Photovoltaic Material: The material which converts sunlight into electricity is called photovoltaic material.

[Amorphous silica]

**Crystalline solid**
1. In a crystalline solid, the particles (atoms, molecules or ions) are arranged in a regular and repetitive three-dimensional arrangement.
2. These solids have sharp melting points.
3. These solids are anisotropic, i.e., their physical properties such as electrical conductivity, refractive index, thermal expansion, etc., have different values in different directions.
4. These solids can undergo a clean cleavage.
5. These solids are generally incompressible.

**Examples:** All the metallic elements like iron, copper, and silver; non-metallic elements like sulphur, phosphorus, and iodine; Compounds like sodium chloride, zinc sulphide, and naphthalene.

**Amorphous solid**
1. In an amorphous solid, the particles (atoms, molecules or ions) are arranged in an irregular and non-repetitive three-dimensional arrangement.
2. Rapidly solidified liquids are amorphous substances, e.g., glass, rubber, etc.
3. These solids are generally isotropic, i.e., physical properties are the same in all directions.
4. These solids on cleavage form smaller pieces with non-planar faces.
5. These solids do not have sharp melting points and boiling points, i.e., they melt gradually over a temperature range.
6. These solids are compressible.

What makes a glass different from a solid such as Quartz? Under what conditions quartz could be converted into glass?

In glass, amorphous silica ($\text{SiO}_2$) is present. $\text{SiO}_4$ tetrahedra have an irregular arrangement.

In quartz, crystalline silica ($\text{SiO}_2$) is present. $\text{SiO}_4$ tetrahedra have a regular arrangement.

When quartz ($\text{SiO}_2$) is melted and the melt is cooled very rapidly, quartz converts into glass.

**Fluid**

 Liquids and gases are called fluids because of their ability to flow. The fluidity is due to the fact that the molecules are free to move about.

Why glass pans fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top?

Due to fluidity property, the glasses flow down very slowly and make the bottom portion slightly thicker.

Why solids are rigid in nature?

The constituent particles in a solid have fixed positions and can only oscillate about their mean positions, for which solids are rigid.

Name the factors which determine the stability of a substance.
1. Intermolecular forces tend to keep the molecules or constituent particles closer.
2. Thermal energy tends to keep them apart by making them move faster.

**Characteristic properties of solid**
1. They have definite mass, volume, and shape.
2. The intermolecular distances are short.
3. The intermolecular forces are strong.
4. Their constituent particles have fixed positions and can only oscillate about their mean positions.
5. They are incompressible and rigid.

**Why glass is considered as a super cooled liquid?**

Amorphous solids have a tendency to flow. Since glass is an amorphous solid, so it is called a supercooled liquid or pseudo solid.

**Why some glass objects from ancient civilizations are found to become milky in appearance?**

Glass becomes crystalline at some temperature. For which glass objects from ancient civilizations become milky in appearance because of some crystallization.
### Types of solid

<table>
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<th>Types of solid</th>
<th>Constituent particles</th>
<th>Attractive forces</th>
<th>Examples</th>
<th>Physical nature</th>
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<td>Molecules</td>
<td>Dispersion or London forces</td>
<td>Ar, CCl₄, H₂, I₂, CO₂</td>
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<td>Insulator</td>
<td>Very low</td>
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<tr>
<td></td>
<td></td>
<td>Dipole-dipole interactions</td>
<td>HCl, SO₂</td>
<td>Soft</td>
<td>Insulator</td>
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<tr>
<td></td>
<td></td>
<td>Hydrogen bonding</td>
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<td>Insulator</td>
<td>Low</td>
</tr>
<tr>
<td>Ionic solids</td>
<td>Ions</td>
<td>coulombic or electrostatic</td>
<td>NaCl, MgO, ZnS, CaF₂</td>
<td>Hard but brittle</td>
<td>Insulator in solid state but conductors in molten state and in aqueous solutions</td>
<td>High</td>
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<tr>
<td>Metallic solids</td>
<td>Positive ions in a sea of delocalised electrons</td>
<td>Metallic bonding</td>
<td>Fe, Cu, Ag, Mg</td>
<td>Hard but malleable and ductile</td>
<td>Conductors in solid state as well as in molten state</td>
<td>Fairly high</td>
</tr>
<tr>
<td>Covalent network solid</td>
<td>Atoms</td>
<td>Covalent bonding</td>
<td>SiO₂ (quartz), SiC, Diamond, AlN</td>
<td>Hard</td>
<td>Insulator</td>
<td>Very high</td>
</tr>
</tbody>
</table>

### Space lattice or crystal lattice

A regular three dimensional arrangement of points in space is called space lattice or crystal lattice. The points represent the constituent particles of the crystal.

**Unit cell**

An unit cell is the smallest portion of the crystal lattice. When it is moved repeatedly a distance equal to its own dimension along each direction, a three dimensional crystal lattice is generated.

**Types of unit cell**

Unit cells are of two types:

1. **Primitive unit cell**
   - It is also called simple unit cell, which has particles as points only at its corners
   - **(Eight lattice points)**

2. **Non-Primitive unit cell / centered unit cell**
   - In this type of unit cells, particles as points are present not only at the corners but also at some other positions.
   - **[Particles as points are located at the corners and also at the centre of the cube]**
   - **Nine lattice points**
   - **Face-centred**
   - **[Particles as points are located at the corners and also in the centre of each face]**
   - **Fourteen lattice points**
   - **End-centred**
   - **Particles as points are located at the corners and also at the centres of any two opposite faces**
   - **Ten lattice points**
Parameters of a unit cell

Depending upon the symmetry of the axial distance (a, b, c) and also the axial angles between the edge (α, β, γ), the various crystals can be divided into seven systems. Further, the seven crystal systems on the basis of unit cells present, classified into fourteen different types of lattices, called Bravais lattices.

1. Cubic - Primitive, Face-centred, Body-centred - NaCl, Zinc blende and Cu
2. Tetragonal - Primitive, Body-centred - SnO₂, TiO₂, CaSO₄, White tin
3. Orthorhombic - Primitive, Face-centred & Body-centred - KNO₃, BaSO₄, Rhombic sulphur
4. Hexagonal - Primitive - Graphite, ZnO, CdS
5. Rhombohedral or Trigonal - Primitive - Calcite (CaCO₃), HgS (cinnabar)
6. Monoclinic - Primitive, End-centred - Na₂SO₄.10H₂O, Monoclinic sulphur
7. Triclinic - Primitive - K₂Cr₂O₇, CuSO₄.5H₂O, H₃BO₃

Rank of unit cell (Z)

The number of particles as points in a unit cell is known as rank. To calculate rank, these points should be noted:-
- A point at each corner of unit cell is counted as \( \frac{1}{8} \)
- The points on an edge are counted as \( \frac{1}{4} \)
- The points at each face are counted as \( \frac{1}{2} \)
- The points within the unit cell is counted as 1

The rank of unit cell of:-
1. Primitive / simple cubic = \( \frac{1}{8} \times 8 = 1 \)
2. Body-centred cubic = \( \frac{1}{8} \times 8 + 1 = 2 \)
3. Face-centred cubic = \( \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4 \)
4. In hexagonal system, each corner atom shared by 6 hexagonal unit cells, each face shared by 2 unit cell and inside the body there are three atoms

\[ Z = \left( \frac{1}{8} \times 12 \text{ corners} \right) + \left( \frac{1}{2} \times 2 \text{ faces} \right) + \left( 3 \text{ inside the body} \right) = 6 \]

Packing in metallic crystal:

The identical solid spheres can be packed in a number of ways.

1. In the first layer, the spheres are arranged in a hexagonal manner in which each sphere is in contact with six other spheres.
2. In the second layer, the spheres will fit into the depression of the first layer.
3. For the third layer, there are two possibilities:
   a) The spheres can be placed in the depression of the second layer i.e. the third layer is directly above the first and the fourth layer is directly above the second. This leads to the arrangement ABABAB...
   b) Alternatively, the sphere can be placed in the depressions of the second layer; do not lie directly above the atoms of the first layer i.e. the spheres in fourth layer lie exactly above the first, fifth above the second, sixth above the third and so on. This leads to the arrangement ABCABCABC...........

This type of arrangement is known as hexagonal close packed (HCP) structure.

   e.g. Zinc, magnesium crystallizes in this type of structure.

This type of arrangement is cubic close packed or face centered cubic arrangement.

   e.g. Cu, Ag, Au crystallizes in this type of structure.

Co-ordination number

It is the number of atoms or spheres that surrounds the single sphere / atom in a crystal.

C.N of tetragonal arrangement = 3
C.N of tetrahedral arrangement = 4
C.N of octahedral arrangement = 6
C.N of body centered cubic arrangement = 8
Any close (tight) packing having C.N = 12 i.e. hcp and ccp i.e. fcc having C.N = 12
Void / Hole / Interstices

The space which is left in between the closest pack arrangement is called void. In close packing two types of voids are created.

[1] Tetrahedral void:
It refers to one empty space surrounded by four spheres which lie at the vertices of a regular tetrahedron. There are eight tetrahedral voids around each sphere.
Coordination number = 4  
Radius ratio = 0.225

The number of tetrahedral voids belonging to a sphere in close packing arrangement

\[
\frac{\text{Number of tetrahedral voids around a sphere}}{\text{Number of sphere around a void}} = \frac{8}{4} = 2
\]

[2] Octahedral void:
It refers to one empty space surrounded by six spheres which lie at the vertices of a regular octahedron. There are six octahedral voids around each sphere.
Coordination number = 6  
Radius ratio = 0.414

The number of octahedral voids belonging to a sphere in close packing arrangement

\[
\frac{\text{Number of octahedral voids around a sphere}}{\text{Number of sphere around a void}} = \frac{6}{6} = 1
\]

Octahedral voids are larger than the tetrahedral voids.

In FCC there are four octahedral voids and eight tetrahedral voids.

A cubic solid is made up of two elements P & Q. Atoms of Q are at the corners of cube and P at the body centre. What is the formula of the compound? What are the coordination number of P & Q?

There are eight corners which are occupied by Q

No of Q per unit cell = \( \frac{1}{8} \times 8 = 1 \)

P is situated at the body centre, So no. of P per unit cell = 1

So formula of the compound = PQ

C.N of P = 8 & C.N of Q = 8

Relationship between edge length (a) and radius of the sphere (r) in unit cell.

For FCC, \( a = 2\sqrt{2}r \)  
For BCC, \( a = \frac{4}{\sqrt{3}}r \)  
For simple cubic, \( a = 2r \)

Packing efficiency

\[
\text{Packing efficiency} = \frac{\text{Volume occupied by all the spheres in a unit cell}}{\text{Volume of unit cell}} \times 100
\]

Packing efficiency,  
For simple cubic = 52.36 %,  
For BCC = 68 %,  
For FCC = 74 %

Calculate the efficiency of packing in case of a metal crystal for Simple cubic, body centred cubic and face centred cubic.

[1] For simple cubic  
\( a = 2r \)  
Rank (Z) = 1

So volume occupied by one sphere in the unit cell = \( \frac{4}{3}r^3 \)  
Volume of the unit cell = \( (2r)^3 = 8r^3 \)

Hence, packing efficiency = \( \frac{\frac{4}{3}r^3}{8r^3} \times 100 = 52.36 \% \)

[2] For body centred cubic  
\( a = \frac{4}{\sqrt{3}}r \)  
Rank (z) = 2

So, volume occupied by two spheres in the unit cell = \( 2 \times \frac{4}{3}r^3 \)  
Volume of unit cell = \( \left[ \frac{4}{\sqrt{3}}r \right]^3 \)

So packing efficiency = \( \frac{2 \times \frac{4}{3}r^3}{\left[ \frac{4}{\sqrt{3}}r \right]^3} \times 100 = 68 \% \)

[3] For face centred cubic  
\( a = 2\sqrt{2}r \)  
Rank (Z) = 4

So, volume occupied by four spheres in the unit cell = \( 4 \times \frac{4}{3}r^3 \)  
Volume of unit cell = \( \left[ 2\sqrt{2}r \right]^3 \)

So packing efficiency = \( \frac{4 \times \frac{4}{3}r^3}{\left[ 2\sqrt{2}r \right]^3} \times 100 = 74 \% \)
Gold (At. radius = 0.144 nm) crystallizes in a FCC unit cell. What is the length of the side of the unit cell?

Atomic radius = 0.144 nm
So, length of side \( a = 2 \sqrt{2} r = 2 \sqrt{2} \times 0.144 = 0.406 \) nm

Aluminum crystallizes in a cubic closed packed structure. Its metallic radius is 125 pm.

1. What is the length of the side of the unit cell?
2. How many unit cells are there in one c.c of aluminum?

1. For FCC, \( a = 2 \sqrt{2} r = 2 \sqrt{2} \times 125 = 354 \) pm, So the edge length of the unit cell = 354 \( \times 10^{-10} \) cm

2. Therefore, number of unit cells in 1 cc of aluminum = \( 1 / (354 \times 10^{-10})^3 \) cm \(^3\) = 2.254 \( \times 10^{22} \) unit cells

Radius ratio in ionic crystal
The ratio of the radius of the smaller sphere with that of the larger is called the radius ratio.

\[
\text{Radius ratio in ionic crystal} = \frac{\text{Radius of cation (} r^+\text{)}}{\text{Radius of anion (} r^-\text{)}}
\]

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Types of packing</th>
<th>Co-ordination number</th>
<th>Radius ratio</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tetrahedral Void</td>
<td>4</td>
<td>0.225 - 0.414</td>
<td>ZnS</td>
</tr>
<tr>
<td>2</td>
<td>Octahedral Void</td>
<td>6</td>
<td>0.414 - 0.732</td>
<td>NaCl</td>
</tr>
<tr>
<td>3</td>
<td>Body centred cubic</td>
<td>8</td>
<td>0.732 - 1.00</td>
<td>CsCl</td>
</tr>
</tbody>
</table>

High pressure increases the coordination number and high temperature decreases the coordination number. Thus, high pressure converts NaCl structure into CsCl structure and high temperature converts CsCl into NaCl.

If the radius of the octahedral void is \( r \) and radius of the atoms in close packing is \( R \), derive relation between \( r \) and \( R \).

The figure shows the cross section of an octahedral void. In Triangle ABC, \( BC^2 = AB^2 + AC^2 \)

\[ \Rightarrow (2R)^2 = (r + R)^2 + (r+R)^2 \]

\[ \Rightarrow 4R^2 = 2(r + R)^2 \]

\[ \Rightarrow 2R^2 = (r + R)^2 \]

\[ \Rightarrow r + R = \sqrt{2} R \]

\[ \Rightarrow \frac{r}{R} + 1 = \sqrt{2} \]

\[ \Rightarrow \frac{r}{R} = \sqrt{2} - 1 = 1.414 - 1 \]

\[ \Rightarrow r = 0.414 R \]

Ferric oxide crystallizes in a hexagonal closed pack array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Deduce the formula of the ferric oxide.

No. of atoms in one unit cell of hcp structure = 6
No. of oxide ions per unit cell = 6
No. of octahedral voids = 6
Since ferric ions occupy only two out of every three octahedral voids, therefore, no. of octahedral voids occupied by ferric ions = \( \frac{2}{3} \times 6 = 4 \)
Stoichiometric ratio of \( Fe^{3+} \) and \( O^{2-} \) is 4 : 6 = 2 : 3
Hence the formula of ferric oxide is \( Fe_2O_3 \)

Analysis shows that nickel oxide has the formula \( Ni_{0.98} O_{1.00} \). What fraction of nickel exist as \( Ni^{2+} \) and \( Ni^{3+} \) ions?

Let amount of \( Ni^{3+} \) be \( x \) mol.
Then amount of \( Ni^{2+} \) is \((0.98 - x)\)
Total oxidation number of \( Ni \) in the compound is \( 3x + 2(0.98 - x) \)
Oxidation number of oxygen is -2
Since the sum of the oxidation number of all the constituents in a compound is zero.

\[ \Rightarrow 3x + 2(0.98 - x) - 2 = 0 \]

\[ \Rightarrow 3x + 1.96 - 2x - 2 = 0 \]

\[ \Rightarrow x = 0.04 \]

Hence, \% of \( Ni^{3+} = \frac{0.04}{0.04 + 0.98} \times 100 = 4.08\% \)
\% of \( Ni^{2+} = 100 - 4.08 = 95.92\% \)

Relationship between density \( (d) \) and the dimension of unit cells.

Let the edge length of unit cell be \( a \)
There fore volume of unit cell = \( a^3 \)
Let no. of atoms in unit cell = \( Z \)
Gm. Atomic mass = \( M \)
There fore mass of one atom = \( M / N_A \)
Where \( N_A = \text{Avogadro's number i.e.} \ 6.023 \times 10^{23} \)
Silver crystallizes in FCC lattice. If edge length of the cell is 4.05 x 10^{-8} cm and density is 10.5 gm/cm³, calculate atomic mass of silver.

Given data-
Edge length (a) = 4.07 X 10^{-8} cm
Density (d) = 10.5 gm/cm³
Since silver crystallizes in fcc lattice, so rank, i.e. the no. of silver atoms per unit cell (z) = 4

N_A = 6.023 X 10^{23}

\[ d = \frac{ZM}{a^3N_A} \]

So
\[ a^3 = \frac{dN_A}{Z} \]

\[ M = \frac{10.5 \times (4.07 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{4} \]

= 107.1 gm/mol

So atomic mass of silver = 107.1 amu

Niobium crystallizes in body-centered cubic structure. If density is 8.55 g/cm³, calculate atomic radius of niobium using its atomic mass 93 u.

Density (d) = 8.55 gm/cc
Atomic mass (M) = 93 gm/mol
Rank (Z) = 2

\[ d = \frac{M}{a^3N_A} \]

\[ a^3 = \frac{8.55 \times 6.023 \times 10^{23}}{2 \times 93} \]

\[ a^3 = 36.09 \times 10^{-24} \text{ C.C} \]

\[ a = (36.09 \times 10^{-24})^{1/3} = 3.305 \times 10^{-8} \text{ cm} \]

In bcc, a = \frac{4}{\sqrt{3}} r
\[ r = \frac{\sqrt{3}}{4} a \]

\[ r = \frac{\sqrt{3}}{4} \times 3.305 \times 10^{-8} \]

= 1.43 \times 10^{-8} \text{ cm} = 14.3 \text{ nm} 

Copper crystallises into a fcc lattice with edge length 3.61 \times 10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g/cm³.

For fcc, rank (Z) = 4
Edge length (a) = 3.61 \times 10^{-8} cm
Mol.mass (M) = 63.5 gm/mol.

\[ d = \frac{ZM}{a^3N_A} \]

\[ d = \frac{4 \times 63.5}{(3.61 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 8.96 \text{ gm/cm³} \]

So, the measured value is nearly equal to the calculated value.

Crystal defect → Internal irregularities of crystals is known as crystal defect.
# Single crystals are formed when the process of crystallization occurs at extremely slow rate.
# Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.
# Line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points.
# Point defects do not disturb the stoichiometric of the solid is known as stoichiometric defect or intrinsic defect or thermodynamic defect.
# Vacancy defect – When some of the lattice sides are vacant, the crystal is said to have vacancy defect. This results the decrease in density of the substance. This defect develops when a substance is heated.
# Interstitial defect - When some constituent particles occupy an interstitial site, the crystal is said to have interstitial defect. This defect increases the density of the substance.

**Schottky defect**

1. It occurs when a pair of ions of opposite charge are missing from the ideal lattice.
2. The presence of a large number of Schottky defect in a crystal lowers its density.
3. This defect occurs if cation and anion having similar size with high coordination number.
4. In sodium chloride, there is one schottky defect for $10^{16}$ ions. One c.c of sodium chloride contains $10^{22}$ ions. Therefore, one cc of sodium chloride possesses $10^6$ schottky pair of ions.

**Frenkel defect**

1. When an ion leaves its position in the lattice and occupy interstitial site leaving a gap in the crystal i.e. it creates a vacancy defect and interstitial defect.
2. This defect will occur if size of cation is smaller than anion, with low coordination number.
3. Frenkel defects are not found in pure alkali halide. Due to larger size of cations, ions can not accommodate in interstitial site.
4. Frenkel defect are found silver halide, because silver ions are smaller in size and can get into the interstitial site.
5. The Frenkel defect does not change the density of the solid.
6. In silver bromide, both Schottky and Frenkel defects are found.

**Metal excess defect**

[a] F-Centers ( Farbe: means colour )

1. When there is an excess of metal ions in non-stoichiometric compounds, the crystal lattice has vacant anion site. The anion sites occupied by electrons are called F-centre.
2. The F-centers are associated with the colour of the compounds. Excess of K in KCl makes the crystal violet. Excess of Li in LiCl makes the crystal pink.
3. Solid containing F-centre are paramagnetic, because the electrons occupying the F-centers are unpaired.
4. When the crystal having F-centers are exposed to light, they become photoconductor.

[b] Metal excess defect due to presence of extra cation at the interstitial site

Zinc oxide is white in colour at room temperature on heating, it looses oxygen and turns yellow.

$$\text{ZnO} \xrightarrow{\text{heating}} \text{Zn}^{2+} + \frac{1}{2} \text{O}_2 + 2e^-$$

Now there is excess of zinc in the crystal and its formula becomes $\text{Zn} \; _{1+x} \; \text{O}$

The excess zinc ions move to interstitial site and the electrons to neighboring interstitial site.
**Metal deficiency defect**
FeO, mostly found with a composition of Fe$_{0.95}$O i.e. range from Fe$_{0.93}$O – Fe$_{0.96}$O. In crystals of FeO, some Fe$^{2+}$ ions are missing and the loss of positive charge is made up by the presence of required number of Fe$^{3+}$ ions.

**Electron sea model of metallic bonding**
[1] A metal consists of a lattice of positive ions (kernel) immersed in a sea of valence electrons (mobile electrons)
[2] The force of attraction between the mobile electrons and the kernels is known as metallic bond.
[3] The electrical and thermal conductivity of metals can be explained by the presence of mobile electrons in metal.

**The Band Model Of Metallic Bonding**
The band model of metal is based on molecular orbital theory. When a large no. of orbital overlap in metal, it results a continuous energy level produced by a large number of molecular orbital is called energy band.

![Energy Band Diagram](image)

The lowest unoccupied energy band is known as **conduction band**
The highest occupied energy band is known as **valence band**
The energy difference between the top of valence band and the bottom of the conduction band is known as **energy gap**.

**Impurity defect (Doping)**
The introduction of defects in a particular crystalline solid by the addition of other elements is known as doping.
Doping increases the conductivity of crystal. For example, if we mix strontium chloride (SrCl$_2$) with sodium chloride, some strontium (Sr$^{2+}$) ions occupy the lattice sites of sodium ions (Na$^+$) and equal number of sodium (Na$^+$) sites remain vacant. Such vacancies in the crystal increase the electrical conductivity because certain ions from the neighboring sites can move into these vacant holes. In this defect the number of positive ions are less as compared to negative ions. Crystals with such defects also act as semiconductor. Since the conductivity is due to holes, these are known as P-type semiconductors.

**If NaCl is doped with 10$^{-3}$ mol % of SrCl$_2$. What is the concentration of cation vacancies?**
The addition of SrCl$_2$ to NaCl produces cation vacancies equal in number to that of Sr$^{2+}$ ions.
No. of moles of SrCl$_2$ added to one mol of NaCl = 10$^{-3}$/100 = 10$^{-5}$ mol.
No. of holes created in one mole of NaCl = 10$^{-5}$ X 6.023 X 10$^{23}$ = 6.023 x 10$^{18}$

**Semiconductor**
These are solids whose conductivity lies in between those of conductors and insulators. The conductivity of semiconductors increases with increase of temperature.

**Intrinsic semiconductor**
An insulator capable of conducting electric current at higher temperature or when irradiated with electromagnetic radiations, are known as intrinsic semiconductor.
This happens because certain covalent bonds are broken and the released electrons are in a position to conduct electric current. e.g. Silicon, Germanium.

**Extrinsic semiconductor**
These are formed when impurities of certain elements are added (doped) to insulator.
N-type semiconductors
It is obtained by doping group – 14 elements with group – 15 elements.
Suppose Si is doped with P with 5 valence electrons, out of 5 valence electrons, only 4 valence electrons are involved in bond formation.
The fifth electron is not bound anywhere and can be easily promoted to the conduction band. The conduction is thus mainly caused by the movement of electrons.

P-type semiconductors
It is obtained by doping group – 14 elements with group – 13 elements.
Suppose Si is doped with Ga which has 3 valence electrons, 3 valence electrons are involved in bond formation with neighboring Si atom.
A vacancy is left which can be filled by the transfer of a valence electron from a neighboring Si atom.
The movement of electron into the vacancy leaves behind a hole which carries positive charge.
Another electron from a neighboring Si atom can move into the hole leaving behind another hole. It appears as if the hole has moved through the lattice.
The movement of positively charged hole is responsible for the conduction of charge.

Non-stoichiometric cuprous oxide, Cu₂O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1. Can you account for the fact that this substance is a p-type semiconductor?
[1] Since Cu₂O is non-stoichiometric oxide, it contains Cu in two oxidation states, +1 and +2.
[2] Cu²⁺ provides an excess of positive charge. As a result an electron from a neighboring Cu⁺ is transferred to Cu²⁺.
[3] The transfer of electron leaves behind a hole, which carries an extra positive charge and a negative hole is created.
[4] It appears that the positive hole moves through the lattice, hence it appears as P-type semiconductor.

12 – 16 and 13 – 15 compounds
Combination of elements of Gr – 13 and Gr – 15 or Gr – 12 and Gr – 16 produce compounds which stimulate average valence of four as in Ge or Si.
12 – 16 compounds → ZnS, CdS, CdSe, HgTe
13 – 15 compounds → InSn, AlP, GaAs

Magnetic properties
[1] Diamagnetic
Diamagnetic substances are the substances which are weakly repelled by a magnetic field. The electrons in diamagnetic substances are all paired. They do not contain unpaired electrons.
e.g. TiO₂, NaCl, C6H6, N2, Zn

[2] Paramagnetic
Paramagnetic substances are those which are attracted by a magnetic field but they lose their magnetism in the absence of magnetic field.
These substances have permanent magnetic dipole, due to presence of atoms, molecules or ions containing unpaired electrons.
e.g. Cu²⁺, Fe³⁺, O₂, NO, CuO, etc.
Substances containing unpaired electrons are further classified as:
(a) **Ferromagnetic substances** -> Ferromagnetic substances are those substances which are strongly attracted by a magnetic field and can be made into permanent magnets. These substances show magnetism even in the absence of a magnetic field. The large magnetism in these substances is due to the spontaneous alignment of magnetic moment, i.e., unpaired electron in the same direction. Example: Iron, cobalt, nickel, gadolinium and CrO₂. CrO₂ is used to make magnetic tapes for audio recording.

(b) **Anti-ferromagnetic substances** -> Anti-ferromagnetic substances are those substances in which equal number of magnetic moments are aligned in opposite directions so as to give zero net moment. Example: MnO, MnO₂ and Mn₂O₃.

(c) **Ferrimagnetic substances**
Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers. They are weakly attracted by magnetic field as compared to ferromagnetic substances. Example: Fe₃O₄ (magnetite) and ferrites like MgFe₂O₄ and ZnFe₂O₄. These substances also lose ferrimagnetism on heating and become paramagnetic.

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**Schematic alignment of magnetic moments in (a) ferromagnetic, (b) antiferromagnetic and (c) ferrimagnetic.**