

The temperature at which the solid and the liquid forms of a substance exist at equilibrium or both the forms have same vapour pressure, is called the melting point. On supplying heat energy, the particles acquire sufficient energy and move away from their fixed positions in space. This results in the formation of liquid state. The solids have definite melting points depending on the strength of binding energy. However, in some solids (amorphous solids) the melting point is not sharp.

### 4.13 FORMS OF SOLIDS

Solids are divided into two classes on the basis of haphazard and regular arrangement of the building constituents.

(i) **Amorphous solids:** The term 'amorphous' has been derived from a Greek word 'Omorphe' meaning shapeless. In amorphous solids the arrangement of building constituents is not regular but haphazard. Although these solids possess some of the mechanical properties such as rigidity, incompressibility, refractive index, etc., but do not have characteristic shapes or geometrical forms. Amorphous solids in many respects resemble liquids which flow very slowly at room temperature and regarded as supercooled liquids in which the cohesive forces holding the molecules together are so great that the material is rigid but there is no regularity of the structure. Glass, rubber, plastics, etc., are some of the examples of amorphous solids.

Amorphous solids do not have sharp melting points. For example, when glass is heated, it softens and then starts flowing without undergoing any abrupt change from solid to liquid state.

Thus, amorphous substances are not true solids but can be regarded as intermediate between liquids and solids.

(ii) **Crystalline solids:** In crystalline solids the building constituents arrange themselves in regular manner throughout the entire three-dimensional network. The ordered arrangement of building constituents (molecules, atoms or ions) extends over a large distance. Thus, crystalline solids have long range order. A crystalline solid consists of a large number of units, called crystals. A crystal is defined as a solid figure which has a definite geometrical shape, with flat faces and sharp edges.

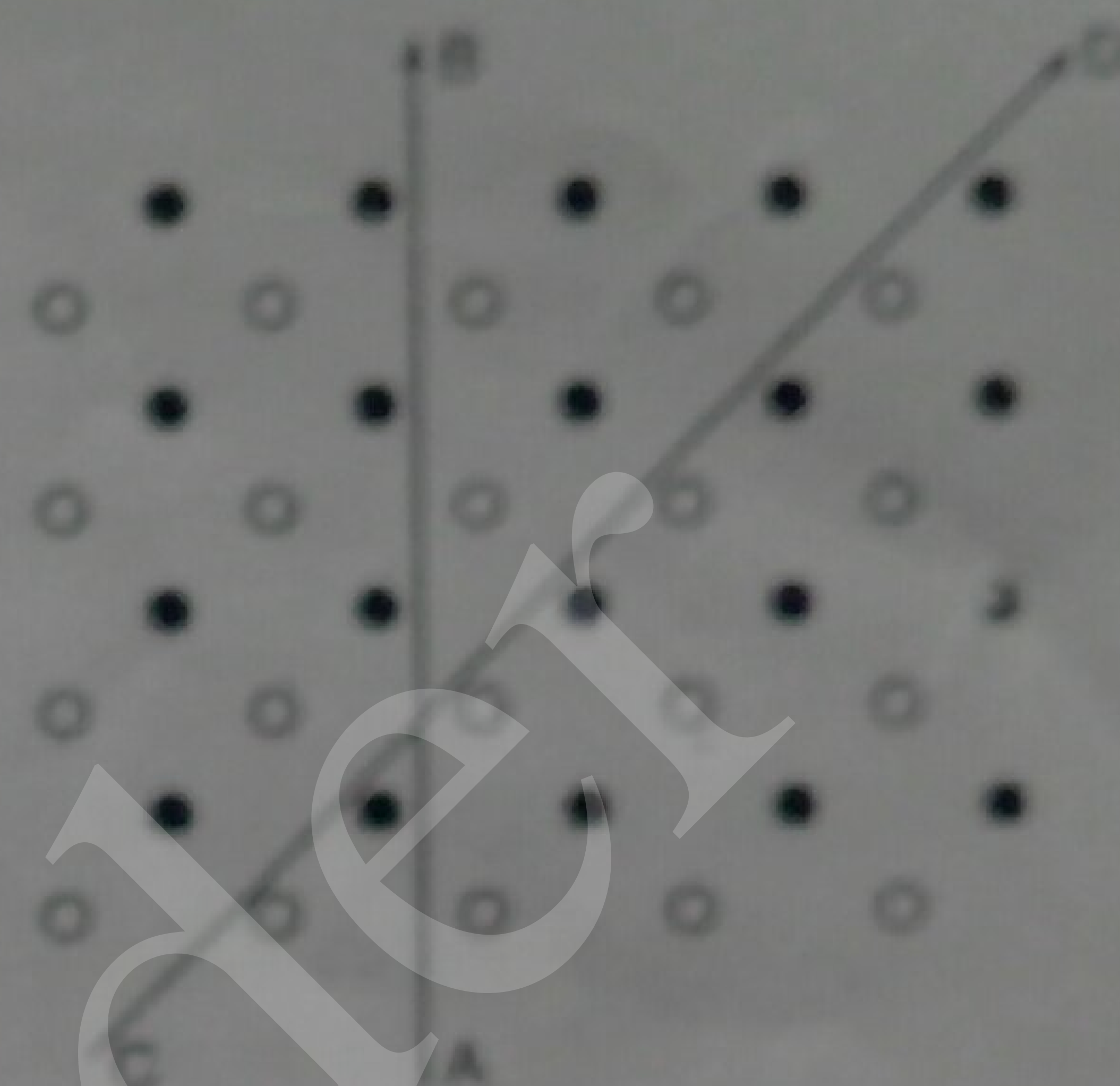
A crystalline substance has a sharp melting point, i.e., it changes abruptly into liquid state. Strictly speaking 'a solid state refers to crystalline state' or 'only a crystalline substance can be considered to be a true solid'.

### 4.14 ISOTROPY AND ANISOTROPY

The substances which show same properties in all directions are said to be isotropic and the substances exhibiting directional differences in properties are termed anisotropic.

Amorphous solids like liquids and gases are said to be isotropic as arrangement of building constituents is random and disordered. Hence, all directions are equal and therefore, properties are same in all the directions.

Crystalline solids are anisotropic. Magnitude of some of the physical properties of crystalline solids such as refractive index, coefficient of thermal expansion, electrical and thermal conductivities, etc., is different in different directions, within the crystal. For example, in the crystal of silver iodide (AgI), the coefficient of thermal expansion is positive in one direction and negative in the other direction.



The phenomenon of anisotropy provides a strong evidence for the presence of ordered molecular arrangement in crystals. This can be explained with the help of Fig. 4.21 in which a simple two dimensional arrangement of two different kinds of atoms has been depicted. When a physical property is measured along the slanting line CD, it will be different from that measured in the direction of vertical line AB, as line CD contains alternate types of atoms while line AB contains one type of atoms only.

### 4.15 DIFFERENCES BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS

Crystalline solids	Amorphous solids
They have definite and regular geometry due to definite and orderly arrangement of atoms, ions or molecules in three dimensional space.	They do not have any pattern of arrangement of atoms, ions or molecules and, thus, do not have any definite geometrical shape.
They have sharp melting points and change abruptly into liquids.	Amorphous solids do not have sharp melting points and do not change abruptly into liquids.
Crystalline solids are anisotropic. Some of their physical properties are different in different directions.	Amorphous solids are isotropic. Their physical properties are same in all directions.
These are considered as true solids.	These are considered pseudo-solids or supercooled liquids.
Crystalline solids are rigid and their shape is not distorted by mild distorting forces.	Amorphous solids are not very rigid. These can be distorted by bending or compressing forces.

Melting point of a solid depends on the structure of the solid. It is used for the identification of solids whether it is crystalline or amorphous.



**Crystalline solids**

Crystals are bound by plane faces. The angle between any two faces is called interfacial angle. For a given crystalline solid, it is a definite angle and remains always constant no matter how the faces develop.

When a crystalline solid is hammered, it breaks up into smaller crystals of the same geometrical shape.

An important property of crystals is their symmetry. There are: (i) plane of symmetry, (ii) axis of symmetry and (iii) centre of symmetry.

**Amorphous solids**

Amorphous solids do not have well defined planes.

When an amorphous solid is broken, the surfaces of the broken pieces are generally not flat and intersect at random angles.

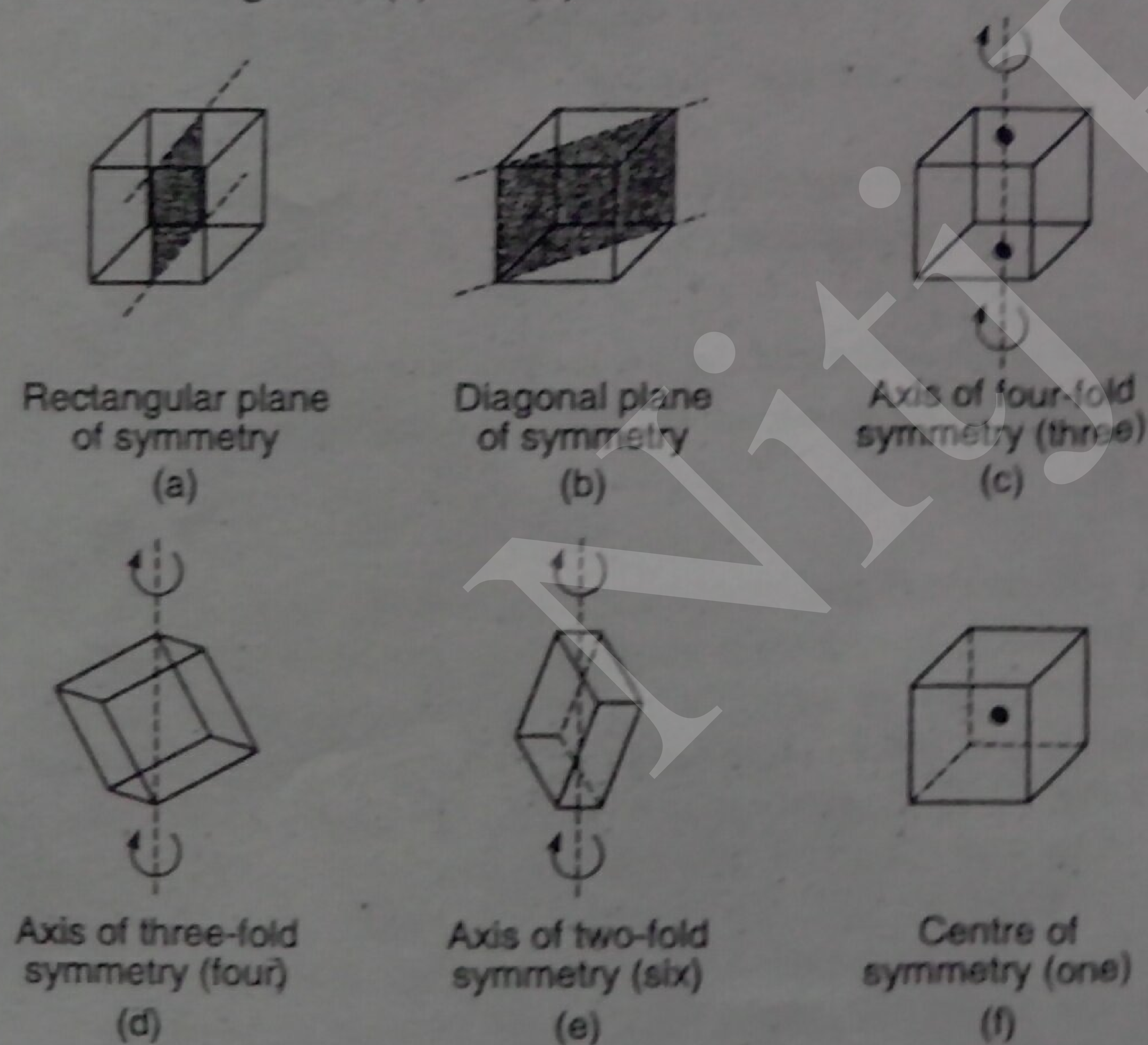
Amorphous solids do not have any symmetry.

**4.16**

**Centre of symmetry:** It is such an imaginary point within the crystal that any line drawn through it intersects the surface of the crystal at equal distances in both directions. A crystal always possesses only one centre of symmetry [Fig. 4.22 (f)].

**Plane of symmetry:** It is an imaginary plane which passes through the centre of a crystal and divides it into two equal portions such that one part is exactly the mirror image of the other.

A cubical crystal like NaCl possesses, in all, nine planes of symmetry; three rectangular planes of symmetry and six diagonal planes of symmetry. One plane of symmetry of each of the above is shown in Fig. 4.22 (a) and (b).



**Axis of symmetry:** It is an imaginary straight line about which, if the crystal is rotated, it will present the same appearance more than once during the complete revolution. The

axes of symmetry are called diad, triad, tetrad and hexad, respectively, if the original appearance is repeated twice (after an angle of  $180^\circ$ ), thrice (after an angle of  $120^\circ$ ), four times (after an angle of  $90^\circ$ ) and six times (after an angle of  $60^\circ$ ) in one rotation. These axes of symmetry are also called two-fold, three-fold, four-fold and six-fold, respectively.

In general, if the same appearance of a crystal is repeated on rotating through an angle of  $\frac{360^\circ}{n}$ , around an imaginary axis, the axis is called an  $n$ -fold axis.

In all, there are 13 axes of symmetry possessed by a cubical crystal like NaCl as shown in Fig. 4.22 (c), (d) and (e).

The total number of planes, axes and centre of symmetry possessed by a crystal are termed as elements of symmetry. A cubic crystal possesses a total of 23 elements of symmetry.

Planes of symmetry =  $(3 + 6) = 9$  [Fig. 4.22 (a) and (b)]

Axes of symmetry =  $(3 + 4 + 6) = 13$  [Fig. 4.22 (c), (d) and (e)]

Centre of symmetry = 1 [Fig. 4.22 (f)]

Total number of symmetry elements = 23

**4.17 SPACE LATTICE AND UNIT CELL**

All crystals are polyhedra consisting of regularly repeating arrays of atoms, molecules or ions which are the structural units. A crystal is a homogeneous portion of a solid substance made of regular pattern of structural units bonded by plane surfaces making definite angles with each other. The geometrical form consisting only of a regular array of points in space is called a lattice or space lattice or it can be defined as an array of points showing how molecules, atoms or ions are arranged in different sites, in three-dimensional space. Fig. 4.23 shows a space lattice. A space lattice can be subdivided into a number of small cells known as unit cells. It can be defined as the smallest repeating unit in space lattice which, when repeated over and over again, results in a crystal of the given substance or it is the smallest block or geometrical figure from which entire crystal can be built up by its translational repetition in three-dimensions. A unit cell of a crystal possesses all the structural properties of the given crystal. For example, if a crystal is a cube, the unit cell must also have its atoms, molecules or ions arranged so as to give a cube.

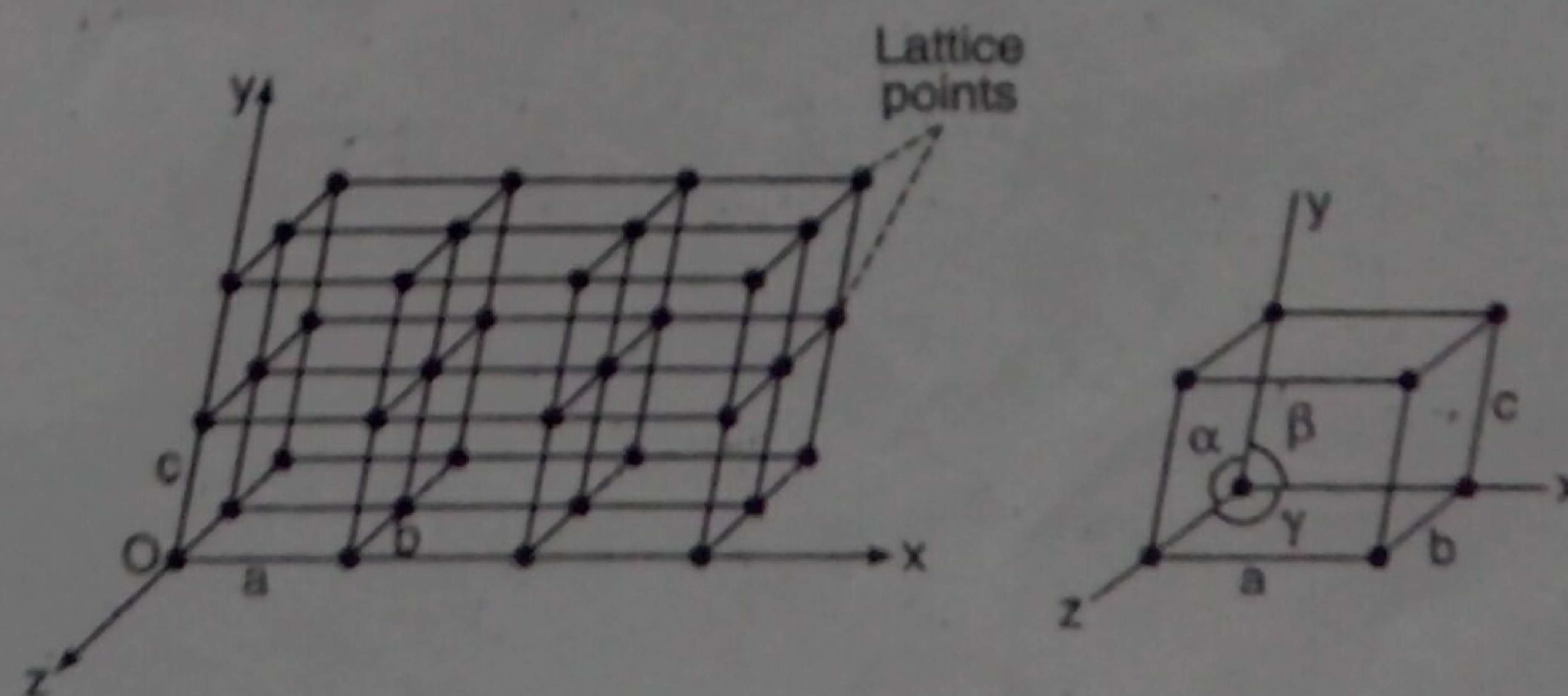


Fig. 4.23 Space lattice and unit cell



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System	Edges	Angles	Maximum symmetry elements	Examples
Cubic $a = b = c, \alpha = \beta = \gamma = 90^\circ$	All the three equal	All right angles	Nine planes, thirteen axes	NaCl, KCl, ZnS, diamond, alums
Orthorhombic $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	All unequal	All right angles	Three planes, three axes	$KNO_3, BaSO_4, K_2SO_4$ , rhombic sulphur.
Tetragonal $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	Two equal	All right angles	Five planes, five axes	$TiO_2, PbWO_4, SnO_2, NH_4Br$
Monoclinic $a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	All unequal	Two right angles	One plane, one axis	Monoclinic sulphur, $KClO_3, CaSO_4 \cdot 2H_2O, Na_2B_4O_7 \cdot 10H_2O$
Triclinic $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	All unequal	None right angles	No planes, no axis	$CuSO_4 \cdot 5H_2O, H_3BO_3, K_2Cr_2O_7$
Hexagonal $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	Two equal	Angle between equal edges = $120^\circ$	Seven planes, seven axes	ZnO, CdS, HgS, SiC, AgI
Rhombohedral $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	All three equal	All equal but none $90^\circ$	Seven planes, seven axes	$NaNO_3, ICl, quartz (CaCO_3)$

Each unit cell has three vectors  $a, b$  and  $c$  as shown in Fig. 4.23. The distances  $a, b$  and  $c$  are the lengths of the edges of the unit cell and angles  $\alpha, \beta$  and  $\gamma$  are the angles between three imaginary axes  $OX, OY$  and  $OZ$ , respectively.

For example: For a crystal system,  $a = b = c$  and  $\alpha = \beta = \gamma \neq 90^\circ$ :

- (a) tetragonal
- (b) hexagonal
- (c) rhombohedral
- (d) monoclinic

[ (c) ]

[ From the table  $a = b = c$  for rhombohedral and cubic system both but  $\alpha = \beta = \gamma \neq 90^\circ$  for rhombohedral only.]

4.18

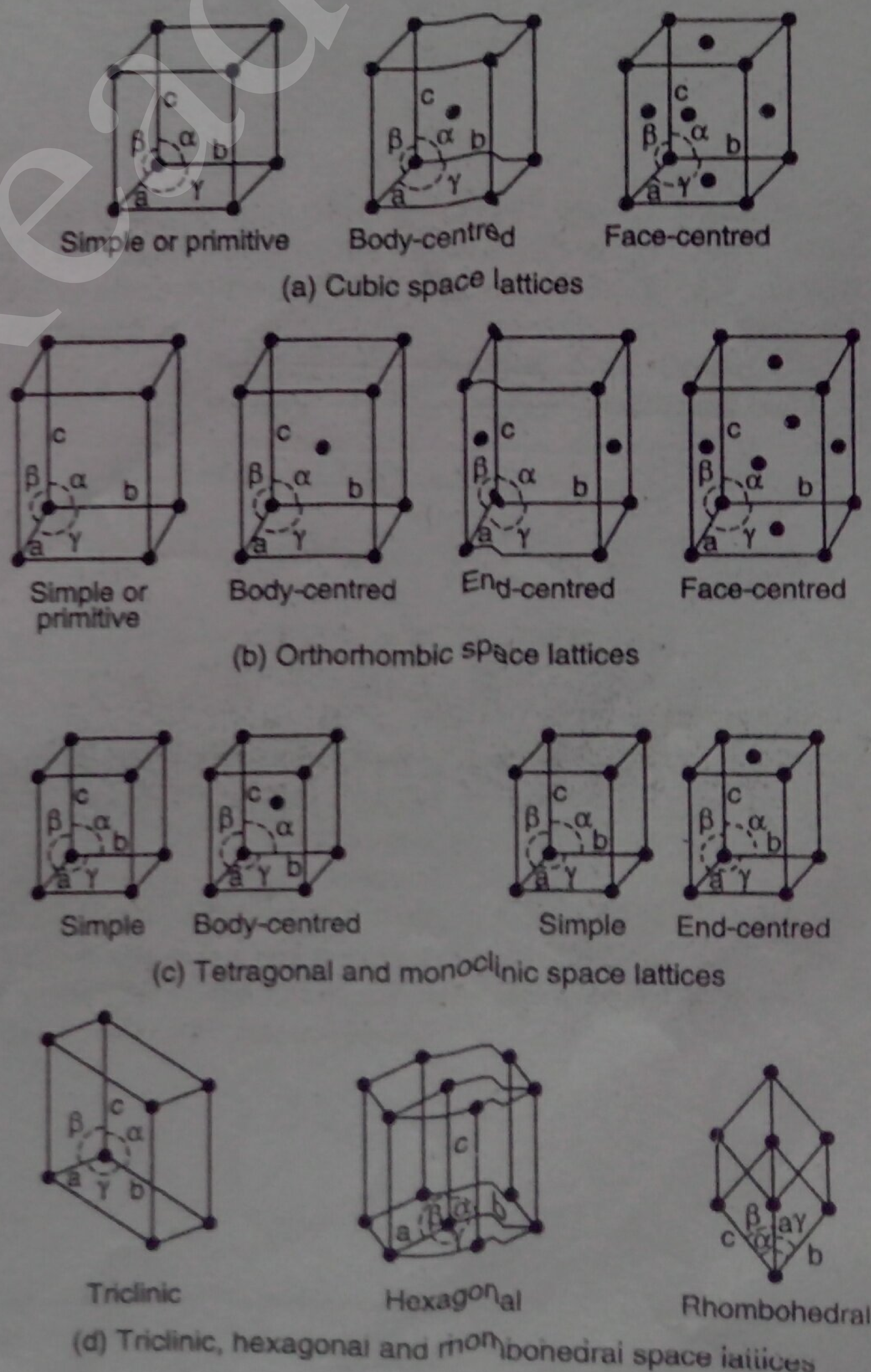
On the basis of geometrical considerations, theoretically there can be 32 different combinations of elements of symmetry of a crystal. These are called 32 systems. Some of the systems have been grouped together. In all, seven types of basic or primitive unit cells have been recognised among crystals. These are cubic, orthorhombic, tetragonal, monoclinic, triclinic, hexagonal and rhombohedral. These are shown in Fig. 4.24 and their characteristics are summarised in the following table.

All crystals do not have simple lattices. Some are more complex. Bravais pointed out that there can be 14 different ways in which similar points can be arranged in a three-dimensional space. Thus, the total number of space lattices belonging to all the seven crystal systems are 14.

The crystals belonging to cubic system have three kinds of Bravais lattices. These are:

There are points only at the corners of each unit.

There are points at the corners as well as at the centre of each of the six faces of the cube.





There are points at the corners as well as in the body-centre of each cube.

The number of Bravais space lattices in a given system is listed in the following table and shown in Fig. 4.24.

Crystal system	No. of space lattices	Lattice type
Cubic	3	Simple, face-centred and body-centred.
Orthorhombic	4	Rectangular and body-centred rectangular prism, rhombic and body-centred rhombic prism.
Tetragonal	2	Simple and body-centred tetragonal prism.
Monoclinic	2	Monoclinic parallelepiped, monoclinic face-centred parallelepiped.
Triclinic	1	Triclinic parallelepiped.
Hexagonal	1	Hexagonal prism.
Rhombohedral	1	Rhombohedron.

In various unit cells, there are three kinds of lattice points: points located at the corners, points in the face-centres and points that lie entirely within the unit cell. In a crystal, atoms located at the corner and face-centre of a unit cell are shared by other cells and only a portion of such an atom actually lies within a given unit cell.

(i) A point that lies at the corner of a unit cell is shared among eight unit cells and, therefore, only one-eighth of each such point lies within the given unit cell.

(ii) A point along an edge is shared by four unit cells and only one-fourth of it lies within any one cell.

(iii) A face-centred point is shared by two unit cells and only one-half of it is present in a given unit cell.

(iv) A body-centred point lies entirely within the unit cell and contributes one complete point to the cell.

Type of lattice point	Contribution to one unit cell
Corner	1/8
Edge	1/4
Face-centre	1/2
Body-centre	1

Total number of constituent units per unit cell

$$= \frac{1}{8} \times \text{occupied corners} + \frac{1}{4} \times \text{occupied edge-centres} + \frac{1}{2} \times \text{occupied face-centres} + \text{occupied body-centre.}$$

Determination of Number of Constituent units per unit cell:

Let edge length of cube =  $a$  cm

Density of substance =  $d$  g cm<sup>-3</sup>

Volume of unit cell =  $a^3$  cm<sup>3</sup>

Mass of unit cell = volume  $\times$  density =  $(a^3 \times d)$  g

$$\text{Number of mol per unit cell} = \frac{a^3 \times d}{M}$$

where,  $M$  = molar mass

Number of molecules per unit cell = Number of mole  $\times$  Avogadro's number

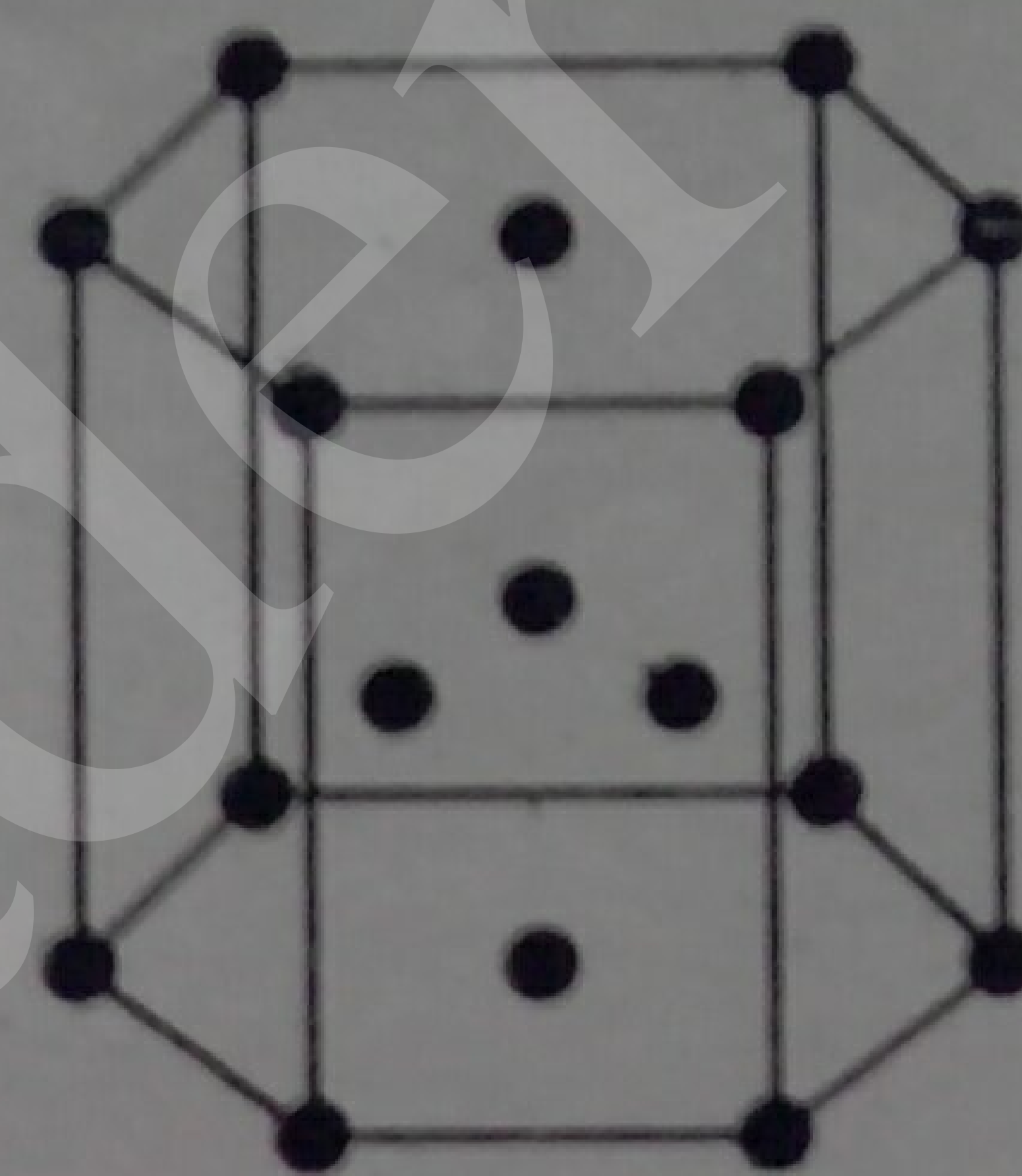
$$Z = \frac{a^3 \times d}{M} \times N = \frac{a^3 \times d \times N}{M}$$

(i) Constituent units at each corner of unit cell is common among six unit cells hence contribute 1/6th to each unit cell.

(ii) Constituent unit at edge is common to three unit cells hence contribute 1/3rd to each unit cell.

(iii) Constituent units present at the body centre is considered in single unit cell.

(iv) Constituent unit at face centre is common between two unit cells hence contribute 1/2 to each unit cell.



In the hexagonal unit cell (Fig 4.25), 12 corners, 2 face centres and 3 constituent units within the unit cells are occupied, hence effective number of constituent units present in the unit cell may be calculated as

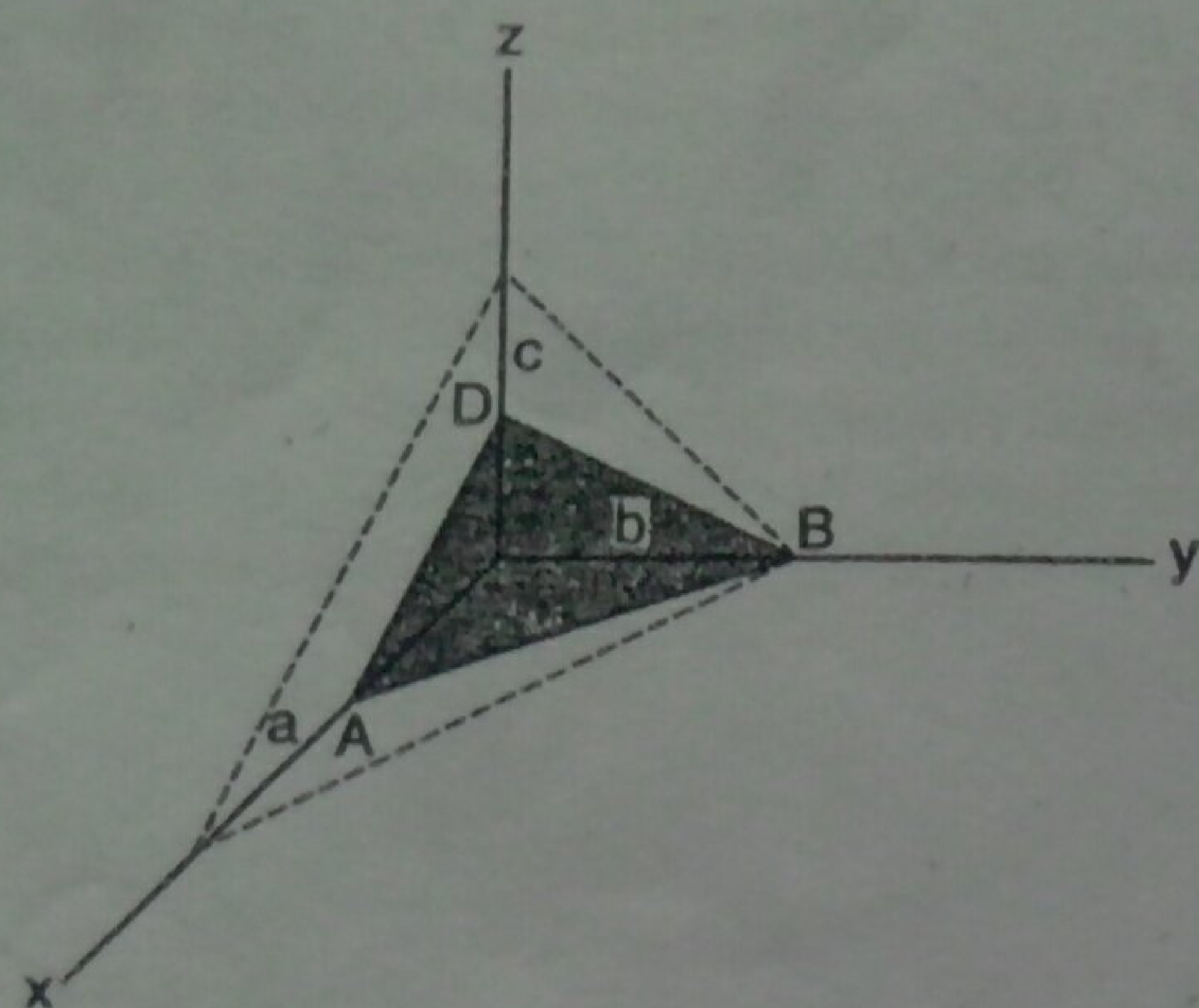
$$\begin{aligned} z &= \frac{1}{6} \times \text{occupied corners} + \frac{1}{2} \times \text{occupied face centres} + \text{Central constituent units} \\ &= \frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 3 \\ &= 6 \end{aligned}$$

#### 4.19 DESIGNATION OF PLANES IN CRYSTALS - MILLER INDICES

Planes in crystals are described by a set of integers ( $h, k$  and  $l$ ) known as Miller indices. Miller indices of a plane are the reciprocals of the fractional intercepts of that plane on the various crystallographic axes. For calculating Miller indices, a reference plane, known as Parametral plane, is selected having intercepts  $a, b$  and  $c$  along  $x, y$  and  $z$ -axes, respectively (Fig. 4.26). Then, the intercepts of the unknown plane are given with respect to  $a, b$  and  $c$  of the parametral plane.



5

Fig. 4.26 Parametral (intercepts  $a, b, c$  along  $x, y$  and  $z$ -axes)

Thus, the Miller indices are:

$$h = \frac{a}{\text{intercept of the plane along } x\text{-axis}}$$

$$k = \frac{b}{\text{intercept of the plane along } y\text{-axis}}$$

$$l = \frac{c}{\text{intercept of the plane along } z\text{-axis}}$$

Consider the shaded plane  $ABD$  in Fig. 4.26. The intercepts of the shaded plane along  $X, Y$  and  $Z$ -axes are  $a/2, b$  and  $c/2$ , respectively. Thus,

$$h = \frac{a}{a/2} = 2;$$

$$k = \frac{b}{b} = 1;$$

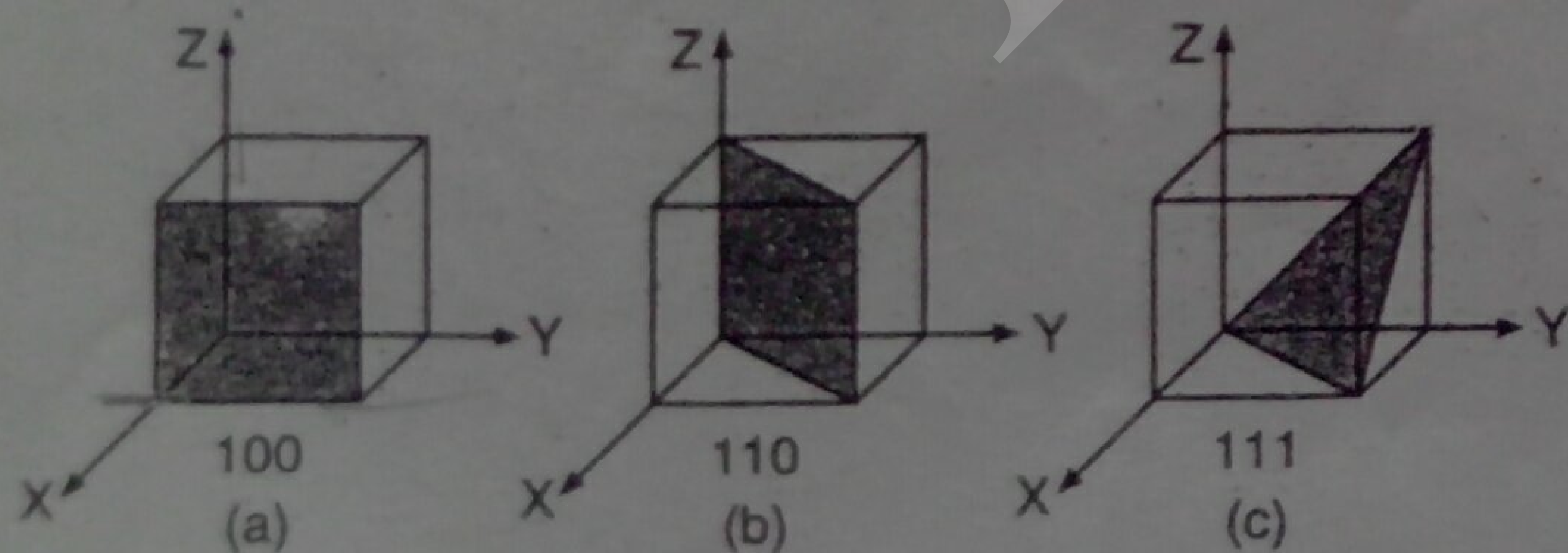
$$l = \frac{c}{c/2} = 2$$

The plane is, therefore, designed as (212) plane.

Note: (i) If a plane is parallel to an axis, its intercept with that axis is taken as infinite and the Miller indices will be zero.

(ii) While defining Miller indices for orthogonal crystal,  $X, Y$  and  $Z$ -axes are considered crystallographic axes.

Some of the important planes of cubic crystals are shown in Fig. 4.27.



In (a) intercepts are	1	$\infty$	$\infty$
So, Miller indices are	1	0	0
The plane is designated (100)			
In (b) intercepts are	1	1	$\infty$
So, Miller indices are	1	1	0
The plane is designated (110)			
In (c) intercepts are	1	1	1
So, Miller indices are	1	1	1
The plane is designated (111)			

The distances between the parallel planes in crystals are designated as  $d_{hkl}$ . For different cubic lattices these interplanar spacings are given by the general formula,

$$d_{(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where,  $a$  is the length of the cube side while  $h, k$  and  $l$  are the Miller indices of the plane.

The spacings of the three planes (100), (110) and (111) of simple cubic lattice can be calculated.

$$d_{(100)} = \frac{a}{\sqrt{1^2 + 0 + 0}} = a$$

$$d_{(110)} = \frac{a}{\sqrt{1^2 + 1^2 + 0}} = \frac{a}{\sqrt{2}}$$

$$d_{(111)} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

The ratio is,

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577$$

Similarly,  $d_{(hkl)}$  ratios for face-centred cubic and body-centred cubic can be calculated. For face-centred cubic,

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1 : 0.707 : 1.154$$

For body-centred cubic,

$$\begin{aligned} d_{(100)} : d_{(110)} : d_{(111)} &= \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} \\ &= 1 : \sqrt{2} : \frac{1}{\sqrt{3}} \\ &= 1 : 1.414 : 0.577 \end{aligned}$$

#### 4.20

Crystallography is the branch of science which deals with the geometry, properties and structure of crystals and crystalline substances. Geometric crystallography is concerned with the external spatial arrangement of crystal planes and geometric shapes of crystals.



Atoms, molecules or ions are too small to be seen with naked eye. The arrangement of particles in crystalline solids is determined indirectly by X-ray diffraction. In 1912, Von Laue showed that any crystal could serve as a three-dimensional grating to the incident electromagnetic radiation with wavelength approximately equal to the internuclear separations ( $\approx 10^{-8}$  cm) of atoms in the crystal. Such radiation is in the X-ray region of the electromagnetic spectrum.

The apparatus used is shown in Fig. 4.28. A monochromatic X-ray beam is directed towards the surface of a slowly rotated crystal so as to vary the angle of incidence  $\theta$ . At various angles, strong beams of deflected X-rays strike the photographic plate. The photographic plate after developing shows a central spot due to primary beam and a set of symmetrically disposed spots due to deflected X-rays. Different kinds of crystals produce different arrangements of spots.

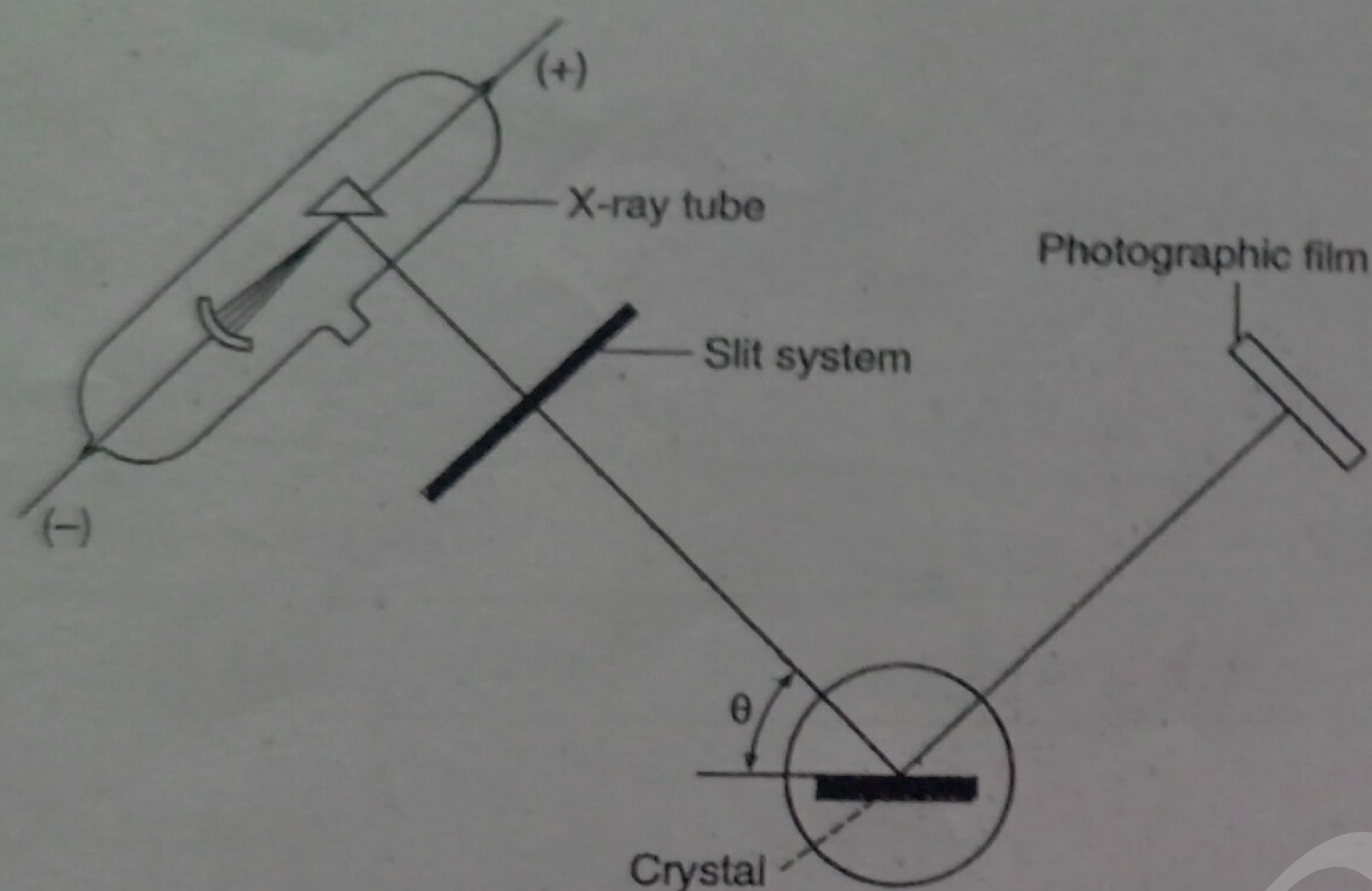


Fig. 4.28 X-ray diffraction of crystals

In 1913, Bragg found that Laue photographs are more easily interpreted by treating the crystals as a reflection grating rather than a diffraction grating. Fig. 4.29 illustrates the way by which the crystal spacings can be determined by use of X-rays of a single wavelength,  $\lambda$ . The rays strike the parallel planes of the crystal at angle  $\theta$ . Some of the rays are reflected from the upper plane, some from the second and some from the lower planes. A strong reflected beam will result only if all the reflected rays are in phase. The waves reflected by different layer planes will be in

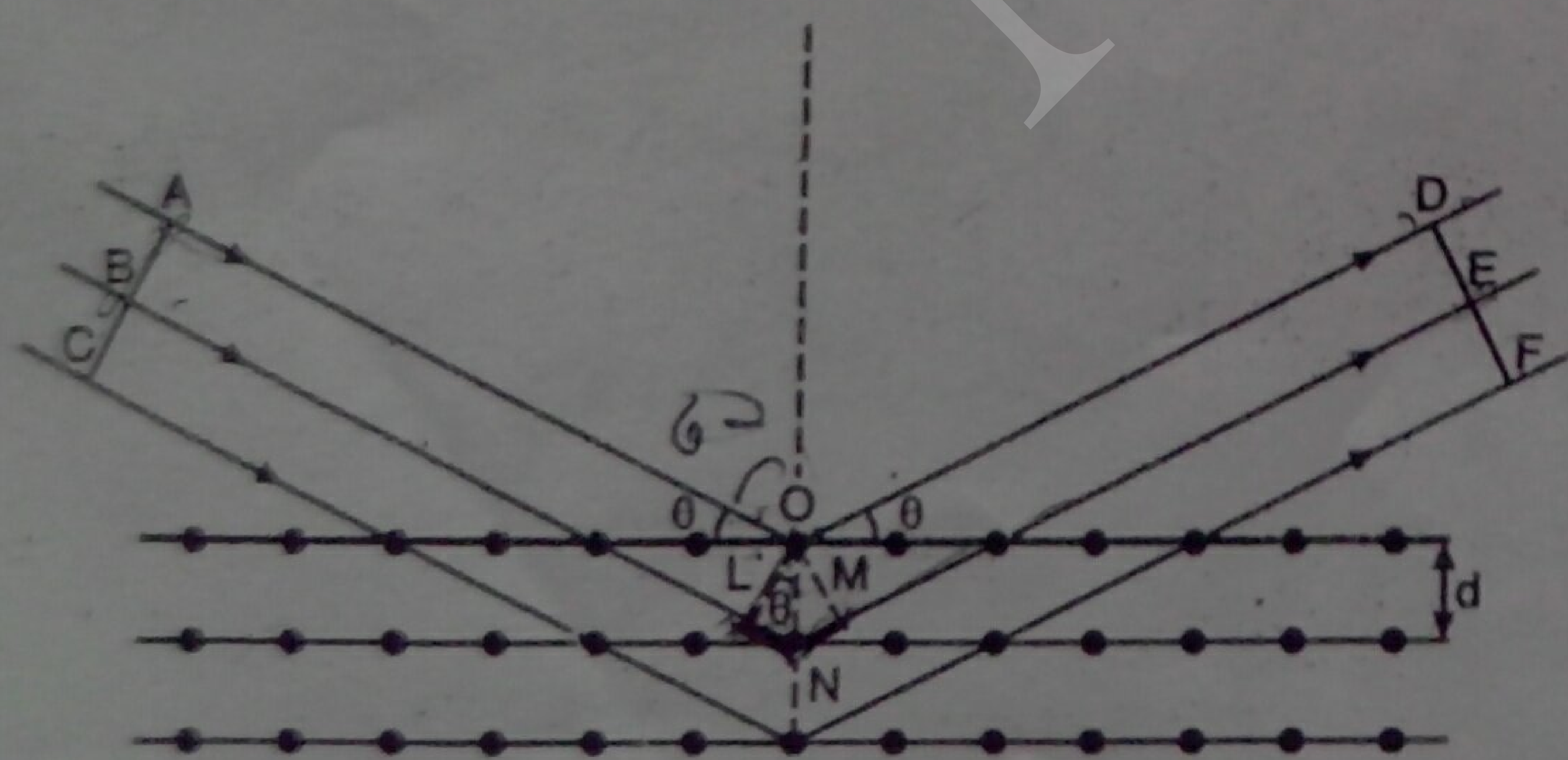


Fig. 4.29 X-ray reflection from crystals

phase with one another only if the difference in the path length of the waves reflected from the successive planes is equal to an integral number of wavelengths.  $OL$  and  $OM$  are the perpendiculars drawn to the incident and reflected beams. The difference in path lengths of waves deflected from the first two planes is given by:

$$LN + NM = n\lambda \quad (n = 1, 2, 3, \dots)$$

Since, the triangles  $OLN$  and  $OMN$  are congruent, hence  $LN = NM$ .

So, Path difference =  $2LN$

as  $LN = d \sin \theta$  where,  $d$  is the distance between two planes.

So, Path difference =  $2d \sin \theta$

When two reflected waves reinforce each other (maximum reflection), the path difference should be  $= n\lambda$  (where,  $n = 1, 2, 3, \dots$ ).

So, for maximum reflection,

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

This relation is called Bragg's equation. Distance between two successive planes  $d$  can be calculated from this equation. With X-rays of definite wavelength, reflections at various angles will be observed for a given set of planes separated by a distance  $d$ . These reflections correspond to  $n = 1, 2, 3$  and so on and are spoken of as first order, second order, third order and so on. With each successive order, the angle  $\theta$  increases and the intensity of the reflected beam weakens.

The values of  $\theta$  for the first order reflection from the three faces of sodium chloride crystal were found to be  $5.9^\circ$ ,  $8.4^\circ$  and  $5.2^\circ$  respectively. As  $n$  and  $a$  are same in each case, the distance  $d$  between successive planes in three faces will be in the ratio of

$$\begin{aligned} \frac{1}{\sin 5.9^\circ} : \frac{1}{\sin 8.4^\circ} : \frac{1}{\sin 5.2^\circ} &= 9.61 : 6.84 : 11.04 \\ &= 1 : 0.70 : 1.14 \\ &= 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} \end{aligned}$$

This ratio corresponds to spacings along the three planes of a face-centred cubic structure. Thus, the NaCl crystal has face-centred cubic structure.

**Example 63.** X-rays of wavelength  $1.54 \text{ \AA}$  strike a crystal and are observed to be deflected at an angle of  $22.5^\circ$ . Assuming that  $n = 1$ , calculate the spacing between the planes of atoms that are responsible for this reflection.

Solution: Applying Bragg's equation,

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

Given,  $n = 1$ ,  $\lambda = 1.54 \text{ \AA}$ ,  $\theta = 22.5^\circ$ .

Using relation  $n\lambda = 2d \sin \theta$ ,

$$d = \frac{1.54}{2 \sin 22.5^\circ} = \frac{1.54}{2 \times 0.383} = 2.01 \text{ \AA}$$

**Example 64.** The first order reflection of a beam of X-rays of wavelength  $1.54 \text{ \AA}$  from the (100) face of a crystal of the simple



**The Bragg Equation.** Bragg pointed out that unlike reflection of ordinary light, the reflection of X-rays can take place only at certain angles which are determined by the wave length of the X-rays and the distance between the planes in the crystal. The fundamental equation which gives a simple relation between the wave length of the X-rays, the interplanar distance in the crystal and the angle of reflection is known as the Bragg equation.

**Derivation of the Bragg Equation.**

Consider Fig. 10. The horizontal lines in this figure represent parallel planes in the crystal structure separated from one another by the distance  $d$ . Suppose a beam of X-rays falls on the crystal at glancing angle  $\theta$ , as shown. Some of these rays will be reflected from the upper plane at the same angle  $\theta$  while some others will be absorbed and not get reflected from the successive layers, as shown. Let the planes ABC and DEF be drawn perpendicular to the incident and reflected beams, respectively. The waves reflected by different layer planes will be in phase with one another (i.e., will coincide with one another in the plane DEF) only if the difference in the path lengths of the waves reflected from the two planes is equal to an integral number of wave lengths. Drawing OL and OM perpendicular to the incident and reflected beams, it will be seen that the difference in the path lengths (say,  $\delta$ ) of the waves from the first two planes is given by

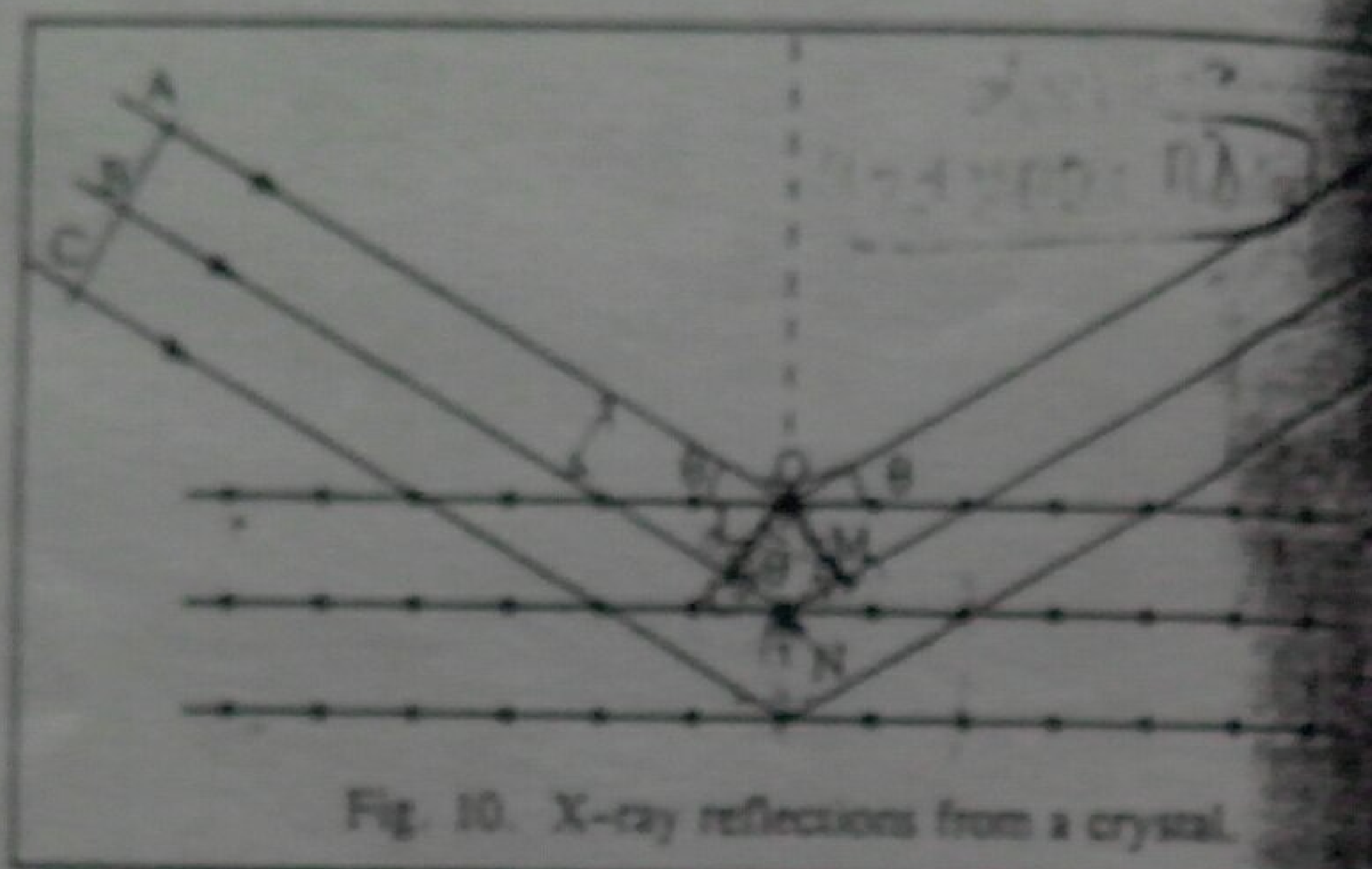


Fig. 10. X-ray reflections from a crystal.

$$\delta = LN + NM$$

This should be equal to a whole number multiple of wave length  $\lambda$ , i.e.,

$$LN + NM = n\lambda$$

Since the triangles OLN and OMN are congruent, hence  $LN = NM$ .

$$2LN = n\lambda \text{ or } 2d \sin \theta = n\lambda$$

This is the Bragg equation. Knowing  $\theta$ ,  $n$  and  $\lambda$ ,  $d$  can be calculated.

For a given set of lattice planes,  $d$  has a fixed value. Therefore, the possibility of getting maximum reflection (i.e., the possibility of getting reflected waves in phase with one another) depends upon  $\theta$ . As  $\theta$  is increased gradually, a number of positions will be found at which the reflections will be maximum. At these positions,  $n$  will have values equal to 1, 2, 3, 4, 5, etc. Generally, in experiments on X-ray reflections,  $n$  is set as equal to 1. If  $\lambda$  is known, it is possible to determine  $d$ , the distance between atomic planes in the crystal by determining  $\theta$  experimentally. On the other hand, if  $d$  is known,  $\lambda$  can be evaluated.

**Experimental Methods.** The X-ray diffraction techniques used in the study of crystals are of two types known as the rotating crystal technique and the powder technique. Both the techniques make use of the X-ray spectrometer, the setting of which for the former technique is shown in Fig. 11.

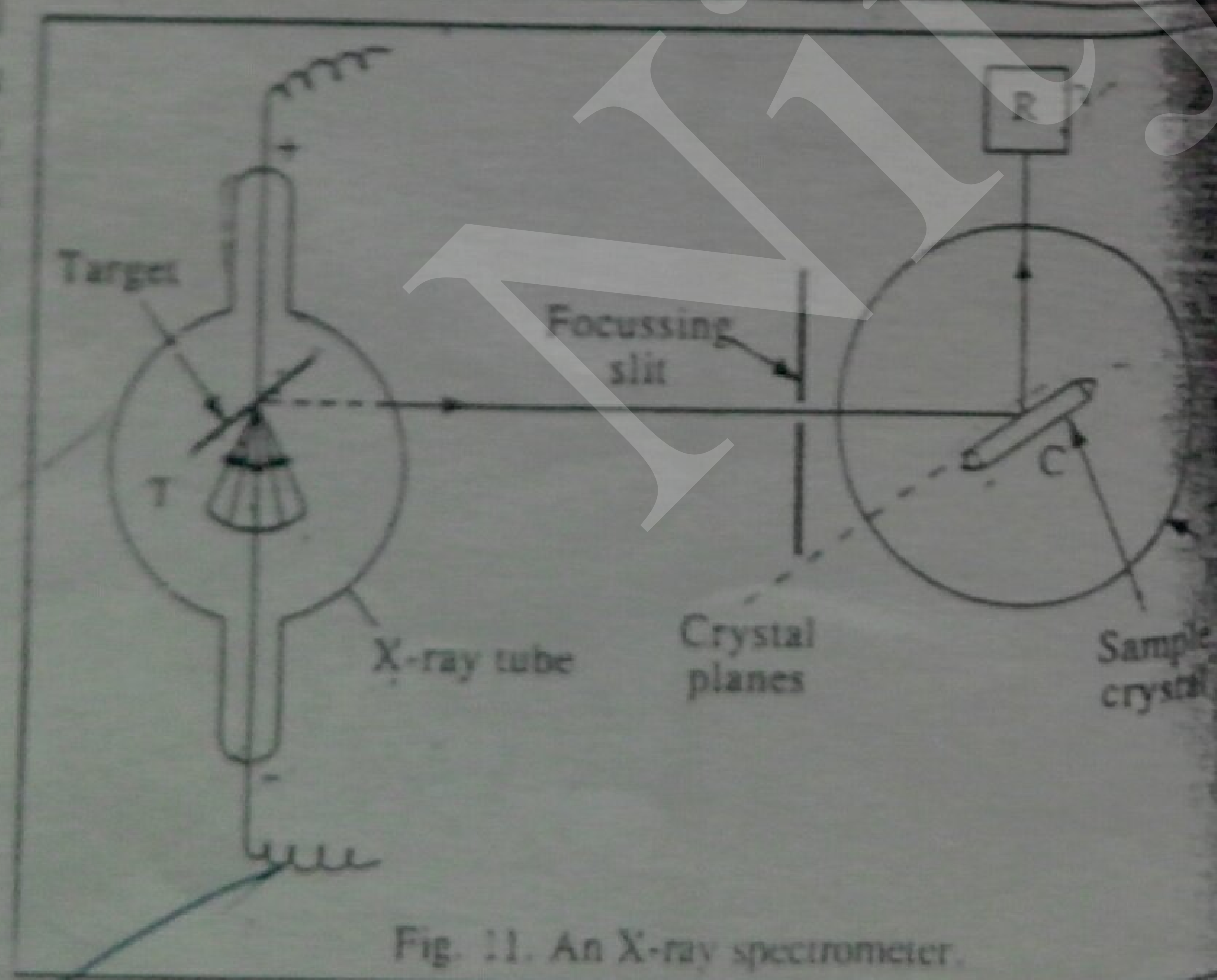


Fig. 11. An X-ray spectrometer.

rays generated in the tube T are passed through a slit so as to obtain a narrow beam which is then allowed to strike a single crystal C mounted on the turn-table. The crystal is rotated gradually by means of the turn-table so as to increase the glancing angle at which the X-rays are incident at the exposed face of the crystal. The intensities of the reflected rays are measured on a recording device R, such as a photographic plate or an ionisation chamber. The angles for which reflections are maximum give the value of  $\theta$ . The process is carried out for each plane of the crystal. The lowest angle at which the maximum reflection occurs corresponds to  $n=1$ . This is called the first order reflection. The next higher angle at which the maximum reflection occurs again, corresponds to  $n=2$ . This is the second order reflection, and so on.

The values of  $\theta$  for the first order reflection from the three faces of sodium chloride crystal are found to be  $5.9^\circ$ ,  $8.4^\circ$  and  $5.2^\circ$ , respectively. Applying the Bragg equation and knowing that  $n$  and  $\lambda$  are the same in each case, the distance  $d$  between successive planes in the three faces will be in the ratio of  $\sin 5.9^\circ : 1/\sin 8.4^\circ : 1/\sin 5.2^\circ = 9.61 : 6.84 : 11.04 = 1.00 : 0.70 : 1.14$

This ratio is very close to that expected to exist between spacings along the three planes of a face-centred cube. Thus, sodium chloride has face-centred cubic structure.

**Powder Method: The Debye-Scherrer Method.**

The powder method is more widely used particularly for crystals with simple structures. The powder, in fact, consists of many small crystals which are oriented in all possible directions. As a result of this, X-rays are diffracted from all sets of planes (e.g., 100, 110, etc.). The scattered rays are detected by using an X-ray sensitive film. The principle of the method is illustrated in Fig. 12. The substance to be examined is finely powdered and is kept in the form of a cylinder inside a glass tube. A narrow beam of X-rays is allowed to pass through the powder. The diffracted X-rays strike a strip of photographic film arranged in the form of a circular arc as shown in the figure.

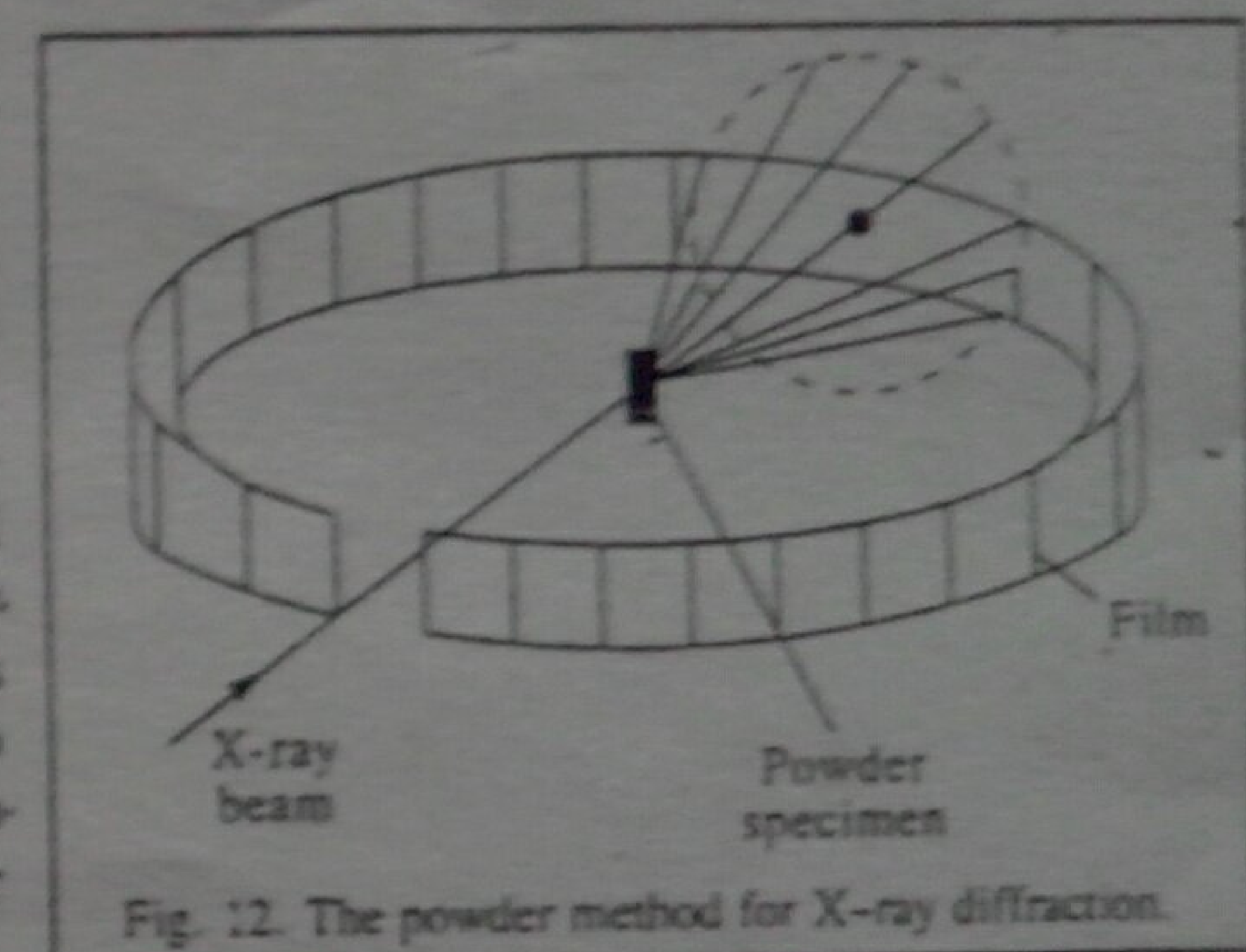


Fig. 12. The powder method for X-ray diffraction.

In this method, no rotation is necessary since the powder sample already contains microcrystals oriented in all possible orientations. Hence, a large number of them will have their lattice planes in the correct positions for maximum X-ray reflection to occur. As a result of this we get lighted areas in the form of arcs of lines at different distances from the incident beam, as shown. These distances can be converted into scattering angles to be used in the Bragg equation for different planes of the crystal.

The British physicists W.H. Bragg (1862-1942) and his son W.L. Bragg (1890-1971) shared the 1915 Nobel Prize for the analysis of crystal structure with X-rays. W.L. Bragg became at 25 the youngest Nobel Laureate in history. The Bragg equation is named after both the father and the son.

**Example 14.**  $KNO_3$  crystallizes in orthorhombic system with the unit cell dimensions  $a=542$  pm,  $b=917$  pm and  $c=645$  pm. Calculate the diffraction angles for first order X-ray reflections from (100), (010) and (111) planes using radiation with wave length = 154.1 pm.

**Solution:**  $2d_{hkl} \sin \theta = n\lambda$

For an orthorhombic system, we have

$$1/(d_{hkl})^2 = (h/a)^2 + (k/b)^2 + (l/c)^2 \tag{Eq. 15}$$

$$1/(d_{100})^2 = (1/542 \text{ pm})^2 + (0/917 \text{ pm})^2 + (0/645 \text{ pm})^2 = (1/542 \text{ pm})^2$$

$$d_{100} = a = 542 \text{ pm}$$

Similarly,  $d_{010} = b = 917 \text{ pm}$  and  $d_{111} = c = 378 \text{ pm}$

For first order reflection,  $n = 1$  Also  $\lambda = 154.1 \text{ pm}$



cubic type occurs at an angle of  $11.29^\circ$ . Calculate the length of the unit cell.

Applying Bragg's equation,

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

Given,  $\theta = 11.29^\circ$ ,  $n = 1$ ,  $\lambda = 1.54 \text{ \AA} = 1.54 \times 10^{-8} \text{ cm}$

$$d = \frac{1.54 \times 10^{-8}}{2 \times \sin 11.29^\circ} = \frac{1.54 \times 10^{-8}}{2 \times 0.1957} = 3.93 \times 10^{-8} \text{ cm}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = a$$

$a = 3.93 \times 10^{-8} \text{ cm} = \text{length of the unit cell}$

**Example 65.** When an electron in an excited state of Mo atom falls from L to K-shell, an X-ray is emitted. These X-rays are diffracted at angle of  $7.75^\circ$  by planes with a separation of  $2.64 \text{ \AA}$ . What is the difference in energy between K-shell and L-shell in Mo, assuming a first order diffraction ( $\sin 7.75^\circ = 0.1349$ )?

According to Bragg's equation:

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

$$1 \times \lambda = 2 \times 2.64 \sin 7.75^\circ = 2 \times 2.64 \times 0.1349$$

$$\lambda = 0.712 \text{ \AA}$$

Energy difference between K and L-shell of Mo

$$= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{0.712 \times 10^{-10}} = 2.791 \times 10^{-15} \text{ J}$$

#### 4.21 ANALYSIS OF CUBIC SYSTEMS

The following characteristics are reflected by cubic systems when analysed mathematically:

It is defined as half the distance between nearest neighbouring atoms in a crystal. It is expressed in terms of length of the edge 'a' of the unit cell of the crystal.

In a simple cubic unit cell, atoms at the corners touch each other along the edge.

Distance between the nearest neighbours,

$$d = AB = a = 2r$$

(where  $r$  = radius of the atom)

or Atomic radius,

$$r = \frac{a}{2} = 0.5a$$

The distance between the two nearest neighbours is represented by length  $AE$  or  $ED$ , i.e., half of the body diagonal,  $AD$ .

$$d = AE = ED = \frac{AD}{2}$$

In  $\Delta ABC$ ,

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

or

$$AC = \sqrt{2}a$$

Now, in  $\Delta ADC$ ,

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

or

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

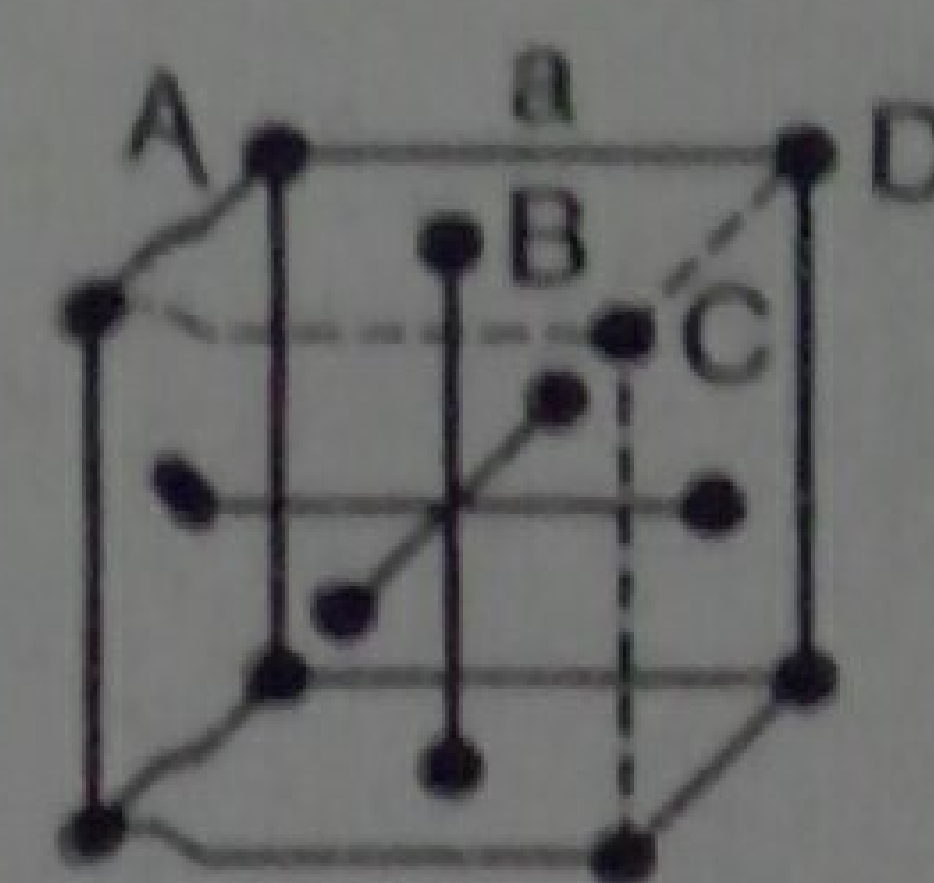
$\therefore$

$$d = \frac{\sqrt{3}}{2}a$$

$$d = 2r = \frac{\sqrt{3}}{2}a$$

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

The distance between the two nearest neighbours is represented by length  $AB$  or  $BC$ , i.e., half of the face diagonal,  $AC$ .



$$d = AB = BC = \frac{AC}{2}$$

In  $\Delta ACD$ ,  $AC^2 = CD^2 + AD^2$

$$= a^2 + a^2 = 2a^2$$

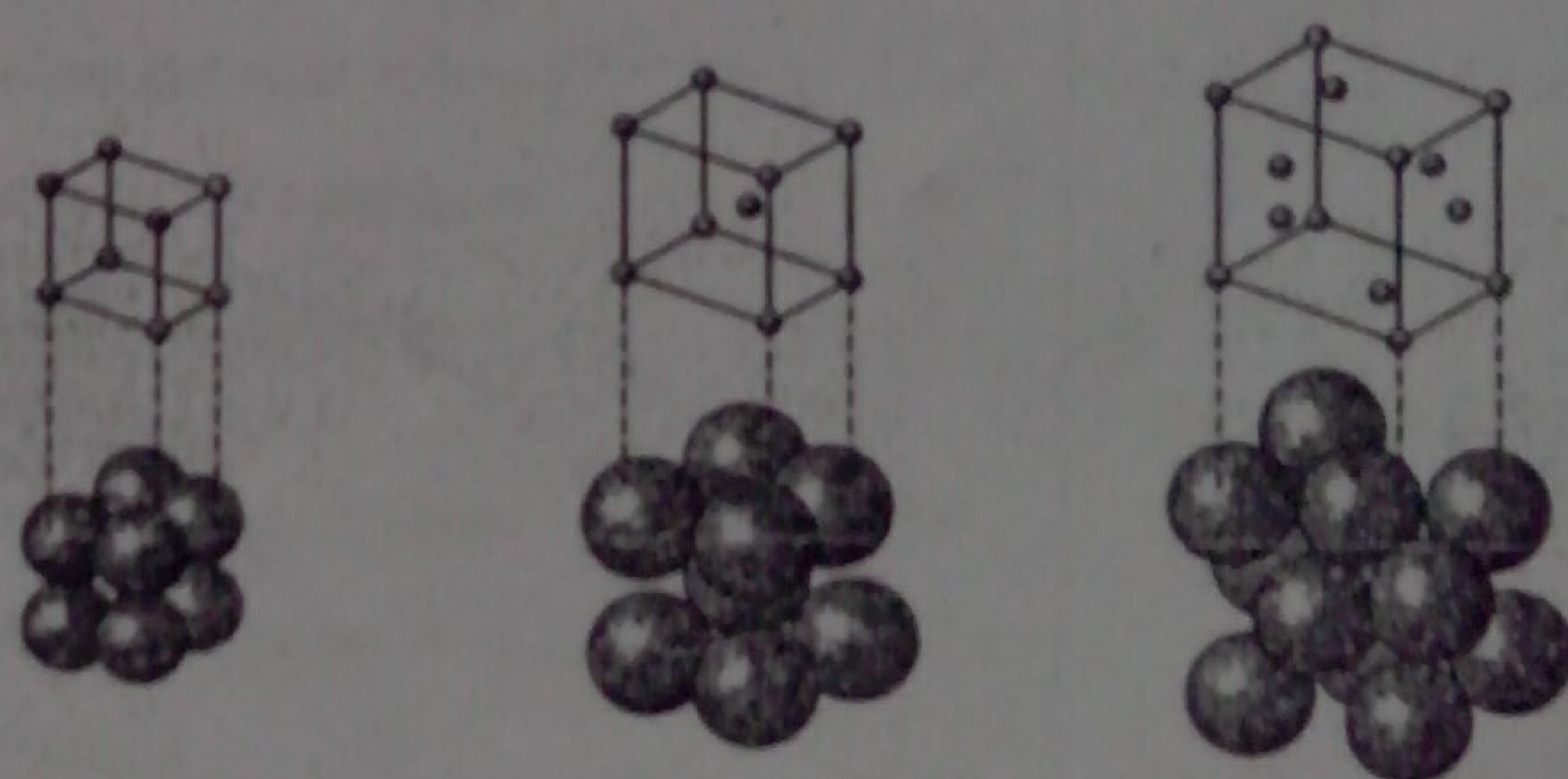
$$AC = \sqrt{2}a$$

or  $d = \frac{AC}{2} = \frac{\sqrt{2}}{2}a = \frac{1}{\sqrt{2}}a$

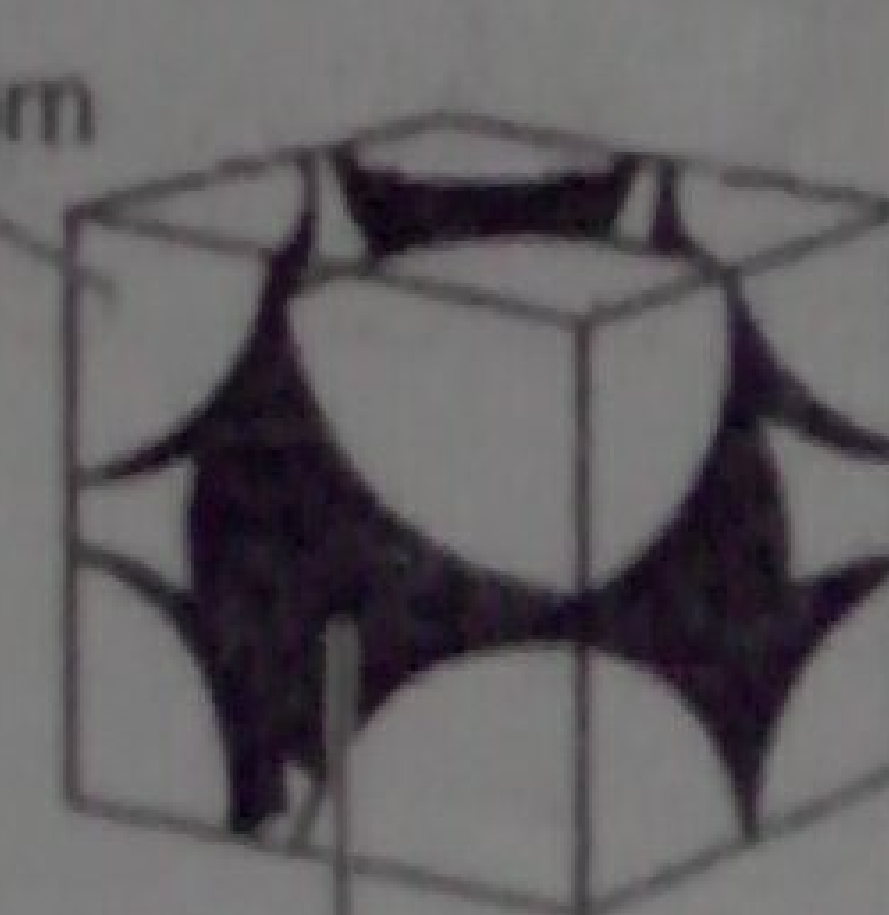
$$d = 2r = \frac{1}{\sqrt{2}}a$$

or Atomic radius,  $r = \frac{1}{2\sqrt{2}}a$

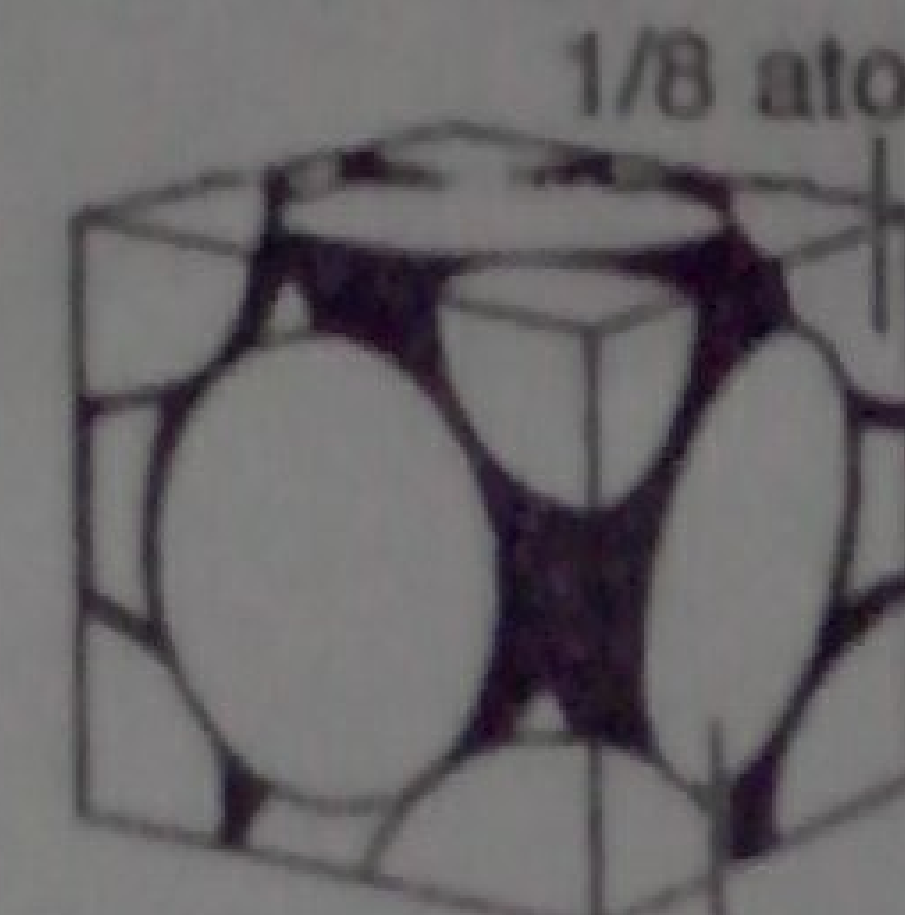
Different types of cubic unit cells are given in following figure:



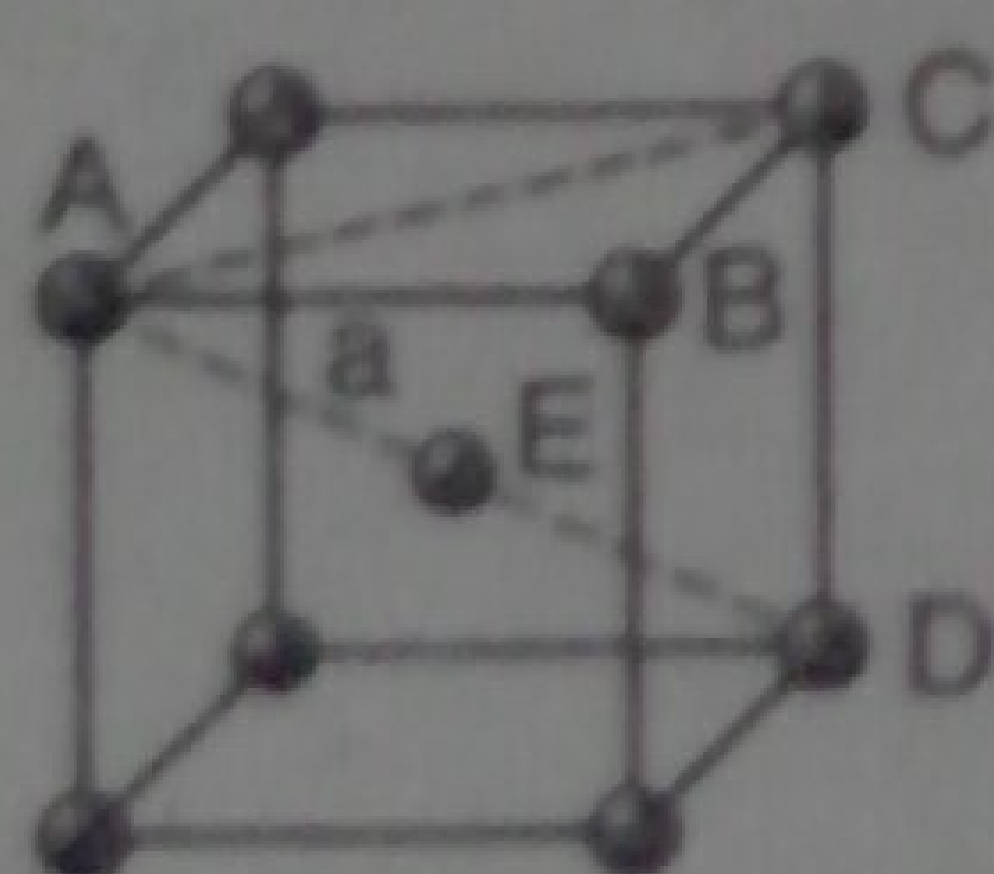
1/8 atom  
Simple cubic  
(a)



1 atom  
Body centred cubic  
(b)



1/2 atom  
Face centred cubic  
(c)





Since, each corner atom is shared by eight surrounding cubes, therefore, it contributes for  $\frac{1}{8}$  of an atom.

Thus, for simple cube =  $8 \times \frac{1}{8} = 1$  atom per unit cell

Since, the structure possesses 8 corner atoms and six at the centre of each face, the contribution will be

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} \quad (\text{Face atom is shared by two cubes})$$

$$= 1 + 3 = 4 \text{ atoms per unit cell}$$

Since, the structure possesses 8 corner atoms and one body-centre, the contribution will be =  $8 \times \frac{1}{8} + 1 = 2$  atoms per unit cell.

It is defined as the number of nearest neighbours that an atom has in a unit cell. It depends upon structure.

$$\text{Coordination number} = 6$$

$$\text{Coordination number} = 12$$

$$\text{Coordination number} = 8$$

Knowing the unit cell dimensions, the theoretical density of a crystal can be calculated as:

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

$$\text{Mass of the unit cell} = \text{number of atoms in the unit cell} \times \text{mass of each atom}$$

$$\text{Mass of each atom} = \frac{\text{Atomic mass}}{\text{Avogadro's number}} = \frac{M}{N_0}$$

$$\text{So, density of a unit cell} = \frac{Z \times M}{N_0 \times V} = \frac{n \times M}{N_0 \times a^3} \quad (\text{For a cube})$$

where,  $Z$  is the number of atoms in a unit cell and  $V$  is the volume of unit cell.

For a cube  $V = a^3$  where,  $a$  is the edge length of the cubic unit cell.

It is defined as the ratio of volumes occupied by atoms in unit cell to the total volume of the unit cell.

$$\text{Packing fraction} = \frac{\text{Volume occupied by atoms in unit cell}}{\text{Total volume of the unit cell}} = \frac{v}{V}$$

Let  $a$  be the cube edge and  $r$  the atomic radius.

$$V = \text{volume of the unit cell} = a^3$$

Since, one atom is present in a unit cell, its

$$\text{Volume, } v = \frac{4}{3} \pi r^3 \quad (r = a/2)$$

$$= \frac{4}{3} \pi \left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}$$

$$\text{Packing fraction} = \frac{v}{V} = \frac{\pi a^3/6}{a^3} = \frac{\pi}{6} = 0.52$$

i.e., 52% of the unit cell is occupied by atoms and 48% is empty.

Since, four atoms are present in a unit cell, their volume is

$$v = 4 \times \left(\frac{4}{3} \pi r^3\right)$$

$$\text{Putting the value of } r = \frac{a}{2\sqrt{2}},$$

$$v = \frac{16}{3} \pi \left(\frac{a}{2\sqrt{2}}\right)^3 = \frac{\pi}{3\sqrt{2}} a^3$$

$$\text{Volume of unit cell, } V = a^3$$

$$\text{Packing fraction} = \frac{\pi a^3}{3\sqrt{2} a^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

i.e., 74% of unit cell is occupied by atoms and 26% is empty.

Since, two atoms are present in a unit cell, their volume is

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

$$\text{Putting the value of } r = \frac{\sqrt{3}}{4} a, \quad v = 2 \times \frac{4}{3} \pi \times \left(\frac{\sqrt{3}}{4} a\right)^3$$

$$= \frac{\sqrt{3} \pi a^3}{8}$$

$$\text{Volume of unit cell, } V = a^3$$

$$\text{Packing fraction} = \frac{\sqrt{3} \pi a^3}{8 a^3} = \frac{\sqrt{3}}{8} \pi = 0.68$$

i.e., 68% of the unit cell is occupied by atoms and 32% is empty.

Characteristics of cubic unit cells are summarised in following tables :

	Simple	Body-centered	Face-centered
Volume, conventional cell	$a^3$	$a^3$	$a^3$
Lattice points per cell	1	2	4
Volume, primitive cell	$a^3$	$\frac{1}{2} a^3$	$\frac{1}{4} a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	$a$	$3^{1/2} a/2$ $= 0.866a$	$a/2^{1/2}$ $= 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2} a$	$a$	$a$
Packing fraction	$\frac{1}{6} \pi$ $= 0.524$	$\frac{1}{6} \pi \sqrt{3}$ $= 0.680$	$\frac{1}{6} \pi \sqrt{2}$ $= 0.740$



12

## Hexagonal Unit Cell

Let us consider hexagonal unit cell of height 'h'; its constituent units are spherical having radius 'r'.

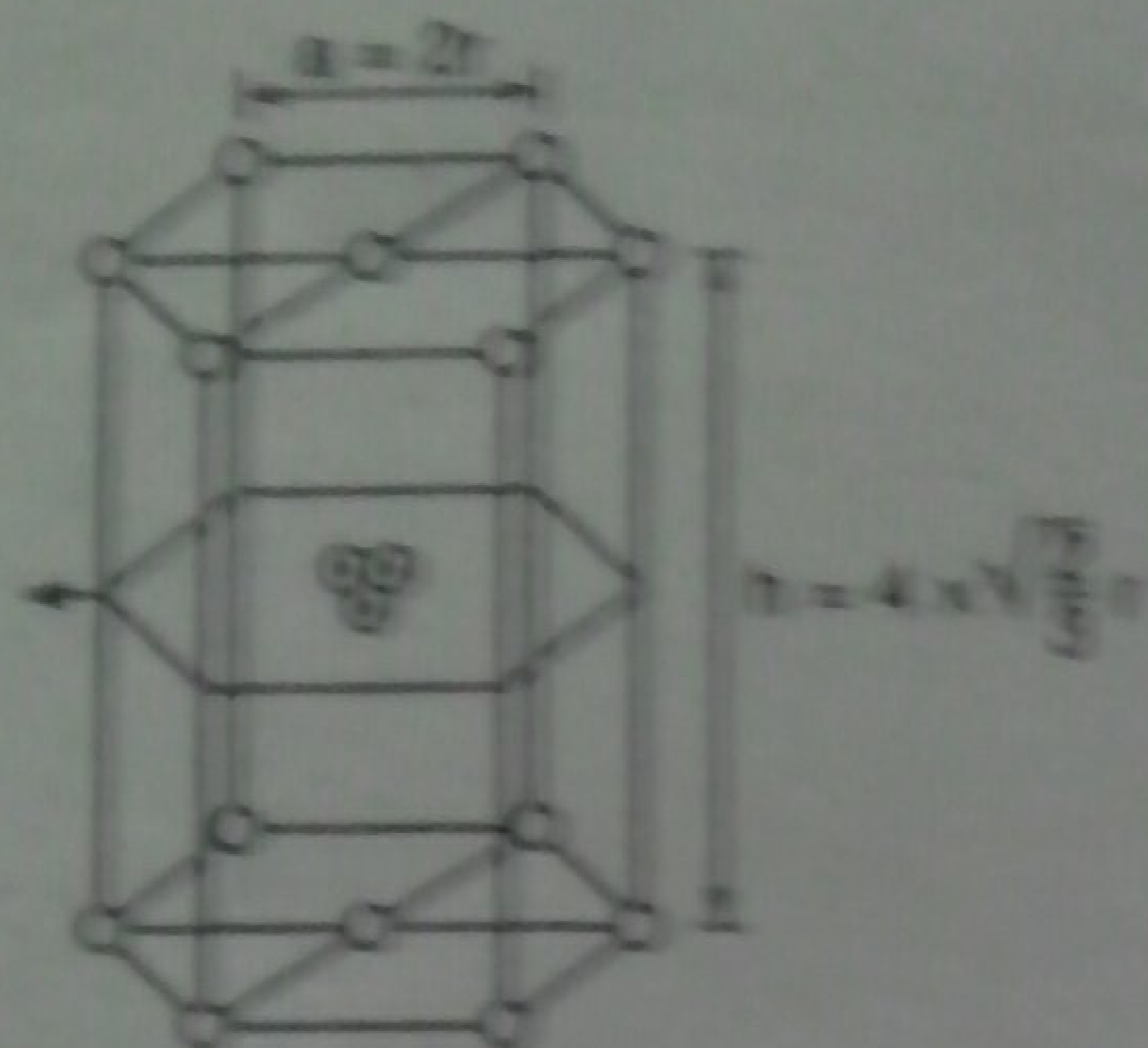


Fig. 4.34 Hexagonal unit cell

Number of constituent units in the hexagonal unit cell = 6.

Thus, occupied volume in the unit cell =  $6 \times \frac{4}{3} \pi r^3$

$$\begin{aligned} \text{Volume of unit cell} &= \text{Area of base} \times \text{height} \\ &= 6 \times \text{Area of equilateral triangle} \times \text{height} \\ &= 6 \times \frac{\sqrt{3}}{4} a^2 \times 4r \frac{\sqrt{2}}{\sqrt{3}} \\ &= 6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4r \frac{\sqrt{2}}{\sqrt{3}} \end{aligned}$$

(Height of the unit cell can be calculated geometrically)

$$\begin{aligned} \text{Percentage occupied space} &= \frac{\text{occupied volume}}{\text{volume of unit cell}} \times 100 \\ &= \frac{6 \times \frac{4}{3} \pi r^3}{6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4r \frac{\sqrt{2}}{\sqrt{3}}} \times 100 = 74.06\% \end{aligned}$$

## SOME SOLVED EXAMPLES

**Example 66.** A compound formed by elements A and B crystallises in cubic structure where A atoms are at the corners of a cube and B atoms are at the face-centre. What is the formula of the compound?

**Solution:** An atom at the corner of the cube contributes  $\frac{1}{8}$  to the unit cell. Hence, number of atoms of A in the unit cell =  $8 \times \frac{1}{8} = 1$ .

An atom at the face of the cube contributes  $\frac{1}{2}$  to the unit cell. Hence, number of atoms of B in the unit cell =  $6 \times \frac{1}{2} = 3$ .

Thus, the formula is  $AB_3$ .

**Example 67.** At room temperature, sodium crystallises in body-centred cubic lattice with  $a = 4.24 \text{ \AA}$ . Calculate the theoretical density of sodium (At. mass of Na = 23.0).

**Solution:** A body-centred cubic unit cell contains 8 atoms at the 8 corners and 1 in the centre.

Hence,

$$\text{Total number of atoms in a unit cell} = 8 \times \frac{1}{8} + 1 = 2$$

$$\text{Volume of unit cell} = a^3 = (4.24 \times 10^{-8})^3 \text{ cm}^3$$

$$\begin{aligned} \text{So, Density} &= \frac{Z \times M}{N_0 \times V} = \frac{2 \times 23}{(6.023 \times 10^{23})(4.24 \times 10^{-8})^3} \\ &= 1.002 \text{ g cm}^{-3} \end{aligned}$$

**Example 68.** The density of KCl is  $1.9893 \text{ g cm}^{-3}$  and the length of a side of unit cell is  $6.29082 \text{ \AA}$  as determined by X-ray diffraction. Calculate the value of Avogadro's number.

**Solution:** KCl has face-centred cubic structure, i.e.,

$$Z = 4$$

$$\text{Avogadro's number} = \frac{Z \times M}{d \times V}$$

Given that,  $d = 1.9893$ ,  $M = 74.5$ ,  $V = (6.29082 \times 10^{-8})^3 \text{ cm}^3$

$$\begin{aligned} \text{Avogadro's number} &= \frac{4 \times 74.5}{1.9893 \times (6.29082 \times 10^{-8})^3} \\ &= 6.017 \times 10^{23} \end{aligned}$$

**Example 69.** Silver crystallises in a face-centred cubic unit cell. The density of Ag is  $10.5 \text{ g cm}^{-3}$ . Calculate the edge length of the unit cell.

**Solution:** For face-centred cubic unit,  $Z = 4$ .

$$\text{We know that, } V = \frac{Z \times M}{N_0 \times d}$$

$$\begin{aligned} &= \frac{4 \times 108}{(6.023 \times 10^{23}) \times 10.5} = 6.83 \times 10^{-23} \\ &= 68.3 \times 10^{-24} \end{aligned}$$

Let  $a$  be the edge length of the unit cell.

$$\text{So, } V = a^3$$

$$\text{or } a^3 = 68.3 \times 10^{-24}$$

$$a = (68.3 \times 10^{-24})^{1/3} \text{ cm}$$

$$= 4.09 \times 10^{-8} \text{ cm}$$

$$= 409 \text{ pm}$$

**Example 70.** An element occurs in bcc structure with a cell edge of  $288 \text{ pm}$ . The density of metal is  $7.2 \text{ g cm}^{-3}$ . How many atoms does 208 g of the element contain?

$$\begin{aligned} \text{Volume of the unit cell} &= (288 \times 10^{-10})^3 \\ &= 23.9 \times 10^{-24} \text{ cm}^3 \end{aligned}$$

$$\text{Volume of 208 g of the element} = \frac{208}{7.2} = 28.88 \text{ cm}^3$$

$$\text{Number of unit cells in } 28.88 \text{ cm}^3 = \frac{28.88}{23.9 \times 10^{-24}}$$

$$= 12.08 \times 10^{23} \text{ unit cells}$$

Each bcc structure contains 2 atoms.



So, Total atoms in  $12.08 \times 10^{23}$  unit cells  
 $= 2 \times 12.08 \times 10^{23}$   
 $= 24.16 \times 10^{23}$

**Example 71.** Lithium forms body-centred cubic crystals. Calculate the atomic radius of lithium if the length of the side of a unit cell of lithium is 351 pm.

**Solution:** In body-centred cubic crystals,

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

$$= \frac{\sqrt{3}}{4} \times 351 \text{ pm} = 151.98 \text{ pm}$$

**Example 72.** Ammonium chloride crystallises in a body-centred cubic lattice with a unit distance of 387 pm. Calculate (a) the distance between oppositely charged ions in the lattice and (b) the radius of the  $\text{NH}_4^+$  ion if the radius of  $\text{Cl}^-$  ion is 181 pm.

**Solution:** (a) In a body-centred cubic lattice, oppositely charged ions touch each other along the cross-diagonal of the cube.

So,  $2r_c + 2r_a = \sqrt{3}a$

or  $r_c + r_a = \frac{\sqrt{3}}{2} a$

$$= \frac{\sqrt{3}}{2} \times 387 = 335.15 \text{ pm}$$

(b) Given that,  $r_a = 181 \text{ pm}$

$$r_c = 335.15 - 181.0 = 154.15 \text{ pm}$$

**Example 73.** The unit cell cube length for LiCl (NaCl structure) is 5.14 Å. Assuming anion-anion contact, calculate the ionic radius for chloride ion.

**Solution:** In a face-centred cubic lattice, anions touch each other along the face diagonal of the cube.

$$4r_{\text{Cl}^-} = \sqrt{2}a$$

$$r_{\text{Cl}^-} = \frac{\sqrt{2}}{4} a$$

$$= \frac{\sqrt{2}}{4} \times 5.14 = 1.82 \text{ Å}$$

Distance between  $\text{Li}^+$  and  $\text{Cl}^-$  ion

$$= \frac{5.14}{2} = 2.57 \text{ Å}$$

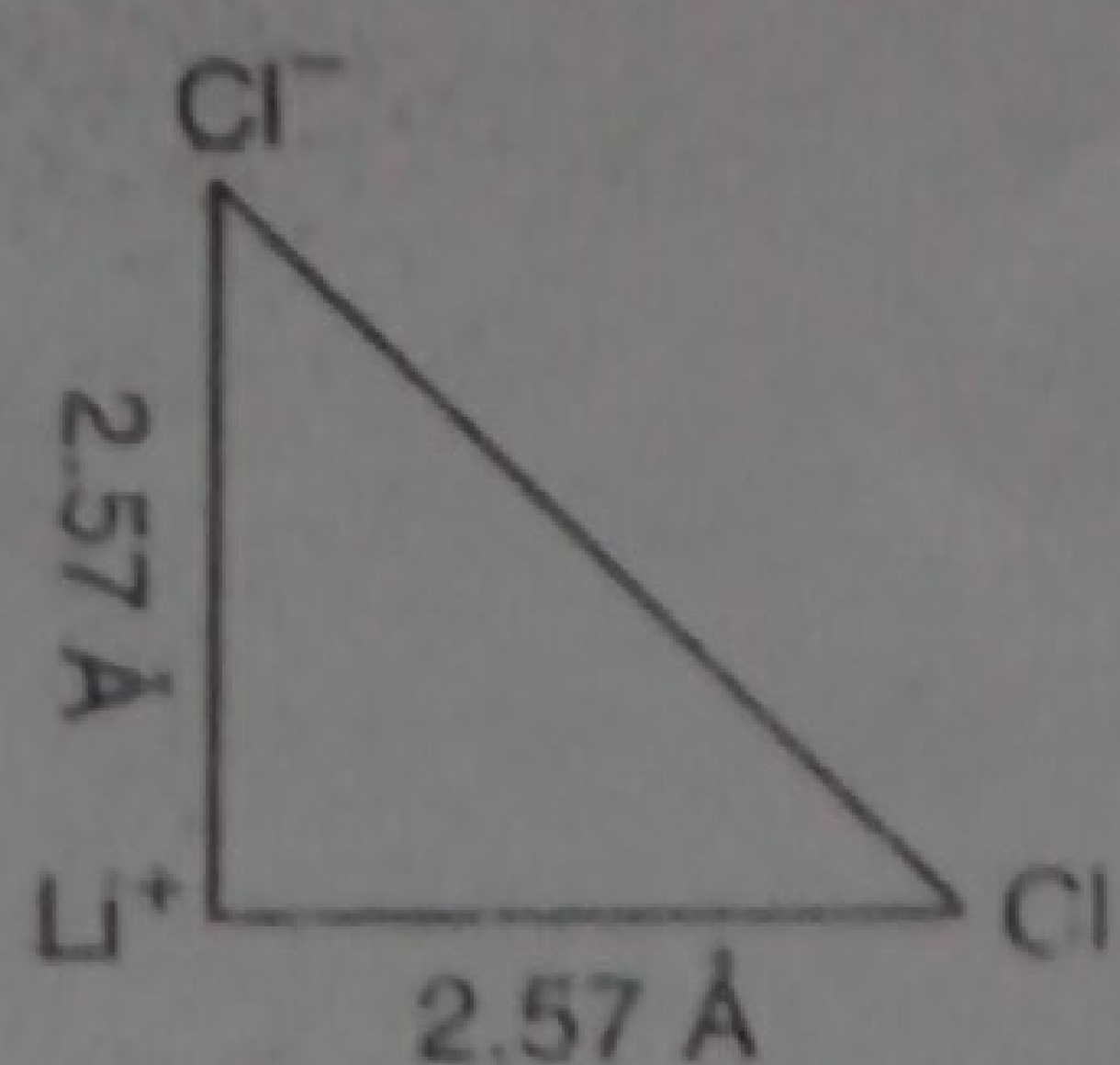
Thus, distance between two chloride ions

$$= \sqrt{(2.57)^2 + (2.57)^2}$$

$$= 3.63 \text{ Å}$$

Hence,

$$\text{radius of } \text{Cl}^- = \frac{3.63}{2} = 1.82 \text{ Å}$$



**Example 74.** The density of crystalline sodium chloride is  $2.165 \text{ g cm}^{-3}$ . What is the edge length of the unit cell. What would be the dimensions of cube containing one mole of NaCl?

**Solution:** We know that,

$$\rho = \frac{N}{a^3} \left( \frac{M}{N_A} \right)$$

where,

$$\rho = \text{density} = 2.165 \text{ g cm}^{-3}$$

$$M = \text{molar mass} = 58.5$$

$$N_A = \text{Avogadro's number} = 6.023 \times 10^{23}$$

$$N = \text{number of formula unit per unit cell}$$

$$= 4 \text{ (for fcc)}$$

$$a^3 = \frac{N}{\rho} \left( \frac{M}{N_A} \right) = \frac{4}{2.165} \left[ \frac{58.5}{6.023 \times 10^{23}} \right]$$

$$= 1.794 \times 10^{-23}$$

$$a = 5.64 \times 10^{-8} \text{ cm}$$

$$\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}} = \frac{58.8}{2.165}$$

$$\text{Edge length (a)} = \left[ \frac{58.8}{2.165} \right]^{1/3} = 3 \text{ cm}$$

**Example 75.** The density of potassium bromide crystal is  $2.75 \text{ g cm}^{-3}$  and the length of an edge of a unit cell is 654 pm. The unit cell of KBr is one of three types of cubic unit cells. How many formula units of KBr are there in a unit cell? Does the unit cell have a NaCl or CsCl structure?

**Solution:** We know that,

$$\rho = \frac{N}{a^3} \left[ \frac{M}{N_A} \right]$$

$$N = \frac{\rho \times a^3 \times N_A}{M}$$

$$= \frac{2.75 \times (654 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{119} = 3.89 \approx 4$$

Number of mass points per unit cell = 4

It is NaCl type crystal, i.e., fcc structure.

**Example 76.** A unit cell of sodium chloride has four formula units. The edge length of unit cell is 0.564 nm. What is the density of sodium chloride?

$$\rho = \frac{ZM}{a^3 N} = \frac{4 \times 58.5}{(5.64 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$$

$$= 2.16 \text{ g cm}^{-3}$$

**Example 77.** Chromium metal crystallises with a body-centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in  $\text{g cm}^{-3}$ ?



14

**Solution:** In body-centred cubic unit cell,

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

where,  $a$  = edge length,  $r$  = radius of atom

$$r = \frac{a\sqrt{3}}{4} = \frac{\sqrt{3} \times 4.29}{4} = 1.8574 \text{ \AA}$$

**Example 78.** When heated above  $916^\circ\text{C}$ , iron changes its crystal structure from body-centred cubic to cubic closed packed structure. Assuming that the metallic radius of the atom does not change, calculate the ratio of density of the bcc crystal to that of the ccp crystal.

**Solution:** In body-centred packing, the efficiency of packing is 67.92%. In the cubic closed packing, the packing efficiency is 74.02%.

Let  $d_1$  be the density when packing efficiency is 74.02% and  $d_2$  is the density when packing efficiency is 67.92%.

$$\frac{d_2}{d_1} = \frac{67.92}{74.02} = 0.918$$

### ILLUSTRATIONS

An element 'A' has face-centred cubic structure with edge length equal to 361 pm. The apparent radius of atom 'A' is:

- (a) 127.6 pm                      (b) 180.5 pm  
(c) 160.5 pm                      (d) 64 pm

[Ans. (a)]

[Hint: For face-centred unit cell,

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

$$\frac{361 \times 1.414}{4} = r$$

$\therefore r = 127.6 \text{ pm}$ ]

The packing fraction of the element that crystallises in simple cubic arrangement is:

- (a)  $\frac{\pi}{4}$                       (b)  $\frac{\pi}{6}$                       (c)  $\frac{\pi}{3}$                       (d)  $\frac{\pi}{2}$

[Ans. (b)]

[Hint: In simple unit cell  $a = 2r$

$$Z = 1$$

$\therefore$  Packing fraction =  $\frac{\text{Occupied volume}}{\text{Total volume}}$

$$= \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

How many unit cells are present in 39 g of potassium that crystallises in body-centred cubic structure?

- (a)  $N_A$                       (b)  $\frac{N_A}{4}$                       (c)  $0.5 N_A$                       (d)  $0.75 N_A$

[Ans. (c)]

[Hint: Number of atoms =  $\frac{\text{Mass}}{\text{Atomic mass}} \times N_A$

$$= \frac{39}{39} \times N_A = N_A$$

In bcc unit cell,  $Z = 2$

$\therefore$  Number of unit cells =  $\frac{N_A}{2} = 0.5 N_A$

Sodium metal exists in bcc unit cell. The distance between nearest sodium atoms is 0.368 nm. The edge length of the unit cell is:

- (a) 0.368 nm                      (b) 0.184 nm  
(c) 0.575 nm                      (d) 0.424 nm  
[Ans. (d)]

[Hint: In bcc unit cell,  $a\sqrt{3} = 4r$

$$a = \frac{4r}{\sqrt{3}} = \frac{2}{\sqrt{3}} \times 2r$$

$$= \frac{2}{\sqrt{3}} \times 0.368 = 0.425 \text{ nm}]$$

If the distance between  $\text{Na}^+$  and  $\text{Cl}^-$  ions in NaCl crystal is 265 pm, then edge length of the unit cell will be?

- (a) 265 pm                      (b) 530 pm                      (c) 795 pm                      (d) 132.5 pm  
[Ans. (b)]

[Hint: In NaCl,

Edge length =  $2 \times$  distance between  $\text{Na}^+$  and  $\text{Cl}^-$  ions  
 $= 2 \times 265 = 530 \text{ pm}$ ]

The interionic distance for caesium chloride crystal will be:

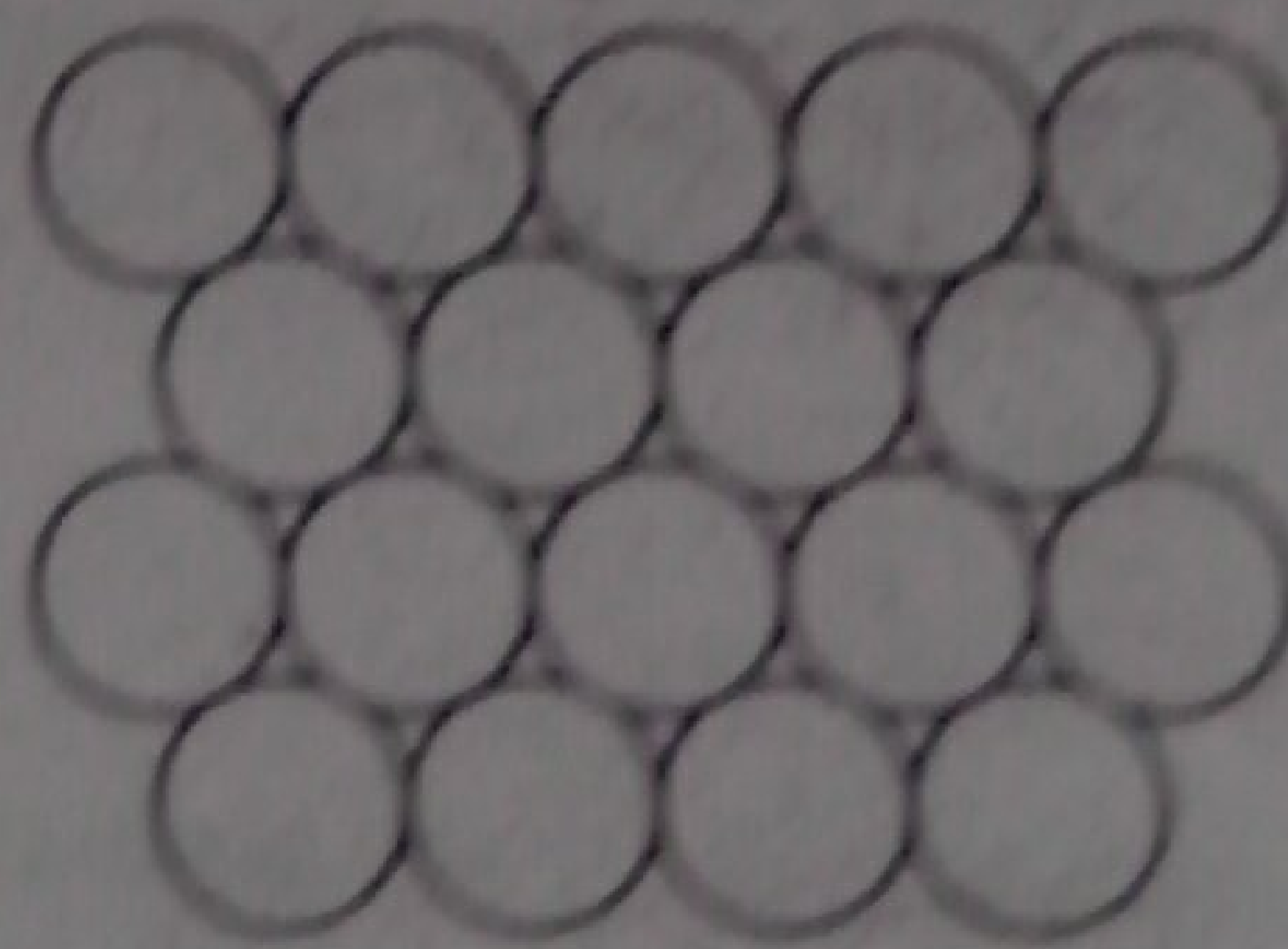
[PMT (MP) 2007]

- (a)  $a$                       (b)  $\frac{a}{2}$                       (c)  $\frac{a\sqrt{3}}{2}$                       (d)  $\frac{2a}{\sqrt{3}}$

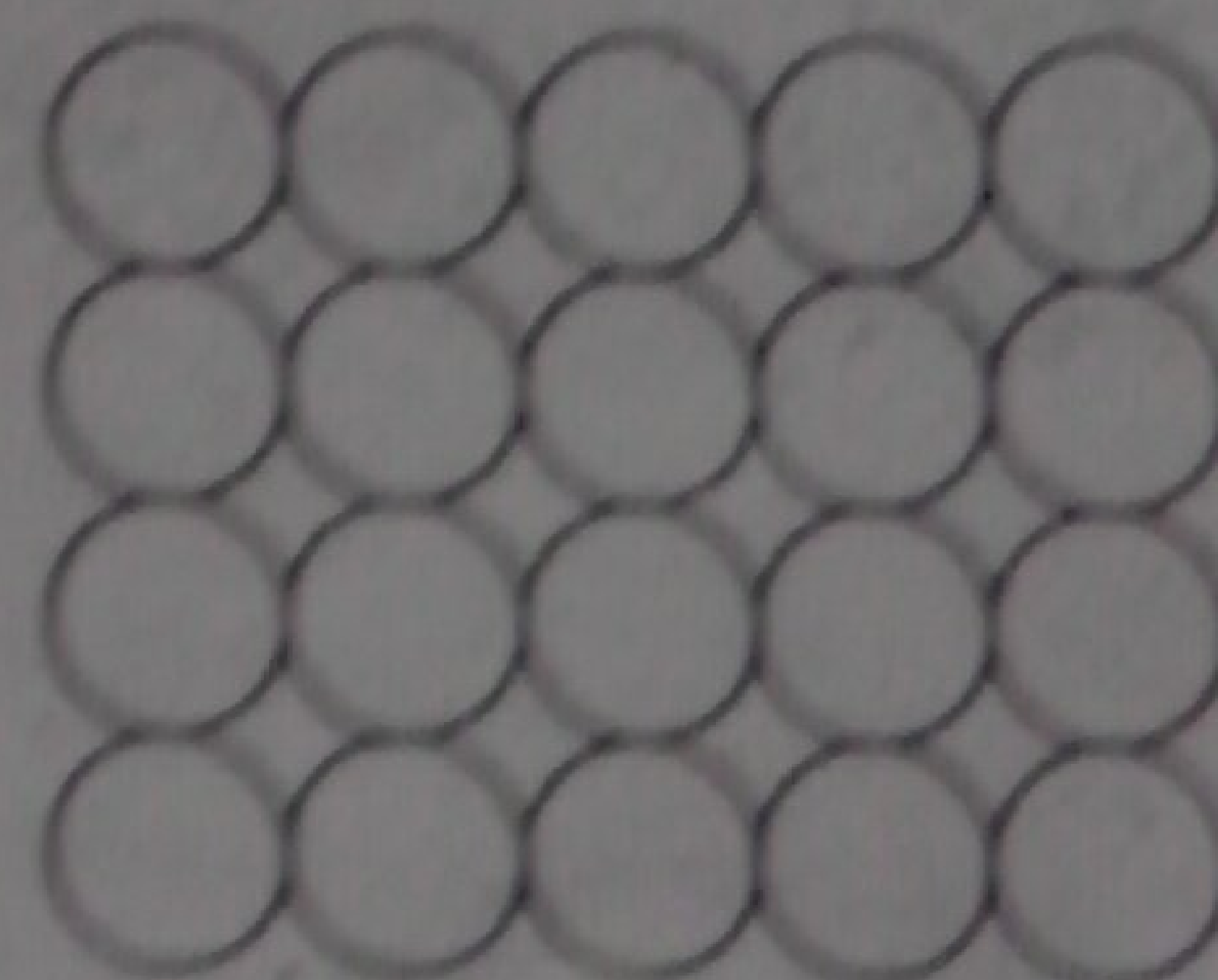
[Ans. (b)]

### 4.22

The constituent particles in the formation of crystals are either atoms, ions or molecules. These particles may be of various shapes and thus, the mode of packing of these particles will change according to their shapes. The simplest way will be to consider these particles as spheres of equal size. The packing of spheres is done in such a way as to use the available space in the most economical manner.



Arrangement (i)



Arrangement (ii)

There are two common ways in which spheres of equal size can be packed. This has been shown in Fig. 4.35. The arrangement (i) is more economical in comparison to arrangement (ii) as 60.4% volume is occupied in arrangement (i) and 52.4% volume in arrangement (ii). Arrangement (i) represents a close packing of spheres.



## MISCELLANEOUS NUMERICAL EXAMPLES

**Example 1.** There is a collection of crystalline substances in a hexagonal closed packing. If the density of matter is  $2.6 \text{ g/cm}^3$ , what would be the average density of matter in collection? What fraction of space is actually unoccupied?

**Solution:** In hexagonal closed packing, the packing efficiency is 74.05%.

$\therefore$  Density of matter = Packing fraction  $\times$  Total density

$$= \frac{74.05}{100} \times 2.6 = 1.93 \text{ g cm}^{-3}$$

$$\% \text{ empty space} = 100 - 74.05 = 25.95\%$$

**Example 2.** The unit cell length of NaCl is observed to be  $0.5627 \text{ nm}$  by X-ray diffraction studies; the measured density of NaCl is  $2.164 \text{ g cm}^{-3}$ . Correlate the difference of observed and calculated density and calculate % of missing  $\text{Na}^+$  and  $\text{Cl}^-$  ions.

**Solution:** We know that,

$$Z = \frac{a^3 \times d \times N}{M}$$

where,  $Z$  = number of constituent units per unit cell

= 4 in fcc

$$a = \text{edge length} = 0.5627 \times 10^{-7} \text{ cm}$$

$d$  = density

$N$  = Avogadro's number

$M$  = molar mass

$$\frac{(0.5627 \times 10^{-7})^3 \times d \times 6.023 \times 10^{23}}{58.5} = 4$$

$$d = 2.1805 \text{ g/cm}^3$$

Observed density =  $2.164 \text{ g/cm}^3$  which is less than calculated density because some places are missing.

Actual constituent units per unit cell can be calculated as:

$$Z = \frac{(0.5627 \times 10^{-7})^3 \times 2.164 \times 6.023 \times 10^{23}}{58.5} = 3.969$$

$$\text{Missing units} = 4 - 3.969 = 0.031$$

$$\% \text{ missing} = \frac{0.031}{4} \times 100 = 0.775\%$$

**Example 3.** In a cubic lattice, the closed packed structure of mixed oxides of the lattice is made up of oxide ions; one eighth of the tetrahedral voids are occupied by divalent ions ( $A^{2+}$ ) while one half of the octahedral voids are occupied by trivalent ions ( $B^{3+}$ ). What is the formula of the oxides?

**Solution:** Let there be  $80 \text{ O}^{2-}$  in the crystal.

$\therefore$  Octahedral voids = 80

Tetrahedral voids = 160

$$A^{2+} \text{ ions} = \frac{1}{8} \times 160 = 20$$

$$B^{3+} \text{ ions} = \frac{1}{2} \times 80 = 40$$

$$A^{2+} : B^{3+} : O^{2-} = 20 : 40 : 80$$

$$= 1 : 2 : 4$$

$\therefore$  Formula is  $AB_2O_4$ .

**Example 4.** At  $1425^\circ\text{C}$ , Fe crystallises in a body-centred cubic lattice whose edge length is  $2.93 \text{ \AA}$ . Assuming the atoms to be packed spheres, calculate:

(a) the radius of the spheres,

(b) the distance between centres of neighbouring spheres,

(c) the number of atoms of Fe per unit lattice and

(d) the total volume occupied by an atom of Fe.

**Solution:** (a)  $a\sqrt{3} = 4r$  where,  $a$  = edge length

$$r = \frac{a\sqrt{3}}{4} = \frac{2.93 \times \sqrt{3}}{4} = 1.268 \text{ \AA}$$

(b) Distance between the centres of neighbouring spheres

$$= 2r = 2 \times 1.268 = 2.537 \text{ \AA}$$

(c) No. of atoms per unit cell =  $8 \times \frac{1}{8} + 1 = 2$ .

(d) Volume occupied by an atom of iron =  $\frac{4}{3} \pi r^3$ .

**Example 5.** In face-centred cubic (fcc) crystal lattice, edge length of the unit cell is  $400 \text{ pm}$ . Find the diameter of the greatest sphere which can be fitted into the interstitial void without distortion of lattice. (IIT 2005)

**Solution:** In fcc unit cell, we can use

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

$$r = \frac{a\sqrt{2}}{4} = \frac{400 \times \sqrt{2}}{4} = 141.4 \text{ pm}$$

For octahedral void,

$$2(r + R) = a$$

$$2R = a - 2r$$

$$2R = a - 2r = 400 - 2 \times 141.4 = 117.16 \text{ pm}$$

Diameter of greatest sphere =  $117.16 \text{ pm}$ .

**Example 6.** The distance between planes of ions parallel to the face of the unit cell of sodium chloride is  $282 \text{ pm}$ . The smallest angle of reflection observed in the X-ray diffraction pattern is  $5.97^\circ$ . Calculate the wavelength of the incident radiation.

**Solution:** Using Bragg's equation,

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

$$1 \times \lambda = 2 \times 282 \times 10^{-12} \sin 5.97$$

$$\lambda = 5.86 \times 10^{-11} \text{ m} = 58.6 \text{ pm}$$

**Example 7.** CsCl has cubic structure of ions in which  $\text{Cs}^+$  ion is present in the body-centre of the cube. If density is  $3.99 \text{ g cm}^{-3}$ :



- (a) Calculate the length of the edge of a unit cell.  
 (b) What is the distance between  $\text{Cs}^+$  and  $\text{Cl}^-$  ions?  
 (c) What is the radius of  $\text{Cs}^+$  ion if the radius of  $\text{Cl}^-$  ion is 180 pm?

We know that,

$$(a) \quad Z = \frac{a^3 \times \rho \times N}{M}$$

$$Z = 1, 1\text{Cs}^+ + 1\text{Cl}^- = 1\text{CsCl}$$

$$M = 168.5$$

$$1 = \frac{a^3 \times 3.99 \times 6.023 \times 10^{23}}{168.5}$$

$$a = 4.123 \times 10^{-8} \text{ cm} = 412 \text{ pm}$$

- (b) Distance between  $\text{Cs}^+$  and  $\text{Cl}^-$  ions

$$= \frac{a\sqrt{3}}{2} = \frac{412 \times \sqrt{3}}{2} = 356.8 \text{ pm}$$

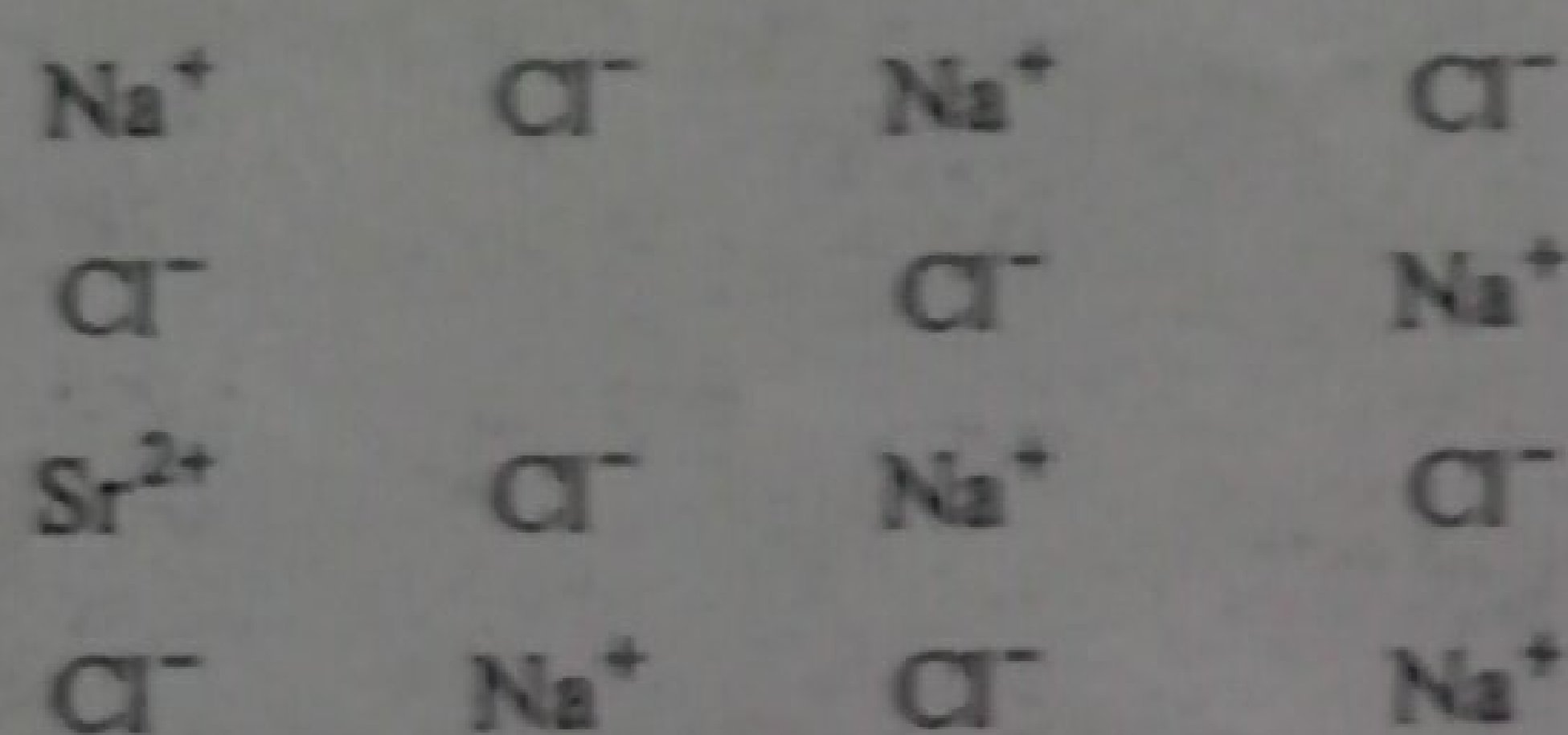
- (c)  $r_{\text{Cs}^+} + r_{\text{Cl}^-} = 356.8$

$$r_{\text{Cs}^+} + 180 = 356.8$$

$$r_{\text{Cs}^+} = 176.8 \text{ pm}$$

**Example 8.** If  $\text{NaCl}$  is doped with  $10^{-3}$  mol per cent of  $\text{SrCl}_2$ , what is the concentration of cation vacancy?

Solution:



Number of cationic vacancies per mol

$$= \frac{10^{-3} \times 6.023 \times 10^{23}}{100} = 6.023 \times 10^{18} \text{ vacancies per mol}$$

**Example 9.** A metal crystallises into two cubic phases, face-centred cubic (fcc) and body-centred cubic (bcc) whose unit lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of fcc and bcc.

Solution: Density of fcc =  $\frac{Z_1 \times \text{At. mass}}{\text{Av. no.} \times V_1}$

and density in bcc =  $\frac{Z_2 \times \text{At. mass}}{\text{Av. no.} \times V_2}$

$$\frac{d_{\text{fcc}}}{d_{\text{bcc}}} = \frac{Z_1}{Z_2} \times \frac{V_2}{V_1}$$

For fcc  $Z_1 = 4; V_1 = a^3 = (3.5 \times 10^{-8})^3$

For bcc  $Z_2 = 2; V_2 = a^3 = (3.0 \times 10^{-8})^3$

$$\frac{d_{\text{fcc}}}{d_{\text{bcc}}} = \frac{4 \times (3.0 \times 10^{-8})^3}{2 \times (3.5 \times 10^{-8})^3} = 1.259$$

**Example 10.** A solid AB has the NaCl structure. If radius of the cation  $A^+$  is 120 pm, calculate the maximum value of the radius of the anion  $B^-$ .

Since, NaCl has octahedral structure,

$$\text{The limiting ratio } \frac{r_A^+}{r_B^-} = 0.414$$

or

$$r_B^- = \frac{r_A^+}{0.414} = \frac{120}{0.414} = 290 \text{ pm}$$

**Example 11.** You are given marbles of diameter 10 mm. They are to be placed such that their centres are lying in a square bond by four lines each of length 40 mm. What will be the arrangement of marbles in a plane, so that, maximum number of marbles can be placed inside the area. Sketch the diagram and derive expression for the number of marbles per unit area.

In order to accommodate maximum number of spheres, there should be hcp (hexagonal closed packing).

Area of square having spherical marbles =  $16 \text{ cm}^2$

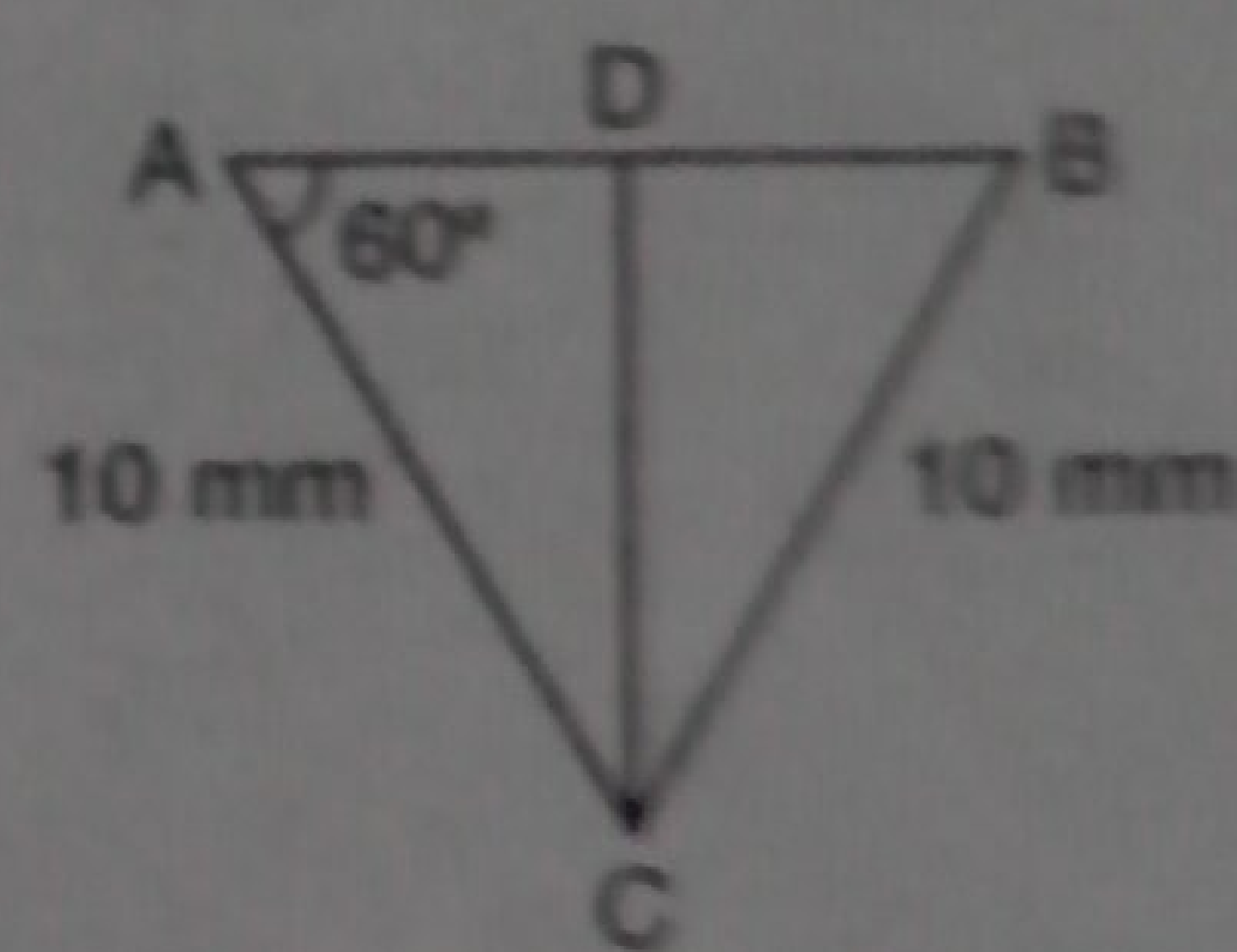
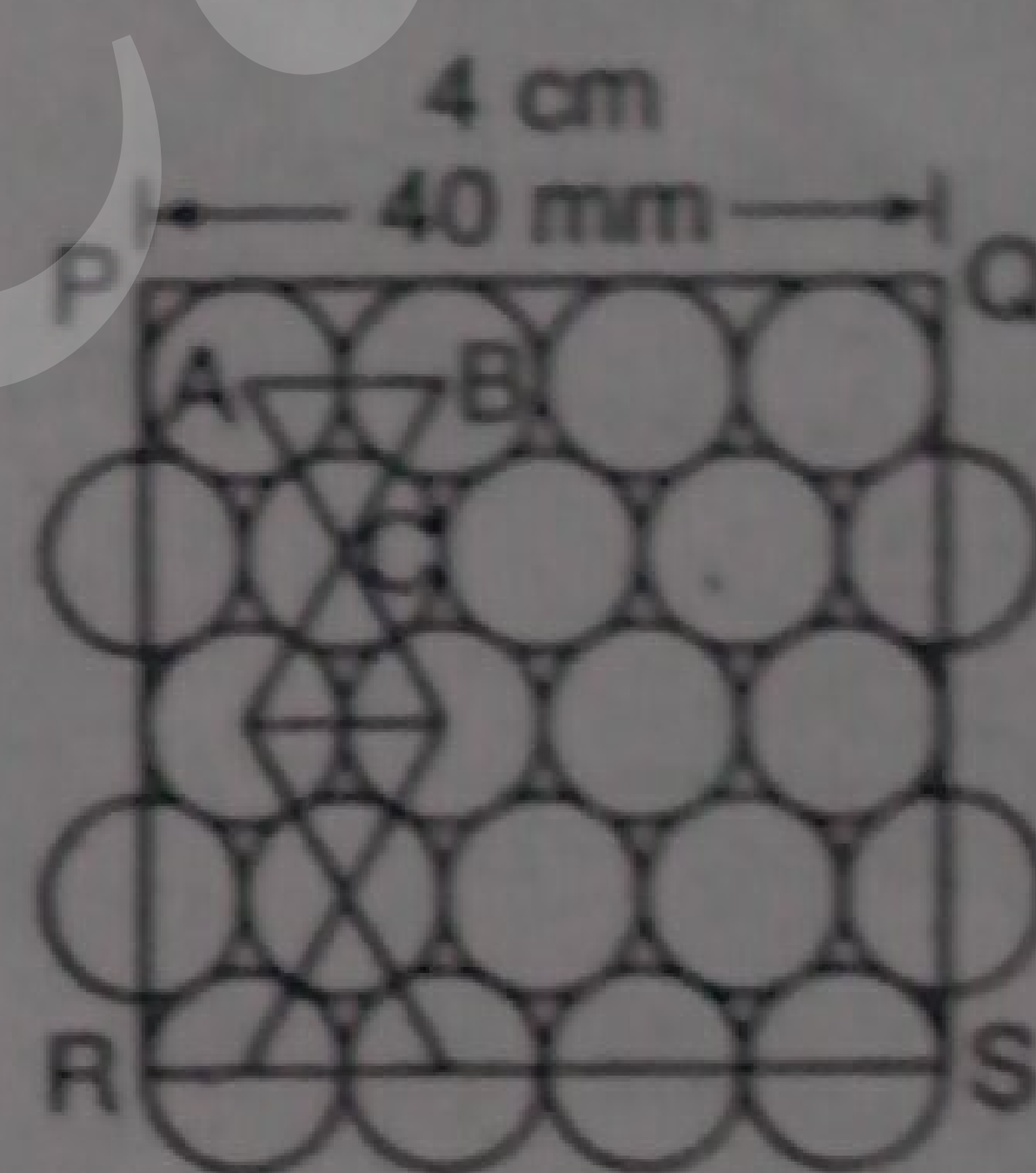
Maximum number of spheres = 14 (full) + 8 (half)

Number of spheres = 18

Per unit area (per  $\text{cm}^2$ ) =  $\frac{18}{16} = 1.125$

Length PQ of square = 4 cm

Length PR =  $5 + 4 \times 5\sqrt{3} = 40 \text{ mm} = 4 \text{ cm}$



$$CD = 10 \sin 60^\circ = \frac{10\sqrt{3}}{2} = 5\sqrt{3}$$

**Example 12.** Calculate the density of diamond from the fact that it has face-centred cubic structure with two atoms per lattice point and a unit cell of edge length 3.569 Å.

Solution:  $Z = 8, M = 12$

$$Z = \frac{l^3 \times \rho \times N}{M}$$

$$\text{Density } \rho = \frac{ZM}{l^3 N} = \frac{8 \times 12}{(3.569 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 3.506 \text{ g cm}^{-3}$$



**Example 13.** An element crystallises into a structure which may be described by a cubic unit cell having one atom at each corner of the cube and two atoms on one of its diagonals. If the volume of this unit cell is  $24 \times 10^{-24} \text{ cm}^3$  and density of element is  $7.2 \text{ g/cm}^3$ . Calculate the number of atoms present in 100 g of the element.

Number of atoms in a unit cell ( $Z$ ) =  $1 + 2 = 3$

$$Z = \frac{l^3 \times \rho \times N}{M}$$

$$M = \frac{l^3 \times \rho \times N}{Z}$$

$$= \frac{24 \times 10^{-24} \times 7.2 \times 6.023 \times 10^{23}}{3} = 34.69$$

$$\begin{aligned} \text{Number of atoms} &= \frac{\text{Mass}}{\text{Molar mass}} \times 6.023 \times 10^{23} \\ &= \frac{100}{34.69} \times 6.023 \times 10^{23} = 3.47 \times 10^{24} \end{aligned}$$

**Example 14.** Analysis shows that nickel oxide has formula  $\text{Ni}_{0.98}\text{O}$ . What fraction of nickel exist as  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  ions?

*Solution:* Let number of  $\text{Ni}^{3+}$  ions =  $x$

$\therefore$  Number of  $\text{Ni}^{2+}$  ions =  $(0.98 - x)$

Since, molecule is neutral, its total charge is zero.

$$(+3 \times x) + (0.98 - x) \times 2 - 2 = 0$$

$$x = 0.04, \text{ i.e., } \text{Ni}^{3+} = 0.04; \text{ Ni}^{2+} = 0.94$$

**Example 15.** Calcium crystallises in face-centred cubic unit cell with  $a = 0.556 \text{ nm}$ . Calculate density if

(i) it contained 0.1% Frenkel defect.

(ii) it contained 0.1% Schottky defect.

*Solution:* (i) Frenkel defect does not alter the density of solid.

$$\begin{aligned} d &= \frac{MZ}{l^3 N} = \frac{40 \times 4}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}} \\ &= 1.5455 \text{ g/cm}^3 \end{aligned}$$

(ii) Schottky defect lowers the density of solid

$$Z = 4 - \frac{4 \times 0.1}{100} = 3.996$$

$$\begin{aligned} d &= \frac{40 \times 3.996}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}} \\ &= 1.5440 \text{ g/cm}^3 \end{aligned}$$

**Example 16.** Density of lithium atom is  $0.53 \text{ g/cm}^3$ . The edge length of Li is  $3.5 \text{ \AA}$ . Find out the number of lithium atoms in a unit cell. Atomic mass of lithium is 6.94.

[CBSE-PMT (Mains) 2005]

*Solution:* 
$$Z = \frac{a^3 \times \rho \times N_A}{M}$$

$$\begin{aligned} &= \frac{(3.5 \times 10^{-8})^3 \times 0.53 \times 6.023 \times 10^{23}}{6.94} \\ &= 2 \end{aligned}$$

**Example 17.** Cu metal crystallises in face centred cubic lattice with cell edge,  $a = 361.6 \text{ pm}$ . What is the density of Cu crystal? (Atomic mass of copper =  $63.5 \text{ amu}$ ,  $N_A = 6.023 \times 10^{23}$ )

We know

$$Z = \frac{a^3 \times d \times N_A}{M}$$

$$\therefore d = \frac{ZM}{a^3 N_A} \quad \text{---(i)}$$

$$Z = 4 \text{ for fcc unit cell; } M = 63.5 \text{ g mol}^{-1}$$

$$a = 361.6 \times 10^{-10} \text{ cm; } N_A = 6.023 \times 10^{23}$$

Putting these values in (i), we get

$$d = \frac{4 \times 63.5}{(361.6 \times 10^{-10})^3 \times 6.023 \times 10^{23}} = 8.94 \text{ g cm}^{-3}$$

**Example 18.** An LPG cylinder weighs  $14.8 \text{ kg}$  when empty. When full, it weighs  $29 \text{ kg}$  and shows a pressure of  $2.5 \text{ atm}$ . In the course of use at  $27^\circ\text{C}$ , the weight of the full cylinder reduced to  $23.2 \text{ kg}$ . Find out the volume of  $n$ -butane in cubic metres used up at  $27^\circ\text{C}$  and  $1 \text{ atm}$ .

[Molecular mass of  $n$ -butane =  $58$ ] [CBSE-PMT (Mains) 2002]

*Solution:* Mass of  $n$ -butane used =  $29 - 23.2 = 5.8 \text{ kg}$

$$\text{Number of moles of butane used} = \frac{5800}{58} = 100$$

$$V = \frac{nRT}{P} = \frac{100 \times 0.0821 \times 300}{1}$$

$$= 2463 \text{ litre}$$

$$= 2.463 \text{ m}^3$$

**Example 19.**  $r_{\text{Na}^+}$  and  $r_{\text{Cl}^-}$  represents radius of  $\text{Na}^+$  and  $\text{Cl}^-$  ions respectively. If ' $n$ ' is the number of  $\text{NaCl}$  units per unit cell then give the equation you will use to obtain molar volume.

[CBSE-PMT (Mains) 2002]

*Solution:* Edge length of unit cell ' $a$ ' =  $2(r_{\text{Na}^+} + r_{\text{Cl}^-})$

$$\text{Volume of unit cell} = a^3 = 8(r_{\text{Na}^+} + r_{\text{Cl}^-})^3$$

Volume occupied by one mole of  $\text{NaCl}$

$$= \frac{8(r_{\text{Na}^+} + r_{\text{Cl}^-})^3}{n} \times N_A$$

where  $N_A = 6.023 \times 10^{23}$

**Example 20.** Two gases A and B of mass  $70.6 \text{ g}$  and  $167.5 \text{ g}$  ( $M_w$  of A =  $32 \text{ amu}$  &  $M_w$  of B =  $20$ ) are mixed. Then total pressure of mixture is  $25 \text{ bar}$ . Calculate partial pressure of A and B.

[CBSE-PMT (Mains) 2002]

*Solution:* Number of moles A,  $n_A = \frac{70.6}{32} = 2.2$



$$\text{Number of moles of B, } n_B = \frac{1675}{20} = 8.375$$

$$\text{Partial pressure of gas A, } p_A = \frac{n_A}{n_A + n_B} \times p$$

$$= \frac{2.2}{2.2 + 8.375} \times 25 = 5.20 \text{ bar}$$

$$p_B = 25 - 5.20 = 19.8 \text{ bar}$$

18

Matter is anything which has mass and occupies space. Matter exists in three states, viz., solid, liquid and gas. Any substance can exist in either of the three states depending on temperature and pressure. Liquid and solid states are condensed states as they have much higher densities. Both liquids and gases are termed as fluids as they have flowing ability.

It is the simplest state and shows greatest uniformity in behaviour. The gases show almost the same behaviour irrespective of chemical nature, colour or odour. The molecules in a gas possess random motion in all directions. A gas has neither a definite shape nor a definite volume. Gases are characterised by low density, high degree of compressibility and expandability. Gases exert uniform pressure on the walls of the container. They diffuse rapidly and intermix to form homogeneous mixtures. All gases obey certain laws called gas laws.

3. Gas laws: Gas laws are based on experiments.

(i) Boyle's law: It states that the volume of the given amount of a gas is inversely proportional to its pressure at a constant temperature.

$$V \propto \frac{1}{P} \text{ or } PV = \text{constant or } P_1V_1 = P_2V_2 = P_3V_3 = \dots$$

$$\text{or } \frac{P_1}{d_1} = \frac{P_2}{d_2} \quad (\text{at constant temperature})$$

where,  $d_1$  and  $d_2$  are the densities of a gas at pressures  $P_1$  and  $P_2$ . The curves between  $P$  and  $V$  at constant temperature are hyperbolas and called isotherms.

(ii) Charles' law: At constant pressure, the volume of a given amount of a gas is directly proportional to its absolute temperature.

$$V \propto T \text{ or } \frac{V}{T} = \text{constant or } \frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \dots$$

Absolute temperature scale or Kelvin scale starts with  $-273^\circ\text{C}$  as zero.

$$\text{Absolute temperature (in K)} = 273 + t^\circ\text{C}$$

The absolute zero is that temperature where no gas can exist. The plots of volume against temperature (at constant pressure) are termed as isobars.

(iii) Pressure law or Gay-Lussac's law: At constant volume, the pressure of a given amount of a gas varies directly as its absolute temperature.

$$P \propto T \text{ or } \frac{P}{T} = \text{constant or } \frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{P_3}{T_3} = \dots$$

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

For one mole of an ideal gas,  $PV = RT$

For  $n$  moles of an ideal gas,  $PV = nRT$

For  $w$  g of the gas (mol. mass  $M$ ),

$$PV = \frac{w}{M} RT$$

$$\text{or } P = \frac{w}{V} \frac{RT}{M} = d \times \frac{RT}{M} \quad (d = \text{density})$$

$R$  is a universal gas constant. It is expressed in the units of work per degree kelvin per mol. Value of  $R$  in different units is

$$R = 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1}$$

$$= 82.1 \text{ mL-atm K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

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

$$= 1.987 = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$$

(iv) Avogadro's law: Equal volumes of all gases contain equal number of molecules under similar conditions of temperature and pressure. Volume occupied by one mole of a gas at NTP ( $0^\circ\text{C}$  and 1 atm) is termed molar volume. It is 22.4 litre or 22400 mL.

[Note: At  $25^\circ\text{C}$  and 1 bar, one mole of a gas has a volume of 25 litre.]

(v) Dalton's law of partial pressures: The total pressure exerted by a mixture of gases which do not react chemically is equal to the sum of their individual pressures (partial pressures) under similar conditions of temperature.

$$P = P_1 + P_2 + P_3 + \dots$$

Partial pressure of a gas = Molar fraction

$\times$  Total pressure of the gas

(vi) Graham's law of diffusion: The property of gases to mix with each other to form homogeneous mixture irrespective of gravity is called diffusion. Effusion is a special case of diffusion in which gas passes through a small aperture.

Under similar conditions of temperature and pressure, the relative rates of diffusion of gases are inversely proportional to the square root of their densities or vapour densities or molecular masses. This is Graham's law of diffusion.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{VD_2}{VD_1}} = \sqrt{\frac{M_2}{M_1}}$$



99. Elevation in boiling point was  $0.52^\circ\text{C}$  when 6 g of a compound was dissolved in 100 g of water. Molecular weight of  $X$  is ( $k_b$  of water is  $5.2^\circ\text{C}$  per 100 g water) [BCECE]  
 (a) 120 (b) 60 (c) 600 (d) 180
100. If 0.15 g of a solute, dissolved in 15 g of solvent, is boiled at a temperature higher by  $0.216^\circ\text{C}$  than that of the pure solvent. The molecular weight of the substance (molal elevation constant for the solvent is  $2.16^\circ\text{C}$ ) is [MHT CET]  
 (a) 100 (b) 10.1 (c) 10 (d) 1.001
101. 20 g of binary electrolyte (mol. wt. = 100) are dissolved in 500 g of water. The depression in freezing point of the solution is  $0.74^\circ\text{C}$  ( $k_f = 1.86 \text{ K m}^{-1}$ ) The degree of ionisation of the electrolyte is [Manipal]  
 (a) 0% (b) 100% (c) 75% (d) 50%
102. The order of osmotic pressure of isomolar solution of  $\text{BaCl}_2$ ,  $\text{NaCl}$  and sucrose is [MP PET]  
 (a)  $\text{BaCl}_2 > \text{NaCl} > \text{sucrose}$   
 (b)  $\text{NaCl} > \text{BaCl}_2 > \text{sucrose}$   
 (c)  $\text{sucrose} > \text{NaCl} > \text{BaCl}_2$   
 (d)  $\text{BaCl}_2 > \text{sucrose} > \text{NaCl}$
103. The vapour pressure of pure liquid is 1.2 atm. When a non-volatile substance  $B$  is mixed in  $A$ , then its vapour pressure becomes 0.6 atm. The mole fraction of  $B$  in the solution is [MP PET]  
 (a) 0.15 (b) 0.25  
 (c) 0.50 (d) 0.75
104. The freezing point of equimolar aqueous solution will be highest for [J&K CET]  
 (a)  $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$  (b)  $\text{La}(\text{NO}_3)_3$   
 (c)  $\text{C}_6\text{H}_{12}\text{O}_6$  (d)  $\text{Ca}(\text{NO}_3)_2$

## Topic 4 Abnormal Molar Masses

2011

1. The degree of dissociation ( $\alpha$ ) of a weak electrolyte,  $A_xB_y$  is related to van't Hoff factor ( $i$ ) by the expression [AIIEE]

$$\begin{aligned} \text{(a) } \alpha &= \frac{i-1}{(x+y-1)} & \text{(b) } \alpha &= \frac{i-1}{x+y+1} \\ \text{(c) } \alpha &= \frac{x+y-1}{i-1} & \text{(d) } \alpha &= \frac{x+y-1}{i-1} \end{aligned}$$

2010

2. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water ( $\Delta T_f$ ), when 0.01 mole of sodium sulphate is dissolved in 1 kg of water, is ( $k_f = 1.86 \text{ K kg mol}^{-1}$ ) [AIIEE]

$$\begin{aligned} \text{(a) } 0.0372 \text{ K} & & \text{(b) } 0.0558 \text{ K} \\ \text{(c) } 0.0744 \text{ L} & & \text{(d) } 0.0186 \text{ K} \end{aligned}$$

2009

3. If the various terms in the below given expressions have usual meanings, the van't Hoff factor ( $i$ ) cannot be calculated by which one of the expressions? [DCE]

$$\begin{aligned} \text{(a) } \pi V &= \sqrt{inRT} \\ \text{(b) } \Delta T_f &= ik_f \cdot m \\ \text{(c) } \Delta T_b &= ik_b \cdot m \\ \text{(d) } \frac{P_{\text{solvent}}^* - P_{\text{solution}}}{P_{\text{solvent}}^*} &= i \left( \frac{n}{N+n} \right) \end{aligned}$$

4. van't Hoff factor of aq.  $\text{K}_2\text{SO}_4$  at infinite dilution has value equal to [AMU]

$$\begin{aligned} \text{(a) } 1 \\ \text{(b) } 2 \\ \text{(c) } 3 \\ \text{(d) between 2 and 3} \end{aligned}$$

2008

5. van't Hoff factor of  $\text{Ca}(\text{NO}_3)_2$  is [BCECE]

$$\begin{aligned} \text{(a) one} & & \text{(b) two} \\ \text{(c) three} & & \text{(d) four} \end{aligned}$$

6. Osmotic pressure observed when benzoic acid is dissolved in benzene is less than that expected from theoretical considerations. This is because [Jamia Millia Islamia]

$$\begin{aligned} \text{(a) benzoic acid is an organic solute} \\ \text{(b) benzoic acid has higher molar mass than benzene} \\ \text{(c) benzoic acid gets associated in benzene} \\ \text{(d) benzoic acid gets dissociated in benzene} \end{aligned}$$

7. van't Hoff factor more than unity indicates that the solute in solution has [Manipal]

$$\begin{aligned} \text{(a) dissociated} \\ \text{(b) associated} \\ \text{(c) Both (a) and (b)} \\ \text{(d) cannot say anything} \end{aligned}$$

8. Abnormal colligative properties are observed only when the dissolved non-volatile solute in a given dilute solution [J&K CET]

$$\text{(a) is a non-electrolyte}$$



90

- (b) offers an intense colour  
 (c) associates or dissociates  
 (d) offers no colour

**2007**

9. When 20 g of naphthoic acid ( $C_{11}H_8O_2$ ) is dissolved in 50 g of benzene ( $k_f = 1.72 \text{ K kg mol}^{-1}$ ), a freezing point depression of 2 K is observed. The van't Hoff factor ( $i$ ) is [IIT JEE]

- (a) 0.5 (b) 1  
 (c) 2 (d) 3

10. Phenol dimerises in benzene having van't Hoff factor 0.54. What is the degree of association? [OJEE]

- (a) 1.92 (b) 0.98  
 (c) 1.08 (d) 0.92

**2006**

11. Observe the following abbreviations

$\pi_{\text{obs}}$  = observed colligative property

$\pi_{\text{cal}}$  = theoretical colligative property assuming normal behaviour of solute.

van't Hoff factor ( $i$ ) is given by

- (a)  $i = \pi_{\text{obs}} \times \pi_{\text{cal}}$  (b)  $i = \pi_{\text{obs}} + \pi_{\text{cal}}$   
 (c)  $i = \pi_{\text{obs}} - \pi_{\text{cal}}$  (d)  $i = \frac{\pi_{\text{obs}}}{\pi_{\text{cal}}}$

[J&amp;K CET]

**2005**

12. The elevation in boiling point of a solution of 13.44 g of  $\text{CuCl}_2$  in 1 kg of water using the following information will be (molecular weight of  $\text{CuCl}_2 = 134.4$  and  $k_b = 0.52 \text{ K m}^{-1}$ ) [IIT JEE]

- (a) 0.16 (b) 0.05  
 (c) 0.1 (d) 0.2

13. If  $\alpha$  is the degree of dissociation of  $\text{Na}_2\text{SO}_4$ , the van't Hoff factor ( $i$ ) used for calculating the molecular mass is [AIIEEE]

- (a)  $1 - 2\alpha$  (b)  $1 + 2\alpha$   
 (c)  $1 - \alpha$  (d)  $1 + \alpha$

14. The van't Hoff factor of  $\text{BaCl}_2$  at 0.01 M concentration is 1.98. The percentage of dissociation of  $\text{BaCl}_2$  at this concentration is [Kerala CEE]

- (a) 49 (b) 69  
 (c) 89 (d) 98  
 (e) 100

**2004**

15. 0.004 M  $\text{Na}_2\text{SO}_4$  is isotonic with 0.01 M glucose. Degree of dissociation of  $\text{Na}_2\text{SO}_4$  is [IIT JEE]

- (a) 75% (b) 50%  
 (c) 25% (d) 85%

**2003**

16. Benzoic acid dissolved in benzene shows a molecular weight of [Manipal]

- (a) 61 (b) 244  
 (c) 366 (d) 122

17. The van't Hoff factor for 0.1 M  $\text{Ba}(\text{NO}_3)_2$  solution is 2.74. The degree of dissociation is [J&K CET]

- (a) 91.3% (b) 87%  
 (c) 100% (d) 74%

## Topic 5

### Distribution Law

**2011**

1. One gram of silver gets distributed between  $10 \text{ cm}^3$  of molten zinc and  $100 \text{ cm}^3$  of molten lead at  $800^\circ\text{C}$ . The percentage of silver still left in the lead layer is approximately [KCET]

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

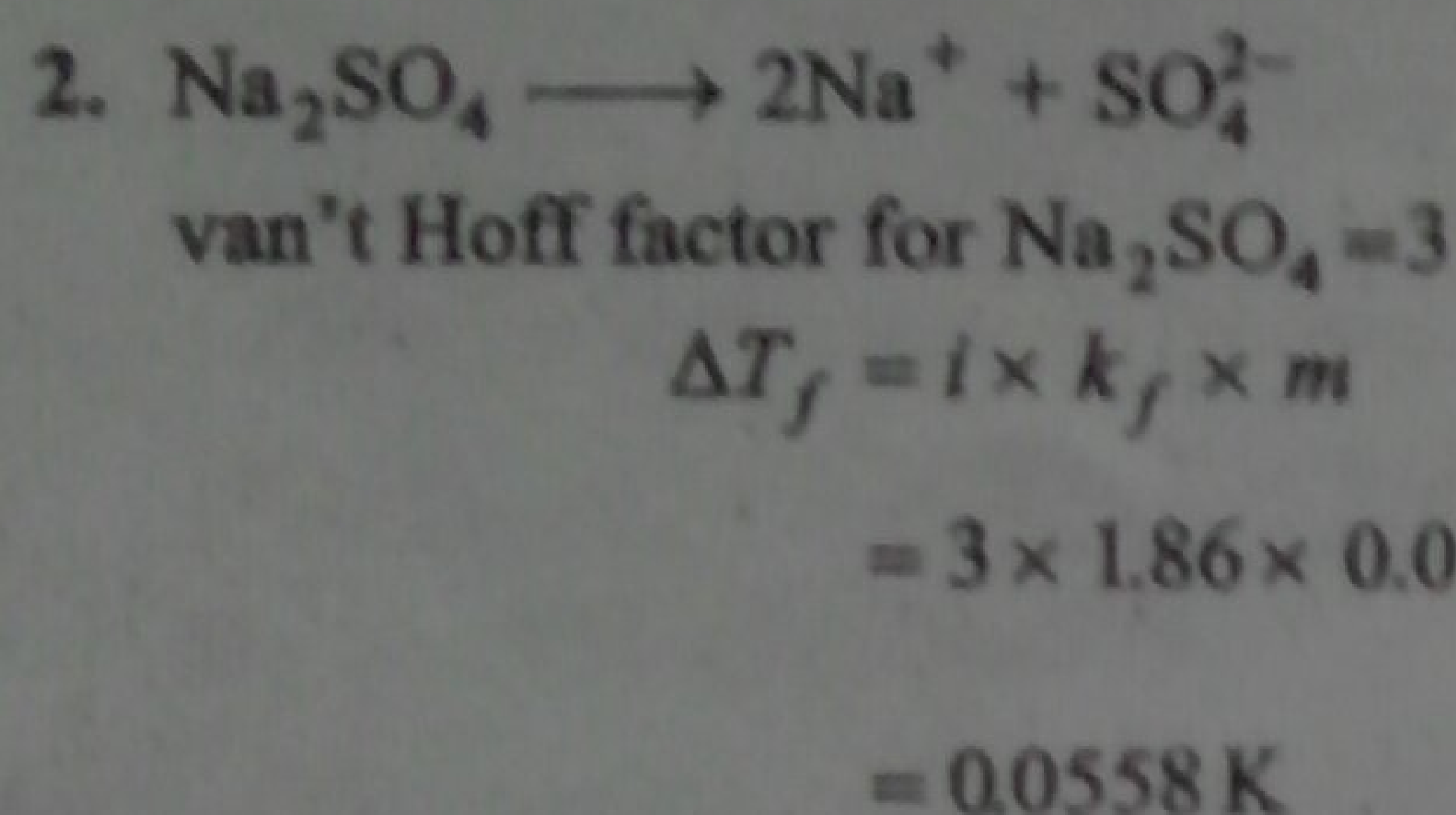
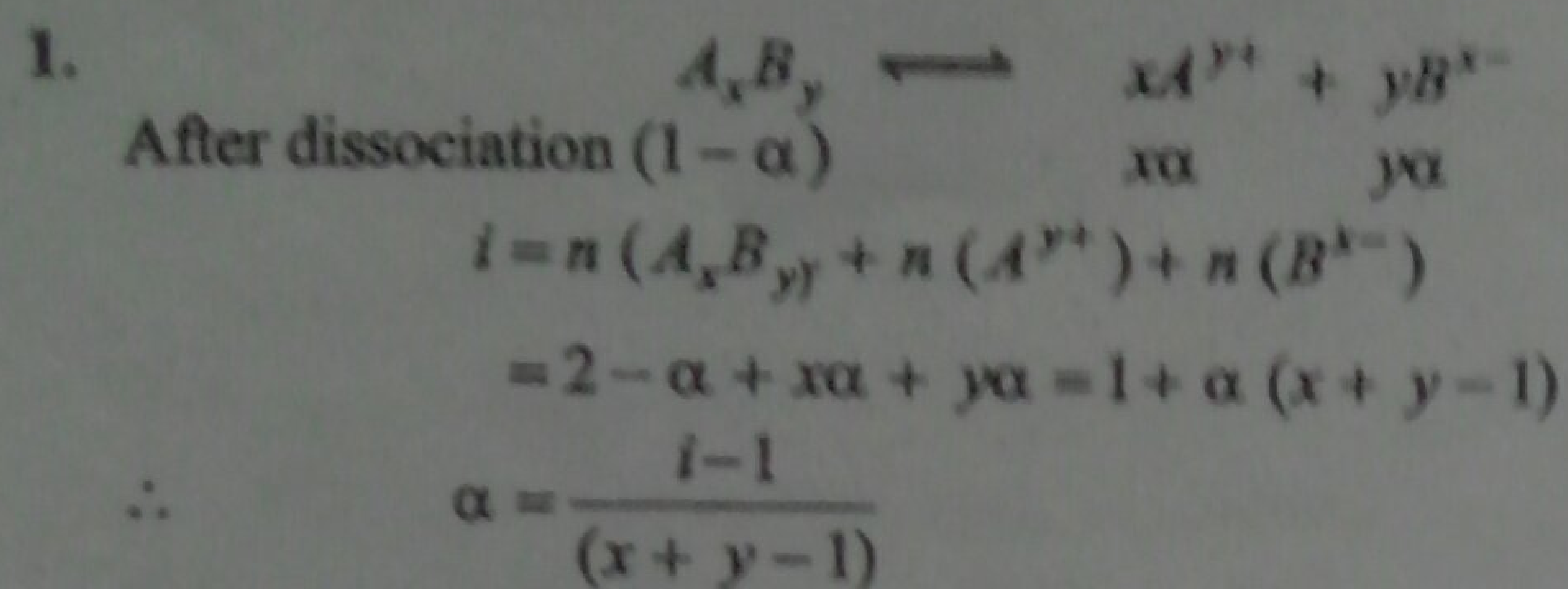
**2006**

2. Distribution law was given by [WB JEE]

- (a) Henry  
 (b) van't Hoff  
 (c) Nernst's  
 (d) Ostwald



## Topic 4 : Abnormal Molar Masses



3. (a) van't Hoff equation is

$$\pi V = inRT$$

(b) For depression in freezing point,

$$\Delta T_f = i \times k_f \times m$$

(c) For elevation in boiling point,

$$\Delta T_b = i \times k_b \times m$$

(d) For lowering of vapour pressure,

$$\frac{P_{\text{solvent}} - P_{\text{solution}}}{P_{\text{solvent}}} = i \left( \frac{n}{N+n} \right)$$



It gives 3 ions, hence, the van't Hoff factor = 3.



It furnishes 3 ions per formula unit. So, its van't Hoff factor is 3.

6. Benzoic acid in benzene exists as a dimer. So, number of molecules decreases and hence, osmotic pressure decreases.

7. van't Hoff factor greater than 1 means observed value is greater than calculated value which is so when the solute dissociates.

8. As the colligative properties depend only upon the number of particles of solute, so if the non-volatile solute dissociates or associates in the solution, the value of colligative properties deviates, i.e., abnormal colligative properties are obtained.

9. Actual molecular weight of naphthoic acid ( $C_{11}H_8O_2$ ) = 172

Molecular mass (calculated)

$$\begin{aligned} &= \frac{1000 \times k_f \times w}{W \times \Delta T_f} \\ &= \frac{1000 \times 1.72 \times 20}{50 \times 2} = 344 \end{aligned}$$

$$\begin{aligned} \text{van't Hoff factor}(i) &= \frac{\text{actual mol. wt.}}{\text{calculated mol. wt.}} = \frac{172}{344} \\ &= 0.5 \end{aligned}$$

10. We have,  $i = 1 - \frac{x}{2}$

where,  $x$  = degree of association

Here,  $i = 0.54$

$$0.54 = 1 - \frac{x}{2}$$

$$\text{or } 0.54 - 1 = -\frac{x}{2}$$

$$\text{or } -0.46 = -\frac{x}{2}$$

$$x = 0.92$$

11. van't Hoff factor ( $i$ ) is given by

$$i = \frac{\text{observed value of colligative property}}{\text{normal value of colligative property}}$$

The normal value of colligative property is the theoretically calculated value assuming no association or dissociation.

$$\therefore i = \frac{\pi_{\text{obs}}}{\pi_{\text{cal}}}$$

12.  $CuCl_2$  is an electrolyte which ionise in solution as follows



At $t = 0$	1 mole	0	0
After ionisation	$(1-\alpha)$ mole	$\alpha$ mole	$2\alpha$ mole

Thus, number of particles after ionisation

$$= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$$

$\therefore$  van't Hoff factor ( $i$ )

$$= \frac{\text{number of particles after ionisation}}{\text{number of particles before ionisation}}$$

$$\text{or } (i) = \frac{1 + 2\alpha}{1} \text{ (On 100\% ionisation } \alpha = 1)$$

$$= \frac{1 + 2 \times 1}{1} = 3$$

The elevation in boiling point (when colligative property is abnormal)

$$\Delta T_b = i \times k_b \times m$$

$m \rightarrow$  molality of solution

Molality of  $CuCl_2$  solution

$$= \frac{\text{weight of } CuCl_2 \text{ in gram}}{\text{mol. weight of } CuCl_2} = \frac{13.44}{134.4} = 0.1 \text{ m}$$

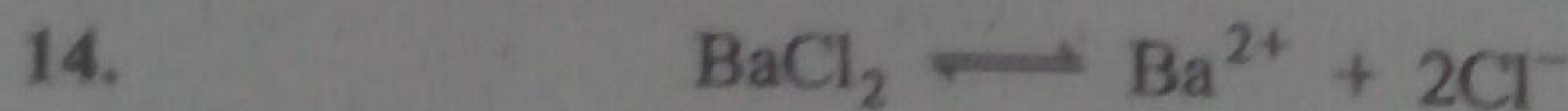
$$\text{Thus, } \Delta T_b = 3 \times 0.52 \times 0.1 = 0.156 \approx 0.16^\circ \text{C}$$



van't Hoff factor  $i = [1 + (y-1)\alpha]$

where  $y$  is the number of ions from one mole solute, (in this case = 3),  $\alpha$  the degree of dissociation.

$$i = (1 + 2\alpha)$$



initial	0.01 M		
at equilibrium	$(0.01 - x)$ M	$x$ M	$2x$ M

$$i = \frac{(0.01 - x) + x + 2x}{0.01}$$



$$= \frac{0.01 + 2x}{0.01} = 1.98$$

$$x = 0.0049$$

$$\% \alpha = \frac{x}{0.01} \times 100 = \frac{0.0049 \times 100}{0.01} = 49\%$$

15. When 0.004 M  $\text{Na}_2\text{SO}_4$  solution is isotonic with 0.01 M solution of glucose, so their osmotic pressures are equal to each other.

Osmotic pressure of 0.01 M glucose  $(\pi)_{\text{glucose}} = CST$

$\therefore C = \text{concentration of solution} = 0.01 \text{ M}$

$S = \text{solution constant} = 0.0821 \text{ L-atm/K/mol}$

$T = \text{absolute temperature}$

$$\therefore \pi_{\text{glucose}} = 0.01 \times 0.0821 \times T \quad \dots(i)$$

$$\pi_{\text{glucose}} = \pi_{\text{Na}_2\text{SO}_4}$$

$\text{Na}_2\text{SO}_4$  is present in ionic state in solution



$$\text{at } t = 0 \quad \begin{array}{ccc} 1 & 0 & 0 \end{array}$$

$$\text{at equilibrium} \quad \begin{array}{ccc} 1 - \alpha & 2\alpha & \alpha \end{array}$$

(where,  $\alpha$  is the degree of dissociation of  $\text{Na}_2\text{SO}_4$ )

$$(\pi_{\text{cal}})_{\text{Na}_2\text{SO}_4} = C \times S \times T = 0.004 \times 0.0821 \times T \quad \dots(ii)$$

By van't Hoff factor

$$\frac{(\pi_{\text{obs}})_{\text{Na}_2\text{SO}_4}}{(\pi_{\text{cal}})_{\text{Na}_2\text{SO}_4}} = \frac{\text{number of particles after dissociation}}{\text{number of particles before dissociation}}$$

$$= \frac{1 - \alpha + 2\alpha + \alpha}{1}$$

$$\therefore \frac{(\pi_{\text{obs}})_{\text{Na}_2\text{SO}_4}}{(\pi_{\text{cal}})_{\text{Na}_2\text{SO}_4}} = \frac{1 + 2\alpha}{1}$$

$$\therefore \frac{0.01 \times 0.0821 \times T}{0.004 \times 0.0821 \times T} = \frac{1 + 2\alpha}{1}$$

$$\text{or } \frac{10}{4} = \frac{1 + 2\alpha}{1} \quad \text{or} \quad 10 = 4 + 8\alpha$$

$$\alpha = \frac{10 - 4}{8} = 0.75$$

$$\% \text{ of } \alpha = 75\%$$

16. Benzoic acid dimerises in benzene.

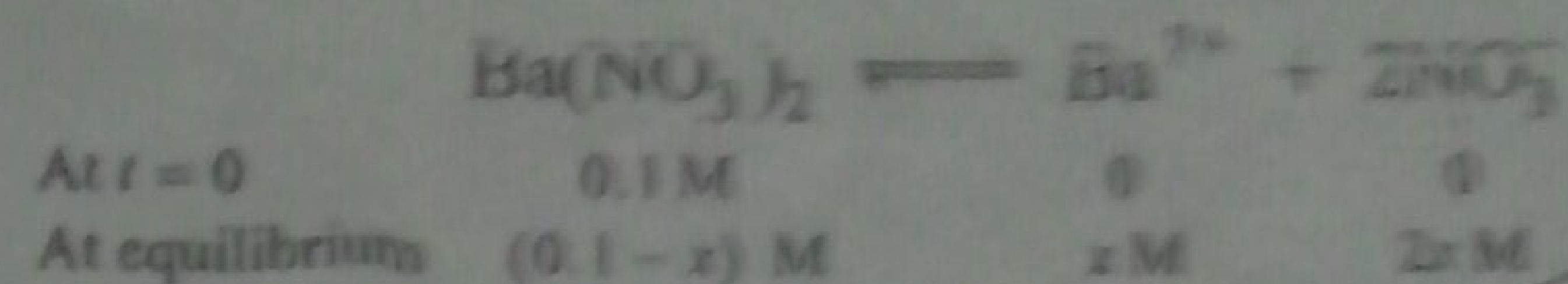
Mol. wt. of benzoic acid

$$= 78 + 12 + 32 = 122$$

Hence, molecular weight of benzoic acid in benzene is

$$= 122 + 122 = 244$$

17.



$$\text{At } t = 0 \quad \begin{array}{ccc} 0.1 \text{ M} & 0 & 0 \end{array}$$

$$\text{At equilibrium} \quad \begin{array}{ccc} (0.1 - x) \text{ M} & x \text{ M} & 2x \text{ M} \end{array}$$

$$i = \frac{(0.1 - x) + x + 2x}{0.1}$$

$$2.74 = \frac{0.1 + 2x}{0.1}$$

$$0.1 + 2x = 0.274$$

$$2x = 0.274 - 0.1 = 0.174$$

$$x = \frac{0.174}{2} = 0.087$$

$$\therefore \text{Degree of dissociation} = \frac{0.087}{0.1} \times 100 = 87\%$$

## Topic 5 : Distribution Law

$$1. K_D = \frac{\text{concentration of } X \text{ in solvent } A}{\text{concentration of } X \text{ in solvent } B}$$

$$\text{Concentration of Ag in } 10 \text{ cm}^3 \text{ Zn} = x$$

$$\text{Concentration of Ag in } 100 \text{ cm}^3 \text{ Pb} = \frac{1-x}{10}$$

$$\text{Concentration of Ag in } 10 \text{ cm}^3 \text{ Pb} = \frac{1-x}{10}$$

$$300 = \frac{x \times 10}{(1-x)} \quad \text{or } x = \frac{300}{100} = 0.967$$

$$= 97\%$$

$$\text{Concentration of Ag in zinc} = 1 - 0.967 = 0.033$$

$$= 3.3\%$$

2. Nernst's distribution law at constant temperature, when, different quantities of a solute are allowed to distribute between two immiscible solvents in contact with each other then at equilibrium the ratio of the concentration of the solute in two layers is constant for similar species which may be present.

Distribution coefficient,

$$K_D = \frac{\text{concentration of } X \text{ in solvent } A (C_1)}{\text{concentration of } X \text{ in solvent } B (C_2)}$$