DAY TWO

States of Matter

Learning & Revision for the Day

- Classification of Matter
- Gaseous State
- Kinetic Theory of Gases
- Liquid State
- Solid State
- Bragg's Law and Its Applications
- Unit Cell and Lattices

Classification of Matter

Anything which has mass and occupies space is called matter. Three states of matter are as follows

1. **Solids** have definite volume, a definite shape and are rigid.
2. **Liquids** have definite volume, but not definite shape and are non-rigid.
3. **Gases** have neither definite shape, nor definite volume and are non-rigid. It is the simplest state and shows great uniformity in behaviour.

- Besides the three states of matter, two more states of matter have been found to exist. These are **plasma** and **Bose-Einstein condensate** (predicted by Albert Einstein and Indian physicist Satyendra Nath Bose).
- If plasma are super-hot and super-excited atoms (a mixture of electrons and positively charged ions formed by superheating, e.g. in the sun), the Bose-Einstein condensate are total opposite, i.e. super-cold and super- unexcited atoms formed by super-cooling to such an extent that the atoms lose their individual identity and condensate to form a single super-atom.

Following two factors determine the physical state of matter:

1. **Thermal agitation** due to kinetic energy of the particles, atoms [or molecules] of a matter are in a state of continuous vibration and agitation. This increases with increase in temperature due to increase in their kinetic energy.
2. **Cohesive forces** (intermolecular forces) may be attractive or repulsive. Attractive intermolecular forces are called van der Waals' forces.

   The nature of intermolecular forces, molecular interactions and effect of thermal energy on the motion of particles helps to determine the state of a substance.

   Attractive intermolecular forces are known as van der Waals' forces. The different types of van der Waals' forces are as follows:

   (i) **Dispersion or London forces** are the forces that exists between non-polar molecules possessing temporary dipole moments. The interaction energy of these forces is proportional to $1/r^6$. [where, r is the distance between two particles].

   (ii) **Dipole-dipole forces** are forces that exists between dipole ends of polar molecules and are strongest of all van der Waals' forces.

Dipole-dipole interaction energy between stationary polar molecules is proportional to $1/r^3$ and that between rotating polar molecules is proportional to $1/r^6$.

(iii) **Dipole-induced dipole forces** are forces that exists between the polar molecules having permanent dipole and the molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electron cloud.

In dipole-induced dipole interactions, the interaction energy is proportional to $1/r^6$.

(iv) **Ion-dipole and ion-Induced dipole forces** are similar to dipole-dipole and induced-dipole interactions but involves only ions, instead of only polar and non-polar molecules. These forces are stronger than dipole-dipole interactions because the charge of any ion is much greater than the charge of a dipole moment.

(v) **Hydrogen bond** it is a special case of dipole-dipole interaction.

(a) In a solid, the cohesive forces predominate the effect of thermal agitation. Consequently, the particles are held together in rigid, highly-oriented and close-packed structure.

(b) In a liquid, the cohesive forces are no longer strong enough, however, these are still sufficient, so that particles cannot escape each others environment, they have sufficient mobility.

(c) In a gas, the thermal agitation dominates the effect of cohesive forces, thus the gas molecules acquire the unrestricted and independent mobility of the vapour state.

Gaseous State

It is the most disordered state of matter. In this state, matter neither have fixed volume nor fixed shape. It takes the shape and volume of the container in which it is placed.

Gases exhibit the following characteristic properties:

- Gases **expand indefinitely**.
- Gases are **highly compressible**.
- Gases intermix freely with one another or move from one place to other without any difficulty. This is known as **diffusion**.
- Pure gases or their mixtures are all **homogeneous in composition**.
- Gases possess very **low density**. The density of gas when compared to that of hydrogen is termed as relative density.
- Due to collision of molecules on the walls of container, **gases exert pressure** which obviously increases due to increase in temperature.
- Gaseous molecules move very rapidly in all directions in a random manner, i.e. gases have **highest kinetic energy**.

Measurable Properties of Gases

The characteristics of gases are described fully in terms of four parameters, i.e. pressure (p), volume (V), temperature (T) and mass or mole, which are termed as **measurable properties**.

(i) **Mass** is expressed in gram or kilogram and is equal to the difference in masses of empty vessel and vessel containing gas.

(ii) **Volume** is equal to the volume of the container and is expressed in terms of litre (L), millilitre (mL), cubic centimetre (cm^3), cubic metre (m^3) or cubic decimetre (dm^3).

$$1\ L = 1000\ mL = 1000\ cm^3 = 1\ dm^3$$

$$1\ m^3 = 10^3 dm^3 = 10^6 cm^3 = 10^6 mL = 10^3 L$$

(iii) **Pressure** is defined as force per unit area. The greater the force acting on a given area, the greater is the pressure. The origin of the force exerted by a gas is the continuous collisions of the molecules against the walls of the container.

The units of pressure are atm, mm Hg, torr etc.

$$1\ atm = 76\ cm\ of\ Hg = 760\ mm\ of\ Hg = 760\ torr$$

$$1\ atm = 101.325\ kPa = 101325\ Pa = 101.325\ Nm^{-2}$$

$$= 1.01325\ bar$$

$$1\ bar = 10^5\ Pa = 0.987\ atm$$

(iv) **Temperature** is the measurement of hotness or coldness of an object. It is measured in Celsius scale or absolute scale (Kelvin scale). Celsius scale was earlier known as the centigrade scale.

Gas Laws

Various types of gas laws are as follows:

1. Boyle's Law (1662)

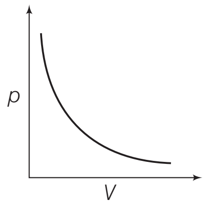
At constant temperature, the pressure of a fixed amount of gas varies inversely with its volume.

At constant temperature (T), $p \propto \dfrac{1}{V}$

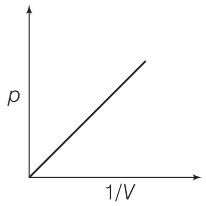
$$pV = \text{constant (for given moles and } T)$$

or $$p_1V_1 = p_2V_2 = \text{constant}$$

The two conventional ways of graphically representing Boyle's law are as follows:



p vs V plot



p vs $1/V$ plot

2. Charles' Law (1787)

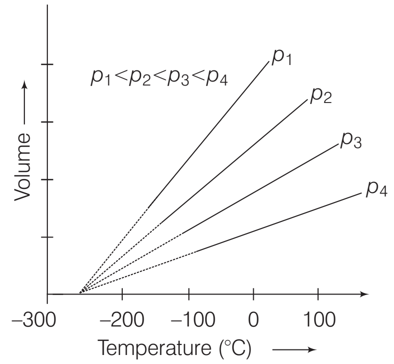
At constant pressure, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.

At constant pressure (p), $V \propto T$

$$\frac{V}{T} = \text{constant (for given } n \text{ and } p)$$

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

- Charle's found that for all gases at given pressure, graph of V vs T is a straight line.



***V* vs *T* graph at different constant pressures**

- Charles' obtained experimentally that for 1°C change in temperature of a gas, the volume get changed by a fraction of $\frac{1}{273}$. Hence, if V_0 be the volume of a gas at 0°C and it is recorded to be V at t°C then

$$V = V_0 + \frac{1}{273.15} t\, V_0$$

$$= V_0\left(1 + \frac{t}{273.15}\right) = \frac{V_0}{273.15} T$$

If temperature is lowered, the volume decreases at constant pressure and become zero at $-273.15°\text{C}$.

Further lowering is not possible thus, it is called the lowest possible temperature or absolute zero of temperature. Scale of temperature based on this choice of zero is called **absolute scale of temperature** or thermodynamic scale of temperature.

$$T(\text{K}) = t\,(°\text{C}) + 273.15$$

3. Gay-Lussac's Law

At constant volume, pressure of a fixed amount of a gas varies directly with the temperature.

At constant volume (V), $p \propto T$

$$\frac{p}{T} = \text{constant}$$

(for given n and V)

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

4. Avogadro's Law

It states that equal volumes of all gases at same pressure and temperature contain equal number of molecules.

$$V \propto n \qquad \text{(at given } T \text{ and } p)$$

or $$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Ideal Gas Equation

The Boyle's law, Charle's law and Avogadro's law can be combined together in a single equation known as **ideal gas equation**.

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

$$pV = nRT \quad \text{or} \quad pV = \frac{w}{M}RT$$

$$\therefore \left[\text{number of moles } n = \frac{w}{M}\right]$$

or $$pM = dRT$$

where, w = mass of gas,

M = molecular weight of gas

d = density of gas,

p = pressure of gas

T = temperature, V = volume

R = universal gas constant.

Values of $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$= 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$

$= 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$

$= 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$

NOTE Standard temperature and pressure (**STP** or **NTP**) means 273.15 K (0°C) temperature and 1 bar (i.e. exactly 10^5 pascal) pressure. At STP, molar volume of an ideal gas is 22.71098 L mol^{-1}.

Dalton's Law of Partial Pressures

- Total pressure exerted by the mixture of non-reacting gases is equal to the sum of the partial pressures of individual gases.

  $p_{\text{Total}} = p_1 + p_2 + p_3 + p_4 + \ldots$ (at constant T, V)
- Partial pressure of a gas (p) = mole fraction (χ) × total pressure exerted by the mixture (p_{total})
- Percentage of a gas in the mixture

  $$= \frac{\text{partial pressure of gas}}{\text{total pressure}} \times 100$$

  $= \text{mole fraction of that gas} \times 100$
- When a gas is collected over the water, the pressure of the gas $p_{\text{observed or moist}}$ = pressure of dry gas + aqueous tension or water vapour pressure.
- Relative humidity (R_H) is given by R_H = partial pressure of water in air/vapour pressure of water.

Graham's Law of Diffusion

According to this law "if a gas is allowed to escape from its container through a small hole into vacuum, the process is called effusion. On the other hand, diffusion is the passage of gas through a porous partition.

- Rate of diffusion or effusion $\propto \dfrac{1}{\sqrt{\text{molecular weight}}}$

$$[\because \text{Molecular weight} = 2 \times \text{vapour density} \Rightarrow M \propto d]$$

Rate of diffusion or effusion $\propto \dfrac{1}{\sqrt{\text{density}}}$

- Rate of diffusion or effusion (r)

$$= \frac{\text{volume diffused or effused}}{\text{time taken}}$$

Hence, $\dfrac{r_1}{r_2} = \dfrac{t_2}{t_1} = \sqrt{\dfrac{d_2}{d_1}} = \sqrt{\dfrac{M_2}{M_1}}$

- If p is not constant $r \propto p$.

$$\therefore \qquad \frac{r_1}{r_2} = \frac{p_1}{p_2}\sqrt{\frac{M_2}{M_1}}$$

Kinetic Molecular Theory of Gases

It is based on the following postulates:

- A gas consists of extremely small discrete molecules. These molecules are so small and so far apart that actual volume of the molecules is negligible as compared to the total volume of the gas.
- Gas molecules are in constant random motion with high velocities that moves in a straight line and changes their directions on collision with other molecules or walls of container.
- The intermolecular forces of attraction are negligible and the effect of gravity on them is also negligible.
- The collisions are perfectly elastic, therefore, there is no loss of kinetic energy during collision. However, there may be redistribution of energy during such a collision.
- The pressure of a gas is caused by the bombardment of moving molecules against the walls of container.
- In a gas, different molecules have different kinetic energies but the average kinetic energy of molecules is proportional to absolute temperature of the gas.
- On the basis of these assumptions, the following mathematical expression for kinetic gas equation is derived.

$$pV = \frac{1}{3} mNu^2$$

or

$$pV = \frac{1}{3} Mu^2$$

$$(\because M = m \times N, \text{ for one mole } m = 1)$$

where, u = rms velocity.

Different kind of velocities of molecules are as follows:

(i) **Root mean square velocity**

$$(u_{\text{rms}}) = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3p}{d}} = \sqrt{\frac{3KT}{M}}$$

For the same gas at two different temperatures, the ratio of RMS velocities will be

$$\frac{u_1}{u_2} = \sqrt{\frac{T_1}{T_2}}$$

For two different gases, the ratio of the RMS velocities will be $\dfrac{u_1}{u_2} = \sqrt{\dfrac{M_2}{M_1}}$

(ii) **Average velocity** $(u_{\text{av}}) = \sqrt{\dfrac{8\,RT}{\pi\,M}} = \sqrt{\dfrac{8KT}{\pi M}}$

(iii) **Most probable velocity** $(u_{\text{mp}}) = \sqrt{\dfrac{2RT}{M}} = \sqrt{\dfrac{2pV}{M}} = \sqrt{\dfrac{2p}{d}}$

Relation between different molecular velocities are as follows:

(i) $u_{\text{mp}} : u_{\text{av}} : u_{\text{rms}} :: \sqrt{2} : \sqrt{\dfrac{8}{\pi}} : \sqrt{3} = 1 : 1.128 : 1.224$

(ii) $u_{\text{av}} = u_{\text{rms}} \times 0.9213$

(iii) Kinetic energy of molecules

KE (per molecule) $= \dfrac{3}{2} KT$

$$\left[\text{where, } K = \frac{R}{N_A}\right], \; K \text{ is Boltzmann constant}$$

$$\frac{R}{N_0} = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}$$

KE (per mol) $= \dfrac{3}{2} pV = \dfrac{3}{2} RT$

At absolute zero, the kinetic energy of gas molecules become zero.

Real Gases

The gas which does not obey gas laws at all conditions of temperature and pressure is called real gas. Real gases obey the gas laws under moderate conditions of temperature and pressure.

Deviation from Ideal Behaviour

At very low temperature and high pressure, real gases show deviation from the ideal gas behaviour.

The causes of deviation are:

(i) At low temperature and high pressure, volume of a real gas is larger than that predicted for an ideal gas as the molecules of gas have their own volume.

(ii) Intermolecular forces are not negligible.

The deviations from ideal gas behaviour are expressed in terms of **compressibility factor** (Z).

Compressibility factor $(Z) = \frac{pV}{nRT} = 1$ (for ideal gas)

Different conditions of compressibility factor (Z) for real gases are as follows:

- $Z < 1$ (as for CH_4, NH_3, CO_2) can be attributed to predominance of attractive forces among the molecules of these gases at the temperature of experimentation.
- $Z > 1$ (for H_2, He) can be attributed to the dominance of strong repulsive forces among the molecules. **Boyle temperature** is the characteristic temperature of the gas at which it obeys ideal gas nature. Below this temperature, the value of Z at first decreases, approaches a minimum and then increases as the pressure increases continuously.

van der Waals' Equation

To rectify the errors caused by ignoring the intermolecular forces of attraction and the volume occupied by molecules, Johannes van der Waals' proposed following equation, which is valid for real gases upto a large range of temperature and pressure.

$$\left[p + \frac{n^2a}{V^2}\right](V - nb) = nRT$$

where, n = number of moles, a = constant (measure of magnitude of attractive forces between the molecules)
b = constant (due to occupied volume of gaseous molecules = co-volume or excluded volume).

Units of 'a' are atm L^2mol^{-2} or atm m^6 mol^{-2} or Nm^4mol^{-2} and that of 'b' are $L\,mol^{-1}$ or dm^3 mol^{-1}.

van der Waals' equation get reduced at different conditions of pressures and temperatures. These are shown below:

1. **When Pressure is Low** At low pressure, V is very large, thus, $(V - b) \approx V$ as b is neglected in comparison to V, therefore equation becomes:

$$\left(p + \frac{a}{V^2}\right)V = RT \text{ or } pV + \frac{a}{V} = RT$$

$$\Rightarrow \quad \frac{pV}{RT} = 1 - \frac{a}{VRT} \quad \Rightarrow \quad Z = \frac{pV}{RT} = 1 - \frac{a}{VRT}$$

At extremely low pressures, $\frac{a}{V}$ is very small as V is very large. Thus, it can be neglected.

$$\therefore \quad pV = RT$$

2. **When Pressure is High** At high pressure, V is quite small, thus, the term $(V - b)$ cannot be neglected while the term $\frac{a}{V^2}$ is quite large but in comparison to high p, $\frac{a}{V^2}$ can be neglected.

$$\therefore \quad p(V - b) = RT$$

$$\Rightarrow \quad pV = RT + pb$$

$$\frac{pV}{RT} = 1 + \frac{pb}{RT} \quad \text{or} \quad Z = 1 + \frac{pb}{RT}$$

3. **When Temperature is High** At high temperature, V is very large, the terms $\frac{a}{V^2}$ and b can be neglected thus, $pV = RT$.
4. **When Temperature is Low** At low temperature, both p and V are small thus, both pressure and volume corrections are appreciable.

The values of van der Waals' constant 'a' and 'b' do not remain constant over the entire range of temperature and pressure. Hence, van der Waals' equation is valid only over specific range of temperature and pressure.

Liquefaction of Gases and Critical Constants

- The phenomenon of converting a gas into liquid is known as **liquefaction** at particular temperature, pressure and volume. When a gas changes into liquid, these conditions are known as **critical conditions** e.g. T_c, V_c, p_c etc.
- **Critical Temperature (T_c)** is the maximum temperature at which a gas can be liquefied. **Critical pressure (p_c)** is the minimum pressure which is required to liquefy a gas. **Critical volume** (V_c) is the volume of one mole of a gas which is occupied at critical temperature.

Critical temperature $(T_c) = \frac{8a}{27\,Rb}$

Critical pressure $(p_c) = \frac{a}{27\,b^2}$

Critical volume $(V_c) = 3\,b$

NOTE
- Relation between critical p, V and T is $p_cV_c = \frac{3}{8}RT_c$

  or $\frac{p_cV_c}{RT_c} = \frac{3}{8}$ $Z < 1$ at critical point.
- At critical point, there is no distinction between gaseous state and liquid state as densities of a substance in gaseous and liquid states are same.

Liquid State

It is the state of matter in which the molecules are held close to each other and execute random motion through intervening spaces.

Liquids have definite volume. They can move past one another freely. They can flow, can be poured and can assume the shape of the container in which these are stored.

Physical Properties of Liquid

1 Vapour Pressure

- Inside a closed vessel, the liquid and its vapours are in dynamic equilibrium. The pressure exerted by the vapours on the walls of the container increases. After sometime, it becomes constant, an equilibrium is established between liquid phase and vapour phase. Vapour pressure at this stage is known as **equilibrium vapour pressure**.

- Since, the vapour pressure is a kinetic phenomena, it is independent of the amount of a liquid. It only depends on the temperature.
- When a liquid is heated in an open vessel, the liquid vapourises from the surface. The temperature at which vapour pressure of the liquid becomes equal to the external pressure, vaporisation can occur throughout the bulk of the liquid is called **boiling point** and the condition is called **boiling**.

2 Viscosity

- The ease with which a fluid can flow is determined by its property, called **viscosity**. It arises due to the internal friction between layers of fluids.
- Viscosity of liquid decreases with increase in temperature because rise in temperature increases the kinetic energy of molecules, this results in decrease in inter-layer friction.

3 Surface Tension

- The force acting along the surface of a liquid at right angle to any line per unit length is called **surface tension**. The unit of surface tension is **Nm^{-1}**. Surface tension decreases with rise in temperature. It is different for different liquids due to different intermolecular forces.
- Due to surface tension, the small drops of liquids are spherical as the liquid tends to have a minimum surface area. Due to surface tension, liquids rise or fall in capillary tube.

Solid State

It is defined as that form of matter which has rigidity and due to which it possesses a definite volume and a definite shape. These characteristics are due to the existence of very strong forces of attraction among the constituent species of the solid.

On the basis of the arrangement of their atoms or ions or molecules, solids are broadly classified into two groups:

1. **Crystalline Solids** They have systematic and regular arrangement of particles and sharp melting point.Crystalline solids are anisotropic, i.e. their physical properties have different values in different directions. On the basis of types of bond present, they are further divided into four groups.
   (a) **Molecular crystal**s or van der Waals' crystals, e.g. $I_2(s)$, $H_2O\ (s)$ etc.
   (b) **Atomic crystals** or (covalent crystals), e.g. graphite, diamond etc.
   (c) **Metallic crystals**, e.g. all metallic solids etc.
   (d) **Ionic crystals,** e.g. NaCl, CsCl, ZnS etc.
2. **Amorphous Solids** They are unsystematic and irregular arrangement of particles. These are isotropic, i.e. their physical properties have same values in different directions.

Bragg's Law and Its Applications

The fundamental relation among the wavelength of the X-rays, the inter-planar distance in the crystal and the angle of reflection is known as the Bragg's law.

$$2d \sin\theta = n\lambda$$

where,

λ = wavelength of X-ray used

θ = angle between incident X-rays and the plane of the crystal

d = distance between planes of the constituent particle in a crystal

n = an integer (1, 2, 3, 4, ...) which represents the serial order of diffracted beams.

Various applications of Bragg's law are as follows:

- Structure of solids are determined by X-ray diffraction methods.
- Structures of complex substances such as proteins and nucleic acids are also determined by this method.

Unit Cell and Lattices

- An array of lattice points showing arrangement of constituent particles in different position in three dimensional space, is known as **space lattice** or **crystal lattice**.
- **Unit cell** is the smallest group of lattice points which when repeated in all directions develop the entire lattice.
- A unit cell is characterised by its dimensions (a, b and c) and angles (α, β, γ). These parameters of a typical unit cell are tabulated as follows:

Seven crystal system and their unit cell parameters

Crystal systems and Bravais lattices	Unit cell parameters
Cubic [primitive, face centred, body centred] e.g. NaCl, KCl, diamond, copper, zinc blende etc.	$a = b = c, \alpha = \beta = \gamma = 90^\circ$
Rhombohedral or trigonal [primitive] e.g. $NaNO_3$, $CaCO_3$, HgS, etc.	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$
Orthorhombic [primitive, face centred, body centred, end centred] e.g. Rhombic sulphur, $BaSO_4$ (baryta), $PbCO_3$ etc.	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
Triclinic (most asymmetric) [primitive] e.g. $K_2Cr_2O_7$, H_3BO_3, $CuSO_4 \cdot 5H_2O$ etc.	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$
Monoclinic [primitive, end centred] e.g. $Na_2SO_4 \cdot 10H_2O$, $Na_2B_2O_7 \cdot 10H_2O$, monoclinic S etc.	$a \neq b \neq c$, $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
Tetragonal [primitive, body centred] e.g. Cassiterite, white tin, rutile etc.	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$
Hexagonal [primitive] e.g. Mg, beryl, ZnO (zincite), PbI_2, graphite etc.	$a = b \neq c$, $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

Various types of unit cells are as follows:

1. **Simple unit cell or primitive unit cell** in which particles are present only at corners.

   $\therefore$ Number of atoms per unit cell $= \frac{1}{8} \times 8 = 1$

2. **Face centred cell** in which the particles are present at the corners as well as at the centre of each face.

   $\therefore$ Number of atoms per unit cell

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

3. **Body centred unit cell** in which the particles are present at the corners of the cube as well as one particle is present at the centre within the body.

   $\therefore$ Number of atoms per unit cell $= \frac{1}{8} \times 8 + 1 = 2$

Coordination Number

The number of atoms in a crystal which surrounds particular atoms as its nearest atoms in its neighbour is called its coordination number. Each coordination number corresponds to a fixed radius ratio (the ratio of radius of cation to that of anion).

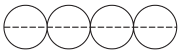
Radius ratio $\left(\frac{r_+}{r_-}\right)$	Coordination number	Structure
< 0.155	2	Linear
0.155 – 0.225	3	Planar triangle
0.225 – 0.414	4	Tetrahedral
0.414 – 0.732	6	Octahedral
0.732 – 1	8	Cubic

Packing in Solids

The packing of spheres of equal size in solids takes place as follows:

1. One Dimensional Packing

When the spheres are placed in horizontal row, touching each other, an edge of the crystal is formed.

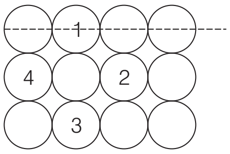


Close packing of spheres in one dimension

2. Two Dimensional Packing

It is done in two different types:

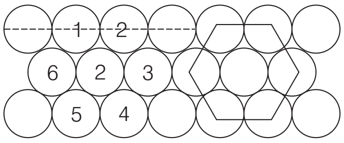
(i) **Square Close Packing** (SCP) The particles, when placed in the adjacent rows show a horizontal as well as vertical alignment and form squares.



Coordination number is 4 (SCP)

Square close packing

(ii) **Hexagonal Close Packing** (HCP) The particles in every next row are placed in the depression between the particles of the first row. The particles in the third row will be vertically aligned with those in the first row.



Coordination number is 6 (HCP)

Hexagonal close packing

3. Three Dimensional Packing

It can be obtained by stacking two dimensional layers one above the other.

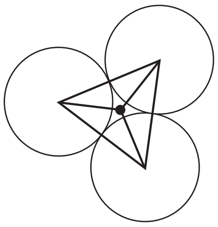
It is of two types:

(i) **Hexagonal Closed Packing** (HCP) The first layer as layer *A* and second layer as layer *B*, the arrangement is called *AB AB* ... pattern or hexagonal closed packing (hcp).

(ii) **Cubic Close Packing** (CCP) When the third layer is placed over the second layer in such a way that spheres cover the octahedral voids, a layer different from layers *A* and *B* is produced. Let us call it as layer *C*. This pattern of stacking spheres is called *ABC ABC* ... pattern or cubic close packing (ccp). It is similar to face centred cubic (fcc) packing.

Voids

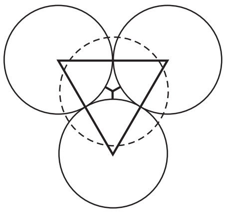
In closely packed structures, the empty space is called interstitial site or void. The void can be a simple triangular space in the case of two dimensional packing and called the **trigonal void**.



Trigonal void

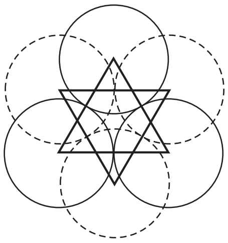
In three dimensional close packing patterns, the voids can be of two types:

1. **Tetrahedral Void** It is a simple triangular space surrounded by four spheres.



Tetrahedral void

2. **Octahedral Void** It is a double triangular void surrounded by six spheres.



Octahedral void

The sizes of above voids can be seen in the increasing order as:

Trigonal < tetrahedral < octahedral are N sphere (atoms or ions) in the packing then.

Number of octahedral voids = N

Number of tetrahedral voids = $2N$

Calculations Involving Unit Cell Parameters

1. **Relation between Edge Length and Radius of Sphere**
   - (i) **Simple cubic**, $r = a/2$

     Percentage of packing fraction = 52 %
   - (ii) **Face centred cubic** for ccp and hcp structures $r = \frac{a}{2\sqrt{2}}$

     Percentage of packing fraction = 74%
   - (iii) **Body centred cubic** $r = \sqrt{\frac{3}{4}}\,a$

     Percentage of packing fraction = 68%
2. **Density of unit cell** $d = \frac{M \times Z}{N_A \times a^3}$

   where, d = density

   M = molecular weight

   Z = number of atoms per unit cell

   N_A = Avogadro number

   a = edge length of unit cell

Structures of Some Ionic Solids

1. **Rock salt** (NaCl) **type** It has fcc arrangement and coordination number $Na^+ = 6, Cl^- = 6$, e.g. LiCl, AgF, AgCl, NH_4Br etc.
2. **CsCl type** It has the bcc arrangement with Cs^+ at the body centre and Cl^- ion at corners of a cube or *vice-versa*. Coordination number $Cs^+ = 8, Cl^- = 8$, e.g. CsCN, TiCl, TiCN etc.
3. **Zinc blende** (ZnS) **type** It has ccp or fcc arrangement. Coordination number $Zn^{2+} = 4, S^{2-} = 4$. Structure of ZnS is identical to diamond, e.g. CuCl, AgI etc.
4. **Fluorite** (CaF_2) **type** It has ccp arrangement. F^- ions occupy all the tetrahedral voids. Coordination number $Ca^{2+} = 8, F^- = 4$, e.g. CdF_2, PbF_2, $BaCl_2$, $SrCl_2$.
5. **Anti fluorite** (A_2B) **type** It has ccp arrangement. The cation occupy half of the tetrahedral voids. Coordination number $Na^+ = 4, O^{2-} = 8$, e.g. Na_2O.
6. On applying pressure, NaCl structure (6:6 coordination) changes into CsCl (8 : 8 coordination) and reverse of this occurs at high temperature.

Imperfections in Solids or Defects

Any departure from perfectly ordered arrangement of atoms in a crystal is called **imperfection or defect**.

The defects are of two types:

(i) **Line defects** are the irregularities or deviations from ideal arrangement in entire rows of lattice points.

(ii) **Point defects** are the irregularities or deviations from ideal arrangement around a point or an atom in crystalline substance.

Points defects are classified into three types. These are as follows:

1. **Stoichiometric Defects** are the point defects that do not disturb the stoichiometry of the solid.
   - These are of two types: Vacancy and interstitial defects.
   - Schottky and Frenkel defects are vacancy and interstitial defects respectively.

Schottky Defect	Frenkel Defect
It is mainly a vacancy defect arises due to equal number of cations and anions missing from the lattice sites.	It is mainly an interstitial defect arises due to the missing of ions (usually cations) from the lattice sites and they occupy the interstitial sites.
This results in the decrease in density of crystal.	It has no effect on the density of crystal.
This type of defect is found in highly ionic compounds with high coordination number, e.g. NaCl, CsCl, AgBr etc.	This type of defect is found in crystals, where the difference in the size of cations and anions is very large, e.g. AgCl, AgBr, ZnS etc.

2. **Non-Stoichiometric Defects** contain the constituent elements is non-stoichiometric ratio due to defects in their crystal structures. These defects result in either **excess of metal atom** or **deficiency of metal atom.**

   In **metal excess defect** due to anionic vacancies, a negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron, thereby maintaining the electrical balance. The electrons, thus trapped in the anion vacancies are called ***F*-centres** because they are responsible for imparting colour to the crystals.

3. **Impurity Defects** is a common method of introducing defects in ionic solids. It is done by adding impurity ions having different charge than host ion.

   These foreign atoms are present at lattice site in substitutional solids and at vacant interstitial sites in interstitial solids.

Electrical Properties of Solids

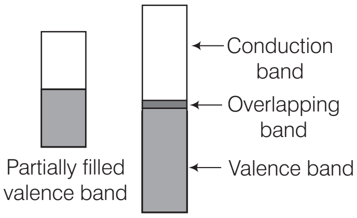
Solids are classified into three groups on the basis their conductivity. These are as follows:

(i) **Conductors** are the solids with conductivity range of the order of 10^4 to $10^7\,\Omega^{-1}\text{m}^{-1}$, e.g. metals.

(ii) **Semiconductors** are the solids with conductivity range $10^{-6} - 10^4\ \Omega^{-1}\ \text{m}^{-1}$, e.g. semi-metals.

(iii) **Insulators** are the solids with conductivity range $10^{-20} - 10^{-10}\ (\Omega\ \text{m})^{-1}$, e.g. non-metals.

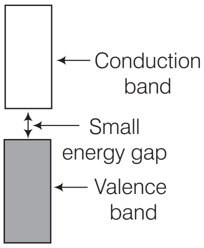
1. In **conductors**, the conduction band is almost overlapping with the valence band, i.e. there is no energy gap present between these two bands or valence band is not completely filled. Electrons can flow easily under the influence of electric field, in both the cases.



Conductors

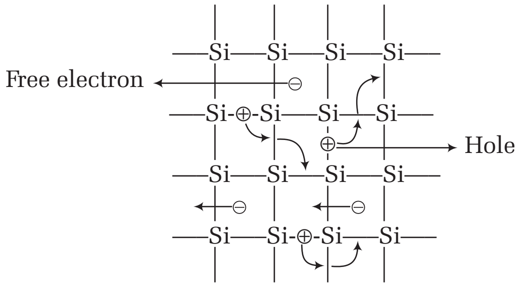
2. In **semiconductors**, the gap between valence band and conduction band is small and therefore, some of the electrons may jump from valence band to conduction band and some conductivity is observed.

   The conductivity here increases with increase in temperature due to lowering of energy gap as shown in the figure.



Semiconductors

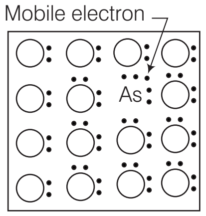
- Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band. Substances like silicon and germanium show this type of behaviour and are called **intrinsic semiconductor (undoped)**.



Electrical conductance

- The conductivity of intrinsic semiconductors is too low. So, their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called **doping**.
- Introduction of impurities in the form of electrons of 13 and 15 group of periodic table in perfect crystal. Such conductors is called **extrinsic conductors.** Depending upon the nature of the elements used for doping, the extrinsic semiconductor can be of two types, *viz*, *n*-type semiconductors and *p*-type semiconductors.

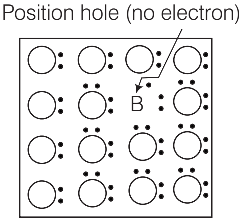
(i) ***n*-type semiconductors** The group 15 elements have 1 electron excess to Si or Ge, after forming 4 covalent bonds with group 14 member (Si or Ge). This excess free electron is responsible for electrical conductivity in them. Group 14 elements when doped with group 15 elements are called ***n*-type semiconductors**. Here, *n* specifies that negative charge flows in them.



n-type semiconductor

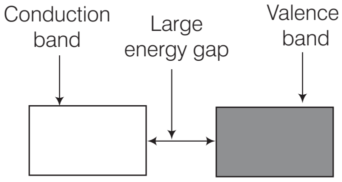
(ii) ***p*-type semiconductors** The group 13 elements have 1 electron short to group 14 elements, thus giving rise to electron deficient band or a hole. Here, such holes are responsible for electrical conductivity.

Thus, group 14 elements when doped with elements of group 13 are called ***p*-type semiconductors**.



p-type semiconductor

3. In case of **insulators**, the energy gap between valence band and conduction band is so large that it cannot even covered up by supplying energy in the form of heat.



Insulator

Magnetic Properties of Solids

- The origin of magnetic properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two type of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis.
- Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment.
- Each electron has a permanent spin and an orbital magnetic moment associated with it whose magnitude is very small and is measured in the unit called Bohr magneton, μ_B. It is equal to $9.27 \times 10^{-24}\ \text{Am}^2$.

Solids can be divided into different classes depending on their response to magnetic field. These are as follows :

1 **Diamagnetic substances** are the substances that are weakly repelled by the magnetic field and do not have any unpaired electron. e.g. TiO_2, V_2O_5, C_6H_6, NaCl etc.

2 **Paramagnetic substances** are the substances that are attracted by the magnetic field and have unpaired electrons. They lose magnetism in the absence of magnetic field. e.g. O_2, Cu^{2+}, Fe^{3+} etc.

3 **Ferromagnetic substances** are attracted by the magnetic field and show permanent magnetism even in the absence of magnetic field. e.g. Fe, Co, Ni and CrO_2. Ferromagnetic property decreases from iron to nickel because number of unpaired electrons decreases.

4 **Antiferromagnetic substances** have net magnetic moment zero due to compensatory alignment of magnetic moments. e.g. MnO, MnO_2, FeO, NiO, Cr_2O_3 etc.

5. **Ferrimagnetic substances** have a net dipole moment due to unequal parallel and anti-parallel alignment of magnetic moments. e.g. Fe_3O_4, ferrites $MgFe_2O_4$ and $ZnFe_2O_4$ etc.

Dielectric Properties of Solids

These are seen in insulators. Insulators show generation of dipoles in them, when they are placed in an electric field. These dipoles are given below:

(i) May align themselves in an order manner, so that there is a net dipole moment in the crystal.

(ii) May align themselves in such a manner that dipole moments may cancel each other.

(iii) It is also possible that there are no dipoles in the crystal but only ions are present.

Some other important dielectric properties of solids are:

1. **Piezoelectricity** It is produced on applying mechanical stress on polar crystals.
2. **Pyroelectricity** It is produced on heating some polar crystals.
3. **Ferroelectricity** Piezoelectric crystals with permanent dipoles are said to have ferroelectricity. e.g. $BaTiO_3$, KH_2PO_4 etc. All ferroelectric solids are piezoelectric but all piezoelectric solids are not ferroelectric, e.g. quartz is piezoelectric but not ferroelectric.
4. **Antiferroelectricity** In antiferroelectric crystals, the dipoles in alternate polyhedra point up and down in such a way that the crystal does not possess any net dipole moment.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is ➞ JEE Main 2015

(a) ion-ion interaction (b) ion- dipole interaction
(c) London force (d) hydrogen bond

2 A certain mass of the oxygen gas occupies 7 L volume under a pressure of 380 mm Hg. The volume of the same mass of the gas at standard pressure with temperature remaining constant shall be

(a) 26.60 L (b) 54.28 L (c) 3.5 L (d) 7 L

3 A bubble of gas released at the bottom of a lake increases to eight times its original volume when it reaches the surface.Assuming that atmospheric pressure is equivalent to the pressure exerted by a column of water 10 m high, what is the depth of the lake?

(a) 90 m (b) 10 m (c) 70 m (d) 80 m

4 Equal weights of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is

(a) 1 : 2 (b) 1 : 1 (c) 1 : 16 (d) 15 : 16

5 Through the two ends of a glass tube of length 200 cm HCl gas and NH_3 are allowed to enter. At what distance, the white ring of ammonium chloride will first appear?

(a) 81.1 cm from HCl end (b) 81.1 cm from NH_3 end
(c) 118.9 cm from HCl end (d) The ring will not form

6 At STP, 0.48 g of O_2 diffused through a porous partition in 1200 s. What volume of CO_2 will diffuse in the same time and under the same conditions?

(a) 286.6 mL (b) 346.7 mL
(c) 112.2 mL (d) 224.8 mL

7 What are the relative rates of diffusion for $^{235}UF_6$ and $^{238}UF_6$?

(a) 1.0043 (b) 2.540 (c) 1.503 (d) 1.119

8 Assuming the same pressure in each case, what is the mass of hydrogen required to inflate a balloon to a certain volume V at 100°C, if 3.5 g helium is required to inflate the balloon to half the volume V at 25°C?

(a) 3.8 g (b) 2.8 g (c) 4.2 g (d) 4.0 g

9 Helium atom is two times heavier than a hydrogen molecule at 298 K. The average kinetic energy of helium is

(a) two times that of hydrogen molecule
(b) same as that of hydrogen molecule
(c) four times that of hydrogen molecule
(d) half that of hydrogen molecule

10 For a monoatomic gas, kinetic energy = E. The relation with rms velocity is

(a) $u = \left(\frac{2E}{M}\right)^{\frac{1}{2}}$ (b) $u = \left(\frac{3E}{2M}\right)^{\frac{1}{2}}$

(c) $u = \left(\frac{E}{2M}\right)^{\frac{1}{2}}$ (d) $u = \left(\frac{E}{3M}\right)^{\frac{1}{2}}$

11 At what temperature, the rms velocity of SO_2 be same as that of O_2 at 303 K?

(a) 273 K (b) 606 K (c) 303 K (d) 403 K

12 The ratio between the root mean square velocity of H_2 at 50 K and that of O_2 at 800 K is

(a) 4 (b) 2 (c) 1 (d) 1/4

13 As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by a factor of which of the following?

(a) $\frac{1}{2}$ (b) $\sqrt{\frac{313}{293}}$ (c) $\frac{313}{293}$ (d) 2

14 To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mole of He and 1.0 mole of an unknown compound (vapour pressure 0.68 atm at 0°C) are introduced.

Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to ➞ AIEEE 2011

(a) 3 (b) 5 (c) 7 (d) 9

15 If 10^{-4} dm^3 of water is introduced into a 1.0 dm^3 flask at 300 K, how many moles of water are in the vapour phase when equilibrium is established?

(Given, vapour pressure of H_2O at 300 K is 3170 Pa;
$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) ➞ AIEEE 2010

(a) 5.56×10^{-3} mol (b) 1.53×10^{-2} mol

(c) 4.46×10^{-2} mol (d) 1.27×10^{-3} mol

16 The compressibility factor for a real gas at high pressure is ➞ AIEEE 2012

(a) $1 + \frac{RT}{pb}$ (b) 1

(c) $1 + \frac{pb}{RT}$ (d) $1 - \frac{pb}{RT}$

17 The compressibility of a gas is less than unity at STP. Therefore,

(a) $V_m > 22.4$ L (b) $V_m < 22.4$ L

(c) $V_m = 22.4$ L (d) $V_m = 44.8$ L

18 If Z is a compressibility factor, van der Waals' equation at low pressure can be written as ➞ JEE Main 2014

(a) $Z = 1 + \frac{RT}{pb}$ (b) $Z = 1 - \frac{a}{VRT}$

(c) $Z = 1 - \frac{pb}{RT}$ (d) $Z = 1 + \frac{pb}{RT}$

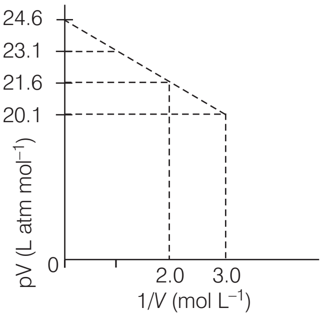
19 In van der Waals' equation of state for a non-ideal gas, the term that accounts for intermolecular force is

(a) $(V - b)$ (b) $(RT)^{-1}$

(c) $\left(p + \frac{a}{V^2}\right)$ (d) RT

20 For one mole of a van der Waals' gas when $b = 0$ and $T = 300$ K, the pV vs $\frac{1}{V}$ plot is shown below. The value of the van der Waals' constant a (atm L mol^{-2}) is

➞ AIEEE 2012



(a) 1.0 (b) 4.5

(c) 1.5 (d) 3.0

21 a and b are van der Waals' constants for gases. Chlorine is more easily liquefied than ethane because

(a) a and b for $Cl_2 >$ a and b for C_2H_6 ➞ AIEEE 2011
(b) a and b for $Cl_2 <$ a and b for C_2H_6
(c) a for $Cl_2 <$ a for C_2H_6 but b for $Cl_2 >$ b for C_2H_6
(d) a for $Cl_2 >$ a for C_2H_6 but b for $Cl_2 <$ b for C_2H_6

22 The value of compression factor, Z for critical constants is

(a) $\frac{1}{2}$ (b) $\frac{3}{4}$

(c) $\frac{2}{3}$ (d) $\frac{3}{8}$

23 Which of the following exists as crystals in the solid state? ➞ JEE Main 2013

(a) Iodine (b) Silicon

(c) Sulphur (d) Phosphorus

24 The number of hexagonal faces that are present in truncated octahedron is ➞ AIEEE 2011

(a) 2 (b) 4 (c) 6 (d) 8

25 The first order diffraction of X-rays from a certain set of crystal planes occur at an angle of 11.8° from the planes. If the planes are 0.281 nm apart, what is the wavelength of X-rays?

(a) 0.281 nm (b) 0.2044 nm
(c) 0.1149 nm (d) 0.1180 nm

26 In diamond, the coordination number of carbon is

(a) four and its unit cell has eight carbon atoms
(b) four and its unit cell has six carbon atoms
(c) six and its unit cell has four carbon atoms
(d) four and its unit cell has four carbon atoms

27 Sodium metal crystallises in a body centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately ➞ JEE Main 2015

(a) 1.86 Å (b) 3.22 Å
(c) 5.72 Å (d) 0.93 Å

28 Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be ➞ AIEEE 2012

(a) 75 pm (b) 300 pm (c) 240 pm (d) 152 pm

29 CsCl crystallises in body centred cubic lattice. If 'a' its edge length, then which of the following expressions is correct? ➞ JEE Main 2014

(a) $r_{\mathrm{Cs}^+} + r_{\mathrm{Cl}^-} = 3a$ (b) $r_{\mathrm{Cs}^+} + r_{\mathrm{Cl}^-} = \frac{3a}{2}$

(c) $r_{\mathrm{Cs}^+} + r_{\mathrm{Cl}^-} = \frac{\sqrt{3}}{2}a$ (d) $r_{\mathrm{Cs}^+} + r_{\mathrm{Cl}^-} = \sqrt{3a}$

30 In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of B is missing from one of the face centred points, the formula of the compound is ➞ AIEEE 2010

(a) A_2B (b) AB_2 (c) A_2B_2 (d) A_2B_5

31 An element having an atomic radius of 0.14 nm crystallises in an fcc unit cell. What is the length of a side of the cell? ➞ JEE Main 2013

(a) 0.56 nm (b) 0.24 nm (c) 0.96 nm (d) 0.4 nm

32 If the distance between Na^+ and Cl^- ion in NaCl crystal is 'a' pm. What is the length of the cell edge? ➞ JEE Main 2013

(a) $4\,a$ pm (b) $\frac{a}{4}$ pm
(c) $2\,a$ pm (d) $\frac{a}{2}$ pm

33 A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a' the closest approach between two atoms in metallic crystal will be ➞ JEE Main 2017

(a) $2a$ (b) $2\sqrt{2}\,a$ (c) $\sqrt{2}\,a$ (d) $\frac{a}{\sqrt{2}}$

34 How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g?

(a) 2.57×10^{21} (b) 5.14×10^{21}
(c) 1.28×10^{21} (d) 1.71×10^{21}

35 Iron crystallises in a bcc system with a lattice parameter of 2.861 Å. Calculate the density of iron in the bcc system (atomic weight of Fe = 56, $N_A = 6.02 \times 10^{23}\ \mathrm{mol}^{-1}$)

(a) 7.94 g mL^{-1} (b) 8.96 g mL g^{-1}
(c) 2.78 g mL^{-1} (d) 6.72 g mL^{-1}

36 Calcium crystallises in a face centred cubic unit cell with $a = 0.556$ nm. Calculate the density, if it contained 0.1% Schottky defects.

(a) 1.5463 g / cm^3 (b) 1.4962 g / cm^3
(c) 1.5448 g / cm^3 (d) 1.5943 g / cm^3

37 To get n-type semiconductor from silicon, it should be doped with a substance with valence

(a) 1 (b) 2
(c) 3 (d) 5

38 Which type of 'defect' has the presence of cations in the interstitial sites? ➞ JEE Main 2018

(a) Schottky defect (b) Vacancy defect
(c) Frenkel defect (d) Metal deficiency defect

39 Which of the following compounds is metallic and ferromagnetic? ➞ JEE Main 2016

(a) $\mathrm{CrO_2}$ (b) $\mathrm{VO_2}$
(c) $\mathrm{MnO_2}$ (d) $\mathrm{TiO_2}$

Direction (Q. Nos. 40-43) *In the following questions Assertion (A) followed by a Reason (R) is given. Choose the correct answer out of the following choices.*

(a) Both A and R are true and R is correct explanation of A
(b) Both A and R are true but R is not correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

40 **Assertion** (A) Average speed of molecules, if a gas in a container moving only in one direction, will be zero.

Reason (R) The molecules of gas are not collected in one direction.

41 **Assertion** (A) The temperature at which vapour pressure of a liquid is equal to the external pressure is called boiling temperature

Reason (R) At high altitude atmospheric pressure is high.

42 **Assertion** (A) Liquids tends to have maximum number of molecules at their surface.

Reason (R) Small liquid drops have spherical shape.

43 **Assertion** (A) Solids containing F-centres are paramagnetic.

Reason (R) F-centres solids possess holes occupied by unpaired electrons.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 A mixture of $NH_3(g)$ and $N_2H_4(g)$ is placed in a sealed container at 300 K. The total pressure is 0.5 atm. When the container is heated to 1200 K, both substances decompose completely according to the equations :

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

and $$N_2H_4(g) \longrightarrow N_2(g) + 2H_2(g)$$

After decomposition, the total pressure at 1200 K is found to be 4.5 atm. What is the per cent of $N_2H_4(g)$ in the original mixture? (assuming ideal behaviour)

(a) 35% (b) 40% (c) 75% (d) 25%

2 For gaseous state, if most probable speed is denoted by C^*, average speed by $\overline{C}$ and mean square speed by C, then for a large number of molecules, the ratio of these speeds are :

(a) $C^* : \overline{C} : C = 1.128 : 1.225 : 1$ (b) $C^* : \overline{C} : C = 1 : 1.128 : 1.225$

(c) $C^* : \overline{C} : C = 1 : 1.125 : 1.128$ (d) $C^* : \overline{C} : C = 1.225 : 1.128 : 1$

3 When 3.2 g sulphur is vaporised at 450°C and 723 mm Hg pressure, the vapours occupy a volume of 780 mL. What is the molecular formula of S vapours?

(a) S_2 (b) S_4 (c) S_6 (d) S_8

4 What is the difference in the density of dry air at 1 atm and 25°C and moist air with 50% relative humidity under the same condition? The vapour pressure of water at 25°C is 23.7 torr and dry air has 75.5% N_2 and 24.5% O_2.

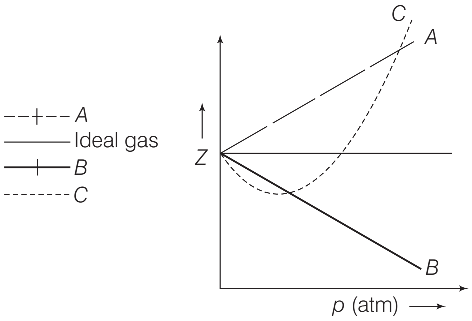
(a) 0.005 kg m^{-3} (b) 0.007 kg m^{-3}

(c) 0.01 kg m^{-3} (d) 0.05 kg m^{-3}

5 In a spinel structure, oxide ions are cubical closed packed whereas 1/8th of tetrahedral voids are occupied by A ions and 1/2 of octahedral voids are occupied by B ions. The charge present on A and B ions will be

(a) A^{2+}, B^{3+} (b) A^{3+}, B^{2+} (c) A^{4+}, B^{2-} (d) A^{-1}, B^{2-}

6 The given graph represents the variation of Z (compressibility factor $= \frac{pV}{nRT}$) *versus* p, for three real gases A, B and C. Identify the only incorrect statement.



(a) For the gas A, $a = 0$ and its dependence on p is linear at all pressures

(b) For the gas B, $b = 0$ and its dependence on p is linear at all temperatures

(c) For the gas C, which is typical real gas for which neither $a = 0$ nor $b = 0$, by knowing the minima and the point of intersection, with $Z = 1$, a and b can be calculated

(d) At high pressure, the slope is positive for all real gases

7 At 100°C and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3}, the volume occupied by water molecules in 1 L of steam at that temperature is

(a) 6 cm^3 (b) 60 cm^3 (c) 0.6 cm^3 (d) 0.06 cm^3

8 Experimentally, it was found that a metal oxide has formula $M_{0.98}$ O. Metal M is present as M^{2+} and M^{3+}. It oxide fraction of the metal which exists as M^{3+} would be

(a) 4.08% (b) 6.05% (c) 5.08% (d) 7.01%

9 Which of the following order of root mean square speed of different gases at the same temperature is true?

(a) $(\mu_{rms})H_2 > (\mu_{rms})CH_4 > (\mu_{rms})NH_3 > (\mu_{rms})CO_2$

(b) $(\mu_{rms})H_2 < (\mu_{rms})CH_4 < (\mu_{rms})NH_3 < (\mu_{rms})CO_2$

(c) $(\mu_{rms})H_2 < (\mu_{rms})CH_4 > (\mu_{rms})NH_3 > (\mu_{rms})CO_2$

(d) $(\mu_{rms})H_2 > (\mu_{rms})CH_4 < (\mu_{rms})NH_3 < (\mu_{rms})CO_2$

10 The behaviour of a real gas is usually depicted by plotting compression factor (Z) *versus* p at *a* constant temperature. At low temperature and low pressure, Z is usually less than one. This fact can be explained by van der Waals' equation when

(a) the constant a is negligible and not b

(b) the constant b is negligible and not a

(c) both the constant a and b are negligible

(d) both the constant a and b are not negligible

11 When a capillary tube of diameter 0.4 mm is dipped in a liquid having density 800 kg m^{-3}, then the height of liquid in the capillary tube rises to 4 cm. The surface tension of liquid is $(g = 9.8 \text{ m/s}^2)$.

(a) 1.6×10^{-2} Nm^{-1} (b) 5.6×10^{-2} Nm^{-1}

(c) 6.3×10^{-2} Nm^{-1} (d) 7.3×10^{-2} Nm^{-1}

12 When a sample of gas is compressed at constant temperature from 15 atm to 6 atm, its volume changes from 76 cm^3 to 20.5 cm^3. Which of the following statements are possible explanations of this behaviour?

I. The gas behaves non-ideally.
II. The gas dimerises.
III. The gas is absorbed into the vessel walls.

(a) I, II and III (b) I and II only

(c) II and III (d) Only I

13 For a crystal, the angle of diffraction (2θ) is 90° and the second order line has a d value of 2.28 Å. The wavelength (in Å) of X-rays used for Bragg's diffraction is

(a) 1.612 (b) 2.00
(c) 2.28 (d) 4.00

14 How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g? (Atomic mass of Na = 23, Cl = 35.5)

(a) 2.57×10^{21} (b) 5.14×10^{21}
(c) 1.28×10^{21} (d) 1.71×10^{21}

15 Schottky defects occur mainly in electrovalent compounds where

(a) positive ions and negative ions are of different size
(b) positive ions and negative ions are of same size
(c) positive ions are small and negative ions are big
(d) positive ions are and negative ions are small

ANSWERS

SESSION 1	**1** (d)	**2** (c)	**3** (c)	**4** (d)	**5** (a)	**6** (a)	**7** (a)	**8** (b)	**9** (b)	**10** (a)
	11 (b)	**12** (c)	**13** (c)	**14** (c)	**15** (d)	**16** (c)	**17** (b)	**18** (b)	**19** (c)	**20** (c)
	21 (d)	**22** (d)	**23** (b)	**24** (d)	**25** (c)	**26** (a)	**27** (a)	**28** (d)	**29** (c)	**30** (d)
	31 (d)	**32** (c)	**33** (d)	**34** (a)	**35** (a)	**36** (c)	**37** (d)	**38** (c)	**39** (a)	**40** (a)
	41 (c)	**42** (d)	**43** (a)							
SESSION 2	**1** (d)	**2** (b)	**3** (d)	**4** (b)	**5** (a)	**6** (c)	**7** (c)	**8** (a)	**9** (a)	**10** (b)
	11 (c)	**12** (d)	**13** (a)	**14** (a)	**15** (b)					

Hints and Explanations

SESSION 1

1 Ion-ion interaction is dependent on the square of distance, i.e.

ion-ion interaction $\propto \frac{1}{r^2}$.

Similarly, ion-dipole interaction $\propto \frac{1}{r^2}$.

London forces $\propto \frac{1}{r^6}$ and dipole-dipole interactions

[H-bonds] $\propto \frac{1}{r^3}$. Thus, H-bonds being dipole-dipole interactions is dependent on the inverse cube of distance between the molecules.

2 At constant temperature,

$$p_1V_1 = p_2V_2 \text{ (Boyle's law)}$$
$$380 \times 7 = 760 \times V_2$$
$$V_2 = \frac{380 \times 7}{760} = 3.5 \text{ L}$$

3 By using Boyle's law,

$$p \times 8\,V = p_1 \times V;\ 8p = p_1$$

p_1 = atmosphere pressure + pressure due to water in lake

∴ Pressure of water in lake = $7p$

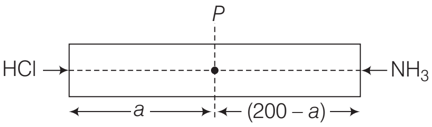
Since, p = pressure exerted by 10 m of water, the depth of the lake = 70 m.

4 $n_{C_2H_6} = \frac{w}{30}, n_{(H_2)} = \frac{w}{2}$

$$p_{H_2} = \frac{w/2}{\frac{w}{2} + \frac{w}{30}} \cdot p = \frac{1}{1 + \frac{1}{15}} = \frac{15}{16} \cdot p$$

Hence, (d) option is correct.

5 Let a cm from HCl end, white fumes of NH_4Cl are noticed.



From Graham's law; $\frac{r_{HCl}}{r_{NH_3}} = \sqrt{\frac{M_{NH_3}}{M_{HCl}}}$

or $$\frac{a}{t} \times \frac{t}{(200 - a)} = \sqrt{\frac{17}{36.5}}$$

[∵ Time of diffusion in tube for both is same.]

∴ $a = 81.1$ cm from HCl end.

6 Volume of O_2 diffused $= \frac{22400 \times 0.48}{32} = 336$ mL

Let the volume of CO_2 diffused be x mL.

Rate of diffusion of $O_2 = \frac{336}{1200}$ mL s^{-1}

Rate of diffusion of $CO_2 = \frac{x}{1200}$ mL s^{-1}

$$\frac{r_{O_2}}{r_{CO_2}} = \frac{V_{O_2}/t}{V_{CO_2}/t} = \sqrt{\frac{M_{CO_2}}{M_{O_2}}}$$

or $$\frac{\frac{336}{1200}}{\frac{x}{1200}} = \sqrt{\frac{44}{32}}$$

∴ $x = 286.6$ mL

7 According to Graham's law of diffusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\therefore \quad \frac{r_{235_{UF_6}}}{r_{238_{UF_6}}} = \sqrt{\frac{352}{349}} = 1.0043$$

8 For H_2 : $p \times V = \frac{w}{2} \times R \times 373$

For He : $p \times \frac{V}{2} = \frac{3.5}{4} \times R \times 298$

Hence, $w_{H_2} = 2.8$ g

9 Average kinetic energy depends only on temperature and does not depend upon the nature of gas.

10 $u_{rms} = \sqrt{\frac{3pV}{M}}$

$pV = nKT$ (K = Boltzmann's constant)

For a molecule, $n = 1$

$pV = KT \quad \Rightarrow \quad u_{rms} = \sqrt{\frac{3KT}{M}}$

Kinetic energy $(E) = \frac{3}{2}KT$ or $KT = \frac{2}{3}E$

$$u_{rms} = \sqrt{\frac{3 \times \frac{2}{3}E}{M}} = \sqrt{\frac{2E}{M}}$$

11 $\frac{u_{rms}\ (SO_2)}{u_{rms}\ (O_2)} = \sqrt{\frac{T\ (SO_2)}{M\ (SO_2)} \times \frac{M\ (O_2)}{T\ (O_2)}}$

i.e. $\quad 1 = \sqrt{\frac{T\ (SO_2)}{64} \times \frac{32}{303}}$ or,

$T(SO_2) = 606$ K

12 $u_{rms} = \sqrt{\frac{3RT}{M}} \therefore \frac{u_1}{u_2} = \sqrt{\frac{3RT_1}{M_1} \times \frac{M_2}{3RT_2}}$

$$= \sqrt{\frac{T_1M_2}{T_2M_1}} = \sqrt{\frac{50 \times 32}{800 \times 2}} = 1$$

13 Average KE $= \frac{3}{2}RT/N_0$

$$\text{KE} \propto T \Rightarrow \frac{(\text{KE})_{313}}{(\text{KE})_{293}} = \frac{313}{293}$$

14 Since, the external pressure is 1.0 atm, the gas pressure is also 1.0 atm as piston is movable. Out of this 1.0 atm, partial pressure due to known compound is 0.68 atm. Therefore, partial pressure of He

$$= 1.00 - 0.68 = 0.32 \text{ atm}$$

$$\text{Volume} = \frac{n_{(He)}\ RT}{p_{(He)}}$$

$$= \frac{0.1 \times 0.082 \times 273}{0.32} = 7 \text{ L}$$

15 $n = \frac{pV}{RT} = \frac{3170 \times 10^{-3}}{8.314 \times 300}$

$$= 1.27 \times 10^{-3} \text{ mol}$$

16 van der Waals' equation for one mole of real gas is $\left(p + \frac{a}{V^2}\right)(V - b) = RT$

When pressure is high $p >> \frac{a}{V^2}$ such that $\left(p + \frac{a}{V^2}\right) = p$

Thus, $p(V - b) = RT \quad \Rightarrow pV = RT + pb$

$\therefore$ Compressibility factor, $Z = \frac{pV}{RT}$

$$= \left(1 + \frac{pb}{RT}\right)$$

17 $Z = \frac{pV}{nRT}$, i.e. $\frac{pV}{nRT} < 1$ or $pV < nRT$

(p = 1 atm at STP)

$V < 1 \times 0.0821 \times 273$ or $V < 22.4$ L

18 To solve this problem, the stepwise approach is required, i.e.

(i) Write the van der Waals' equation, then apply the condition that at low pressure, volume become high, i.e. $V - b \approx V$

(ii) Now, calculate the value of compressibility factor (Z).

$[Z = pV / RT]$

According to van der Waals' equation, $\left(p + \frac{a}{V^2}\right)(V - b) = RT$

At low pressure,

$\left(p + \frac{a}{V^2}\right)V = RT \Rightarrow pV + \frac{a}{V} = RT$

$$pV = RT - \frac{a}{V}$$

Divide both side by RT,

$$\frac{pV}{RT} = 1 - \frac{a}{RTV}$$

19 Intermolecular forces are given by the term $\left(p + \frac{a}{V^2}\right)$.

20 $\left(p + \frac{a}{V^2}\right)V = RT \Rightarrow pV = RT - \frac{a}{V} \quad \dots \text{(i)}$

Eq. (i) is a straight line equation between pV and $\frac{1}{V}$ where slope is $-a$.

Equating with slope of the straight line given in the graph

$$-a = \frac{20.1 - 21.6}{3 - 2} = -1.5, \ a = 1.5$$

21 van der Waas' constant a is due to force of attraction and b is due to finite size of molecules. Thus, greater the value of a and smaller the value of b, larger the liquefaction.

Thus, $a\ (Cl_2) > a\ (C_2H_6)$ and $b\ (Cl_2) < b\ (C_2H_6)$.

22 We know that, $p_c = \frac{a}{27b^2}$, $V_C = 3b$

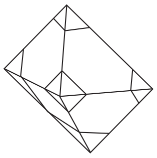
and $T_c = \frac{8a}{27Rb}$

$$= \frac{p_c V_c}{T_c} = \frac{a \times 3b \times 27Rb}{27b^2 \times 8a} = \frac{3}{8}R$$

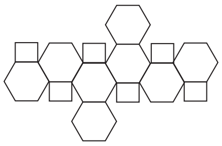
Compression factor, $Z = \frac{p_c V_c}{RT_c} = \frac{3}{8}$

23 Silicon exists as covalent crystal in solid state. (Network like structure, like diamond).

24 The truncated octahedron is the 14 faced Archimedean solid, with 14 total faces : 6 squares and 8 regular hexagonals. The truncated octahedron is formed by removing the six right square pyramids one from each point of a regular octahedron.



Truncated octahedron



Truncated octahedron unfolded in two dimensions

25 Given, $n = 1, d = 0.281 \times 10^{-9}$ m,

$\theta = 11.8°$

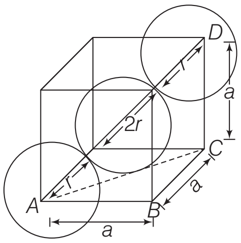
$$\therefore \quad \lambda = \frac{2 \times 0.281 \times 10^{-9} \times \sin 11.8}{1}$$

$$= 2 \times 0.281 \times 10^{-9} \times 0.2044$$

$$= 0.1149 \text{ nm}$$

26 The space lattice of diamond is fcc. The primitive basis has two identical atoms $(0,0,0), \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$ associated with each point of the fcc lattice. Thus, the conventional unit cube contains eight atoms. Also, diamond is tetrahedral.

27



From this figure,

$(AC)^2 = (AB)^2 + (BC)^2 = a^2 + a^2 = 2a^2$

Also, $(AD)^2 = (AC)^2 + (DC)^2$

$(4r)^2 = 2a^2 + a^2, 16r^2 = 3a^2, r = \frac{\sqrt{3}}{4}a$

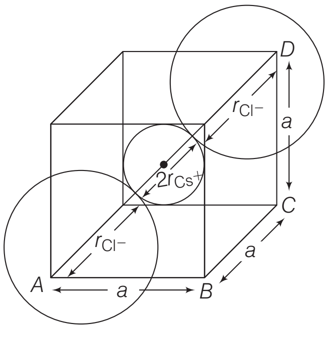
Now, when Na metal crystallises in bcc unit cell with unit cell edge length $a = 4.29\text{Å}$

$\therefore \quad r = \frac{\sqrt{3}}{4} \times 4.29\text{Å} = 1.86\text{Å}$

28 Atomic radius of lithium $= \frac{\sqrt{3}}{4}a$

$= \frac{1.73}{4} \times 351 = 151.8 \text{ pm} \approx 152 \text{ pm}$

29 CsCl crystal has bcc structure.



$AD^2 = AC^2 + CD^2 = (a\sqrt{2})^2 + a^2 = 3a^2$

$\Rightarrow AD = a\sqrt{3}$

Also, $AD = r_{Cl^-} + 2r_{Cs^+} + r_{Cl^-} = a\sqrt{3}$

$\Rightarrow \quad r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$

30 Number of atoms (A) per unit cell

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

Number of atoms (B) per unit cell

$= (6 - 1) \times \frac{1}{2} = \frac{5}{2}$

($\because$ One B atom is missing.)

Thus, formula is $A_1B_{5/2}$ or A_2B_5.

31 For fcc unit cell,

$r = \frac{\sqrt{2}}{4}a$

$\Rightarrow 0.14 = \frac{\sqrt{2}}{4}a$

$a = \frac{4 \times 0.14}{\sqrt{2}} = 0.396 \text{ nm} = 0.4 \text{ nm}$

32 Length of the edge of NaCl unit cell

$= 2 \times$ distance between Na^+ and Cl^-

$= 2 \times a = 2a$ pm

33 For fcc arrangement, $4r = \sqrt{2}a$

where, r = radius and a = edge length

$\therefore$ Closest distance $= 2r = \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}}$

34 Mass of one unit cell $= V \times d = a^3 \times d$,

Density $= \frac{Z \cdot M}{a^3 \cdot N_0}$

Mass of 1 unit cell $= \frac{a^3 \times Z \times M}{a^3 \times N_0} = \frac{ZM}{N_0}$

$= \frac{4 \times 58.5}{6.02 \times 10^{23}} = 38.87 \times 10^{-23}\text{g}$

Number of unit cells in 1g

$= \frac{1}{38.87 \times 10^{-23}} = 2.57 \times 10^{21}$

35 $d = \frac{ZM}{N_A a^3}$ (for bcc, $Z = 2$)

$d_{Fe} = \frac{(2) \times 56.0 \text{ g mol}^{-1}}{(6.02 \times 10^{23}\text{mol}^{-1})\ (2.861 \times 10^{-8})^3 \text{ cm}^3}$

$= 7.94 \text{ g cm}^{-3}$

36 $d = \frac{ZM}{N_0 a^3} \Rightarrow Z = 4 \times \left(1 - \frac{0.1}{100}\right) = 3.996$

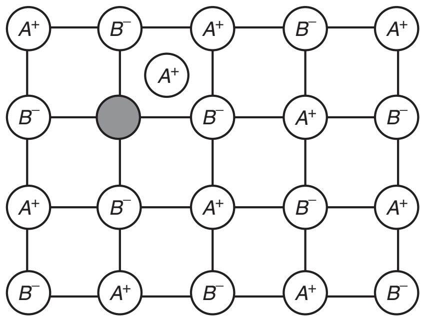
(because it contains 0.1% Schottky defect)

$d = \frac{3.996 \times 40}{6.02 \times 10^{23} \times (0.556 \times 10^{-7})^3}$

$= 1.5448 \text{ g/cm}^3$

37 For the preparation of n-type semiconductor from silicon, it should be doped with a substance of 5 valence electrons.

38 It is the "Frenkel defect" in which cations leave their original site and occupy interstitial site as shown below:



39 Only three elements iron (Fe), cobalt (Co) and nickel (Ni) show ferromagnetism at room temperature. CrO_2 is also a metallic and ferromagnetic compound which is used to make magnetic tapes for cassette recorders.

40 Both Assertion and Reason are true, Reason is a correct explanation for Assertion. Because motion of gas in one direction gives zero average speed.

41 Assertion is true but Reason is false. Because at high altitude, atmospheric pressure is low.

42 Both Assertion and Reason are false. Liquids tends to possess minimum number of molecules on the surface due to surface tension.

43 Both Assertion and Reason are true. Reason is a correct explanation for Assertion. Because F-centre contains unpaired electron and show paramagnetic character.

SESSION 2

1 Let the moles of NH_3 and N_2H_4 in original mixture are n_1 and n_2 respectively.

From given decomposition reactions :

2 moles of NH_3 produce total 4 moles of N_2 and H_2.

1 mole of N_2H_4 produces total 3 moles of N_2 and H_2.

Hence, total moles after decomposition $= 2n_1 + 3n_2$

Ideal gas equation : $pV = nRT$

Now, (0.5 atm) $V = (n_1 + n_2) R$ (300 K) ...(i)

and (4.5 atm)

$V = (2n_1 + 3n_2) R$ (1200 K) ...(ii)

On dividing the two equations and rearranging

$\frac{2n_1 + 3n_2}{n_1 + n_2} = \frac{9}{4}$ or $\frac{2(n_1 + n_2) + n_2}{n_1 + n_2} = \frac{9}{4}$

or $\frac{n_2}{n_1 + n_2} = \frac{9}{4} - 2 = \frac{1}{4}$

$\therefore$ % of N_2H_4 is $\frac{n_2}{n_1 + n_2} \times 100 = 25\%$

or $\frac{1}{4} \times 100 = 25\%$

2 $C^* = \sqrt{\frac{2RT}{M}}, \quad \overline{C} = \sqrt{\frac{8RT}{\pi M}}, \quad C = \sqrt{\frac{3RT}{\pi M}}$

$\therefore \quad C^* : \overline{C} : C = 1 : 1.128 : 1.225$

3 Given, $p = (723/760)$ atm, $w = 3.2$ g

$$T = 273 + 450 = 723 \text{ K}$$

$$\Rightarrow \quad V = (780/1000) \text{ L}$$

$$\because \quad pV = \frac{w}{M} RT$$

$$\therefore M = \frac{3.2 \times 0.0821 \times 760 \times 1000 \times 723}{723 \times 780}$$

$$= 256$$

$\because$ 32 g sulphur has 1 atom of S.

$\therefore$ 256 g S has 256/32 = 8 atoms of S

$\therefore$ Molecular formula $= S_8$

4 $M_{\text{(dry air)}}$

$$= \frac{M_1(O_2)\, x_1 (\% \text{ of } O_2) + M_2\, (N_2)\, x_2\, (\% \text{ of } N_2)}{x_1 + x_2}$$

$$= \frac{32 \times 24.5 + 28 \times 75.5}{100} = 28.98 \text{ g mol}^{-1}$$

$$d_{\text{(dry air)}} = \frac{pM_{\text{(air)}}}{RT} = \frac{1 \times 28.98}{0.0821 \times 298.15}$$

$$= 1.184 \text{ g L}^{-1} = 1.184 \text{ kgm}^{-3}$$

Relative humidity (50 %)

$$= \frac{\text{partial pressure of } H_2O \text{ in air}}{\text{vapour pressure of } H_2O}$$

$$p\,(H_2O) = 0.50 \times 23.7 \text{ torr}$$

$$= 11.85 \text{ torr} = \frac{11.85}{760} \text{ atm}$$

$$= 0.0156 \text{ atm}$$

% of H_2O vapour in air

$$= \frac{0.0156 \times 100}{1} = 1.56\%$$

% of N_2 and O_2 in air

$$= 100 - 1.56 = 98.44\%$$

$M_{\text{(wet air)}}$

$$= \frac{28.98 \times 98.44 \text{ (air)} + 18 \times 1.56 \text{ (water vapour)}}{100}$$

$$= 28.81 \text{ g mol}^{-1}$$

$$\therefore d_{\text{(wet air)}} = \frac{pM_{\text{(wet air)}}}{RT}$$

$$= \frac{1 \times 28.81}{0.0821 \times 298.15}$$

$$= 1.177 \text{ g L}^{-1}$$

$$= 1.177 \text{ kg m}^{-3}$$

Difference

$$= 1.184 - 1.177$$

$$= 0.007 \text{ kg m}^{-3}$$

5 In cubic closed packing, there will be four oxide ions;

$8 \times \frac{1}{8}$ = one A ion and $4 \times \frac{1}{2} = 2B$ ions.

Hence, formula will be $\overset{+2}{A}\, \overset{+3}{B_2}\, \overset{-2}{O_4}$.

6 van der Waals' equation is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

When $a = 0$, $p\,(V - b) = RT$

or $\quad pV = RT + pb$

or $\quad \frac{pV}{RT}$, i.e. $\quad Z = 1 + \frac{pb}{RT}$.

Thus, $Z > 1$ and increases with increase of pressure. Hence, (a) is correct.

When $b = 0$, $\left(p + \frac{a}{V^2}\right) V = RT$

or $pV + \frac{a}{V} = RT$ or $\frac{pV}{RT}$, i.e. $Z = 1 - \frac{a}{VRT}$.

Thus, $Z < 1$ and decreases with increase of pressure. Hence, (b) is correct. (d) is also correct and only wrong statement is (c).

7 Mass of 1L steam

$= 1000 \times 0.0006 = 0.6$ g

= mass of liquid water

Volume of water = 0.6 cc

($d = 1 \text{ g cm}^{-3}$).

Same volume will be occupied by water molecules in steam.

8 Given, metal oxide $= M_{0.98}O$

Let x ions are of M in + 3 states,
Therefore, $3x + (0.98 - x) \times 2 = 2$,
$x = 0.04$

$$\% \text{ of } M \text{ in } +3 \text{ states} = \frac{0.04}{0.98} \times 100$$

$$= 4.08\%$$

9 The correct order of root mean square speed of different gases at the same temperature is

$$(\mu_{rms})_{H_2} > (\mu_{rms})_{CH_4} > (\mu_{rms})_{NH_3} > (\mu_{rms})_{CO_2}$$

We know that,

$$\mu_{rms} \propto \frac{1}{M}$$

More the mass of the molecule, less is the μ_{rms}.

10 At low temperature and low pressure, Z is usually less than one. This fact can be explained by van der Waals' equation when the constant b is negligible and not a.

11 $T = \frac{rhdg}{2}$

$$= \frac{(4 \times 10^{-4}) \times (0.04) \times 800 \times 9.8}{2}$$

$$(r = 0.4 \text{ mm} = 4 \times 10^{-4} \text{ m})$$

$$= 4 \times 10^{-4} \times 0.04 \times 400 \times 9.8$$

$$= 4 \times 4 \times 4 \times 98 \times 10^{-5}$$

$$= 6.3 \times 10^{-2} \text{ Nm}^{-1}$$

12 When a sample of gas is compressed at constant temperature from 15 atm to 6 atm, its volume changes from 76 cm^3 to 20.5 cm^3. This behaviour shows that gas behaves non-ideally.

13 Given, angle of diffraction $(2\theta) = 90°$,

$$\theta = 45°$$

Distance between two planes,
$d = 2.28$ Å, $n = 2$

Bragg's equation is $n\lambda = 2d \sin\theta$

$$2 \times \lambda = 2 \times 2.28 \times \sin 45°$$

$$\lambda = 1.612$$

14 Mass of one unit-cell (m) = volume × density

$$= a^3 \times d$$

$$= a^3 \times \frac{MZ}{N_0 a^3}$$

$$\frac{Mz}{N_0} \times m = \frac{58.5 \times 4}{6.02 \times 10^{23}} \text{ g}$$

$\therefore$ Number of unit cell in 1 g

$$= \frac{1}{m} = \frac{6.02 \times 10^{23}}{584 \times 4} = 2.57 \times 10^{21}$$

15 Schottky defects occur mainly in electrovalent compounds where positive ions and negative ions are of same size.