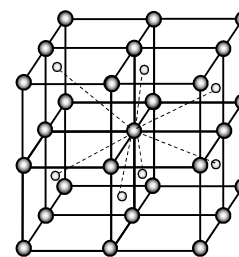


We know solids are the substances which have definite volume and definite shape. A solid is nearly incompressible state of matter. This is because the particles or units (atoms, molecules or ions) making up the solid are in close contact and are in fixed positions or sites. Now, let us study some characteristic properties of solids.



Characteristic Properties of Solids

Solids can be distinguished from liquids and gases due to their characteristic properties. Some of these are as follows:

- Solids have definite volume, irrespective of the size of the container.
- Solids are rigid and have definite shape.
- Solids are almost incompressible.
- Many solids are crystalline in nature. *These crystals have definite pattern of angles and planes.*
- The density of solids is generally greater than that of liquids and gases.
- Solids diffuse very slowly as compared to liquids and gases.
- Most solids melt on heating and become liquids. The temperature at which the solid melts and changes into liquid state under normal atmospheric pressure is called its normal melting point.
- *Solids are not always crystalline in nature.*
- Solids can be broadly classified into following two types :
 - (i) Crystalline solids/True solids
 - (ii) Amorphous solids/Pseudo solids

(1) Difference between crystalline and amorphous solids

Property	Crystalline solids	Amorphous solids
Shape	<i>They have long range order.</i>	<i>They have short range order.</i>
Melting point	<i>They have definite melting point</i>	<i>They do not have definite melting point</i>
Heat of fusion	<i>They have a definite heat of fusion</i>	<i>They do not have definite heat of fusion</i>
Compressibility	<i>They are rigid and incompressible</i>	<i>These may not be compressed to any appreciable extent</i>
Cutting with a sharp edged tool	<i>They are given cleavage i.e. they break into two pieces with plane surfaces</i>	<i>They are given irregular cleavage i.e. they break into two pieces with irregular surface</i>
Isotropy and Anisotropy	<i>They are anisotropic</i>	<i>They are isotropic</i>
Volume change	<i>There is a sudden change in volume when it melts.</i>	<i>There is no sudden change in volume on melting.</i>
Symmetry	<i>These possess symmetry</i>	<i>These do not possess any symmetry.</i>
Interfacial angles	<i>These possess interfacial angles.</i>	<i>These do not possess interfacial angles.</i>

Note : **Isomorphism and polymorphism** : Two substances are said to be isomorphous if these possess similar crystalline form and similar chemical composition e.g., Na_2SeO_4 and Na_2SO_4 . NaNO_3 and KNO_3 are not isomorphous because they have similar formula but different crystalline forms. The existence of a substance in more than one crystalline form is known as polymorphism e.g., sulphur shows two polymorphic forms viz. rhombic and monoclinic sulphur.

Glass is a supercooled liquid.

(2) **Classification of solids** : Depending upon the nature of interparticle forces the solids are classified into four types :

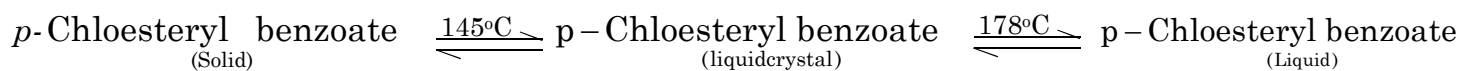
Types of Solid	Constituents	Bonding	Examples	Physical Nature	M.P.	B.P.	Electrical Conductivity
Ionic	Positive and negative ions network systematically arranged	Coulombic	NaCl , KCl , CaO , MgO , LiF , ZnS , BaSO_4 and K_2SO_4 etc.	Hard but brittle	High ($\approx 1000\text{K}$)	High ($\approx 2000\text{K}$)	Conductor (in molten state and in aqueous solution)
Covalent	Atoms connected in covalent bonds	Electron sharing	SiO_2 (Quartz), SiC , C (diamond), C (graphite) etc.	Hard	Very high ($\approx 4000\text{K}$)	Very high ($\approx 500\text{K}$)	Insulator except graphite

Molecular	Polar or non-polar molecules	(i) Molecular interactions (intermolecular forces) (ii) Hydrogen bonding	$I_2, S_8, P_4, CO_2, CH_4, CCl_4$ etc. Starch, sucrose, water, dry ice or drikold (solid CO_2) etc.	Soft Soft	Low ($\approx 300 K$ to $600 K$) Low ($\approx 400 K$)	Low ($\approx 450 K$ to $800 K$) Low ($\approx 373 K$ to $500 K$)	Insulator Insulator
Metallic	Cations in a sea of electrons	Metallic	Sodium, Au, Cu, magnesium, metals and alloys	Ductile malleable	High ($\approx 800 K$ to $1000 K$)	High ($\approx 1500 K$ to $2000 K$)	Conductor
Atomic	Atoms	London dispersion force	Noble gases	Soft	Very low	Very low	Poor thermal and electrical conductors

(i) **Liquid Crystal** : *There are certain solids which when heated undergo two sharp phase transformations one after the other. Such solids first fuse sharply yielding turbid liquids and then further heating to a higher temperature these sharply change into clear liquids. The first temperature at which solids changes into turbid liquid is known as **transition point** and the second temperature at which turbid liquid changes into clear liquid is known as **melting point**.*

Such substances showing liquid crystal character are as follows :

p-chloesteryl benzoate, *p*-Azoxyamisole, Diethylbenzidine etc.



A liquid crystal reflects only one colour, when light falls on it. If the temperature is changed it reflects different colour light. So, such liquid crystals can be used to detect even small temperature changes. The liquid crystals are of two types : (i) Nematic liquid crystals, (needle like), (ii) Smectic liquid crystals (soap like)

(ii) **Dispersion forces or London forces in solids :** When the distribution of electrons around the nucleus is not symmetrical then there is formation of instantaneous electric pole. Field produced due to this distorts the electron distribution in the neighbouring atom or molecule so that it acquires a dipole moment itself. The two dipole will attract and this makes the basis of London forces or dispersion forces these forces are attractive in nature and the interaction energy due to this is proportional to $\left(\frac{1}{r^6}\right)$. Thus, these forces are important at short distances (≈ 500 pm). This force also depends on the polarisability of the molecules.

(3) **Amorphous Solids (Supercooled liquid) :** Solids unlike crystalline solids, do not have an ordered arrangement of their constituent atoms or ions but have a disordered or random arrangement, are called amorphous solids. Ordinary glass (metal silicate), rubber and most of the plastics are the best examples of amorphous solids. In fact, any material can be made amorphous or

glassy either by rapidly cooling or freezing its vapours for example, SiO_2 crystallises or quartz in which SiO_4^{4-} tetrahedra are linked in a regular manner but on melting and then rapid cooling, it gives glass in which SiO_4^{4-} tetrahedron are randomly joined to each other.

Properties of Amorphous solids

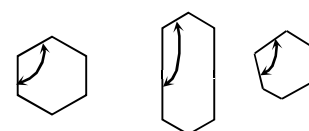
- (i) *Lack of long range order / Existence of short range order* : Amorphous solids do not have a long range order of their constituent atoms or ions. However, they do have a short range order like that in the liquids.
- (ii) No sharp melting point/Melting over a range.
- (iii) Conversion into crystalline form on heating.

Uses of Amorphous solids

- (i) The most widely used amorphous solids are in the inorganic glasses which find application in construction, house ware, laboratory ware etc.
- (ii) Rubber is amorphous solid, which is used in making tyres, shoe soles etc.
- (iii) Amorphous silica has been found to be the best material for converting sunlight into electricity (in **photovoltaic cells**).

Crystallography

“The branch of science that deals with the study of structure, geometry and properties of crystals is called crystallography”.



Constancy of interfacial angles

(1) Laws of crystallography :

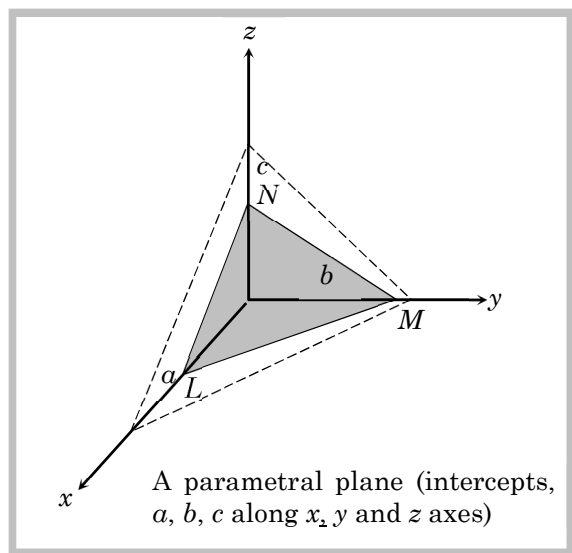
Crystallography is based on three fundamental laws. Which are as follows

(i) *Law of constancy of interfacial angles* : This law states that angle between adjacent corresponding faces of the crystal of a particular substance is always constant inspite of different shapes and sizes. The size and shape of crystal depend upon the conditions of crystallisation. This law is also known as **Steno's Law**.

(ii) *Law of rational indices* : This law states that the intercepts of any face of a crystal along the crystallographic axes are either equal to unit intercepts (i.e., intercepts made by unit cell) a, b, c or some simple whole number multiples of them e.g., $na, n'b, n''c$, where n, n' and n'' are simple whole numbers. The whole numbers n, n' and n'' are called **Weiss indices**. This law was given by **Hally**.

(iii) *Law of constancy of symmetry* : According to this law, all crystals of a substance have the same elements of symmetry.

(2) **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. Then, the intercepts of the



unknown plane are given with respect to a , b and c of the parametral plane.

Thus, the Miller indices are :

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

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

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

Consider a plane in which Weiss notation is given by $\infty a : 2b : c$. The Miller indices of this plane may be calculated as below.

(i) Reciprocals of the coefficients of Weiss indices = $\frac{1}{\infty}, \frac{1}{2}, \frac{1}{1}$

(ii) Multiplying by 2 in order to get whole numbers = 0, 1, 2

Thus the Miller indices of the plane are 0, 1, and 2 and the plane is designated as the (012) plane, *i.e.* $h=0, k=1, l=2$.

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

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

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

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

Negative signs in the Miller indices is indicated by placing a bar on the intercept.

All parallel planes have same Miller indices.

- The Miller indices are enclosed within parenthesis. *i.e.*, brackets.
Commas can be used for clarity.

Examples based on crystallography

Example 1 : Calculate the Miller indices of crystal planes which cut through the crystal axes at (i) $(2a, 3b, c)$, (ii) $(\infty, 2b, c)$

(a) 3, 2, 6 and 0, 1, 2

(b) 4, 2, 6 and 0, 2, 1

(c) 6, 2, 3 and 0, 0, 1

(d) 7, 2, 3 and 1, 1, 1

Solution: (a)

(i)	x	y	z	
	$2a$	$3b$	c	Intercepts
	$\frac{2a}{a}$	$\frac{3b}{b}$	$\frac{c}{c}$	Lattice parameters
	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{1}$	Reciprocals
	3	2	6	Multiplying by <i>LCM</i> (6)

Hence, the Miller indices are (3, 2, 6)

(ii)	x	y	z	
	∞	$2b$	c	Intercepts
	$\frac{\infty}{a}$	$\frac{2b}{b}$	$\frac{c}{c}$	Lattice parameters
	$\frac{1}{\infty}$	$\frac{1}{2}$	$\frac{1}{1}$	Reciprocals
	0	1	2	Multiplying by <i>LCM</i> (2)

Hence, the Miller indices are (0, 1, 2).

Example 2 : Calculate the distance between 111 planes in a crystal of Ca . Repeat the calculation for the 222 planes. ($a=0.556nm$)

(a) 016.1 nm

(b) 01.61 nm

(c) 0.610 nm

(d) None of the above

Solution: (b) We have, $d = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}}$; $d_{111} = \frac{0.556}{\sqrt{1^2 + 1^2 + 1^2}} = 0.321nm$

and $d_{222} = \frac{0.556}{\sqrt{2^2 + 2^2 + 2^2}} = 0.161nm$

The separation of the 111 planes is twice as great as that of 222 planes.

Study of Crystals

(1) **Crystal :** It is a homogeneous portion of a crystalline substance, composed of a regular pattern of structural units (ions, atoms or molecules) by plane surfaces making definite angles with each other giving a regular geometric form.

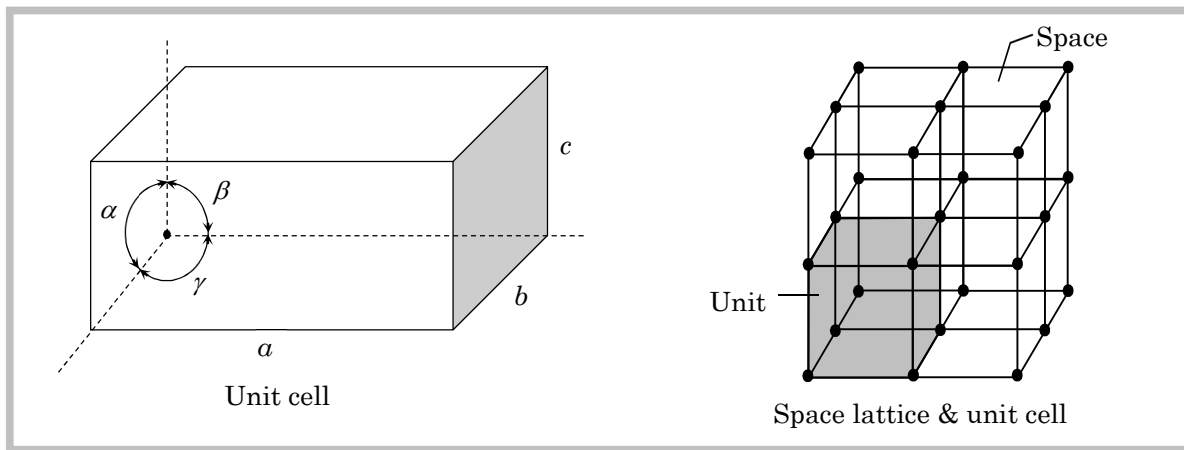
(2) **Space lattice and Unit cell :** A regular array of points (showing atoms/ions) in three dimensions is commonly called as a space lattice, or lattice.

(i) Each point in a space lattice represents an atom or a group of atoms.

(ii) Each point in a space lattice has identical surroundings throughout.

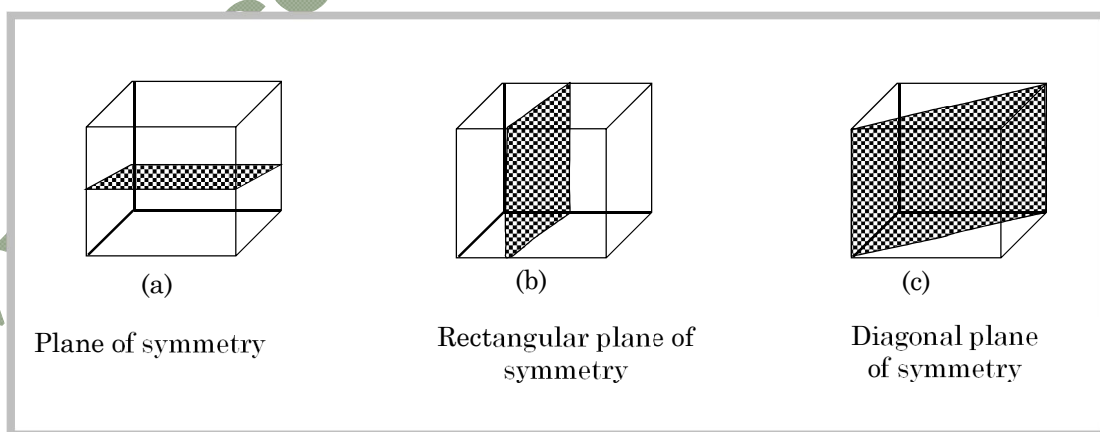
A three dimensional group of lattice points which when repeated in space generates the crystal called unit cell.

The unit cell is described by the lengths of its edges, a , b , c (which are related to the spacing between layers) and the angles between the edges, α , β , γ .



(3) **Symmetry in Crystal systems** : *Law of constancy of symmetry* : According to this law, all crystals of a substance have the same elements of symmetry. A crystal possess following three types of symmetry :

(i) *Plane of symmetry* : It is an imaginary plane which passes through the centre of a crystal can divides it into two equal portions which are exactly the mirror images of each other.



(ii) *Axis of symmetry* : An axis of symmetry or axis of rotation is an imaginary line, passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete revolution *i.e.*, in a rotation through 360° . Suppose, the same appearance of crystal is repeated, on rotating it through an angle of $360^\circ/n$, around an imaginary axis, is called an ***n*-fold axis** where, *n* is known as the order of axis. By order is meant the value of *n* in $2\pi/n$ so that rotation through $2\pi/n$, gives an equivalent configuration. For example, If a cube is rotated about an axis passing perpendicularly through the centre so that the similar appearance occurs four times in one revolution, the axis is called a four – fold or a tetrad axis, [Fig (iii)]. If similar appearance occurs twice in one complete revolution *i.e.*, after 180° , the axis is called two-fold axis of symmetry or diad axis [Fig (i)]. If the original appearance is repeated three times in one revolution *i.e.* rotation after 120° , the axis of symmetry is called three-fold axis of symmetry or triad axis [Fig (ii)]. Similarly, if the original appearance is repeated after an angle of 60° as in the case of a hexagonal crystal, the axis is called six-fold axis of symmetry or hexad axis [Fig (iv)].

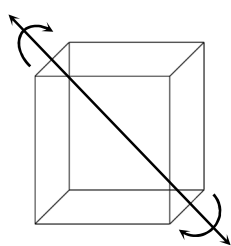


Fig. (i) Axis of two fold symmetry.

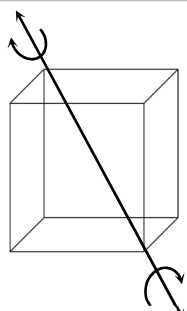


Fig. (ii) Axis of three fold symmetry.

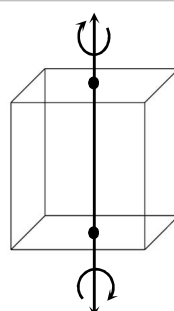


Fig. (iii) Axis of four fold symmetry.

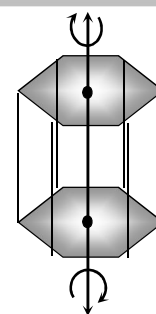
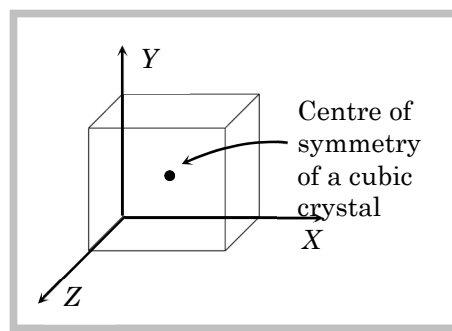


Fig. (iv) Axis of six fold symmetry.

(iii) **Centre of symmetry** : It is an imaginary point in the crystal that any line drawn through it intersects the surface of the crystal at equal distance on either side.



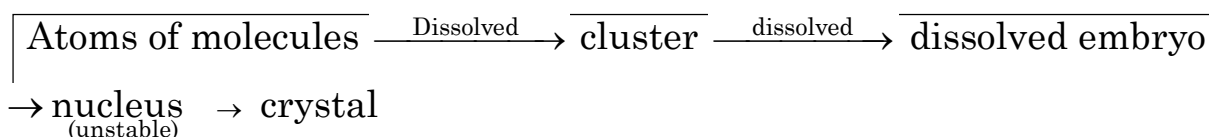
Note : \square Only simple cubic system have one centre of symmetry. Other system do not have centre of symmetry.

(4) **Element of symmetry** : (i) The total number of planes, axes and centre of symmetries possessed by a crystal is termed as elements of symmetry.

(ii) A cubic crystal possesses total 23 elements of symmetry.

(a) Plane of symmetry	(3 + 6)	= 9
(b) Axes of symmetry	(3 + 4 + 6)	= 13
(c) Centre of symmetry	(1)	= 1
Total symmetry		= 23

(5) **Formation of crystals** : The crystals of the substance are obtained by cooling the liquid (or the melt) of the solution of that substance. The size of the crystal depends upon the rate of cooling. If cooling is carried out slowly, crystals of large size are obtained because the particles (ions, atoms or molecules) get sufficient time to arrange themselves in proper positions.

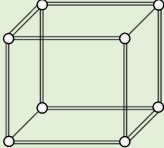
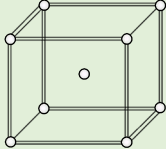
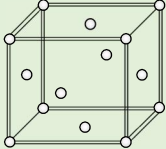


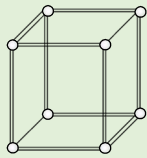
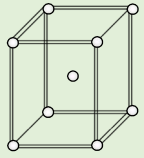
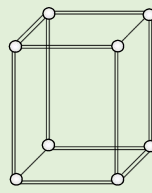
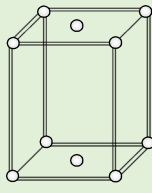
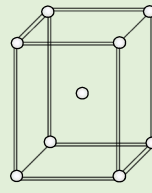
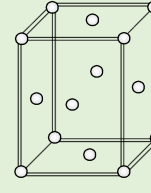
(If losing units dissolves as embryo and if gaining unit grow as a crystals).

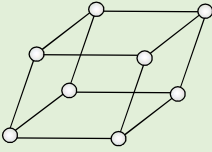
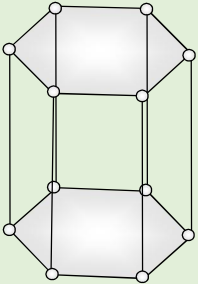
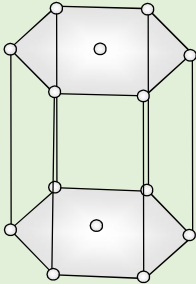
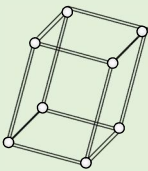
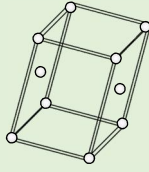
(6) **Crystal systems** : Bravais (1848) showed from geometrical considerations that there can be only 14 different ways in which similar points can be arranged. Thus, there can be only 14 different space lattices. These 14 types of lattices are known as **Bravais Lattices**. But on the other hand Bravais showed that there are only seven types of crystal systems. The seven crystal systems are :

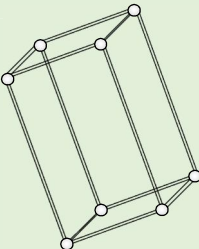
- (a) Cubic
- (b) Tetragonal
- (c) Orthorhombic
- (d) Rhombohedra
- (e) Hexagonal
- (f) Monoclinic
- (g) Triclinic

Bravais lattices corresponding to different crystal systems

Crystal system	Space lattice			Examples
<p>Cubic</p> <p>$a = b = c$,</p> <p>Here a, b and c are parameters (dimensions of a unit cell along three axes) size of crystals depend on parameters.</p> <p>$\alpha = \beta = \gamma = 90^\circ$</p> <p>$\alpha$, β and γ are three angles between the axes.</p>	<p>Simple : Lattice</p> <p>points at the eight corners of the unit cells.</p> 	<p>Body centered</p> <p>: Points at the eight corners and at the body centred.</p> 	<p>Face centered :</p> <p>Points at the eight corners and at the six face centres.</p> 	<p>Pb, Hg, Ag, Au, Cu, ZnS, diamond, KCl, NaCl, Cu_2O, CaF_2 and alums. etc.</p>

<p>Tetragonal</p> <p>$a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$</p>	<p>Simple : Points at the eight corners of the unit cell.</p> 		<p>Body centered : Points at the eight corners and at the body centre</p> 		<p>SnO_2, TiO_2, ZnO_2, ZrSiO_4. PbWO_4, white Sn etc.</p>
<p>Orthorhombic c (Rhombic)</p> <p>$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$</p>	<p>Simple: Points at the eight corners of the unit cell.</p> 	<p>End centered : Also called side centered or base centered. Points at the eight corners and at two face centres opposite to each other.</p> 	<p>Body centered : Points at the eight corners and at the body centre</p> 	<p>Face centered: Points at the eight corners and at the six face centres.</p> 	<p>KNO_3, K_2SO_4, PbCO_3, BaSO_4 rhombic sulphur, MgSO_4. $7\text{H}_2\text{O}$ etc.</p>

<p>Rhombohedral or Trigonal</p> <p>$a = b = c,$ $\alpha = \beta = \gamma \neq 90^\circ$</p>	<p>Simple : Points at the eight corners of the unit cell</p> 		<p>$\text{NaNO}_3,$ $\text{CaSO}_4,$ calcite, quartz, As, Sb, Bi etc.</p>
<p>Hexagonal</p> <p>$a = b \neq c,$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$</p>	<p>Simple : Points at the twelve corners of the unit cell out lined by thick line.</p> 	<p>or Points at the twelve corners of the hexagonal prism and at the centres of the two hexagonal faces.</p> 	<p>$\text{ZnO}, \text{PbS},$ $\text{CdS}, \text{HgS},$ graphite, ice, Mg, Zn, Cd, etc.</p>
<p>Monoclinic</p> <p>$a \neq b \neq c,$ $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$</p>	<p>Simple : Points at the eight corners of the unit cell</p> 	<p>End centered : Point at the eight corners and at two face centres opposite to the each other.</p> 	<p>$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O},$ $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O},$ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O},$ monoclinic sulphur etc.</p>

Triclinic $a \neq b \neq c,$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple : Points at the eight corners of the unit cell. 	$\text{CaSO}_4 \cdot$ $5\text{H}_2\text{O},$ $\text{K}_2\text{Cr}_2\text{O}_7,$ $\text{H}_3\text{BO}_3,$ etc.
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Note : Out of seven crystal systems triclinic is the most unsymmetrical ($a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$).

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