistors, which are used for detecting or amplifying radio or audio signals
- •In making a solar cell, which is a photo diode used for converting light energy into electrical energy
- •A large number of compounds (solid) have been prepared by the combination of groups 13 and 15 or 12 and 16 to stimulate average valence of four as in Si or Ge.
- •Examples of compounds of groups 13 15 are InSb, AlP, GaAs
- •Examples of compounds of groups 12 16 are ZnS, CdS, CdSe, HgTe
- •Some transition metal oxides like TiO, CrO₂, ReO₃ behave like metals.
- •For example, ReO₃ resembles metallic copper in its conductivity and appearance
- •Some oxides like VO, VO₂, VO₃, TiO₃ show metallic or insulating properties depending on temperature.

Magnetic Properties

- •Each electron in an atom behaves like a tiny magnet.
- •The magnetic moment of an electron originates from its two types of motion.
- •Orbital motion around the nucleus
- •Spin around its own axis
- •Thus, an electron has a permanent spin and an orbital magnetic moment associated with it.
- •An orbiting electron
- •A spinning electron



- •Based on magnetic properties, substances are classified into five categories -
- •Paramagnetic
- •Diamagnetic
- •Ferromagnetic
- •Ferrimagnetic
- •Anti-ferromagnetic

Para magnetism

The substances that are attracted by a magnetic field are called paramagnetic substances.

Some examples of paramagnetic substances are O_2 , Cu^{2+} , Fe^{3+} and Cr^{3+} .

➢Paramagnetic substances get magnetized in a magnetic field in the same direction, but

 \succ lose magnetism when the magnetic field is removed.

➤To undergo paramagnetic, a substance must have one or more unpaired electrons. This is because the unpaired electrons are attracted by a magnetic field, thereby causing paramagnetic.

<u>Diamagnetism</u>

➤The substances which are weakly repelled by magnetic field are said to have diamagnetism.

➤Example – H₂O, NaCl, C₆H₆

Diamagnetic substances are weakly magnetized in a magnetic field in opposite direction.

>In diamagnetic substances, all the electrons are paired.

Magnetic characters of these substances are lost due to the cancellation of moments by the pairing of electrons.

<u>Ferromagnetism</u>

•The substances that are strongly attracted by a magnetic field are called ferromagnetic substances.

•Ferromagnetic substances can be permanently magnetized even in the absence of a magnetic field.

•Some examples of ferromagnetic substances are iron, cobalt, nickel, gadolinium and CrO_{2} .

•In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called domains, and each domain acts as a tiny magnet. In an un-magnetized piece of a ferromagnetic substance, the domains are randomly oriented, so their magnetic moments get cancelled. However, when the substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field. As a result, a strong magnetic effect is produced. This ordering of domains persists even after the removal of the magnetic field. Thus, the ferromagnetic substance becomes a permanent magnet.

•Schematic alignment of magnetic moments in ferromagnetic substances is as follows:

<u>Ferrimagnetism</u>

•The substances in which the magnetic moments of the domains are aligned in parallel and antiparallel directions, in unequal numbers, are said to have ferrimagnetism.

- •Examples include Fe₃O₄ (magnetite), ferrites such as MgFe₂O₄ and ZnFe₂O₄.
- •Ferrimagnetic substances are weakly attracted by a magnetic field as compared to ferromagnetic substances.
- •On heating, these substances become paramagnetic.
- •Schematic alignment of magnetic moments in ferrimagnetic substances is as follows:



<u>Anti-ferromagnetism</u>

•Antiferromagnetic substances have domain structures similar to ferromagnetic substances, but are oppositely oriented.

•The oppositely oriented domains cancel out each other's magnetic moments.

•Schematic alignment of magnetic moments in anti-ferromagnetic substances is as follows:



THANK YOU

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