Chemistry Notes for class 12

Chapter 1 The Solid State

Solids

Solids are the chemical substances which are characterised by define shape and volume, rigidity, high density, low compressibility. The constituent particles (atoms, molecules or ions) are closely packed and held together by strong interparticle forces

Types of Solids

The solids are of two types : Crystalline solids and amorphous solids.

Distinction Between Crystalline and Amorphous Solids

Crystalline solid	Amorphous solids
These have definite and regular arrangement of the constituent particles in space.	These doesn't have any regular arrangement of the constituent particles in space
These are true solids	Theseare super cooled liquids or pseudo soilds
3 These have long order arrangement of the particles	These have short order arrangement of particle.
These are anisotropic in nature, i.e., their physical properties are different in different directions.	These are isotropic in nature i.e., their physical properties are same in all the directions.
They have sharp melting points.	They melt over a certain range of temperature
They undergo a clean cleavage when cut.	. They undergo irregular cleavage when cut.

Types of crystalline solids.

See table no.1.2 in ncert page 6

Crystal lattice and unit cell.

If 3 D arrangement of particles in crystal is represented diagrammatically, in whichb each particle is depicted as a point, this arrangement is called crystal lattice.

Its characteristics:

1. Each point is called lattice point.
2. The point represent the constituent particle (atom,ion,molecule etc)
3. When these lattice points are joined by straight lines, it gives geometry of the crystal.

Unit Cell

> The smallest geometrical portion of the crystal lattice which can be used as repetitive unit to build up the whole crystal is called unit cell.

Types of Unit Cell

(i)   Simple or primitive Unit cell In which the particles are present at the corners only.

(ii)   Face centred unit cell In which the particles are present at the corners as well as at the centre of each of six faces.

(iii)   Body centred unit cell In which the particles are present at the corners as well as at the centre of the unit cell.

Seven Crystal Systems

There are many crystal forms, which have been grouped into 14 types of space lattices, called Bravais Lattices, on the basis of their symmetry and seven different crystal systems on the basis of interfacial angles(alpha,beta,gamma) and axis(a,b,c).

See table 1.3 ncert pg8

Packing Fraction

It is defined as the ratio of the volume of the unit cell that is occupied by the spheres to the volume of the unit cell. **(done in shortcut)**

(i) Primitive cubic unit cell Atoms touch each other along edges.

Hence, $d = a$ or $r = a / 2$

(r = radius of atom and a = edge length)

Therefore, PF = $4 / 3 \pi r^3 / (2r)^3$ = 0.524 **or 52.4%**

(ii) Face centred cubic unit cell Atoms touch each other along the face diagonal.

Hence, $d = a / \sqrt{2}$

or $r = \sqrt{2}a / 4$

Therefore; PF = $4 * 4 / 3 \pi r^3 / (4r / \sqrt{2})r^3$ = 0.74 **or 74%**

(iii) Body centred cubic unit cell Atoms touch each other along the body diagonal.

Hence, $\sqrt{3}a / 2$

or $r = \sqrt{3}a / 4$

Therefore; PF = $2 * 4 / 3 \pi r^3 / (4r / \sqrt{3})r^3$ = 0.68 or **68%**

Coordination Number

It is defined as the number of particles immediately adjacent to each particle in the crystal lattice.

[In simple cubic lattice, CN is 6, in body centred lattice, CN is 8 and in face centred cubic lattice, CN is 12].

High pressure increases CN and high temperature decreases the CN.

Close Packing in Crystals

Two Dimensional Packing of Constituent Particles

(i) Square close packing Space occupied by spheres is 52.4%.

(ii) Hexagonal close packing Space occupied by spheres is 60.4%.Hence. It is more efficient.

Three Dimensional Packing of Constituent Particles

(i) ABAB arrangement gives hexagonal close packing (hcp).(covering tetrahedral void on 2nd layer)

(ii) ABCABC arrangement gives cubic close packing or face centred CUbIC packing (ccp or fcc).(covering octahedral voids of 2nd layer)

 In both these arrangements 74 % space is occupied. Coordination number in hcp and ccp arrangement is 12 while in bcc arrangement, it is 8.

(Close packing of atoms in cubic structure = fcc > bcc > sc. All noble gases have ccp structure except He (hcp structure).

Void or Space or Holes

Empty or vacant space present bet ween spheres of a unit cell, is called void or space or hole or interstitial void. When particles are closed packed resulting in either ccp or hcp structure, two types of voids are generated:

 Tetrahedral voids are holes or voids surrounded by four spheres Present at the corner of a tetrahedron. Coordination number of a tetrahedral void is 4.

 Octahedral voids are holes surrounded by six spheres located on a regular tetrahedron. Coordination number of octahedral void is 6.

[**The number of octahedral voids present in a lattice is equal to the number of close packed particles. The number of tetrahedral voids present in a lattice is twice to the number of close packed particles.]**

Density of Unit Cell (d)

Density of unit ce11 = mass of unit cell / volume of unit cell

d = Z * M / a3 = ZM / a3 * NA

(The density of the unit cell is same as the density of the substance.)

where, d = density of unit cell, M = molecular weight, Z = no. of atoms per unit cell

NA = Avogadro number, a = edge length of unit cell.

Imperfections in Solids

 In a crystalline solid, the atoms, ions and molecules are arranged in a definite repeating pattern, but some defects may occur in the pattern. Deviations from perfect arrangement may occur due to rapid cooling or presence of additional particles.

The defects are of two types, namely point defects and line defects.

Point Defects

Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance Point defects can be classified into three types : (1) stiochiometric defects (2) impurity defects (3) non–stoichiometric defects

1. Stoichiometric Defect : These are point defects that do not disturb the -stoichiometric of the solid. They are also called intrinsic or thermodynamic defects.

In case non ionic compound its of two types

Vacancy defect and interstitial defect.

In ionic solids, basically these are of two types, **Frankel defect and Schottky defect**

FRENKEL DEFECT	SCHOTTKY DEFECT
Interstitial defect	Vacancy defect
Density constant	Density decreases
Neutrality is maintained	Neutrality is maintained
Large difference in the size of ions	Ions are of comparable sizes

AgBr has both Schottky and Frenkel defects. Frenkel defects are not found in pure alkali metal halides because cations are of large size.

2. Impurity Defect

It arises when foreign atoms or ions aloe present in the lattice. In case of ionic compounds, the impurity is also ionic in nature. When the impurity has the same charge as the host ion. it just substitutes some of the host ions.

Impurity defects can also be introduced by adding impurity ions having different charge than host ions. e.g. molten NaCl containing a little amount of SrCI2 is crystallised. In such cases,

(Cationic vacancies produced = [number of cations of higher valence * Difference in valence of the host cation and cation of higher valence)

3. Non-Stoichiometric Defect

Non-stoichiometric crystals are those which do not obey the law of constant proportions. The numbers of positive and negative ions present in such compounds are different from those expected from their ideal chemical formulae. However, the crystal as a whole in neutral.

Types of n-stoichiometric defects are as follows:

(i)   Metal excess defect:

1. Metal excess defect due to anionic vacancies: Alkyl halides like NaC1 and KCl show this type of defect. F Centres are the sites from where anions are missing and the vacant sites are occupied by electrons**. F-centres contribute colour and paramagnetic nature** of the crystal [F stands for German wo\d Farbe meaning colour).

2. Metal excess defect due to presence of extra cations at interstitial sites, e.g., zinc oxide is white in colour at room temperature. On heating, it loses oxygen and turns yellow.

$$ZnO \text{--------} \rightarrow Zn^{2+} + 1/2 \ O_2 + 2e\text{-}$$
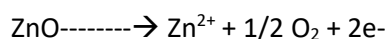
(ii)   **Metal deficiency defect**:
(Due to cation vacancy) It is due to the absence of a metal ion from its lattice site and charge is balanced by ion having higher positive charge. Transition metals exhibit this defect, e.g., FeO, which is found in the composition range from Fe0.93 O to Fe0.96O. In crystal of FeO, some Fe $^{2+}$ cations are missing and the loss of positive charge is made up by the presence of required number of Fe $^{3+}$ ions.

Electrical properties of solids

[The electricity produced on heating a polar crystal is called 'pyroelectricity'.]

When mechanical stress is applied on polar crystals, electricity produced due to displacement of ions is called 'piezoelectricity'

Semiconductors

Electronic conductors having electrical conductivity in the range of $10^4 - 10^7$ Ω-1 cm-1 are known as semiconductors. Examples Si, Ge Sn (grey), Cu2O, SiC and GaAs.

Intrinsic Semiconductors

Pure substances that are semiconductors are known as Intrinsic Semiconductors e.g., Si, Ge

Extrinsic Semiconductors

Their conductivity is due to the presence of impurities. They are formed by doping. It is defined as addition of impurities to a semiconductor to increase the conductivity. Doping of Si or Ge is carried out with P, As, Sb, B, Al or Ga.

(i**) n·type semiconductors** Silicon doped with 15 group elements like phosphorus is called ntype semiconductor. The conductivity is due to the presence of negative charge (electrons),

(ii**) p·type semiconductors** Silicon doped with 13 group element like gallium is called p-type semiconductor. The conductivity is due to the presence of positive holes.

 Some typical 13-15 compounds are InSb, AlP and GaAs and SOme typical 12-16 compounds are ZnS, CdS. CdSe and HgTe. ⷮ These exhibit electrical and optical properties of great use in electronic industry.

Magnetic Properties of Solids

Solids can be divided into different classes depending on their response to magnetic field.

1 **Diamagnetic Substances**

These are weakly repelled by the magnetic field and do not have any unpaired electron, e.g., TiO2, V2O5, C6H6, NaCI, etc.

2**. Paramagnetic Substances**

These are attracted by the magnetic field and have unpaired electrons These lose magnetism in the absence of magnetic field, e.g., O2, Cu2+, Fe3+, etc.

3. **Ferromagnetic Substances**

These are attracted by the magnetic field and show permanent magnetism even ill the absence of magnetic field e.g., Fe, Co and Ni.

4**. Anti-ferromagnetic Substances**: These substances have net magnetic moment zero due to compensatory alignment of magnetic moments, e.g., MnO, MnO2, FeO, etc.

5. **Ferrimagnetic Substance**: These substances have a net dipole moment due to unequal parallel and anti-parallel alignment of magnetic moments, e.g., Fe3O4, ferrites, etc.

(note: see diagrams wherever needed)