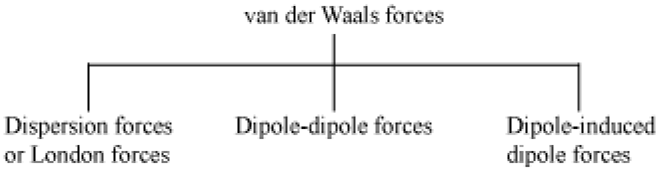
States of Matter

Intermolecular Forces

- Attractive and repulsive forces between interacting particles (atoms and molecules)

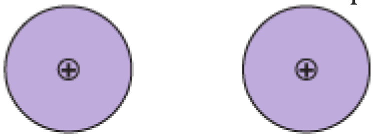
- Do not include ionic and covalent bonds

- Attractive intermolecular forces are known as van der Waals forces.

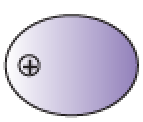


- **Dispersion Forces or London Forces**

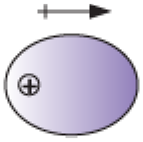
- Forces of attraction between two temporary dipoles
- Occur between atoms or non-polar molecules



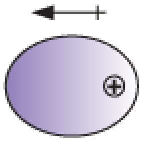
- Symmetrical distribution of electronic charge cloud
- Atoms or non-polar molecules have no dipole moment as they are electrically symmetrical. However, for some reason, momentarily an atom or non-polar molecule becomes electrically unsymmetrical. As a result, instantaneous dipole is developed on that atom for a very short time. This instantaneous dipole induces dipole on another atom close to it.



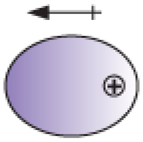
Atom with instantaneous dipole, more electron density on the right hand side



Atom with induced dipole



Atom with more electron density on the left hand side

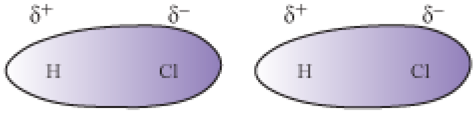


Atom with induced dipole

- $E \propto \frac{1}{r^6}$, where E = Interaction energy
- r = Distance between two interacting particles
- Occur only at short distances (~500 pm)
- Depend on the polarisability of the particle

- **Dipole-Dipole Forces**

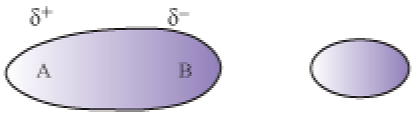
- Forces between molecules possessing permanent dipole
- London force < Dipole-dipole force < Ion-ion force
- Increase with decrease in distance
- For stationary polar molecules,
- $E \propto \frac{1}{r^3}$
- And for rotating polar molecules,
- $E \propto \frac{1}{r^6}$
- Where, E = Interaction energy
- r = Distance between the polar molecules
- Polar molecule can also interact by London forces, because of which the overall intermolecular forces in polar moecules increase.
- Dipole-dipole interaction between two HCl molecules:



- Dipole-dipole interaction between two HCl molecules

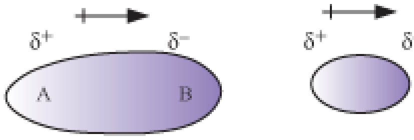
- **Dipole-Induced Dipole forces**

- Forces between polar molecules and non-polar molecules
- Occur because polar molecule induces dipole on non-polar molecule



Permanent dipole (a polar molecule)

Non-polar molecule



- Permanent dipole (a polar molecule)

Induced dipole in a non-polar molecule

- Depends upon the dipole moment present in the permanent dipole and the polarisability of the non-polar molecule.
- $E \propto \frac{1}{r^6}$, where E = Interaction energy
- r = Distance between the two molecules
- Intermolecular forces between polar and non-polar molecules = London forces + Dipole-induced dipole forces

Ion-dipole Interaction

- An ion can interact with the oppositely charged site of a polar molecule to form an attractive force of interaction between the ion and polar molecule.
- Strength of interaction depends upon magnitude of dipole moment and size of the polar molecule and charge and size of the ion.
- Since charge density on a cation is higher than on an anion, as a result interaction between a cation and a polar molecule is stronger than between an anion of same charge and the polar molecule.

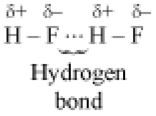
Hydrogen Bonding

- Special case of dipole-dipole interaction

- Force between hydrogen attached to an electronegative atom of one molecule and an electronegative atom of different molecule

- Limited to electronegative atoms N, O, and F (sometimes Cl also)

- Formation of hydrogen bond:



$$\overset{\delta+}{H}-\overset{\delta-}{F}\underbrace{\cdots}_{\text{Hydrogen bond}}\overset{\delta+}{H}-\overset{\delta-}{F}$$

Repulsive Forces

- Increases with decrease in distance

- Due to this reason ,

- solids are harder to compress than liquids

- liquids are harder to compress than gases

Thermal Energy

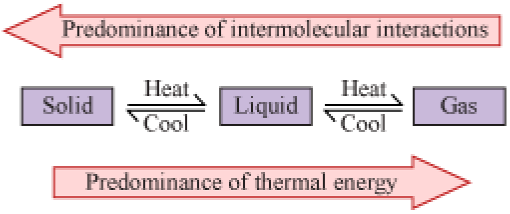
- Energy of a body resulting from atomic and molecular motion
- Measure of average kinetic energy of particles of matter
- Directly proportional to temperature

Intermolecular Forces vs. Thermal Interaction

- Intermolecular forces ––– hold molecules together

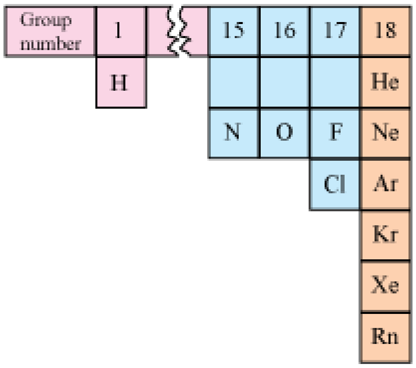
  Thermal interactions ––– keep molecules apart

- Intermolecular forces and thermal energy balance each other to different extent resulting in the three states of matter (solid, liquid, and gas).



The Gaseous State

- Physical Properties:
- Can be compressed to a large extent
- Exerts pressure equally in all directions
- Much less denser than solids and liquids
- Does not have any shape and volume
- Mixes evenly and completely in all proportions
- Reason for these properties:
- Negligible intermolecular forces of interaction
- Eleven elements which exist as gases under normal atmospheric condition are as follows:



Group number	1		15	16	17	18
	H					He
			N	O	F	Ne
					Cl	Ar
						Kr
						Xe
						Rn

Measurable Properties of Gases

- Mass: Mass of one mole of gas molecules is equal to the molar mass in grams.
- Volume: The volume of a gas is the volume of the container in which it is stored.
- Temperature: The degree of hotness or coldness of a body.
- Pressure: It is the force exerted by the molecules of the gas per unit area on the walls on the container.
- Density: It is the mass of the gas per unit volume.

Boyle's Law and Charle's Law

Boyle’s Law

- Relation between pressure (*p*) and volume (*V*)

- Statement – At constant temperature, the pressure of a fixed amount (number of moles, *n*) of a gas is inversely proportional to its volume.

- Explanation – Based on kinetic theory:
- Number of particles and their average kinetic energy is constant for a given mass of gas.
- When volume of a certain mass of gas is reduced to half, the particles have lesser space to move around.
- The number of collision of the particles with the walls of the container doubles, thus increasing the pressure to twice the original value.
- Mathematically,

$$p \propto \frac{1}{V} \text{(at constant } T \text{ and } n\text{)}$$

$\Rightarrow p = k_1 \frac{1}{V}$, where k_1 = Proportionality constant

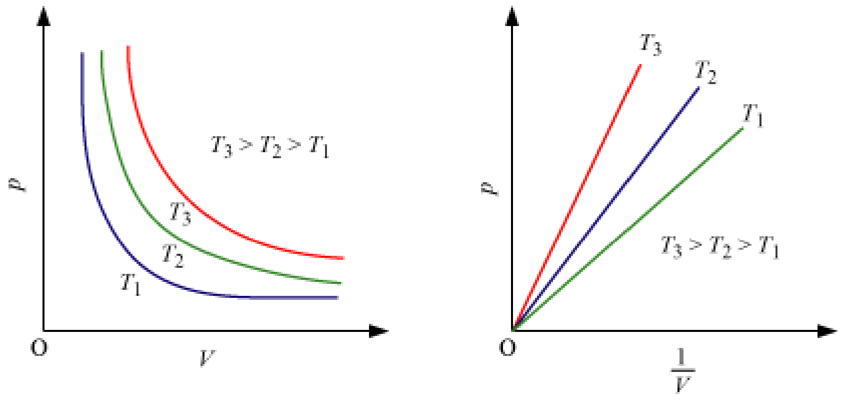
$$\Rightarrow pV = k_1$$

- From the above equation, it is found that at constant temperature, the product of pressure and volume of a fixed amount of a gas is constant.

- The value of k_1 depends upon

  - amount of the gas
  - temperature of the gas
  - units of p and V

Graphical representation of Boyle's law



p vs V graph

p vs $\frac{1}{V}$ graph

  - Each line is called isotherm (at constant temperature plot).

- If at constant temperature,

  V_1 = Volume of a gas at pressure p_1

  V_2 = Volume of the same gas at pressure p_2

  Then,

  $p_1V_1 = p_2V_2$ = Constant

  $$\Rightarrow \frac{p_1}{p_2} = \frac{V_2}{V_1}$$

- Relationship between density (d) and pressure (p):

We know that,

$$d = \frac{m}{V}$$

Where, m = Mass of a gas

V = Volume of the gas

$$\Rightarrow d = \left(\frac{m}{k_1}\right)p \quad \left(\text{since } p = k_1\frac{1}{V}\right)$$
$$\Rightarrow d = k'p$$
$$\Rightarrow d \propto p$$

- From the above equation, it is known that density is proportional to the pressure of a fixed amount of a gas.
- Significance of Boyle's law:
  - Mountaineers carry oxygen cylinders with them as at higher altitudes as the pressure is low.

Example

Rita has two cylinders. One is empty and the other contains compressed nitrogen at 25 atm. She wants to distribute the gas in the two cylinders. To do so, she connects the two cylinders. If the volume of the cylinder containing the gas is 50 L and that of the empty one is 80 L, then what will be the pressure inside the two cylinders?

Solution:

According to Boyle's law,

$$p_1V_1 = p_2V_2$$

Given, p_1 = 25 atm

V_1 = 50 L

V_2 = (50 + 80) L = 130 L

Now, 25 atm × 50 L = p_2 × 130 L

$$\Rightarrow p_2 = \frac{25 \times 50}{130} \text{atm}$$
$$= 9.62 \text{ atm}$$

Hence, the pressure inside the cylinders is 9.62 atm.

Charles' Law

- Relation between temperature (*T*) and volume (*V*)

- Statement − At constant pressure, the volume of a fixed amount of a gas is directly proportional to its absolute temperature.
- Explanation − On the basis of kinetic theory
- Average kinetic energy of the particles of a gas is directly proportional to the absolute temperature of the gas
- When temperature is increased at constant pressure, the kinetic energy of the particles increases.
- The number and intensity of collisions with the walls of the container increase, thereby increasing the volume at constant pressure.

- Mathematically,

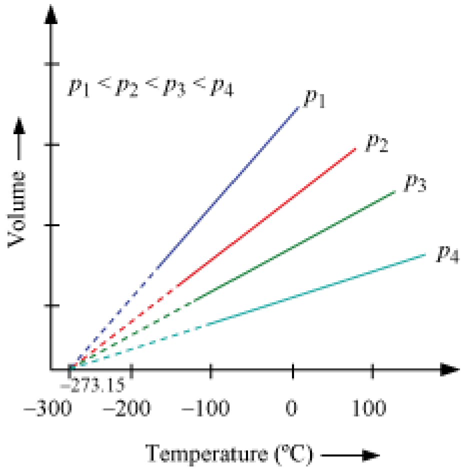
  $V \propto T$

  $\Rightarrow V = k_2 T$, where k_2 = Proportionality constant

- The value of k_2 depends upon

  - pressure of the gas
  - amount of the gas
  - unit of volume

- Graphical representation



  - Straight line
  - Interception on zero volume at 273.15°C
  - Each line is called isobar (constant pressure plot).

- Derivation

For each degree rise in temperature, volume of a gas increases by $\frac{1}{273.15}$ of the original volume of the gas at 0°C.

Suppose, V_0 = Volume of a gas at 0°C

V_t = Volume of the same gas at t°C

Then,

$$V_t = V_0 + \frac{t}{273 \cdot 15} V_0$$

$$\Rightarrow V_t = V_0 \left(1 + \frac{t}{273 \cdot 15} \right)$$

$$\Rightarrow V_t = V_0 \left(\frac{273 \cdot 15 + t}{273 \cdot 15} \right) \qquad \text{(i)}$$

According to Kelvin temperature scale (also called absolute temperature scale or thermodynamic scale),

$T = 273.15 + t$

$T_0 = 273.15$

From equation (i), we obtain

$$V_t = V_0\left(\frac{T_t}{T_0}\right)$$

$$\Rightarrow \frac{V_t}{V_0} = \frac{T_t}{T_0}$$

Or, we can write

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$

$$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\Rightarrow \frac{V}{T} = \text{constant} = k_2$$

$$\Rightarrow V = k_2 T$$

- Significance of Charle's law:
- Hot air is filled in the balloons used for meteorological purposes.

Example

It is desired to increase the volume of 5 L of a gas by 40% without changing the pressure. To what temperature should the gas be heated if its initial temperature is 298 K?

Solution:

Desired increase in the volume of gas = 40% of 5 L

$$= \frac{40}{100} \times 5 \text{ L}$$

= 2 L

Therefore, final volume of the gas = (5 + 2) L = 7 L

Applying Charles' law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Now, V_1 = 5 L

T_1 = 298 K

V_2 = 7 L

Therefore, $\frac{5\ \text{L}}{298\ \text{K}} = \frac{7\ \text{L}}{T_2}$

$$\Rightarrow T_2 = \frac{7\ \text{L} \times 298\ \text{K}}{5\ \text{L}}$$
$$= 417.2\ \text{K}$$

Standard Temperature and Pressure(STP)

The pressure and temperature of the gas keeps varying frequently. Hence, we choose a standard value for temperature and pressure to which the gas volumes can be referred. The standard value chosen are 0°0°C or 273K for temperature and 1 atm or 760 mm of Hg for pressure and are commonly known as **S.T.P.**

Diffusion

Diffusion is defined as the random movement of gaseous molecules from regions of higher concentration to regions of lower concentration. It is a physical process and can only occur if the gases do not react with each other.

Graham's Law of Diffusion:

It states that the rate of diffusion of gas is inversely proportional to the square root of its density at the given temperature and pressure.

r∝1d√ r= Kd√ or K=rd−−√r= rate of diffusiond=density of gasK= proportionality constant Relationship between diffusion and massr= Kd√r∝Kmv√   as d=m (mass)v (volume)Hence, r=Kvm−−√   or   r∝1m√r∝1d r= Kd or K=rdr= rate of diffusiond=density of gasK= proportionality constantRelationship between diffusion and massr= Kdr∝Kmv   as d=m (mass) v (volume)Hence, r=Kvm   or   r∝1m

It means that the rate of diffusion is inversely proportional to the square root of mass of the gas.

Gay- Lussac's Law and Avogadro's Law

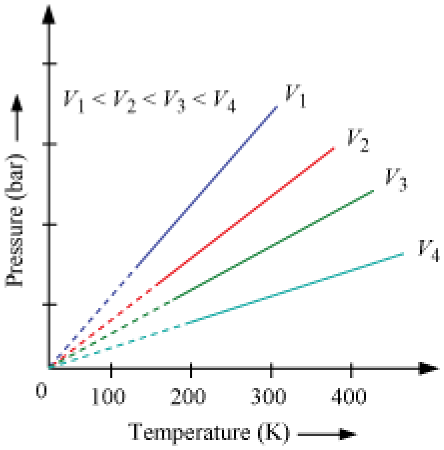
Gay-Lussac's Law

- Relation between pressure and temperature
- Statement – At constant volume, the pressure of a fixed amount of a gas is directly proportional to the temperature.
- Mathematically,

$p \propto T$

$\Rightarrow \frac{p}{T}$ = constant = k_3

- Graphical representation at constant volume



- Each line is called isochore (constant volume plot).
- If at constant volume,

p_1 = Pressure of a gas at T_1

p_2 = Pressure of the same gas at T_2

Then,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Example

An iron tank contains helium at a pressure of 3.0 atm at 300 K. The tank can withstand a maximum pressure of 12.0 atm. The building in which the tank has been placed catches fire. Predict whether the tank will blow up first or melt. (Given, melting point of iron is 1808 K)

Solution:

To calculate the pressure built up in the tank at the melting point of iron, we have to apply Gay-Lussac's law.

According to Gay-Lusaac's Law,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Here, p_1 = 3.0 atm

T_1 = 300 K

T_2 = 1808 K

Now, $\frac{3.0 \text{ atm}}{300 \text{ K}} = \frac{p_2}{1808 \text{ K}}$

$$\Rightarrow p_2 = \frac{3.0 \times 1808}{300} \text{ atm}$$

= 18.08 atm

It is found that pressure of the gas in the tank is much more than 12 atm at the melting point. Hence, the tank will blow up before reaching the melting point.

Avogadro Law

- Relation between volume (V) and amount of substance (number of moles n)
- Statement – Under the same conditions of temperature and pressure, equal volumes of all gases contain equal number of molecules.

That is, at constant temperature and pressure, the volume of a gas depends upon the amount (number of mole n) of the gas.

Mathematically,

$V \propto n$

$\Rightarrow V = k_4 n$

Where, k_4 = Proportionality constant

- Avogadro constant = Number of molecules present in one mole of a gas = 6.022×10^{23}
- At STP (273.15 K and 1 bar), molar volume of an ideal gas is 22.71098 L mol^{-1}.
- If m = Mass of a gas

  M = Molar mass of the gas

  Then,

  $$n = \frac{m}{M}$$

  Therefore, $V = k_4 \frac{m}{M}$ (Since $V = k_4 n$)

  $$\Rightarrow M = k_4 \frac{m}{V}$$

  $$\Rightarrow M = k_4 d \quad \left(\text{Density, } d = \frac{m}{v}\right)$$

- From the above equation, it can be concluded that at a given temperature and pressure, density of a gas is directly proportional to its molar mass.

Ideal Gas Equation, Dalton's Law of Partial Pressure

Ideal Gas

- The gas which strictly follows Boyle’s law, Charles’ law and Avogadro law
- The intermolecular forces are assumed to be absent between the molecules of an ideal gas.

- Under a certain specific condition (when the intermolecular forces are negligible), real gases follow the above laws.

Ideal Gas Equation

- Equation obtained by the combination of Boyle's law, Charles' law and Avogadro law

Boyle's law: $V \propto \frac{1}{p}$ …(At constant T and n)

Charles' law: $V \propto T$ …(At constant p and n)

Avogadro law: $V \propto n$ …(At constant p and T)

By combining the above three laws, we have

$$V \propto \frac{nT}{p}$$

$$\Rightarrow V = \mathrm{R}\frac{nT}{p}$$

$\Rightarrow pV = n\mathrm{R}T$…….(i)

R = Proportionality constant, known as Universal Gas Constant

Equation (i) is called ideal gas equation.

- At STP, for one mole of a gas, R = 8.314 $\mathrm{JK^{-1}\ mol^{-1}}$

Or, R = 8.20578×10^{-2} L atm $\mathrm{K^{-1}\ mol^{-1}}$

- It is also called the equation of state
- Reason: It relates between four variables and describes the state of a gas.
- **Combined gas law:**

If the temperature, volume and pressure of a fixed amount of a gas vary from T_1, V_1 and p_1 to T_2, V_2 and p_2, then we have

$$\frac{p_1V_1}{T_1} = n\text{R} \qquad \text{(ii)}$$

$$\frac{p_2V_2}{T_2} = n\text{R} \qquad \text{(iii)}$$

From equations (ii) and (iii), we have

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \qquad \text{(iv)}$$

Equation (iv) is called combined gas law.

Examples

1. A vessel of 200 mL capacity contains a certain amount of gas at 27°C and 0.9 bar pressure. The gas is then transferred into another vessel of capacity 150 mL at 27°C. What would be the pressure of the gas in the vessel of capacity 150 mL?

Solution:

According to combined gas law,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

Here, initial pressure of the gas, $p_1 = 0.9$ bar

Final pressure of the gas, $p_2 = ?$

Initial volume of the gas, $V_1 = 200$ mL

Final volume of the gas, $V_2 = 150$ mL

Initial temperature of the gas, $T_1 = (27 + 273)$ K = 300 K

Final temperature of the gas, $T_2 = (27 + 273)$ K = 300 K

Now, $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

$$\Rightarrow \frac{0.9 \times 200}{300} = \frac{p_2 \times 150}{300}$$

$$\Rightarrow p_2 = \frac{0.9 \times 200 \times 300}{150 \times 300}$$

= 1.2 bar

Hence, the pressure of the gas in the vessel of capacity 150 mL would be 1.2 bar.

2. How many grams of nitrogen are present in an 8.21 L sample of a gas at 5 atm and −23°C?

Solution:

It is given that,

$V = 8.21$ L

$p = 5$ atm

$T = (-23 + 273)\text{K} = 250$ K

Here, $R = 0.0821$ L atm K^{-1} mol^{-1}

From the ideal gas equation, we have

$pV = nRT$

$$\Rightarrow n = \frac{pV}{RT}$$

$$= \frac{5 \text{ atm} \times 8.21 \text{ L}}{0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 250 \text{ K}}$$

= 2 mol

Molar mass of nitrogen gas= 28 g

This means that 1 mole of nitrogen gas weighs 28 g.

Therefore, 2 moles of nitrogen gas will weigh 2 × 28 g, i.e., 56 g.

Thus, at 5 atm and −23°C, 56 g of nitrogen gas are present in an 8.21 L sample of the gas.

- Relation between density and molar mass of a gaseous substance:

  $pV = nRT$

  $\Rightarrow pV = \frac{m}{M}RT$ ($n = \frac{m}{M}$ Where, m = Mass of the gas, M = Molar mass of the gas)

  $\Rightarrow \frac{m}{MV} = \frac{p}{RT}$

  $\Rightarrow \frac{d}{M} = \frac{p}{RT}$ (Where, Density, $d = \frac{m}{V}$)

  $\Rightarrow M = \frac{dRT}{p}$

  Dalton's Law of Partial Pressures

- Partial pressure: Pressure exerted by the individual gases in a mixture
- Statement: At constant temperature, the total pressure exerted by a mixture of two or more non-reacting gases, enclosed in a definite volume, is equal to the sum of the partial pressures of the individual gases.
- Mathematically,

  $P_{\text{total}} = p_1 + p_2 + p_3 + \ldots\ldots\ldots\ldots$ (At constant T and V)

  Where, p_{total} = Total pressure exerted by the mixture

  $p_1 + p_2 + p_3, \ldots$ = Partial pressures of the individual gases

- $p_{\text{dry gas}} = p_{\text{total}}$ − Aqueous tension

  Where, $p_{\text{dry gas}}$ = Pressure of dry gas

  p_{total} = Total pressure

- Aqueous tension: Pressure exerted by saturated water vapour

- Partial pressure in terms of mole fraction:

  Suppose three gases are enclosed in a vessel of volume, V at temperature, T and exert partial pressures, p_1, p_2 and p_3 respectively.

  Then, we have

$$p_1 = \frac{n_1 \mathrm{R}T}{V}$$
$$p_2 = \frac{n_2 \mathrm{R}T}{V}$$
$$p_3 = \frac{n_3 \mathrm{R}T}{V}$$

  Where, n_1, n_2, n_3 = Number of moles of the gases

  Now, $p_{\text{total}} = p_1 + p_2 + p_3$

$$= n_1 \frac{\mathrm{R}T}{V} + n_2 \frac{\mathrm{R}T}{V} + n_3 \frac{\mathrm{R}T}{V}$$
$$= (n_1 + n_2 + n_3) \frac{\mathrm{R}T}{V}$$

  By dividing p_1 by p_{total}, we have

$$\frac{p_1}{p_{\text{total}}} = \left(\frac{n_1}{n_1 + n_2 + n_3} \right) \frac{\mathrm{R}TV}{\mathrm{R}TV}$$
$$\Rightarrow \frac{p_1}{p_{\text{total}}} = \frac{n_1}{n_1 + n_2 + n_3}$$
$$\Rightarrow \frac{p_1}{p_{\text{total}}} = \frac{n_1}{n} \quad (n = n_1 + n_2 + n_3)$$
$$\Rightarrow \frac{p_1}{p_{\text{total}}} = x_1$$
$$\Rightarrow p_1 = x_1 p_{\text{total}}$$

- x_1 is called the mole fraction of the first gas

- General equation

  $p_i = x_i \, p_{\text{total}}$

p_i = Partial pressure of *i*th gas

x_i = Mole fraction of *i*th gas

Example

A gaseous mixture of oxygen and nitrogen contains 22.4 g of oxygen and 145.6 g of nitrogen. The pressure of the mixture is 700 Nm^{-2}. What are the respective partial pressures of oxygen and nitrogen in the mixture?

Solution:

Molar mass of O_2 = 32 g mol^{-1}

Molar mass of N_2 = 28 g mol^{-1}

Therefore, number of moles of O_2 in the mixture $= \frac{22.4\text{g}}{32 \text{ g mol}^{-1}} = 0.7 \text{ mol}$

Number of moles of N_2 in the mixture $= \frac{145.6 \text{ g}}{28 \text{ g mol}^{-1}}$

= 5.2 mol

Hence, mole fraction of O_2, $x_{O_2} = \frac{0.7}{0.7+5.2}$

$= \frac{0.7}{5.9}$

= 0.119

Mole fraction of N_2, x_{N_2} = 1 − 0.119

= 0.881

Given, total pressure, p_{total} = 700 Nm^{-2}

Therefore, partial pressure of O_2, p_{O_2} = x_{O_2} p_{total}

= 0.119 × 700 Nm^{-2}

= 83.3 Nm^{-2}

And, partial pressure of N_2, $p_{N_2} = x_{N_2}$ p_{total}

= 0.881 × 700 Nm^{-2}

= 616.7 Nm^{-2}

Kinetic Molecular Theory of Gases

Kinetic Molecular Theory of Gases

The kinetic theory explains the macroscopic properties of gases, such as temperature, pressure and volume, considering their molecular composition and motion.

Postulates:

- A gas consists of very small particles, atoms and molecules, which move in a random motion.
- These particles have the same mass.
- There is no force of attraction between these particles.
- The volume of the particles is negligible compared to the total volume of the gas.
- Collision of the gas particles takes place either with other particles or with the wall of the container.
- The average kinetic energy of gas particles depends only on the temperature of the system. The total kinetic energy of gas particles remains constant.
- Pressure of the gas arises due to the collision of its molecules with the wall of the container.

On the basis of the above postulates, the equation derived as **kinetic gas equation** is:

PV=13mNAc2rmsPV=13mNAcrms2
Here, *m* is the mass of one molecule, N_A is the Avogadro number and c2rmscrms2is the root mean square speed.

Pressure due to an Ideal Gas

Different Types of Molecular Speeds

Root mean square speed:

crms=n1C1+n2C2+n3C3+...n1+n2+n3+...−−−−−−−−−−−−−−√=3RTM−−−−√=3PVM−−−−√crms=n1C1+n2C2+n3C3+...n1+n2+n3+...=3RTM=3PVM
Here, n_1 is the number of molecule having speed C_2, n_2 is the number of molecule having speed C_2 and so on.
Also, R is the gas constant, T is the temperature, M is the molar mass of the gas, P is the pressure of the gas and V is the volume of the gas.

Most probable speed:
cmp=2RTM−−−−√cmp=2RTM
Here, M is the molar mass of the gas, R is the gas constant and T is the temperature.

Average speed:
cav=n1C1+n2C2+n3C3+...n1+n2+n3+...=8RTM−−−−√cav=n1C1+n2C2+n3C3+...n1+n2+n3+...=8RTM
Here, n_1 is the number of molar having speed C_2, n_2 is the number of molecule having speed C_2 and so on.
Also, R is the gas constant, T is the temperature and M is the molar mass of the gas.

Some Important Relations

Relationship between different types of speeds:

c_{mp}:c_{av}:c_{rms}::1:1.128:1.224
c_{av} = 0.9213 c_{rms}
c_{rms} = 1.086 c_{av}
c_{mp} = 0.816 c_{rms}

Relationship between average kinetic energy of gas and temperature:

The average kinetic energy of a gas molecule can be calculated on the basis of gas equation.
K.E=32RTNA=32kT [RNA=k]K.E=32RTNA=32kT RNA=k
Here, k is Boltzmann's constant and R is the universal gas constant.

Maxwell Distribution of Molecular Velocity

Gas is a collection of tiny particles that are separated from each other by a large empty space; these particles move rapidly in a random motion in all directions. Because of this motion, molecules frequently collide with one another as well as with the wall of the container, thereby resulting in the change in their velocity and direction. Although the molecules in a given sample do not have the same velocity, the fraction of molecules possessing particular velocities remains constant at constant temperature.

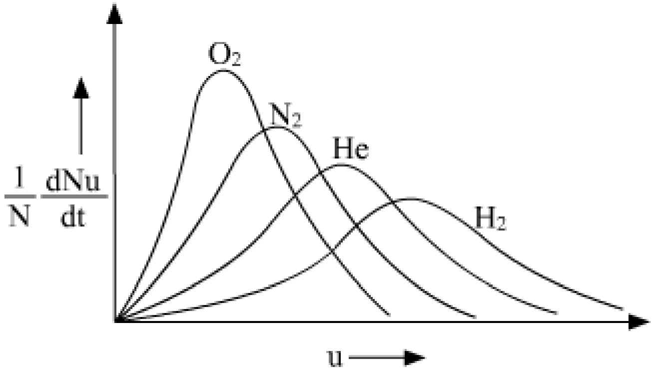
Important features of Maxwell's distribution curve:

- The fraction of molecules having very high or very low molecular speeds is very small. Most number of molecules have speed near to the most probable speed, c_{mp}.

- The total area under the curve gives a measure of the total number of molecules possessing a particular velocity.

- The distribution of molecules is also dependent on the molecular mass of a gas. At constant temperature, a gas with higher molecular mass shows a narrow distribution of speeds compared to that shown by a low-molecular-weight gas.

Maxwell Distribution of Molecular Velocity



- The fraction of molecules with speeds greater than the minimum increases with the increase in speed, reaches to the maximum value and then starts to decrease.

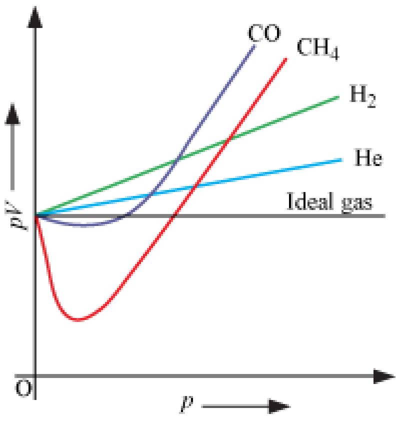
- At constant temperature, the fraction of molecules having a certain speed remains the same, even though the molecules change their speeds continuously because of collisions.

Behaviour of Real Gas

- Real gases show deviation from ideal gas behaviour.

- According to Boyle's law, at constant temperature, pV of a gas is constant, and the pV vs p graph is a straight line parallel to the x-axis at all pressures.

  But real gases do not behave like this.



- Reasons for deviation from the ideal gas behaviour − The two postulates of the kinetic theory which do not hold good:
    - There is no force of attraction and repulsion between the molecules of a gas.
    - Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.
- van der Waals equation:
    - Real gas deviates from ideal gas behaviour as there are forces of attraction and repulsion between the molecules of a gas. At high pressure, while striking the walls of a container, the molecules of a gas are dragged back by other molecules due to the existing force of attraction; therefore, the pressure exerted by the gas is lower than the pressure exerted by an ideal gas.

$$p_{\text{ideal}} = \underset{\substack{\text{Observed}\\ \text{pressure}}}{p_{\text{real}}} + \underset{\substack{\text{Correction}\\ \text{term}}}{\frac{an^2}{V^2}}$$

Where,

n = Number of moles of the gas

V = Volume of the gas

a = van der Waals constant, whose value depends upon the nature of the gas

- Also, at high pressure, the molecules come almost in contact with each other. As a result, repulsive forces come into play which cause the molecules to behave as small but impenetrable spheres. The volume occupied by the gas molecules becomes significant. This is because the movement of the gas particles is restricted to the volume ($V - nb$), instead of V. Here, nb is the approximate total volume of the molecules themselves, excluding the spaces between them.

This means, $V = V - nb$

- Therefore, the ideal gas equation $pV = n\mathrm{R}T$ can be rewritten as

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = n\mathrm{R}T$$

This equation is called Van der Waals equation.

- Significance of 'a':

It is the measure of the magnitude of attractive forces between the molecules of a gas.

Unit: atm L^2 mol^{-2} or bar L^2 mol^{-2}

Larger the value of 'a', larger will be the intermolecular force of attraction.

It is independent of pressure and temperature.

- Significance of 'b':

It is the measure of the effective size of gas molecules.

Unit: L mol^{-1}

- Real gases behave like ideal gas under certain specific conditions when the intermolecular forces are negligible.
- When pressure approaches zero, real gases behave like ideal gas.
- When the volume of a gas is so large that the volume occupied by the molecules is negligible, the gas shows ideal gas behaviour.
- Compressibility factor (Z):
- It is the measure of deviation from ideal behaviour.
- $$Z = \frac{pV}{n\mathrm{R}T}$$

Or

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

- For ideal gas, $Z = 1$
- At low pressure, $Z \approx 1$

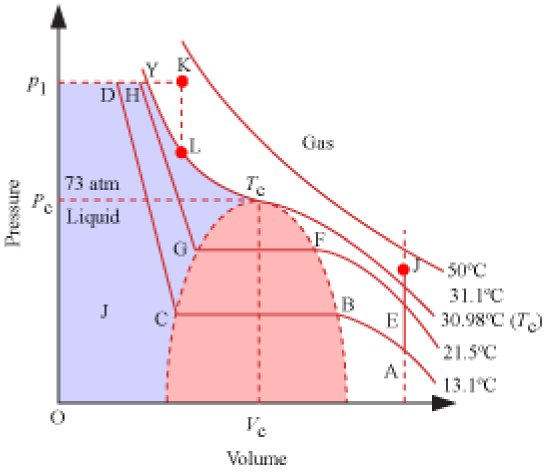
  At high pressure, $Z > 1$

  At intermediate pressure, $Z < 1$
- Boyle temperature or Boyle point:
- The temperature at which a real gas shows ideal gas behaviour over an appreciable range of pressure
- Depends upon the nature of the gas
- Above Boyle point – positive deviation from ideal behaviour
- Below Boyle point – negative deviation from ideal behaviour
- At low pressure and high temperature, gases behave ideally.

Liquefaction of Gases

A gas can be liquefied by increasing its pressure and decreasing its temperature.

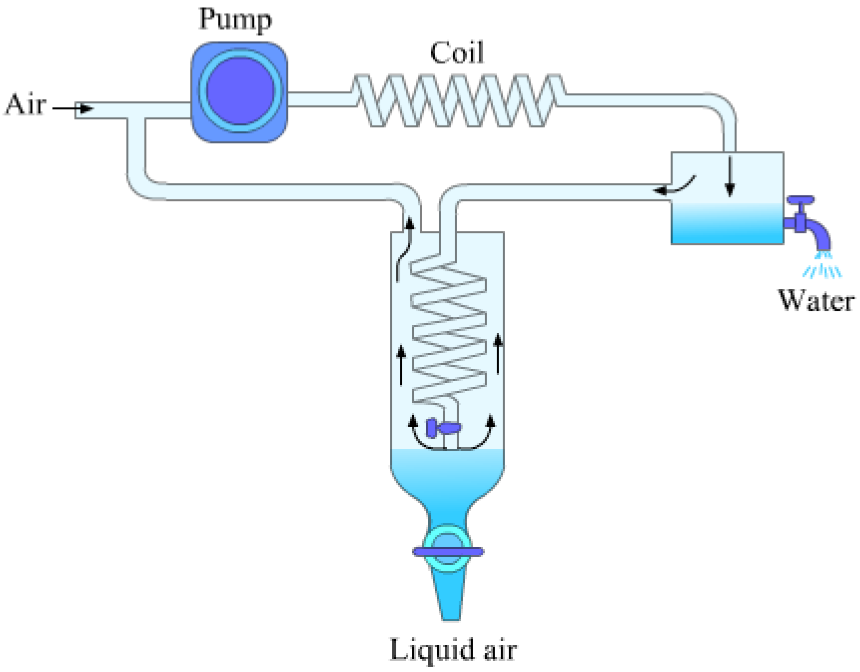
- Critical temperature (T_c) – The temperature above which a gas cannot be liquified, no matter how high pressure may be applied on it.
- Critical pressure (p_c) – the pressure of a gas at critical temperature
- Critical volume (V_c) – the volume of 1 mole of a gas at critical temperature
- Isotherm of carbon dioxide is shown in the figure.



- Critical temperature, critical pressure and critical volume are called critical constants.

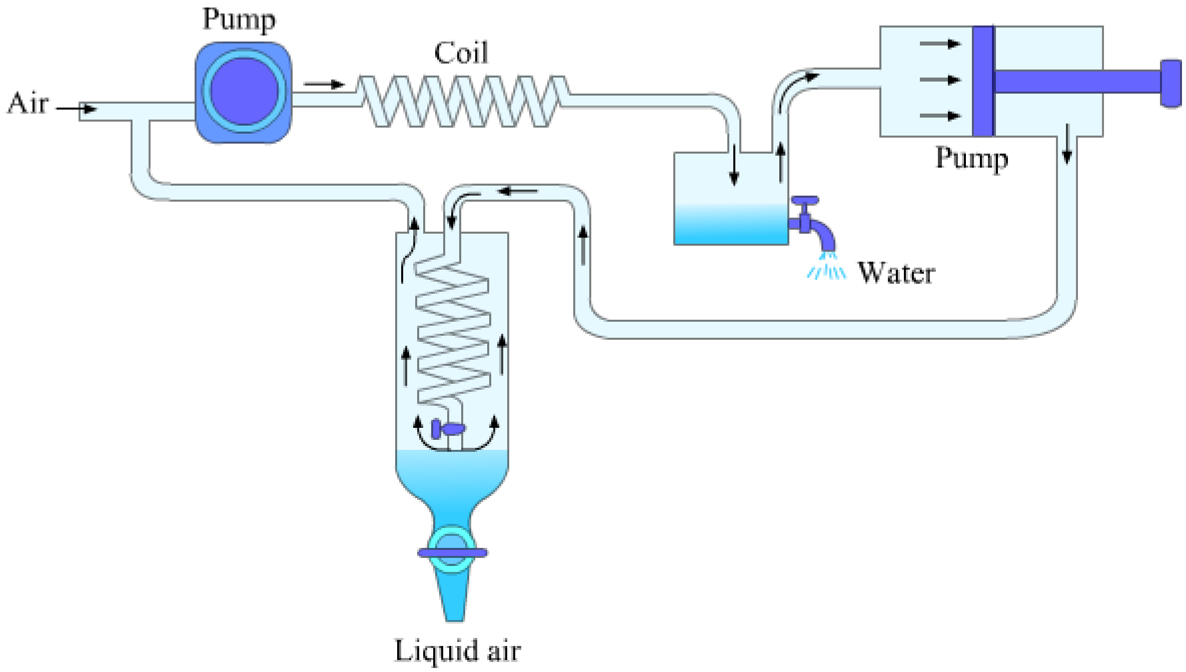
Linde Process for Liquefaction of Air

- First of all compress the air by pressure pump about pressure of 100 atmospheres. Due to such process air gets heated.
- Now remove the heat by passing the air through cooled coil in the presence of circulation of ammonia and cold water.
- Due to this water vapour condense and liquefied. Remove this water from the condenser.
- Next step is to pass the air through long copper coil which is maintained at liquid air temperature.
- Air becomes cool under high pressure and comes out from container through small orifice.
- Gas expanded at atmospheric pressure and further cooling take place by Joule-Thomson effect.
- Now copper coils cooled by this cold air. Again air taken into the the pump and entire cycle is repeated again and again.
- Finally when air becomes liquefied, it is removed from the bottom of the container.



Linde-Claude Process for Liquefaction of Air

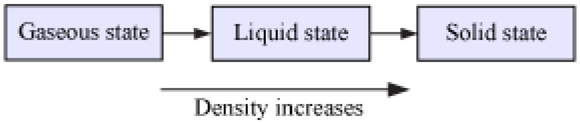
- This is the modification process of Linde which is called Linde-Claude process.
- In this process gas becomes easily liquefied which does not occur in Linde process.
- Additional work done by the gas in the process of moving piston in cylindrical piston arrangement at the stage of removal of the condensed water from the compressed air before it is entering the chamber of copper coil.
- Such addition work is done by adiabatically in the cost of internal energy and cooling takes place again.
- Now the process again continued by entering the gas in the coil and gas is liquefied more effectively.



Vapour Pressure of Liquids

Liquid State

- Intermolecular forces are stronger than those in gaseous state
-



- Liquids have definite volume. Reason: Molecules do not separate due to intermolecular force of attraction.
- Liquids can flow. Reason: Molecules can freely move past one another.

Physical Property of Liquid – Vapour Pressure

- Equilibrium vapour pressure or saturated vapour pressure: Vapour pressure in the state of equilibrium between liquid phase and vapour phase
- Boiling point: The temperature at which the vapour pressure of a liquid is equal to the external pressure

- Normal boiling point − Boiling point at 1 atm pressure

- Standard boiling point − Boiling point at 1 bar pressure

- The standard boiling point of a liquid is slightly lower than its normal boiling point. Reason − 1 atm pressure is slightly greater than 1 bar pressure.

- Example − Water has a normal boiling point of 100°C (373 K) and a standard boiling point of 99.6°C (372.6 K).

- The boiling point of a liquid is lower at high altitudes than at sea level. Reason − Atmospheric pressure is lower at high altitudes than at sea level.

  This means that the boiling point of a liquid can be varied by changing the pressure over the liquid.

- Boiling does not take place when a liquid is heated in a closed vessel.
- The vapour pressure increases on continuously heating a liquid.
- Since liquid is denser than vapour, hence at first a clear boundary is visible between the liquid and vapour phase.
- As the temperature is further increased, the density of liquid decreases while that of vapour decreases. At a particular temperature the density of the two phases becomes equal and the boundary between them disappears. This is known as critical temperature.

Surface Tension

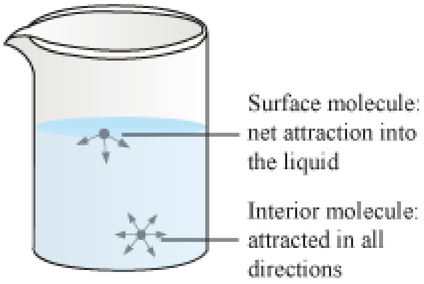
Surface Tension

- Force acting per unit length perpendicular to the line drawn on the surface of liquid

- Denoted by Greek letter γ (gamma)

- Unit = Nm^{-1}

- Reason for surface tension − A molecule in the bulk of liquid does not experience any net force as it experiences equal intermolecular forces from all the sides. However, there are no intermolecular forces above a molecule on the surface of liquid. Therefore, a molecule on the surface of liquid experiences net attractive force towards the interior of the liquid.



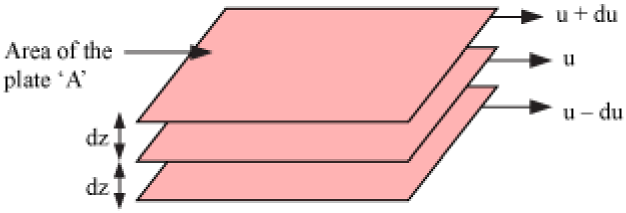
- As a result of surface tension, liquid tends to minimize their surface area.

Surface energy

- Energy required to increase the surface area of the liquid by one unit
- Unit = Jm^{-2}
- Liquid droplets are spherical because sphere has minimum surface area and liquids tend to have minimum surface area due to surface tension.
- Surface tension causes capillary action.
- Dependence of surface tension:
- The surface tension between the molecules increase with increase in attractive force.
- The surface tension decrease with the increase in temperature because with the increase in temperature, kinetic energy of particles increases and hence, effectiveness of intermolecular attraction decreases.

Viscosity

- Resistance toflow
- Stronger the intermolecular forces, higher is the viscosity.
- Laminar flow- Type of flow which involves a regular velocity gradation in passing from one layer to the next
- For a given layer in a flowing liquid, the layer above it accelerates its flow while the layer below it retards its flow.



Velocity gradient $= \frac{du}{dz}$ (change in velocity with distance)

Where, dz = Distance

du = Change in velocity

We can write,

$F \propto A$

Where, F = Force required to maintain the flow of layers

A = Area of contact

And, $F \propto \frac{du}{dz}$

Therefore, $F \propto A\frac{du}{dz}$

$$\Rightarrow F = \eta A \frac{du}{dz}$$

Where, η = Proportionality constant known as coefficient of viscosity

- Viscosity coefficient
- Force when velocity gradient is unity and the area of contact is unit area
- Measure of viscosity
- SI unit = Ns m^{-2}

1 Ns m^{-2} = 1 Pa S = 1 kg m^{-1} s^{-1}

CGS unit = poise

1 poise = 1 g cm^{-1} s^{-1} = 10^{-1} kg m^{-1} s^{-1}

- Greater the viscosity, more slowly the liquid flows.
- Glass is an extremely viscous liquid.
- With increase in temperature, viscosity of liquids decreases.
- Reason − With increase in temperature, kinetic energy of molecule increases and therefore, it is easier to overcome the intermolecular forces to slip past one another between the layers.

Amorphous and Crystalline Solids & Classification of Crystalline Solids

Amorphous and Crystalline Solids

- Based on the nature of the order of arrangement of the constituent particles, solids are classified as amorphous and crystalline.
- 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	When cut with a sharp-edged tool, they cut into two pieces with irregular shapes	4	When cut with a sharp-edged tool, they split into two pieces with plain and smooth newly generated surfaces.
5	Do not have definite heat of fusion	5	Have definite and characteristic heat of fusion
6	Isotropic in nature	6	Anisotropic in nature
7	Pseudo solids or super-cooled liquids	7	True solids

Classification of Crystalline Solids

- Based on the nature of intermolecular forces, crystalline solids are classified into four categories –

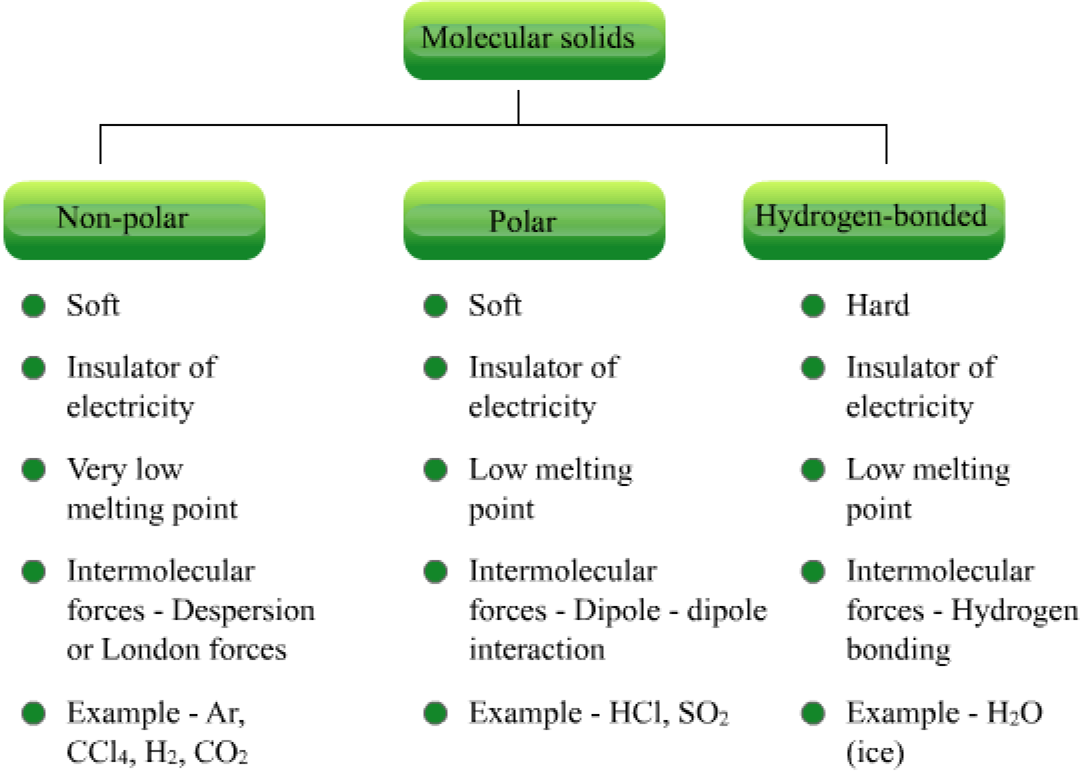
- Molecular solids

- Ionic solids

- Metallic solids

- Covalent solids

- Constituent particles are molecules



Non-polar
- Soft
- Insulator of electricity
- Very low melting point
- Intermolecular forces - Despersion or London forces
- Example - Ar, CCl_4, H_2, CO_2

Polar
- Soft
- Insulator of electricity
- Low melting point
- Intermolecular forces - Dipole - dipole interaction
- Example - HCl, SO_2

Hydrogen-bonded
- Hard
- Insulator of electricity
- Low melting point
- Intermolecular forces - Hydrogen bonding
- Example - H_2O (ice)

- Ionic solids

- Constituent particles are ions
- Hard but brittle
- Insulators of electricity in solid state, but conductors in molten state and in aqueous solution
- High melting point
- Attractive forces are Coulombic or electrostatic
- Example – NaCl, MgO, ZnS

- Metallic solids

- In metallic solids, positive ions are surrounded and are held together in a sea of delocalised electrons.
- Hard but malleable and ductile
- Conductors of electricity in solid state as well as molten state
- Fairly high melting point
- Particles are held by metallic bonding
- Example – Fe, Cu, Mg

- Covalent or network solids

- Constituent particles are atoms
- Hard (except graphite, which is soft)
- Insulators of electricity (except graphite, which is a conductor of electricity)
- Very high melting point and can decompose before melting
- Particles are held by covalent bonding
- Example – SiO_2 (quartz), SiC, diamond, graphite

Add to your knowledge

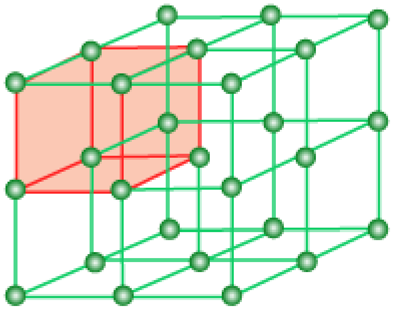
The property by virtue of which two or more crystalline solids having similar chemical composition exist in the same crystalline form is called **isomorphism**. For example: Na_3PO_4.

The property by virtue of which a particular substance exists in more than one crystalline form is called polymorphism. For example: existence of calcium carbonate in two crystalline forms called calcite and aragonite.

Crystal Lattices and Unit Cells

Crystal Lattice

- Regular three-dimensional arrangement of points in space



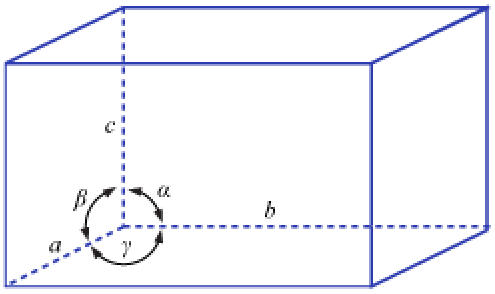
- There are 14 possible three-dimensional lattices, known as Bravais lattices.
- Characteristics of a crystal lattice:
- Each point in a lattice is called lattice point or lattice site.
- Each lattice point represents one constituent particle (atom, molecule or ion).
- Lattice points are joined by straight lines to bring out the geometry of the lattice.

Unit Cell

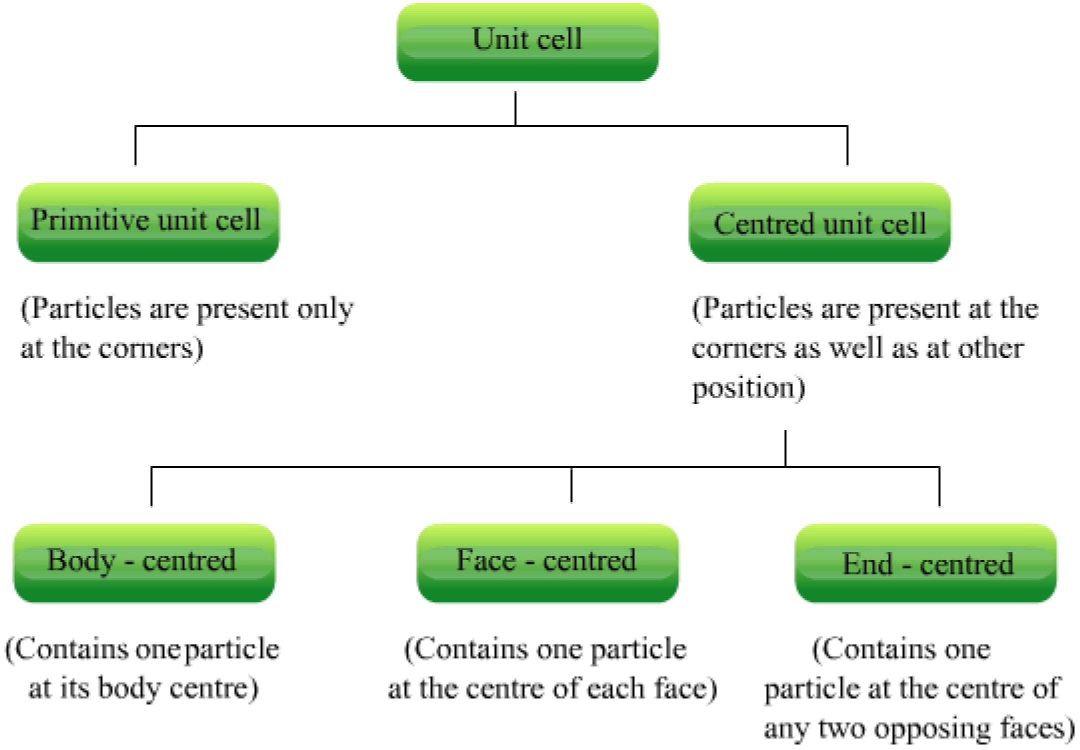
- Smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice
- Characterised by –

  (i) Its dimensions along the three edges a, b and c

  (ii) Angles between the edges α, β and γ

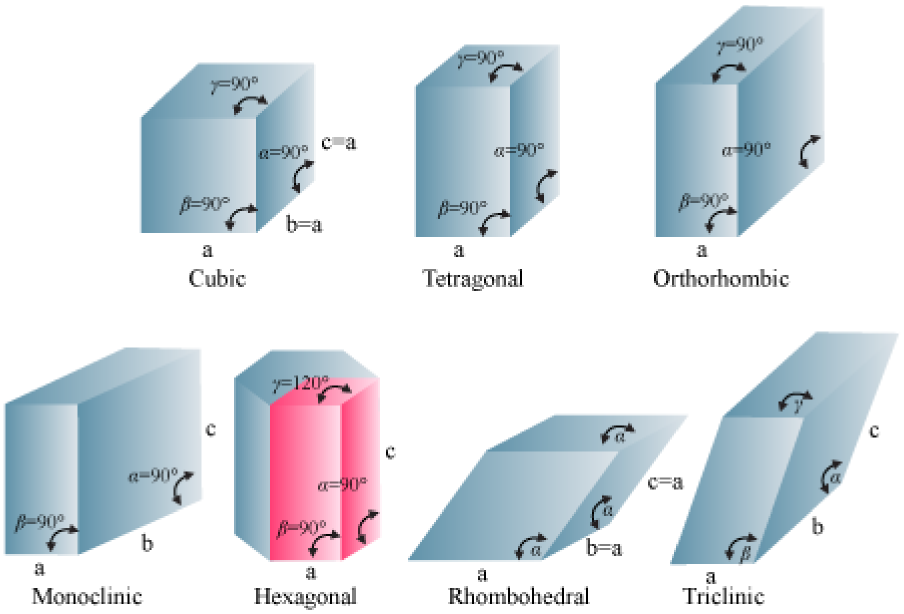


- The unit cells can be classified as follows:



Seven Crystal Systems

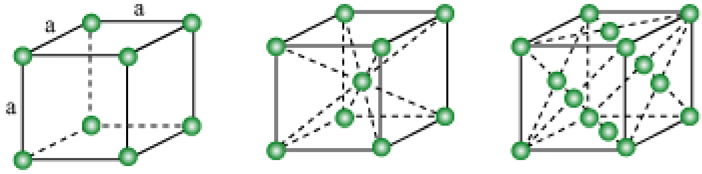
There are seven types of primitive unit cells, as given in the following table.



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

Crystal Class	**Axial Distances**	**Axial Angles**	**Possible Types of Unit Cells**	**Examples**
1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Primitive, body-centred, face-centred	KCl, NaCl
2. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, body-centred	SnO_2, TiO_2
3. Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, body-centred, face-centred, end-centred	KNO_3, $BaSO_4$
4. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$; $\gamma = 120°$	Primitive	Mg, ZnO
5. Trigonal or Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Primitive	($CaCO_3$) Calcite, HgS (Cinnabar)
6. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$; $\beta \neq 90°$	Primitive and end-centred	Monoclinic sulphur, $Na_2SO_4.10H_2O$
7. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive	$K_2Cr_2O_7$, H_3BO_3

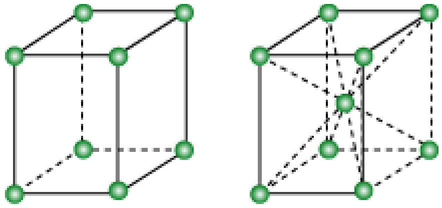
- **Unit cells of 14 types Bravais lattices:**
-
- Cubic lattices: All sides are of the same length, and the angles between the faces are 90° each



Primitive (or simple) Body-centred Face-centred

Cubic

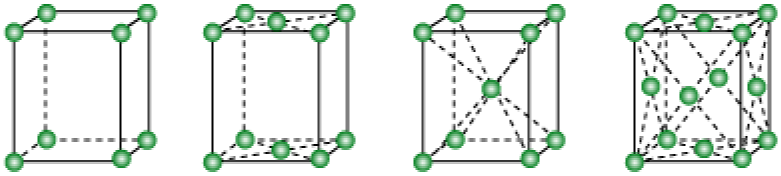
- Tetragonal lattices: One side is different in length from the other two, and the angles between the faces are 90° each



Primitive Body-centred

Tetragonal

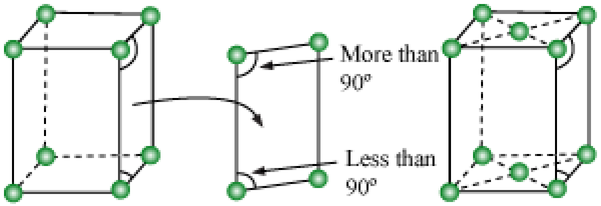
- Orthorhombic lattices: Unequal sides; angles between the faces are 90° each



Primitive End-centred Body-centred Face-centred

Orthorhombic

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



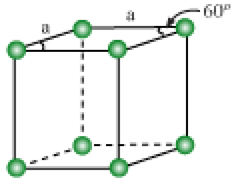
Primitive End-centred

Monoclinic

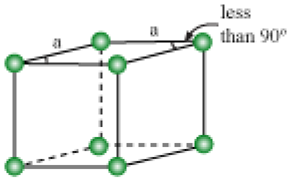
- Hexagonal lattice: One side is different in length from the other two, and the marked angles on two faces are 60°

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

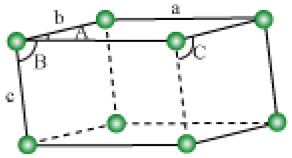
- Triclinic lattice: Unequal sides; unequal angles, with none equal to 90°



Hexagonal



Rhombohedral



Triclinic

Questions asked in previous years' board examinations

Ques. Name the type of structure possessed by a unit cell of CsCl.

Sol: A unit cell of CsCl possesses body-centred cubic structure.

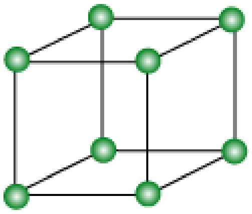
Number of Atoms in a Unit Cell

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.

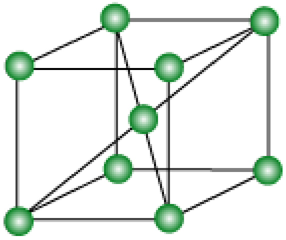
Total number of atoms in one unit cell

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

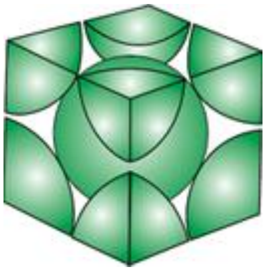
Let us see the packing in a simple cubic unit cell through this video.

Body-Centred Cubic Unit Cell

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



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



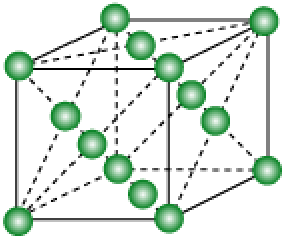
Total number of atoms in one unit cell

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

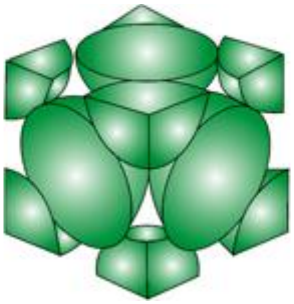
$$= 8 \times \frac{1}{8} + 1$$
$$= 2$$

Face-Centred Cubic Unit Cell

Open structure for a face-centred 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

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

Now, let us visualise the packing in face-centred cubic lattice through this video.

Questions asked in previous years' board examinations
Ques. What is the total number of atoms per unit cell in a face-centred cubic (fcc) structure?

Sol: The total number of atoms per unit cell in a face-centred cubic (fcc) structure is 4 (8 corner atoms $\times\frac{1}{8}$ atom per unit cell + 6 face-centred atoms $\times\frac{1}{2}$ atom per unit cell)

Ques. What is the number of atoms per unit cell in a body-centred cubic structure?

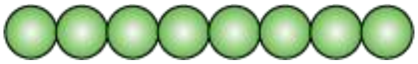
Sol: The number of atoms per unit cell in a body-centred cubic structure is 2 (8 corner atoms × $\frac{1}{8}$ atom per unit cell + 1 body-centre atom).

Closed-Packed Structures

Coordination number − The number of nearest neighbours of an atom

Close-Packing in One dimension

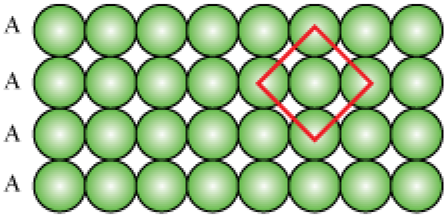
- Only one way of arrangement, i.e., the particles are arranged in a row, touching each other



- Coordination number = 2

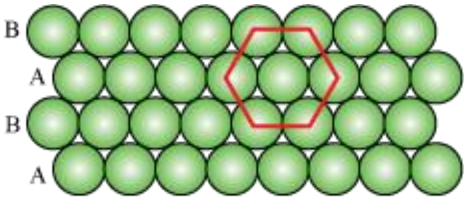
Close-Packing in Two Dimensions

- 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

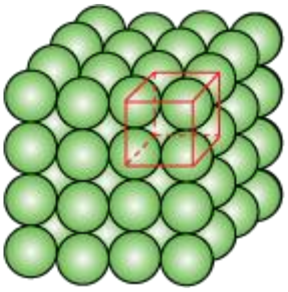
Three-dimensional close-packing is obtained by stacking two-dimensional layers (square close-packed or hexagonal close-packed) one above the other.

- 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

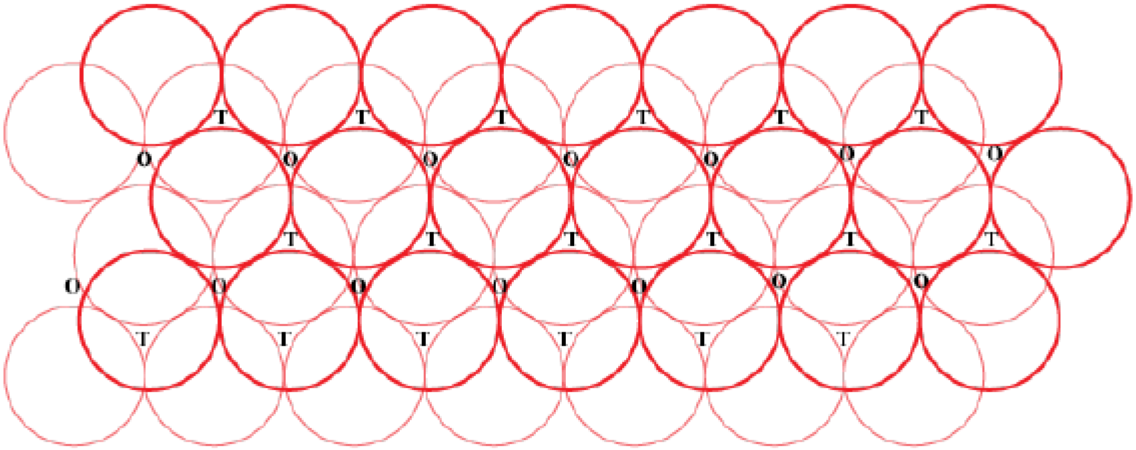
- By stacking two-dimensional hexagonal close-packed layers

- 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.



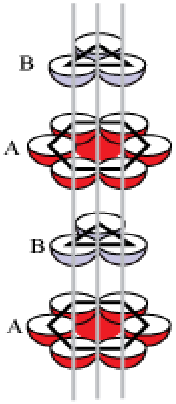
Here, T = Tetrahedral void, O = Octahedral void

Number of octahedral voids = Number of close-packed particles

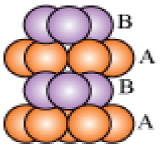
Number of tetrahedral voids = 2 × Number of close-packed particles

- Placing the third layer over the second layer: There are two ways –

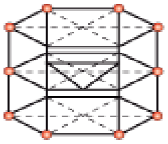
- Covering tetrahedral voids: ABAB … pattern. The particles in the third layer are exactly aligned with those in the first layer. It results in a hexagonal close-packed (*hcp*) structure. Example: Arrangement of atoms in metals like Mg and Zn



Hexagonal packing

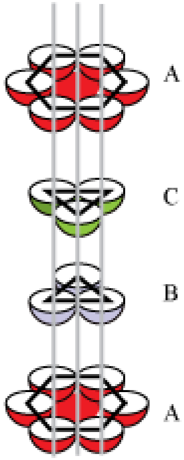


Hexagonal

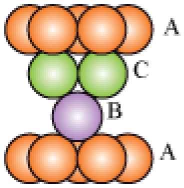


hcp

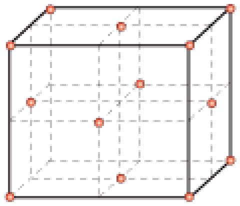
- Covering octahedral voids: ABCABC … octahedral voids. The particles in the third layer are not aligned either with those in the first layer or with those in the second layer, but with those in the fourth layer aligned with those in the first layer. This arrangement is called ‘C’ type. It results in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



Cubic close packing



Cubic



fcc

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

- Both *hcp* and *ccp* structures are highly efficient in packing (packing efficiency = 74%)

Questions asked in previous years’ board examinations

Ques. What is the coordination number of each type of ions in a rock-salt type crystal structure?

Sol: In rock salt or common salt, every Na^+ ion is surrounded by 6 Cl^- ions and each Cl^- ion is surrounded by 6 Na^+ ions. Thus, the coordination number of each type of ion in rock salt is 6.

Ques. What is the maximum possible coordination number of an atom in an *hcp* crystal structure of an element?

Sol: The maximum possible coordination number of an atom in an *hcp* crystal structure of an element 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 × 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.

Example

A compound is formed by two elements X and Y. The atoms of element X form*hcp* lattice and those of element Y occupy $\frac{1}{4}$ th of the tetrahedral voids. What is the formula of the compound formed?

Solution:

It is known that the number of tetrahedral voids formed is equal to twice the number of atoms of element X.

It is given that only $\frac{1}{4}^{\text{th}}$ of the tetrahedral voids are occupied by the atoms of element Y.

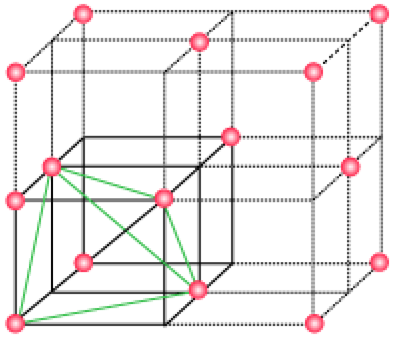
Therefore, ratio of the number of atoms of X and Y = $1:2\times\left(\frac{1}{4}\right)$

= 2: 1

Hence, the formula of the compound formed is X_2Y.

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.

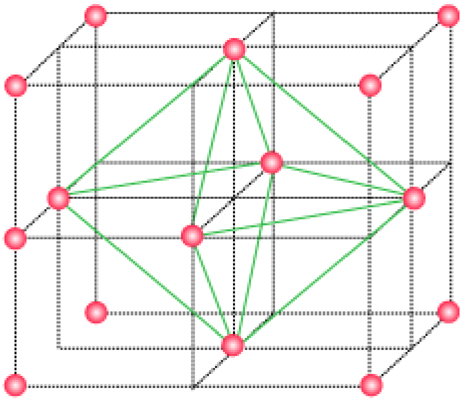


- This implies that one tetrahedral void is present in each small cube. Therefore, a total of eight tetrahedral voids are present in one unit cell.

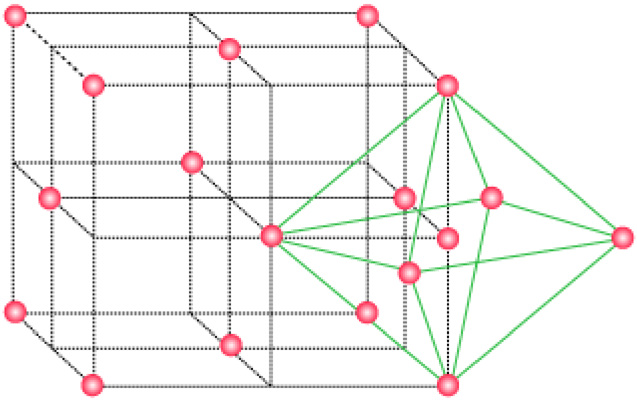
- Since each unit cell of *ccp* structure has 4 atoms, the number of tetrahedral voids is twice the number of atoms.

Locating Octahedral Voids

- When the six atoms of the face centres 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 $\frac{1}{4}^{th}$ 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 cell.

Now, let us see the stacking of two layers and the formation of the two types of voids by means of this video.

Add to your knowledge

In NaCl, the Na^+ ions occupy all the octahedral voids. In ZnS, Zn^{2+} are in alternate tetrahedral voids. In CaF_2, F^- ions occupy all the tetrahedral voids.

In Fe_3O_4, if Fe^{2+} ions are replaced by divalent cations such as Mg^{2+} and Zn^{2+}, then the compounds obtained are called ferrites.

Questions asked in previous years' board examinations

Ques. A cubic solid is made of two elements X and Y. Atoms Y are at the corners of the cube and X at the body centre. What is the formula of the compound?

Sol: The atom at the body centre makes a contribution of 1 to the unit cell, while the atom at the corner makes a contribution of $\frac{1}{8}$ to the unit cell.

Thus, number of atoms Y per unit cell

= Number of atoms × Contribution per unit cell

= 8 (at the corners) × $\frac{1}{8}$ atoms per unit cell

= 1

Thus, number of atoms X per unit cell

= Number of atoms × contribution per unit cell

= 1 (at the body centre) × 1

= 1

Thus, the formula of the given compound is XY.

Packing Efficiency & Calculations Involving Unit Cell Dimensions

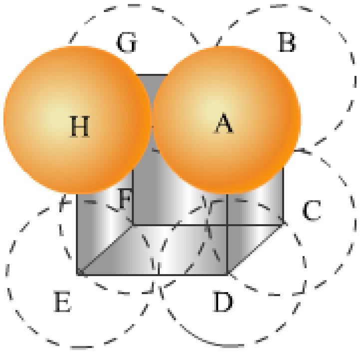
Packing Efficiency

- Percentage of total space filled by particles

Calculations of Packing Efficiency in Different Types of Structures

- **Simple cubic lattice**

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:

$a = 2r$

Now, volume of the cubic unit cell = a^3

= $(2r)^3$

= $8r^3$

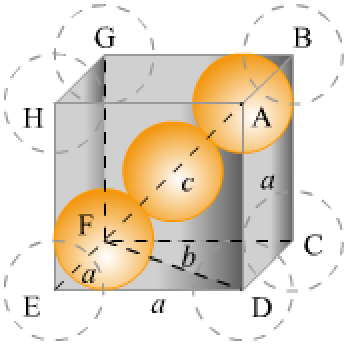
The number of particles present per simple cubic unit cell is 1.

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

Hence, packing efficiency $= \frac{\text{Volume of one particle}}{\text{Volume of cubic unit cell}} \times 100\%$

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100\ \%$$
$$= \frac{1}{6}\pi \times 100\ \%$$
$$= \frac{1}{6} \times \frac{22}{7} \times 100\ \%$$
$$= 52.4\ \%$$

- **Body-centred cubic structures**



It can be observed from the above figure that the atom at the centre is in contact with the other two atoms diagonally arranged.

From ΔFED, we have

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

From ΔAFD, we have

$$c^2 = a^2 + b^2$$
$$\Rightarrow c^2 = a^2 + 2a^2 \qquad \left(\text{Since } b^2 = 2a^2\right)$$
$$\Rightarrow c^2 = 3a^2$$
$$\Rightarrow c = \sqrt{3}a$$

Let the radius of the atom be r.

Length of the body diagonal, $c = 4r$

$$\Rightarrow \sqrt{3}a = 4r$$
$$\Rightarrow a = \frac{4r}{\sqrt{3}}$$

or, $r = \frac{\sqrt{3}a}{4}$

Volume of the cube, $a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3$

A body-centred cubic lattice contains 2 atoms.

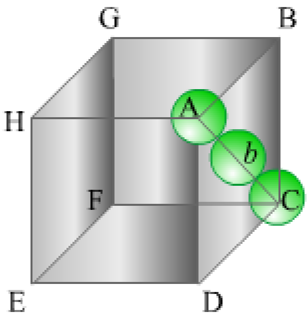
$$\text{So, volume of the occupied cubic lattice } = 2 \times \frac{4}{3}\pi r^3$$
$$= \frac{8}{3}\pi r^3$$

$$\therefore \text{Packing efficiency} = \frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100\ \%$$

$$= \frac{\frac{8}{3}\pi r^3}{\left(\frac{4}{\sqrt{3}}r\right)^3} \times 100\ \%$$
$$= \frac{\frac{8}{3}\pi r^3}{\frac{64}{3\sqrt{3}}r^3} \times 100\ \%$$
$$= 68\ \%$$

- ***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 ΔABC, we have

$$\begin{aligned}
&AC^2 = BC^2 + AB^2\\
&\Rightarrow b^2 = a^2 + a^2\\
&\Rightarrow b^2 = 2a^2\\
&\Rightarrow b = \sqrt{2a}
\end{aligned}$$

Let *r* be the radius of the atom.

Now, from the figure, it can be observed that:

$$\begin{aligned}
&b = 4r\\
&\Rightarrow \sqrt{2}a = 4r\\
&\Rightarrow a = 2\sqrt{2}r
\end{aligned}$$

Now, volume of the cube, $a^3 = \left(2\sqrt{2}r\right)^3$

We know that the number of atoms per unit cell is 4.

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

$$\therefore \text{ Packing efficiency} = \frac{\text{Volume occupied by four spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100\ \%$$

$$= \frac{4 \times \frac{4}{3}\pi r^3}{\left(2\sqrt{2}r\right)^3} \times 100\ \%$$

$$= \frac{\frac{16}{3}\pi r^3}{16\sqrt{2}r^3} \times 100\ \%$$

$$= 74\%$$

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

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 substance

Then, volume of the unit cell = a^3

Again, let

z = Number of atoms present in one unit cell

m = Mass of each atom

Now, mass of the unit cell = Number of atoms in the unit cell × Mass of each atom

$= z \times m$

But, mass of an atom, $m = \frac{M}{N_A}$

Therefore, density of the unit cell,

$$d = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$$

$$\Rightarrow d = \frac{z \cdot m}{a^3}$$

$$\Rightarrow d = \frac{z \cdot M}{a^3 \cdot \mathrm{N_A}}$$

Let us calculate the density of an element crystallising in face-centred cubic lattice.

Questions asked in previous years' board examinations

Ques. The density of copper metal is 8.95 g cm^{-3}. If the radius of copper atom is 127.8 pm, is the copper unit cell a simple cubic, a body-centred cubic or a face centred cubic structure? (Given: At. Mass of Cu = 63.54 g mol^{-1} and $\mathrm{N_A} = 6.02 \times 10^{23}\ \text{mol}^{-1}$)

Sol: We know that density, $d = \frac{z \times M}{a^3 \times \mathrm{N_A}}$ ...(i)

For SCC: $z = 1$ and $a = 2r$

For BCC: $z = 2$ and $a = \frac{4}{\sqrt{3}} r$

For FCC: $z = 4$ and $a = \frac{4}{\sqrt{2}} r$

Substituting the values of z and a in equation (i) we can calculate the value of density.

It is given that $M = 63.54$ g mol^{-1}

$\mathrm{N_A} = 6.02 \times 10^{23}\ \text{mol}^{-1}$

$r = 127.8 \times 10^{-10}$ cm

$$\text{so } d = \frac{z\times 63.54}{a^3\times 6.02\times 10^{23}} = \frac{z\times 10.55\times 10^{-23}}{a^3}$$

$$\text{For SCC: } d = \frac{(1)\times 10.55\times 10^{-23}}{\left(2\times 127.8\times 10^{-10}\right)^3}$$

$$= \frac{10.55}{1.67} = 6.31\ \text{g/cm}^3$$

$$\text{For BCC: } d = \frac{(2)\times 10.55\times 10^{-23}}{\left(\frac{4}{\sqrt{3}}\times 127.8\times 10^{-10}\right)^3}$$

$$= \frac{21.10}{2.57} = 8.2\ \text{g/cm}^3$$

$$\text{For FCC: } d = \frac{4\times 10.55\times 10^{-23}}{\left(\frac{4}{\sqrt{2}}\times 127.8\times 10^{-10}\right)^3}$$

$$= \frac{42.2}{4.73} = 8.92\ \text{g/cm}^3$$

The given value of density is 8.95 g/cm^3. Hence, from the given data, we can conclude that copper unit cell is face centred cubic or fcc.

Ques. Iron has a body-centred cubic unit cell with a cell edge of 286.65 pm. The density of iron is 7.87 g cm^{-3}. Use this information to calculate Avogadro's number.

(At. Mass of Fe = 56 g mol^{-1})

Sol: In a body-centred cubic unit cell, number of atoms present = 2

At mass of iron = 56 g mol^{-1}

Density of iron = 7.87 g cm^{-3}

Mass of iron = 7.87 × Volume

Volume in BCC = (a)^3

= (286.65)^3 pm

= 2.34 × 10^{-23} cm

Mass = $7.87 \times 2.34 \times 10^{-23}$ g

$$\text{Avogadro's number} = \frac{\text{No.of atoms} \times \text{Molar mass}}{\text{Given mass}}$$

$$= \frac{2 \times 56}{7.87 \times 2.34 \times 10^{-23}}$$

∴ Avogadro's number = 6.022×10^{23}

Ques. An element has a body-centred cubic structure with a cell edge of 288 pm. The density of the element is 7.2 g cm^{-3} Calculate the number of atoms presents in 208 g of the element.

Sol: Cell edge (a) = 288 pm

Volume of unit cell = a^3

= $(288 \text{ pm})^3$

= $(288 \times 10^{-10} \text{ cm})^3$

= 2.389×10^{-23} cm^3

Volume of 208 g of the element = $\frac{\text{Mass}}{\text{Density}}$

$$= \frac{208 \text{ g}}{7.2 \text{ g cm}^{-3}}$$

= 28.89 cm^3

Number of unit cells = $\frac{\text{Total volume}}{\text{Volume of a unit cell}}$

$$= \frac{28.89 \text{ cm}^3}{2.389 \times 10^{-23} \text{ cm}^3}$$

= 12.09×10^{23}

In a bcc structure, the number of atoms per unit cell = 2

∴ Number of atoms in 208 g of the given element = $2 \times 12.09 \times 10^{23}$

$= 24.18 \times 10^{23}$

Ques. Aluminium metal forms a cubic close-packed crystal structure. Its atomic radius is 125×10^{-12} m.

(a) Calculate the length of the side of the unit cell.

(b) How many such unit cells are there in 1.00 m^3 of aluminium?

Soli:

(a) For a cubic close-packed crystal structure,

Radius of an atom, $r = \frac{a}{2\sqrt{2}}$

Where, a → Edge length

Therefore, $a = 2\sqrt{2}r$

$$= 2\sqrt{2} \times 125 \times 10^{-12}$$
$$= 354 \times 10^{-12}\,\text{m}$$

Hence, the length of the side of the unit cell is 354×10^{-12} m.

(b) Volume of the unit cell = a^3

$$= \left(354 \times 10^{-12}\,\text{m}\right)^3$$
$$= 4.436 \times 10^{-29}\ \text{m}^3$$

$$\text{Therefore, the number of unit cells in 1.00 m}^3\text{ of aluminium} = \frac{1}{4.436 \times 10^{-29}\,\text{m}^3}$$
$$= 2.25 \times 10^{28}$$

Ques. Calculate the density of silver which crystallises in the face-centred cubic structure. The distance between the nearest silver atoms in this structure is 287 pm.

Sol: Given, molar mass of Ag, M = 107.87 g mol^{-1}

$N_A = 6.02 \times 10^{23}$ mol^{-1}

In case of fcc lattice, number of atoms per unit cell, $z = 4$

Distance between two nearest Ag atoms = 287 pm

$$\Rightarrow \frac{\text{Face diagonal}}{2} = 287\,\text{pm}$$
$$\Rightarrow \frac{\sqrt{2}a}{2} = 287\,\text{pm}$$
$$\Rightarrow a = 287 \times \sqrt{2}\,\text{pm}$$
$$\Rightarrow a = 287 \times 1.414\,\text{pm}$$
$$\Rightarrow a = 405.818\text{ pm}$$

Thus, edge length = 406 pm (approx)

$= 406 \times 10^{-12}$ m

Therefore, density of silver is given by

$$d = \frac{z.M}{a^3.\text{N}_\text{A}}$$
$$= \frac{4 \times 107.87\text{ g mol}^{-1}}{\left(406 \times 10^{-12}\text{ m}\right)^3 \times \left(6.02 \times 10^{23}\text{ mol}^{-1}\right)}$$
$$= 1.07 \times 10^7\,\text{g m}^{-3}$$
$$= 1.07 \times 10^4\ \text{kg m}^{-3}$$

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:

- Stoichiometric defects

- Impurity defect

- Non-stoichiometric defects

  Stoichiometric Defects

- Do not disturb stoichiometry of the solid

- Also called intrinsic or thermodynamic defects

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

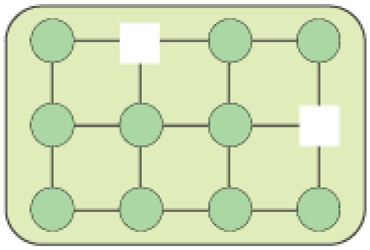
- **Vacancy defect**

- When some of the lattice sites are vacant

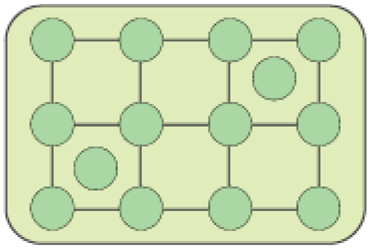
- Shown by non-ionic solids

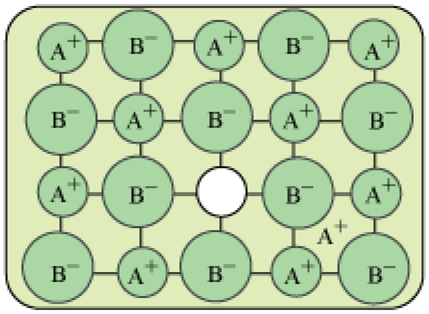
- Created when a substance is heated

- Results in the decrease in density of the substance

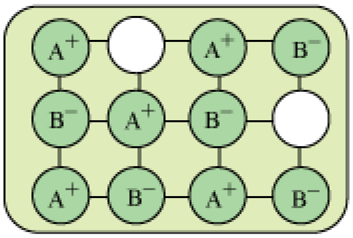


- **Interstitial defect**
- Shown by non-ionic solids
- Created when some constituent particles (atoms or molecules) occupy an interstitial site of the crystal.



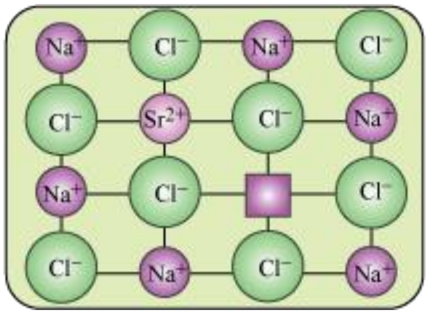
- Ionic solids show these two defects as Frenkel defect and Schottky defect.
- **Frenkel defect**
- Shown by ionic solids containing large differences in the sizes of ions
- Created when the smaller ion (usually cation) is dislocated from its normal site to an interstitial site
- Creates a vacancy defect 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 10^6 Schottky pairs per cm^3, at room temperature.
- Shown by ionic substances containing similar-sized cations and anions; for example, NaCl, KCl CsCl, AgBr



Impurity Defect

- Point defect due to the presence of foreign atoms
- For example, if molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} ions. Each Sr^{2+} ion replaces two Na^+ ions, occupying the site of one ion, leaving the other site vacant. The cationic vacancies thus produced are equal in number to those of Sr^{2+} ions.



- Solid solution of $CdCl_2$ and AgCl also shows this defect

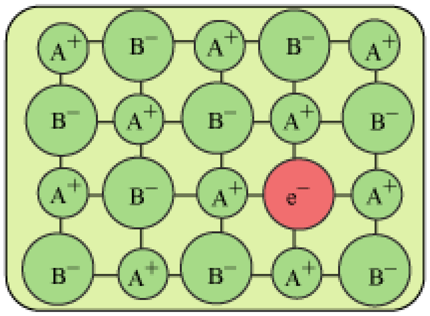
Non-Stoichiometric Defects

- Result in non-stoichiometric ratio of the constituent elements

- Two types –
- Metal excess defect
- Metal deficiency defect

Metal excess defect

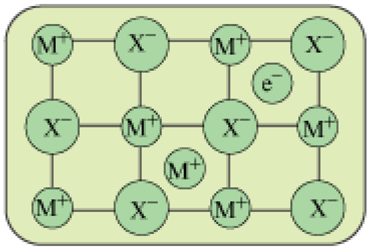
- Metal excess defect due to anionic vacancies:
- Alkali metals like NaCl and KCl show this type of defect.
- When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse from the crystal to its surface and combine 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.

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

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.



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.

Questions asked in previous years' board examinations

Ques. Which point defect in crystals of a solid decreases the density of the solid?

Sol: Vacancy defect decreases the density of a substance. Vacancy defect in ionic solids is known as Schottky defect.

Ques. Which point defect in crystals does not affect the density of the relevant solid?

Sol: Frenkel defect in crystals does not affect the density of the relevant solid.

Ques. Which point defect in its crystal units alters the density of a solid?

Sol: Schottky defect in crystals units alters the density of a solid.

Ques. How would you account for the following?

(i) Frenkel defects are not found in alkali metal halides.

(ii) Schottky defects lower the density of related solids.

(iii) Impurity doped silicon is a semiconductor.

Sol: (i) Frenkel defects are shown by ionic solids having large differences in the sizes of ions. Solids such as ZnS, AgCl show these defects due to the small size of Zn^{2+} and Ag^{+} ions, and the large size of anions. Alkali metals are not so small so as to show these defects. Hence, Frenkel defects are not found in alkali metal halides.

(ii) Schottky defects are basically vacancy defects in ionic solids. In these defects, lattice sites become vacant. As a result, the density of the substance decreases.

(iii) Silicon is an intrinsic semi-conductor in which conductivity is very low. To increase its conductivity, silicon is doped with an appropriate amount of suitable impurity. When doped with electron-rich impurities such as P or As, *n*-type semi-conductor is obtained, and when doped with electron-deficient impurities, *p*-type semi-conductor is obtained. In *n*-type semiconductor, negatively charged electron is responsible for increasing conductivity, and in *p*-type semiconductor, electron hole is responsible for increasing conductivity.

Ques. What are the types of lattice imperfections found in crystals?

Sol: Two types of lattice imperfections are found in crystals.

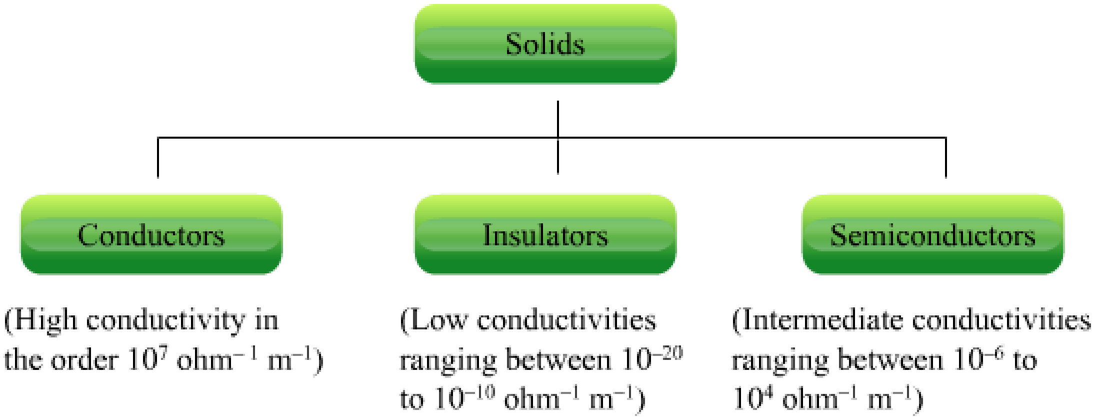
(i) Point defects (irregularities in arrangement around a point or an atom)

(ii) Line defects (irregularities in arrangement in entire rows of lattice points)

Ques. Explain interstitial defect with examples.

Sol: Interstitial defect is shown by non-ionic solids. This type of defect is created when some constituent particles (atoms or molecules) occupy an interstitial site of the crystal. The density of a substance increases because of this defect.

Electrical Properties

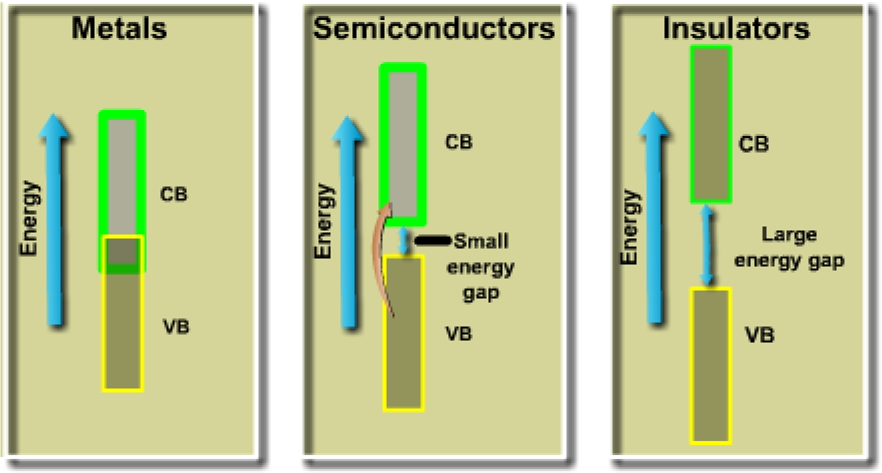


Conduction of Electricity in Metals

- 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.



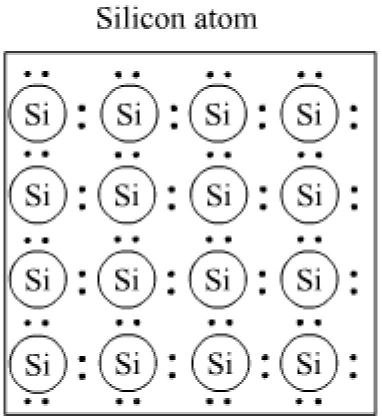
CB: Conduction band
VB: Valence band

- 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.

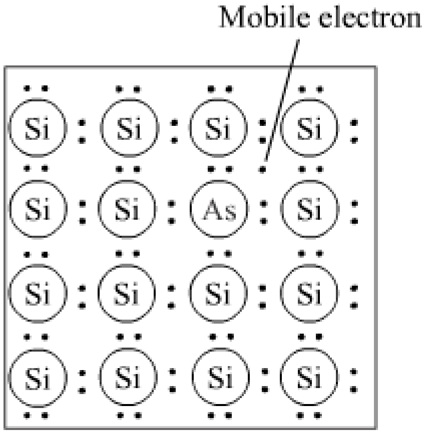
- There are two types of semiconductors:

1. *n* – type semiconductor
2. *p* – type semiconductor

- *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

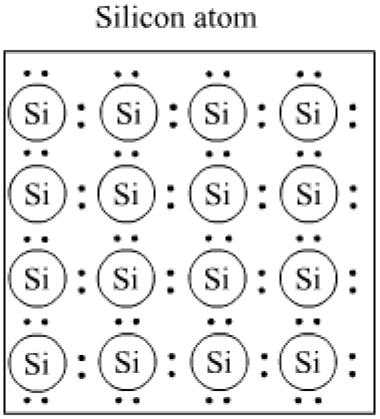


Perfect crystal

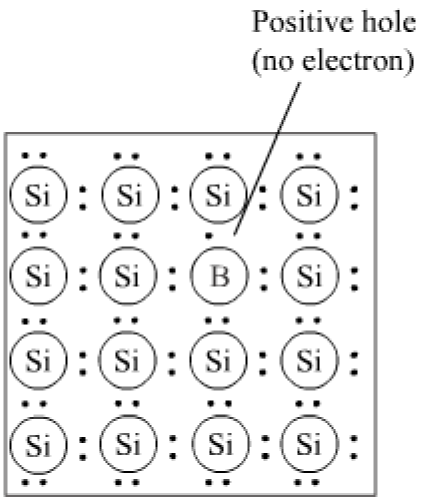


n-type

- *p* – type semiconductor
- 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, CrO_2, ReO_3 behave like metals.
- For example, ReO_3 resembles metallic copper in its conductivity and appearance
- Some oxides like VO, VO_2, VO_3, TiO_3 show metallic or insulating properties depending on temperature.

Do you know?

Polyacetylene, an organic compound shows conductivity when exposed to iodine vapours.

Questions asked in previous years' board examinations

Ques. What is semiconductor? Describe the two main types of semiconductors and explain mechanisms for their conduction.

Sol: Solids having intermediate conductivities (from 10^{-6} to 10^{4} Ω^{-1} m^{-1}) are calledsemiconductors. Germanium and silicon are two examples of semi-conductors. These substances act as insulators at low temperatures and as conductors at high temperatures. There are two types of semiconductors:

***n*-type semiconductor:**

When the crystal of a semiconductor is doped with group-15 elements (P, As, Sb or Bi), only four of the five valence electrons of the doped atoms participate in forming covalent bonds with the atoms of the semiconductors. The fifth electron is free to conduct electricity. As these crystals contain extra electrons, these are known as *n*-type semiconductors.

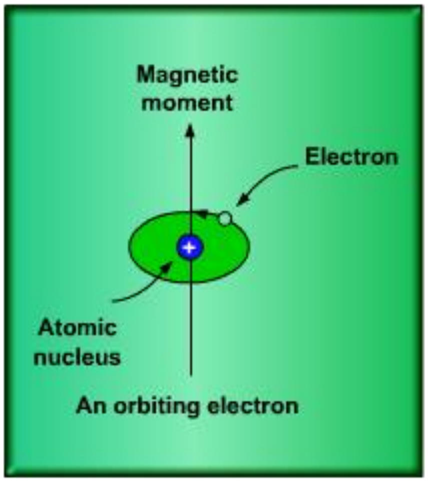
***p*-type semiconductor:**

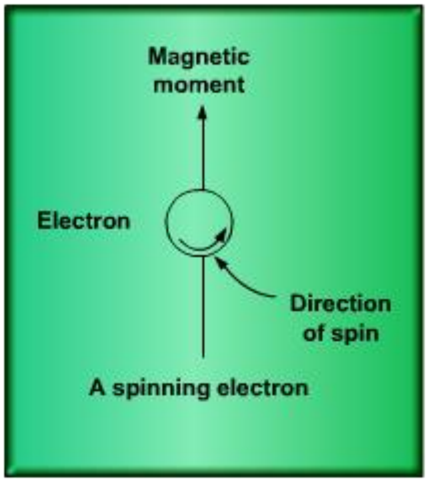
When the crystal of a semiconductor is doped with group-13 elements (Al, Ga or In), only three covalent bonds are formed by the atoms of the doped atoms as they contain three valence electrons. A hole is created at the place where the electron is absent. The presence of such holes increases the conductivity of the semiconductor as the neighbouring electrons can move into these holes, thereby creating newer holes. As these crystals contain lesser electrons than un-doped crystals, they are known as *p*-type semiconductors.

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

Paramagnetism

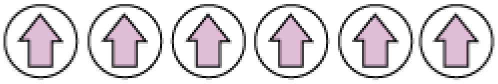
- The substances that are attracted by a magnetic field are called paramagnetic substances.
- Some examples of paramagnetic substances are O_2, Cu^{2+}, Fe^{3+} and Cr^{3+}.
- Paramagnetic substances get magnetised in a magnetic field in the same direction, but lose magnetism when the magnetic field is removed.
- To undergo paramagnetism, a substance must have one or more unpaired electrons. This is because the unpaired electrons are attracted by a magnetic field, thereby causing paramagnetism.

Diamagnetism

- The substances which are weakly repelled by magnetic field are said to have diamagnetism.
- Example – H_2O, NaCl, C_6H_6
- Diamagnetic substances are weakly magnetised 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.

Ferromagnetism

- The substances that are strongly attracted by a magnetic field are called ferromagnetic substances.
- Ferromagnetic substances can be permanently magnetised 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-magnetised 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:



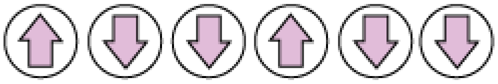
Ferrimagnetism

- The substances in which the magnetic moments of the domains are aligned in parallel and anti-parallel directions, in unequal numbers, are said to have ferrimagnetism.
- Examples include Fe_3O_4 (magnetite), ferrites such as $MgFe_2O_4$ and $ZnFe_2O_4$.

- 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:

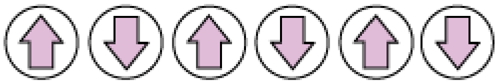


Anti-ferromagnetism

- Antiferromagnetic substanceshave 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:



Do you know?

When a substance offers no resistance to the flow of electric current, it is said to be superconducting. This phenomenon was first discovered by Kammerlingh Onnes.

Questions asked in previous years’ board examinations

Ques. What type of substances exhibits antiferromagnetism?

Sol: Antiferromagnetism is exhibited by substances which have domain structure similar to ferromagnetic substances, but are oppositely oriented (thereby cancelling out each other’s magnetic moment), e.g., MnO.

Ques. Explain each of the following with a suitable example:

(i) Paramagnetism

(ii) Piezoelectric effect

Sol: (i) *Paramagnetism*:

The phenomenon due to which a substance gets attracted towards a magnetic field is called paramagnetism. The substances attracted by a magnetic field are called paramagnetic substances. Some examples of paramagnetic substances are O_2, Cu^{2t}, Fe^{3t} and Cr^{3t}.

Paramagnetic substances get magnetised in a magnetic field in the same direction, but lose magnetism when the magnetic field is removed. To undergo paramagnetism, a substance must have one or more unpaired electrons. This is because the unpaired electrons are attracted by a magnetic field, thereby causing paramagnetism.

(ii) *Piezoelectric effect*:

The production of electricity due to the displacement of ions, on the application of mechanical stress, or the production of mechanical stress and/or strain due to atomic displacement, on the application of an electric field is known as piezoelectric effect. Piezoelectric materials are used in transducers − devices that convert electrical energy into mechanical stress/strain or vice-versa. Some piezoelectric materials are lead-zirconate ($PbZrO_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), quartz, etc.

Ques. What makes alkali metal halides sometimes coloured, which are otherwise colourless?

Alkali metal halides have anionic sites occupied by unpaired electrons. These are called F-centres, and impart colour to the crystals of alkali metal halides. For example, the excess of lithium in LiCl makes it pink.