1. Details of Module and its structure

| Module Detail | Chemistry |
| :--- | :--- |
| Subject Name | Chemistry 03 (Class XII, Semester 01) |
| Course Name | The Solid State: Part 2 |
| Module Name/Title | lech_10102 |
| Module Id | Knowledge about solids and there characteristics |
| Pre-requisites | After going through this lesson, the learners will be able to: |
| Objectives | 1. Crystal lattice and unit cells |
|  | 2. Close packing of particles; <br> 3. Different types of voids and close packed structures; <br> 4. Calculate the packing efficiency of different types of cubic <br> unit cells |
| Keywords | 5. Correlate the density of a substance with its unit cell <br> properties |

## 2. Development Team

| Role | Name | Affiliation |
| :--- | :--- | :--- |
| National MOOC <br> (NMC) | Coordinator Prof. Amarendra P. Behera | CIET, NCERT, New Delhi |
| Program Coordinator | Dr. Mohd. Mamur Ali | CIET, NCERT, New Delhi |
| Course Coordinator (CC) / PI | Prof. Alka Mehrotra <br> Prof. R. K. Parashar | DESM, NCERT, New Delhi <br> DESM, NCERT, New Delhi |
| Course Co-Coordinator / Co-PI | Dr. Aerum Khan | CIET, NCERT, New Delhi |
| Subject Matter Expert (SME) | Mrs. Preeti Kiran | Kendriya Vidyalaya No 1 AFS, <br> Hindan |
| Review Team | Dr. Neeti Misra | Achraya Narendra Dev College, <br> New Delhi <br> CIET, NCERT, New Delhi |

## Table of Contents:

## 1. Introduction

2. Unit cell and Crystal lattice

### 2.1 Types of Unit Cells

### 2.2 Number of Atoms in a Unit Cell

## 3. Close packed structures

## 4. Types of packing in solids

### 4.1 Formula of a Compound and Number of Voids Filled

5. Packing efficiency

### 5.1 In a Simple Cubic Lattice

### 5.2 In a Body-centred Cubic Structures

### 5.3 In a Face-centred Cubic (HCP and CCP) Structures

### 5.4 Calculation involving dimensions of the Unit Cell

## 6. Summary

## 1. Introduction

In the previous module you have learned that when there is a regular arrangement of constituent particles in the solid, it is known as crystalline solid. In this module you will be studying about diagramatic representation of the regular arrangement of crystal as crystal lattice followed by types of packing and packing efficiency.

## 2. Unit Cell and Crystal Lattice

The main characteristic of crystalline solids is a regular and repeating pattern of constituent particles. If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called crystal lattice. Thus, a regular three dimensional arrangement of points in space is called a crystal lattice. A portion of a crystal lattice is shown in Fig. 1


Fig. 1: A portion of a three dimensional cubic lattice and its unit cell.
There are only 14 possible three dimensional lattices. These are called Bravais Lattices (after the French mathematician who first described them).

## The following are the characteristics of a crystal lattice:

(a) Each point in a lattice is called lattice point or lattice site.
(b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.
(c) Lattice points are joined by straight lines to bring out the geometry of the lattice. Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

A unit cell is characterised by:
(i) Its dimensions along the three edges, $\mathrm{a}, \mathrm{b}$ and c . These edges may or may not be mutually perpendicular.
(ii) Angles between the edges, $\alpha$ (between b and c) $\beta$ (between a and c) and $\gamma$ (between a and b). Thus, a unit cell is characterised by six parameters, $a, b, c, \alpha, \beta$ and $\gamma$.


Fig. 2: Illustration of parameters of a unit cell.

### 2.1 Types of Unit Cells

Unit cells can be broadly divided into two categories, i) Primitive and ii) Centred unit cells.
(a) Primitive Unit Cells : When constituent particles are present only on the corner positions of a unit cell, it is called a primitive unit cell.
(b) Centred Unit Cells : When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a centred unit cell. Centred unit cells are of three types:
(i) Body-Centred Unit Cell: It contains one constituent particle (atom, molecule or ion) at its bodycentre and eight particles at its corners.
(ii) Face-Centred Unit Cell: It contains one constituent particle present at the centre of each face, along with eight particles at its corners.
(iii) End-Centred Unit Cell: In this one constituent particle is present at the centre of any two opposite faces along with eight particles at its corners.

In all, there are seven types of primitive unit cells as shown in Fig. 3.


Fig. 3: Seven primitive unit cells in crystals
The characteristics of the seven crystal systems along with the centred unit cells they can form have been listed in Table 1.

Table 1: Seven Primitive Unit Cells and their Possible Variations as Centred Unit Cells

| Crystal System | Possible Variations | Axial distances or edge lengths | Axial angles | Examples |
| :---: | :---: | :---: | :---: | :---: |
| Cubic | Primitive, Bodycentred, Face- centred | $a=b=c$ | $\alpha=\beta=\gamma=90^{\circ}$ | NaCl, Zinc blende, Cu |
| Tetragonal | Primitive, <br> centred Body- | $a=b \neq c$ | $\alpha=\beta=\gamma=90^{\circ}$ | $\begin{aligned} & \text { White tin, } \mathrm{SnO}_{2} \text {, } \\ & \mathrm{TiO}_{2}, \mathrm{CaSO}_{4} \\ & \hline \end{aligned}$ |
| Orthorhombic | Primitive, Bodycentred, Face centred, End- centred | $a \neq b \neq c$ | $\alpha=\beta=\gamma=90^{\circ}$ | Rhombic sulphur, $\mathrm{KNO}_{3}, \mathrm{BaSO}_{4}$ |
| Hexagonal | Primitive | $a=b \neq c$ | $\begin{aligned} & \alpha=\beta=90^{\circ} \\ & \gamma=120^{\circ} \end{aligned}$ | $\begin{aligned} & \text { Graphite, } \mathrm{ZnO} \text {, } \\ & \text { CdS } \end{aligned}$ |
| Rhombohedral or Trigonal | Primitive | $a=b=c$ | $\alpha=\beta=\gamma \neq 90^{\circ}$ | Calcite ( $\mathrm{CaCO}_{3}$ ), <br> HgS (cinnabar) |
| Monoclinic | Primitive, End- centred | $a \neq b \neq c$ | $\begin{aligned} & \alpha=\gamma=90^{\circ} \\ & \beta \neq 90^{\circ} \end{aligned}$ | Monoclinic sulphur, $\mathrm{Na}_{2} \mathrm{SO}_{4} \mathrm{H}_{4} \mathrm{H}_{2} \mathrm{O}$ |
| Triclinic | Primitive | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90{ }^{\circ}$ | $\begin{aligned} & \hline \mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}, \mathrm{CuSO}_{4} . \\ & 5 \mathrm{H}_{2} \mathrm{O}, \mathrm{H}_{3} \mathrm{BO}_{3} \end{aligned}$ |



Primitive (or simple)


Body-centred


Face-centred

The three cubic lattices: all sides of same length, angles between faces all $90^{\circ}$


Primitive


Body-centred

The two tetragonal: one side different in length to the other, two angles between faces all $90^{\circ}$


Primitive


End-centred


Body-centred


Face-centred
The four orthorhombic lattices: unequal sides, angles

$$
\text { between faces all } 90^{\circ}
$$


Primitive
The two monoclinic lattices: unequal sides, two faces have angles different to $90^{\circ}$

onal latticeone side different in length to the other two, the marked angles on two faces are $60^{\circ}$


Triclinic lattice-
unequal sides $a, b, c$,
$\mathrm{A}, \mathrm{B}, \mathrm{C}$ are unequal
angles with none equal to $90^{\circ}$

Fig. 4: Unit Cells of 14 Types of Bravais Lattices

### 2.2 Number of Atoms in a Unit Cell

We know that any crystal lattice is made up of a very large number of unit cells and every lattice point is occupied by one constituent particle (atom, molecule or ion). Let us now work out what portion of each particle belongs to a particular unit cell.

We shall consider three types of cubic unit cells and for simplicity assume that the constituent particle is an atom.

## Primitive Cubic Unit Cell

Primitive cubic unit cell has atoms only at its corner. Each atom at a corner is shared between eight adjacent unit cells as shown in Fig.5, four unit cells in the same layer and four unit cells of the upper (or lower) layer. Therefore, only $\frac{1}{8}$ th of an atom (or molecule or ion) actually belongs to a particular unit cell.


Fig. 5: In a simple cubic unit cell, each corner atom is shared between 8 unit cells.
In Fig.6, a primitive cubic unit cell has been depicted in three different ways. Each small sphere in Fig. 6 (a) represents only the centre of the particle occupying that position and not its actual size. Such structures are called open structures. The arrangement of particles is easier to follow in open structures. Fig. 6 (b)depicts space-filling representation of the unit cell with actual particle size and Fig. 6. (c) shows the actual portions of different atoms present in a cubic unit cell. In all, since each cubic unit cell has 8 atoms on its corners, and each corner atom contributes $1 / 8^{\text {th }}$ portion to the unit cell
the total number of atoms in one unit cell is $8 \times \frac{1}{8}=1$ atom.


Fig. 6: A primitive cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.

## Body-centred cubic (bcc) unit cell

A body-centred cubic unit cell has an atom at each of its corners and also one atom at its body centre. Fig. 7 depicts (a) open structure (b) space filling model and (c) the unit cell with portions of atoms actually belonging to it. It can be seen that the atom at the body centre wholly belongs to the unit cell in which it is present. Thus in a body-centered cubic (bcc) unit cell:
(i) 8 corners $\times \frac{1}{8}$ per corner atom $=8 \times \frac{1}{8}=1$ atom
(ii) 1 body centre atom $=1 \times 1=1$ atom
$\because$ Total number of atoms per unit cell $=2$ atoms


Fig.7: A body-centred cubic unit cell (a) open structure (b) space filling structure (c) actual portions of atoms belonging to one unit cell.

## Face- Centred Cubic Unit Cell

A face-centred cubic (fcc) unit cell contains atoms at all the corners and at the centre of all the faces of the cube. It can be seen in Fig. 8 that each atom located at the face-centre is shared between two adjacent unit cells and only $1 / 2$ of each atom belongs to a unit cell. Fig. 9 depicts (a) open structure (b) space-filling model and (c) the unit cell with portions of atoms actually belonging to it. Thus, in a face-centred cubic (fcc) unit cell:
(i) 8 corners atoms $\times \frac{1}{8}$ atom per unit cell $=8 \times \frac{1}{8}=1$ atom
(ii) 6 face-centred atoms $\times \frac{1}{2}$ atom per unit cell $=6 \times \frac{1}{2}=3$ atoms
$\therefore$ Total number of atoms per unit cell $=4$ atoms

Table 2 summarizes the number of atoms present in one unit cell of three different types of cubic unit cell.


Fig. 8: An atom at face centre of unit cell is shared between 2 unit cells

(a)

(b)

(b)

Fig 9: A face-centred cubic unit cell (a) open structure (b) space filling structure (c) actual portions of atoms belonging to one unit cell.

Table 2: Number of atoms per unit cell (Z):

| Type of unit cell | Number of <br> atoms <br> at corners | Number of <br> atoms <br> in centre of <br> faces | Number of <br> atoms <br> at the <br> centre of <br> unit cell | Total <br> (Z) |
| :--- | :--- | :--- | :--- | :--- |
| Primitive cube | $8 \times 1 / 8=1$ | 0 | 0 | 1 |
| Body Centered Cube <br> (B.C.C) | $8 \times 1 / 8=1$ | 0 | 1 | 2 |
| Face Centered Cube <br> (F.C.C) | $8 \times 1 / 8=1$ | $6 \times 1 / 2=3$ | 0 | 4 |

## 3. Close Packed Structures

In solids, the constituent particles are closely packed, leaving the minimum vacant space. Let us consider the constituent particles as identical hard spheres and build up the three dimensional structure in three steps.

## (i) Close Packing in One Dimension:

There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange them in a row and touching each other (Fig. 10)

Fig. 10: Close packing of spheres in one dimension

The number of nearest neighbours of a particle is called its coordination number. Thus, in one dimensional close packed arrangement, the coordination number is 2 .

## (ii) Close Packing in Two Dimensions:

Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres. It can be generated in two different ways.
(a) Square close packing: The second row may be placed in contact with the first one such that the spheres of the second row are exactly above those of the first row. The spheres of the two rows are aligned horizontally as well as vertically. If we call the first row as ' $A$ ' type row, the second row being exactly the same as the first one, is also of 'A' type. Similarly, we may place more rows to obtain AAA type of arrangement as shown in Fig. 11.


Fig. 11: Square close packing of spheres in two dimensions
In this arrangement, each sphere is in contact with four of its neighbours. Thus, the two dimensional coordination number is 4 . Also, if the centres of these 4 immediate neighbouring spheres are joined, a square is formed. Hence this packing is called square close packing.
(b) Hexagonal close packing: The second row may be placed above the depressions of the first row. If the arrangement of spheres in the first row is called ' $A$ ' type, the one in the second row is different and may be called ' B ' type. This arrangement is of ABAB type as shown in Fig. 12.


Fig. 12: Hexagonal close packing of spheres in two dimensions

In this arrangement, each sphere is in contact with six of its neighbours and thus the coordination number is $\mathbf{6}$. The centres of these six spheres are at the corners of a regular hexagon hence this packing is called two dimensional hexagonal close packing.
The hexagonal close packing structure is a more efficient close packing structure than square close packing structure.
In the two dimensional structures there are empty spaces which are known as voids. In two dimensional hexagonal close packing these voids are triangular in shape. Therefore, these voids are called triangular voids. The triangular voids are of two different types. In one row, the apex of the triangles are pointing upwards and in the next layer downwards.

## (iii) Close Packing in Three Dimensions :

Three dimensional close packed structure can be generated by placing two dimensional close packing layers one over the other. Since there are two types of two dimensional close packing structures, their stacking will result in different types of three dimensional structures. hexagonal close packed layers one over the other.
(i) Three dimensional close packing from two dimensional square close-packed layers: While placing the second square close-packed layer above the first we follow the same rule that was followed when one row was placed adjacent to the other. The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically as shown in Fig. 13.

Similarly, we may place more layers one above the other. If the arrangement of spheres in the first layer is called 'A' type, all the layers have the same arrangement. Thus this lattice has AAA.... type pattern. The lattice thus generated is the simple cubic lattice, and its unit cell is the primitive cubic unit cell (See Fig. 6).


Fig. 13: Simple cubic lattice formed by A A A .... arrangement
(ii) Three dimensional close packing from two dimensional hexagonal close packed layers: Three dimensional close packed structure can be generated by placing second layer over the first layer and then placing the third layer over the second layer. The placement of the third layer can be done in two ways giving rise to different types of three dimensional lattices. So, three dimensional hexagonal close packing involves three steps:
(a)In the first layer the spheres are arranged in a hexagonal manner in which each sphere is in contact with six other spheres.
(b) In the formation of second layer the spheres of the second layer fit into the depression of the first hexagonal close packed layer called ' A '. The depressions are actually the triangular voids of the two dimensional layer. As seen earlier, the triangular voids are of two types and they lie alternate to each other. To achieve a close packed structure, the spheres of the second layer occupy triangular voids (depressions) of one type. Since the spheres of the second layer are aligned differently, let us call the second layer as B. Wherever a sphere of the second layer is above the void of the first layer (or vice versa), a tetrahedral void is formed. These voids are called tetrahedral voids because a tetrahedron is formed when the centres of these four spheres are joined. They have been marked as ' $T$ ' in Fig. 14 . One such void has been shown separately in Fig. 15. It can be observed from Fig. 14 that not all the triangular voids of the first layer are covered by the spheres of the second layer. In such places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these voids do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as ' O ' in Fig.14. Such voids are surrounded by six spheres and are called octahedral voids. One such void has been shown separately in Fig. 15. The number of tetrahedral and octahedral voids depend upon the number of spheres involved in close packed structure.


Fig. 14: A stack of two layers of close packed spheres and voids generated in them. $\mathrm{T}=$ Tetrahedral void; $\mathrm{O}=$ Octahedral void


(a)



(b)


Octahedron
(c)

Fig 15: Tetrahedral and octahedral voids (a) top view (b) exploded side view and (c) geometrical shape of the void.

Let the number of close packed spheres be N , then,
The number of octahedral voids generated $=\mathrm{N}$
The number of tetrahedral voids generated $=2 \mathrm{~N}$
(c) Placing third layer over the second layer: For the third layer, there are two possibilities:
i) Covering Tetrahedral Voids: Tetrahedral voids of the second layer may be covered by the spheres of the third layer. In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as ABAB ....... pattern. This structure is called hexagonal close packed (hcp).


Fig. 16:(a) Hexagonal cubic close-packing exploded view showing stacking of layers of spheres (b) four layers stacked in each case and (c) geometry of packing.
(ii) Covering Octahedral Voids: The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called " C ' type. Only when fourth layer is placed, its spheres are aligned with layer A. This leads to the arrangement ABCABCABC...........Theresulting three dimensional structure is calledcubic closed packed (сср) (or) face centred cubic (fcc) structure.

(b)
(a)

Fig. 17(a) ABCABC... arrangement of layers when octahedral void is covered (b) fragment of structure formed by this arrangement resulting in cubic closed packed (сср) or face centred cubic (fcc) structure.

### 4.1Formula of a Compound and Number of Voids Filled

Earlier in this module, we have learnt that when particles are close packed resulting in either сср or $h с p$ structure, two types of voids are generated. While the number of octahedral voids present in a lattice is equal to the number of close packed particles, the number of tetrahedral voids generated is twice this number. In ionic solids, the bigger ions (usually anions) form the close packed structure and the smaller ions (usually cations) occupy the voids. If the latter ion is small enough then tetrahedral voids are occupied, if bigger, then octahedral voids.

Not all octahedral or tetrahedral voids are occupied. In a given compound, the fraction of octahedral or tetrahedral voids that are occupied, depends upon the chemical formula of the compound, as can be seen from the following examples.

## Solved Example 1

A compound is formed by two elements X and Y . Atoms of the element Y (as anions) make $c c p$ and those of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

## Solution:

The $c c p$ lattice is formed by the element Y . The number of octahedral voids generated would be equal to the number of atoms of Y present in it. Since all the octahedral voids are occupied by the atoms of X , their number would also be equal to that of the element Y . Thus, the atoms of elements X and Y are present in equal numbers or 1:1 ratio. Therefore, the formula of the compound is XY .

## Solved Example 2

Atoms of element B form hcp lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by the elements $A$ and $B$ ?

## Solution:

The number of tetrahedral voids formed is equal to twice the number of atoms of element B and only $2 / 3$ rd of these are occupied by the atoms of element A .
Hence the ratio of the number of atoms of $A$ and $B$ is $2 \times(2 / 3): 1$ or $4: 3$ and the formula of the compound is $\mathrm{A}_{4} \mathrm{~B}_{3}$.

## 5. Packing Efficiency

In whatever way the constituent particles (atoms, molecules or ions) are packed, there is always some free space in the form of voids. Packing efficiency is the percentage of total space filled by the particles. Let us calculate the packing efficiency in different types of structures.

### 5.1 In a Simple Cubic Lattice

In a simple cubic lattice the atoms are located only on the corners of the cube.
The edge length or side of the cube $=$ ' $a$ ',
The radius of each particle $=r$
From the Fig 18 , $\mathrm{a}=2 \mathrm{r}$
The volume of the cubic unit cell $=\mathrm{a}^{3}=(2 \mathrm{r})^{3}=8 \mathrm{r}^{3}$
Since a simple cubic unit cell contains only 1 atom
The volume of one atom occupied space $=4 / 3 \pi r^{3}$
Packing efficiency $=($ Volume of one atom / Volume of cubic unit cell) $\times 100 \%$

$$
\begin{aligned}
& =4 / 3 \pi r^{3} / 8 r^{3} \times 100 \% \\
& =52.38 \%=52.4 \%
\end{aligned}
$$



Fig 18: Packing in a Simple cubic lattice

### 5.2 In a Body-Centred Cubic Structures

In a Body centered cubic lattice the atoms are located at the corners of the cube and one atom at the center of the cube. From Fig. 19 it is clear that the atom at the centre will be in touch with the other two atoms diagonally arranged.
In $\triangle$ EFD
$\mathrm{b}^{2}=\mathrm{a}^{2}+\mathrm{a}^{2}=2 \mathrm{a}^{2}$
$\mathrm{b}=\sqrt{ } 2 \mathrm{a}$
Now in $\triangle$ AFD
$c^{2}=a^{2}+b^{2}=a^{2}+2 a^{2}=3 a^{2}$
$c=\sqrt{ } 3 \mathrm{a}$
The length of the body diagonal c is equal to 4 r , Therefore,
$\sqrt{ } 3 \mathrm{a}=4 \mathrm{r}$

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

Thus, $\quad r=\frac{\sqrt{ } 3 a}{4}$
Total number of atoms is 2 , and their volume $=2 \times(4 / 3) \pi r^{3}$
Volume of the cube, $a^{3}=\frac{4}{\sqrt{3}} r^{3}$
Therefore ,
Packing efficiency $=\frac{\text { Volume occupied by two spheres in the unit cell }}{\text { Total volume of the unit cell }} \times 100 \%$

$$
\frac{2 \times\left(\frac{4}{3}\right) \pi r^{3} \times 100}{[4 / \sqrt{3} r]^{3}}=\frac{(8 / 3) \pi r^{3}}{64 /(3 \sqrt{3}) r^{3}} \times 100=68 \%
$$



Fig. 19: Body-centred cubic unit cell (sphere along the body diagonal are shown with solid boundaries).

### 5.3 In a Face-Centred Cubic (HCP and CCP) Structures

In Fig. 20 let the unit cell edge length be ' $a$ ' and face diagonal $\mathrm{AC}=\mathrm{b}$.
In $\triangle \mathrm{ABC}$
$\mathrm{AC}^{2}=\mathrm{b}^{2}=\mathrm{BC}^{2}+\mathrm{AB}^{2}=\mathrm{a}^{2}+\mathrm{a}^{2}=2 \mathrm{a}^{2}$
Or $\mathrm{b}=\sqrt{ } 2 \mathrm{a}$
If $r$ is the radius of the sphere, we find
$b=4 r=\sqrt{ } 2 a$
or $\mathrm{a}=4 \mathrm{r} / \sqrt{ } 2=2 \sqrt{ } 2 \mathrm{r}$
Also $\mathrm{r}=a /(2 \sqrt{ } 2)$
We know, that each unit cell in fcc structure has 4 atoms.
Total volume of four spheres is equal to $4 \times(4 / 3) \pi r^{3}$
Volume of the cube is $\mathrm{a}^{3}$ or $(2 \sqrt{ } 2 \mathrm{r})^{3}$
Therefore ,
Packing efficiency $=\frac{\text { Volume occupied by four spheres in the unit cell }}{\text { Total volume of the unit cell }} \times 100 \%$
$\frac{4 \times\left(\frac{4}{3}\right) \pi r^{3} \times 100}{(2 \sqrt{2 r})^{3}} \cdot \frac{\left(\frac{16}{3}\right) \pi r^{3} \times 100}{16 \sqrt{2 r^{3}}} .=74 \%$
Thus, we may conclude that ccp and hcp structures have maximum packing efficiency.


Fig. 20: Cubic close packing other sides are not provided with spheres for sake of clarity.

### 5.4 Calculation involving dimensions of the Unit Cell

Let us write the formula of density of the unit cell,

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

Calculation of the volume of the unit cell:
Cell edge of the unit cell $=a \mathrm{~cm}$
Volume of the unit cell $=a^{3} \mathrm{~cm}^{3}$
Calculation of the mass of the unit cell:
Mass of the unit cell $=($ Number of atoms per unit cell $) \times($ mass of each atom $)$
We know that mass of one mole ( $6.023 \times 10^{23}$ ) atoms or molecules is equal to its molar mass.
$\therefore$ Mass of 1 atom $=$ molar mass $/ N_{\mathrm{A}}=M / N_{\mathrm{A}}$
$\therefore$ Mass of the unit cell $=(\mathrm{z}) \times\left(M / N_{\mathrm{A}}\right)$
$\therefore$ Density of the unit cell $=d=\frac{Z \times\left(M / N_{A}\right)}{a^{3}}=\frac{Z \times M}{N_{A} a^{3}}$
Where z = Number of atoms per Unit cell, $N_{\mathrm{A}}=$ Avogadro's number

## Solved Example 3

An element has a body-centred cubic (bcc) structure with a cell edge of 288 pm . The density of the element is $7.2 \mathrm{~g} / \mathrm{cm} 3$. How many atoms are present in 208 g of the element?

## Solution:

Volume of the unit cell $=(288 \mathrm{pm})^{3}$
$=\left(288 \times 10^{-12} \mathrm{~m}\right)^{3}=\left(288 \times 10^{-10} \mathrm{~cm}\right)^{3}$
$=2.39 \times 10^{-23} \mathrm{~cm}^{3}$

Volume of 208 g of the element = mass / density
$=208 \mathrm{~g} / 7.2 \mathrm{~g} \mathrm{~cm}^{-3}$
$=28.88 \mathrm{~cm}^{3}$
Number of unit cells in this volume $=28.88 \mathrm{~cm}^{3} /\left(2.39 \times 10^{-23} \mathrm{~cm}^{3}\right.$ per unit cell $)$
$=12.08 \times 10^{23}$ unit cells

## Solved Example 4

Silver crystallizes in an fcc lattice. The edge length of its unit cell is $4.077 \times \mathbf{1 0}^{-8} \mathbf{c m}$ and its density is $10.5 \mathrm{~g} / \mathrm{cm}^{3}$. Calculate on this basis the atomic mass of silver. $\left(\mathrm{N}_{\mathrm{A}}=6.023 \times 1 \mathbf{1 0}^{23}\right)$ Solution:

Since the lattice is fcc, the number of silver atoms per unit cell $=\mathrm{z}=4$
Molar mass of silver $=M$
Edge length of unit cell $=a=4.077 \times 10^{-8} \mathrm{~cm}$
Density $=10.5 \mathrm{~g} / \mathrm{cm}^{3}$
We know that, $d=(\mathrm{z} \times M) /\left(N_{A} \times a^{3}\right)$
Atomic size $=\mathrm{M}=\left(d \times N_{A} \times a^{3}\right) / z=10.5 \times 6.023 \times 10^{23} \times\left(4.077 \times 10^{-8}\right)^{3} / 4$

$$
=107.1 \mathrm{~g} \mathrm{~mol}^{-1} .
$$

## 6. Summary

The constituent particles in crystalline solids are arranged in a regular pattern which extends throughout the crystal. This arrangement is often depicted in the form of a three dimensional array of points which is called crystal lattice. Each lattice point gives the location of one particle in space. In all, fourteen different types of lattices are possible which are called Bravais lattices. Each lattice can be generated by repeating its small characteristic portion called unit cell. A unit cell is characterised by its edge lengths and three angles between these edges. Unit cells can be either primitive which have particles only at their corner positions or centred. The centred unit cells have additional particles at their body centre (body-centred), at the centre of each face (face-centred) or at the centre of two opposite faces (endcentred).There are seven types of primitive unit cells. Taking centred unit cells also into account, there are fourteen types of unit cells in all, which result in fourteen Bravais lattices.

Close-packing of particles result in two highly efficient lattices, hexagonal close-packed (hcp) and cubic close-packed (ccp). The latter is also called face-centred cubic (fcc) lattice. In both of these packing $74 \%$ space is filled. The remaining space is present in the form of two types of voids-octahedral voids and tetrahedral voids. Other types of packing are not closepackings and have less efficient packing of particles. While in body-centred cubic lattice (bcc) $68 \%$ space is filled, in simple cubic lattice only $52.4 \%$ space is filled.

