T.Y.B.Sc. Chemistry

Paper –II Inorganic Chemistry

Sem- IV

Chapter -3. Ionic Solids

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3. IONIC SOLID

Introduction : Crystaline and Amorphous Solids

In crystalline solid, there is regular arrangement of atom, ions or molecules & these particles are held together by strong force. Due to this solids are rigid, having definite shape. The solids can be crystalline or amorphous. These regular arrangements of solid are responsible for their characteristic properties.

Characteristic properties of solid state:

a. Solids have definite mass, volume and shape
b. Solids are incompressible and rigid
c. In solids, intermolecular distances are very short
d. In solids, intermolecular forces are very strong
e. The constituent particles of solids have fixed positions.
f. The constituent particles of solids can only oscillate about their mean positions.

Classification of solid:

They are classified into crystalline & amorphous solids.

1. Crystalline solid:

These solids have regular arrangement & particle in crystal. They have typical geometrical forms. A crystalline substance has sharp Melting Point. The constituent particles of crystalline solid are arranged in regular pattern which is repeated periodically over the entire crystal. Such type of arrangement is called long range order. Crystalline solids are anisotropic in nature, i.e. many physical properties, such as electrical resistance, refractive index, etc. are different along different axes. Crystal of NaCl, Quartz, Ice, HCl, Iron, etc. are some examples of crystalline solid.

Characteristics of crystalline solid –

- Crystalline solids have definite characteristic geometrical shape.
- Crystalline solids have sharp characteristic melting point.
- Crystalline solids have definite and characteristic heat of fusion.
- Crystalline solids produce pieces with plain and smooth surface when cutwith a tool of sharp edge.
- Crystalline solids are anisotropic in nature.
- Crystalline solids are true solid.
- Constituent particles of crystalline solids are arranged in long range order.

2. Amorphous solid:

These solids possess random arrangement of Constituent units. Amorphous solids do not have definite meeting point. Solids having irregular shapes of particles are known as Amorphous Solids. The word 'Amorphous' came from Greek 'Amorphos' which means no shape. The constituent particles of amorphous solids have only short range order of arrangement, i.e. regular and periodical arrangement of particles is seen to a short distance only. The structures of amorphous solids are similar to that of liquids. Glass, rubber, plastics, etc.

are some of the examples of amorphous solids. Amorphous solids are isotropic in nature, i.e. physical properties of amorphous solids are same in all directions.

Characteristic of amorphous solid –

- Particles of amorphous solids are irregular in shape.
- Amorphous solids soften gradually over a range of temperature.
- Amorphous solids produce pieces of irregular shapes when they are cut intotwo pieces.
- Amorphous solids do not have definite heat of fusion.
- Amorphous solids are isotropic in nature, i.e. they have same physical properties in all directions.
- Amorphous solids are not true solids and hence these are also known asPseudo Solid or Super Cooled Liquid.
- The arrangement of constituent particles is in short range order.

Difference between crystalline & amorphous solid:

Crystalline solid	Amorphous solid
1) It is homogeneous solid.	1) It may not homogeneous.
2) They have definite geometry.	2) They do not have definite geometry.
3) They have definite & orderly arrangement of particles.	3) They have completely random particle arrangement.
4) It has sharp M.P. i.e. it changes sharply into liquid state.	4) It does not have sharp M.P. It softens on heating & starts flowing.
5) The crystal has plane faces.	5) It does not have plane faces.
6) It is Anisotripic- its physical properties are different in differentdirection.	6) It is isotropic – its physical properties are same in all directions.
7) e.g. NaCl, sugar, sulphur etc.	7) e.g. Rubber, Glass, plastic etc.

Crystalline solids are divided into four types –

1) Molecular solid, 2) Metallic solid, 3) Covalent solid, 4) Ionic solid

Molecular Solids: - Solids are having molecules as their constituent particles are called Molecular solids. Example: Hydrogen (H_2), Chlorine(Cl_2), Water(H_2O), HCl,solid carbon dioxide(CO_2), sucrose($C_{12}H_{22}O_{11}$), etc.

Metallic Solids: – All metals are referred as Metallic solids. Their constituent particles are positive ions. These positive ions are surrounded by free moving electrons. Eg. – Iron (Fe), Aluminium (Al), etc.

Covalent Solids: – Crystalline solids are formed by non-metals because of formation of covalent bonds between the adjacent molecules throughout the crystal. These are also known as Network Solids. These are also called giant molecules. Eg. – Diamond, Graphite, Silicon carbide, etc.

Ionic solids: - Solids, in which ions are the constituent particles, are called ionic solids. These solids are formed because of three dimensional arrangements of cations and anions bound together with strong electrostatic forces. Ionic solid made up of positive & negative ions. These ions are held together by electrostatic interaction of oppositely charged ions. This electrostatic force of attraction between cation of anion is called Ionic bond. Eg. NaCl, the Na^+Cl^- ion are held by electrostatic force & compound is ionic. The formation of bond takes place by complete transfer of one or more electrons from the valence shell of one atom to valence shell of another atom. Generally element achieve octate configuration either by losing or gaining electron.

Characteristic Properties of Ionic compounds: -

1) **Ionic bond:** - The cation & anion held together by electrostatic force of attraction.
2) **Hardness:** - Ionic compounds are very hard. Hardness depends on ionic charge & interionic distance. As interionic distance decrease, & ionic charge increases, hardness of crystal is increases.
3) **Melting point and Boiling point:** - Ionic compounds have high M. P. & B. P.
4) **Electrical conductivity:** - Ionic compound in solid state do not conduct electricity. Because ions are fixed & tight. But in molten state or in solution ions are free. These free ions can move & hence conduct electric current.
5) **Solubility:** - The ionic compounds are polar and are soluble in polar solvents with high dielectric constant. The polar solvent such as water dissolves ionic compounds. The solubility is mainly due to the lowering of inter-ionic electrostatic attraction and ion-solvent interaction. Ionic compounds are insoluble in nonpolar solvent such as CCl_4, C_6H_6, etc.
6) Ionic compounds are ionisable in fused state or in solution. The solutions of these compounds are good conductors of electricity.

Crystallography: -

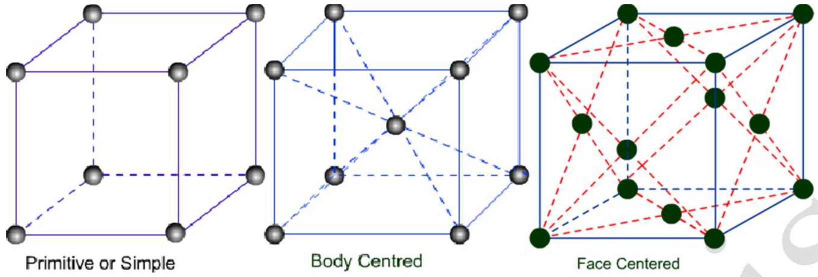
It is a special branch of science, which deals with properties of crystals such as geometry, structure, is called as **Crystallography**.

- **Unit cell: -** It is smallest building unit of crystal. The crystal consists of infinite number of unit cell. In unit cell atoms, ions or molecules are symmetrically arranged.
- **Lattice:-** It is define as an infinite set of points repeated regularly through space. The lattices are one-dimensional (1-D), two-dimensional (2-D) & three- dimensional (3-D).
- **Crystal Lattice: -** The definite and ordered arrangement of the constituent atoms, ions or molecules extends over large distance in crystal is called crystal lattice.

- **Space lattice: -** The positions of atom, ion or molecule in crystal, relative to one another in space. Such representation is called space lattice.

Types of Unit cell: -

The unit cell is the smallest portion as well as complete representation of crystal. The crystal is made up of infinite number of unit cells. There are main three types such as simple cubic, body centered cubic and face centered cubic…



1) Simple cubic unit cell: - The atoms are placed one at each corner of cube.
2) Body centered cubic unit cell: - There is an atom at each corner and oneat the center of the cube.
3) Face centered cubic unit cell: - There is an atom at each corner and onein the each face of cube.

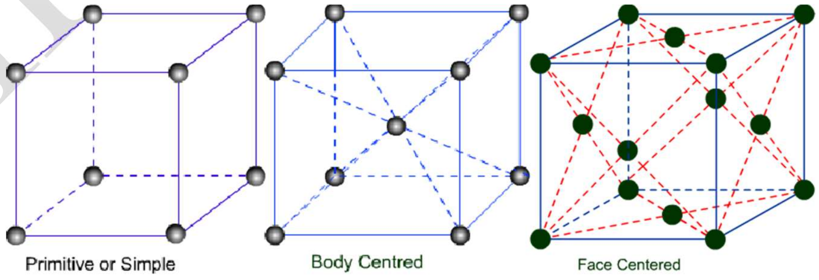
The unit cell in 3-D lattice is characterized by the length a, b, c and angle □□ □□ □□

Bravais Lattices

There are only 14 possible crystal lattices, which are called Bravais Lattices.

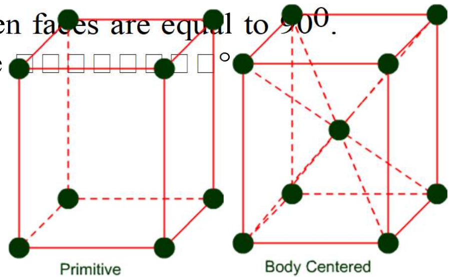
Cubic Lattice – There are **three types** of lattice possible for cubic lattice. Primitive or Simple, Body centred, Face centred lattices. In these types of lattices all sides are of equal length. The angles between their faces are 90^0 in a cubic lattice.

Length: a=b=c and Angle □□□□□□□□□°



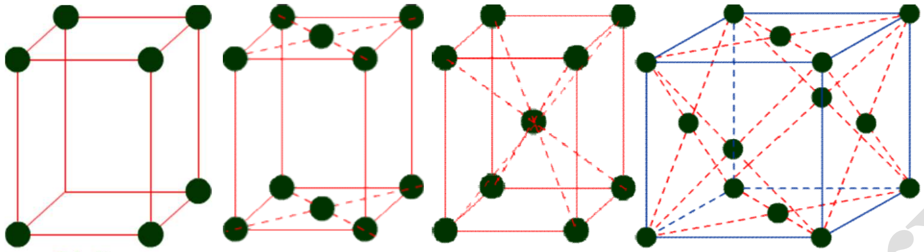
Tetragonal Lattice – There are **two possible** types of tetragonal lattices. Primitive and Body centred unit cells. In these lattices one side is different in length and angles between faces are equal to 90^0.

Length: a=b□c and angle □□□□□□□□□°



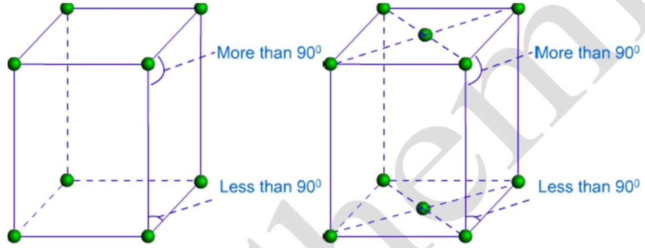
Orthorhombic Lattice – Four types of orthorhombic lattice are possible. They are **four types** Primitive, End-centred, Body centred and Face centred. They have unequal sides. The Angles between their faces are equal to 90^{0}.

Length: a≠b≠c and angle $\alpha=\beta=\gamma=90°$


Primitive End Centered Body Centered Face Centered

Monoclinic Lattice – There are **two possible types** of monoclinic lattice. They are Primitive and End centred. They have unequal sides and two faces have angles other than 90^{0}.

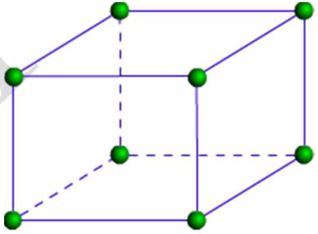
Length: a≠b≠c and angle $\alpha=\beta=90°$ and $\gamma\neq120°$



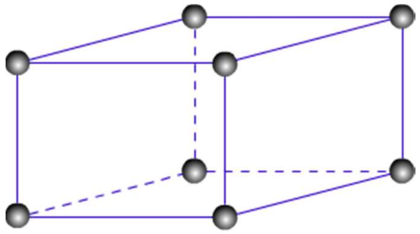
Primitive End Centered

Hexagonal lattice – Hexagonal lattice is of **one type** only. It has one side is different in length to the other two and the angles on two faces are 60^{0}.

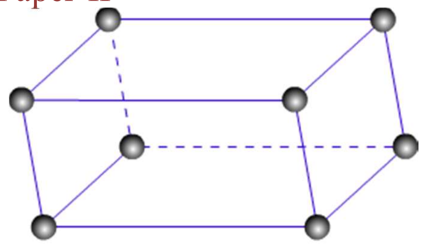
Length: a=b≠c and angle $\alpha=\beta=90°$ and $\gamma=120°$


Hexagonal Lattice

Rhombohedral Lattice – Only one type of lattice is possible for Rhombohedral lattice. It has **two types** such as all sides equal and angles on two faces are less than 90^{0}.

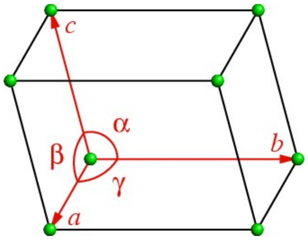

Rhombohedral Lattice

Length: a=b=c and angle $\alpha=\beta=\gamma\neq90°$



Triclinic Lattice

Triclinic Lattice – Triclinic lattice has only **one type** of lattice. It has unequalsides and none of the angles between faces are equal to 90^0.
Length: $a \neq b \neq c$ and angle $\alpha \neq \beta \neq \gamma \neq 90°$



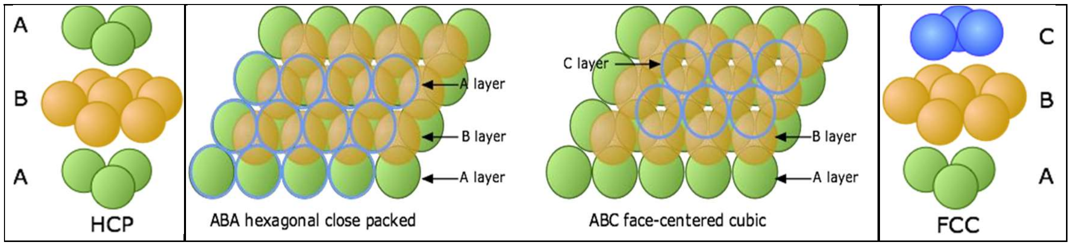
Close packing: -

The arrangement of maximum number of ions or atoms into smallest possible space is called **close packing**. In crystal atoms, ions or molecules are arranged in regular way in three-dimensional space.

Each constituent atom or ions.in crystal is packed as closely as possible. This arrangement has minimum energy and possesses maximum stability.
There are mainly two types Hexagonal close packed and Cubic close packed.

1) Hexagonal Close Packed structure (H.C.P.): -

In close packed structure ions are packed together in the tightest way. The structure consists of number of layers one over other. Each atom is surrounded by six nearest neighbors lying in plane. The symmetry is **hexagonal.** The close packed layers of ions are arranged in an alternation sequence usually A B A B A B ……. In this case each third layer will be directly above the first layer. This ABAB… pattern of layers gives lattice with hexagonal unit cell. Thus it is called hexagonal close packed (HCP) structure.



2) Cubic Close Packed (C.C.P.) or Face Centered Cubic (F.C.C): -

In the CCP arrangement sphere of the third layer are placed exactly above the gap of first layer. In ccp structure, the sequence of close packed layers of ions repeats every fourth layer of ions is exactly same & lies directly above first layer. The sequence is ABC ABC ABC ……… This arrangement of lattice is corresponds with Face Centered Cubic (FCC) unit cell. Hence the crystal structure obtained is CCP or FCC.

The voids OR Holes: -

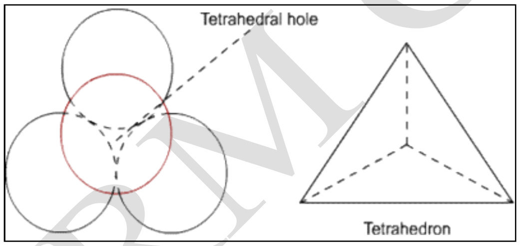
The unoccupied volume between layers of close packed arrangement of sphere is called as voids or holes. There are two types of holes in crystal lattice.

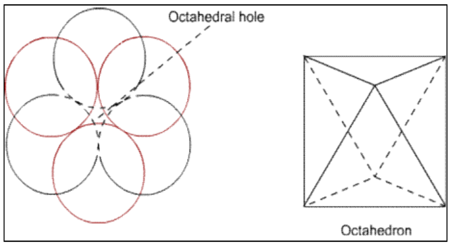
1) Tetrahedral Holes: -

These holes are bounded by four spheres. The four-sphere lie at the regular tetrahedron & space between them is called as tetrahedral holes. The co-ordination number of tetrahedral hole is four.

2) Octahedral holes: -

There are holes bounded by six spheres. The octahedral hole is formed between CCP or HCP structure. In the HCP, there are two tetrahedral & one octahedral hole is present. The co-ordination number of octahedral hole is six.



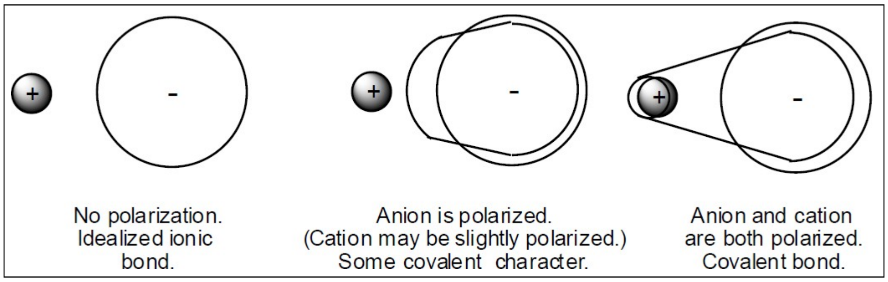


The octahedral holes are larger than tetrahedral holes. The size of each hole is depends on size of the sphere, i.e. larger size of the sphere; it is greater size of hole made by them.

Polarization of Ions & Fajan's Rules: -

In ionic compounds when cation & anion are close to each other, the net positive charge on cation attracts electron cloud of anion towards itself due to electrostatic force of attraction. Size of anion is larger than cation. Due to this force electron cloud of anion are elongated towards cation. The distortion of the electron cloud of one ion by the electron cloud of the other ion is called as **polarization** of anion by the cation or distortion or deformation. As distortion is increased, the bond between anion and cation takes more covalent characters.

When ion is easily polarizable, the valence electrons will be shared between the ions and therefore ionic character of bond will change into covalent bond characters. The net result of the ion polarization is the degree of the electron sharing or increase in the degree of covalent characters.



The polarization of ionic bond depends upon capacity of cation to cause polarization & capacity of anion to get polarized. With polarization, ionic compound convert into covalent character.

he polarization of ion depends upon –

1. Size of cation or anion.
2. Charge on cation or anion
3. Electronic configuration & cation.

Fajan's Rules: -

The polarization of ion is increased with increase in degree of covalent character. The covalent characters are favored by- a) Small size of cation b) Large size of anion, c) High charge on cation or anion or both

1. Covalent bonding character increases with **decreasing cation size** or **increasing cation charge**. The high charge density of small and/or highly charged cations is able to exert a powerful polarizing effect which distorts the electron cloud around the anion. Compare NaCl (mp 800°C) with $CaCl2$ (mp 772°C; charge effect) and KI (mp 686°C) with LiI (mp 449°C; size effect).
2. Covalent character increases with an **increase in anion charge or anion size**. The electrons of larger, more negatively charged anions are more loosely held because they are more shielded from the nuclear charge. Thus, these anions are more easily polarized by cations. Compare LiBr with $Li3P$ (charge effect), and LiF (mp 845°C) with LiI (mp 449°C; size effect).
3. Covalent character is greater for cations with a **non-noble gas electron configuration** (i.e., 18-electron, pseudo-noble-gas cations) than for cations with a true noble-gas configuration (8-electron cations).

Favorable conditions for

Ionic character	Covalent character
1) Low positive charge.	1) High positive charge.
2) Large cation.	2) Small cation.

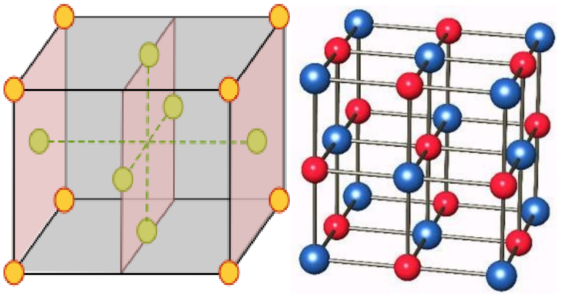
3) Small anion.	3) Large anion.

Structures of Ionic compounds: -

The large no. of simple ionic substance crystallizes in one of the following six common structure:-

1) Face Centered Cubic (FCC): - NaCl structure
2) Body Centered Cubic (BCC): - CsCl structure
3) Cubic Close Packing (CCP): - Zinc blende (ZnS) structure
4) Hexagonal Close Packing (HCP): - Wurtzite (ZnS) structure
5) Fluorite: - CaF_2 structure
6) Rutile: - TiO_2 structure

Lattice	Co. No.	Radius Ratio
FCC-NaCl	6:6	0.42 –0.73
BCC- CsCl	6:6	> 0.73
CCP- Zinc blende	4:4	0.21 to 0.42
HCP- Wurtzite	4:4	0.21 to 0.42
Fluorite-CaF_2	8:4	>0.73
Rutile – TiO_2	6:3	0.42 to 0.73



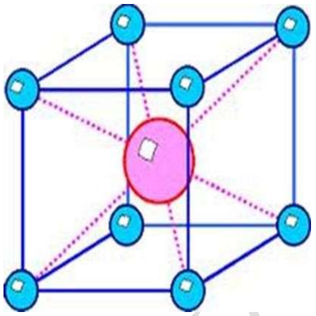
1) Sodium Chloride Structure: NaCl(FCC): -

The radius ratio for Na^+ and Cl^- ion is 0.95/1.81 = 0.525. For the octahedral structure with coordination number 6, radius ratio between 0.41 to 0.73. Hence for NaCl crystal has FCC type structure. Central Na^+ ion is surrounded by six Cl^- ions octahedrally.

The sodium chloride structure is known as "Rock salt structure ". The Na^+ ions are found at 8 corner of cube & also at center of each face the arrangements of ion in crystal lattice is called as face centered cubic (FCC). Another examples: -

$CaCO_3$, CaC_2, etc.

2) Caesium Chloride Structure: CsCl (BCC): -



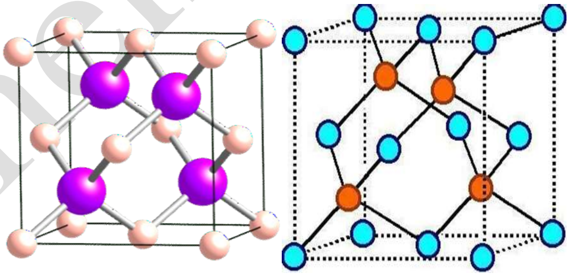
The radius ratio for Cs^+ and Cl^- ion is 1.69 /1.81 0.93. This value is close to one, the Coordination Number should be eight & cubic structure. The Cs^+ & Cl^- ions have same size. These ions have simple cubic structure. Each Cs^+ ion has 8 Cl^- ions as nearest neighbors. The Co. No. of both these ions is 8. Each Cs^+ ion occupies center of cube and Cl^- ion occupies 8 corners of cube. The structure is neither close packed nor BCC.

In BCC center of corner atoms are same, but in CsCl structure center and corner atoms are different. But itis nearest to Body centered cubic structure.

Another examples: - CsBr, CsI, NH_4Cl But CsF is a NaCl type structure.

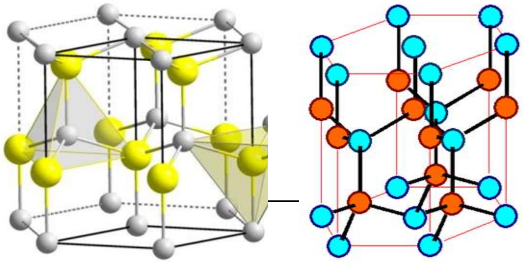
Effect of temp: - CsCl converted into NaCl structure -At 490^0c. NH_4Cl having CsClstructure is converted into NaCl structure - at 184^0c.

3) Zinc Blende Structure: ZnS (CCP):



The radius ratio of Zn^{2+} & S^{2-} is 0.4. This value suggests that Co. No. is 4. Each Zn^{2+} ions is in contact with only four S^{2-} ions. The s^{2-} ions are in cubic close packed arrangement in zinc blendes structure.

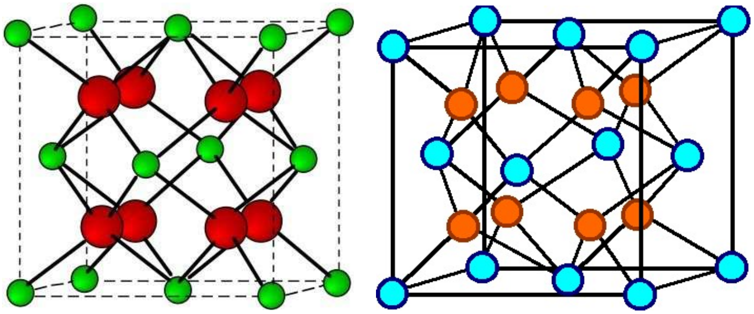
4) Wurtzite structure: ZnS (HCP): -



In this structure sulphide ion are present in hexagonal Closed Packed (HCP). In two close packed layers of sphere (A B A B…sequence) tetrahedral & octahedral holes are formed. The Co. No. of Zn^{2+} & S^{2-} ions are 4.

Another examples: - CuX, CuO, CuS, etc.

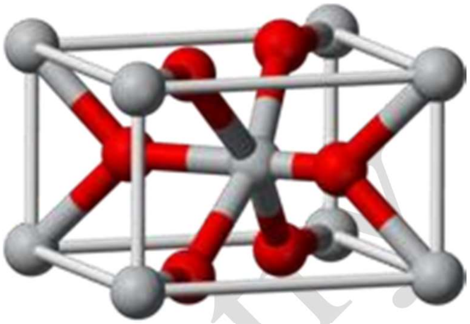
5) Fluorite structure (CaF_2): -



In fluorite structure of CaF_2, each Ca^{2+} ion is surrounded by eight F^- ion at corners of cube, i.e. Face

Centered Cubic & each F^- ion is surrounded by four Ca^{2+} ion arranged octahedrally. The Co. No. of Ca^{2+} are 8 & F^- is 4.

Examples: - Difluorides of Ca, Ba, Cd, Hg, etc.



6) Rutile Structure (TiO_2): -

The radius ratio of TiO_2 is in between 0.41 to 0.73 each Ti^{4+} ion is surrounded by six O^{2-} ions octahedrally & each O^{2-} ion surrounded by three Ti^{4+} ions triangularly. The Co. No. of O^{2-} ion is 6 while Ti^{4+} ion is 3.

Another Examples: - MgF_2, FeF_2, CoF_2, SnO_2, etc.

Ionic Radii: -

Definition:-

a) The space occupied by an ion in any direction in lattice is called as an ionicradii.

b) The distance bet nucleus of an ion & its electron cloud.

The x – ray analysis used to measure internuclear distance between two ions in ionic compound & expressed in (n.m.). The internuclear distance between two ions will be equal to the sum of the ionic radii of two ions as they touching one another.

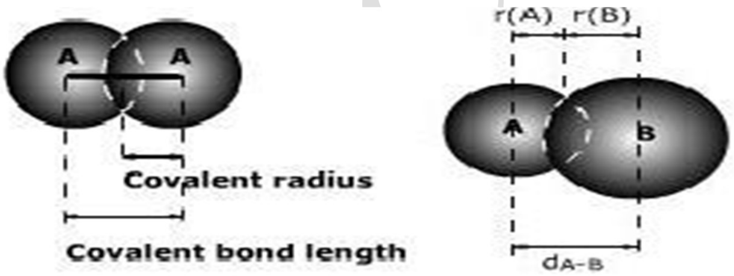


Figure shows the radius of atom A, in homo-nuclear diatomic molecule and internuclear distance of molecule AB, in hetero-nuclear diatomic molecule. Where, r_A = radius of cation, and r_B = radius of anion.

Palings univalent radii: -

Paling determined the ionic radii of univalent ion such as the ions of alkali metals & halogens. He studies four ionic compounds – NaF, KCl, RbBr, CsI.

He selects these four compounds because,

1) They have same radius ratio (0.75)
2) The bond is ionic character.
3) The cation & anion are is electronic.
4) All have NaCl type structure.

Assumptions: -

1) The measured internuclear distance, **$d = r_c + r_a$**.
2) The ratio r_c / r_a should be inversely proportional to the ratio of effective nuclear charge.

   $r_c / r_a = Z_{eff}\ r_a / Z_{eff}\ r_c$

While, Effective nuclear charge (**Z_{eff}**) = Actual nuclear charge – Screening constant.

The screening constant for Neon configuration is 4.15.

Example:- NaF,

For Na^+ having actual nuclear charge of 11 & F^- having actual nuclear charge of 9Z_{eff} for Na^+ = 11- 4.15 = 6.85

Z_{eff} for F^- = 9 –4.15 =4.85

According to Assumption No.- 2

$r_{Na^+} / r_{F^-} = 4.85 / 6.85 = 0.71$ ----------------------------1.

The measured interionic distance in NaF is 2.31 Å.

$r_{Na^+} + r_{F^-} = 2.31$--2.

On solving equation (1)

$r_{Na^+} = 0.71 \times r_{F^-}$

By substituting value of r_{Na^+} in eq. (2), we get

$(0.71 \times r_{F^-}) + r_{F^-} =$

$2.31, r_{F^-} \times (0.71 + 1)$

$= 2.31$

$1.71\ r_{F^-} = 2.31$

$r_{F^-} = 2.31 / 1.71 = 1.35$ Å

Hence, $r_{Na^+} = 2.31 - 1.35 = 0.96$ Å

$r_{Na^+} = 0.96$ Å & $r_{F^-} = 1.35$ Å

Pauling univalent Radii are given below in Å

For cations: - Na^+ = 0.96, K^+ = 1.33, Rb^+ = 1.48, Cs^+ = 1.69For anions: - F^- = 1.36, Cl^- = 1.81, Br^- = 1.95, I^- = 2.16

The ionic radius of cation is always smaller than parent atom. Where as ionic radius of anion is always greater than parent atom.

Pauling crystal Radii: -

Pauling ionic radii for univalent ions quite match with observed inter ionic distance. But in polyvalent ion it is fails.

Eq. 1) Calculated univalent radii of Mg^{2+} - 0.82 & O_2^-- 1.76 Å.

Hence $r_{Mg^{2+}} + r_{O^{2-}}$ = 0.82 +1.76 =2.58 Å. But observed Mg –0 distance is 2.05 Å. The calculated values do not agree with the observed value because the ions (Mg^{2+})are not univalent. It is divalent.

Eq. 2) Univalent radii of Ca^{2+} = 1.18 Å, O^{2-} = 1.76 Å, Inter ionic distance (d) = 2.94 Å, observed distance = 2.39 Å.

Conversion of univalent radii to crystal radii: -

$$\mathbf{r_{cry} = r_{un} \times Z^{-2/(n-1)}}$$

Where $\mathbf{r_{cry}}$ = crystal radius, $\mathbf{r_{un}}$ = univalent radius, **Z**= charge on ion, **n** = Born exponent constant, *Born exponents for: - He* (Li^+, Be^{2+}) *n = 5, Ne* (Na^+, Mg^{2+}, O^{2-}, F^-) *n = 7, Ar* (K^+, Ca^{2+}, Cl^-) *n = 9, Kr* (Rb^+, Br^-) *n = 10, Xe* (Cs^+, I^-) *n = 12*

For Mg^{2+} ion, r_{un} of Mg^{2+} = 0.82, Z = 2, n = 7

Crystal radius $r_{cry} = 0.82 \times 2^{-2/(7-1)} = 0.65$ Å For O^{2-} ion

r_{un} of O^{2-} = 1.76, Z = 2, n = 7

Crystal radians $r_{cry} = 1.76 \times 2^{-2/(7-1)} = 1.40$ Å Observed inter ionic distance,

$$d = r_C + r_A = 0.65 + 1.40 = 2.05 \text{ Å}.$$

Trends in the value of ionic radii: -

1) There is decrease in ionic radii values with increase in atomic number of elements.
2) This decrease is observed for …
   a. d-block elements
   b. lanthanide elements and
   c. actinide elements
3) for a series of isoelectronic ions O^{2-}, F^-, Mg^{2+}, Al^{3+} the ionic radii decreases with increase in atomic number.
4) The cation with low charge is larger in size than the ion with higher charge for same elements. eg. Fe^{2+} has larger radii than Fe^{3+} ion.
5) In a group, the ionic radii is increases in atomic number.

Radius Ratio Effect:-

Radius Ratio =Radius of Cation / Radius of Anion, i.e. $r_C / r_A < 1$.

The effect of radius ratio in determining the Coordination number and shapes of ionic solids is known as Radius Ratio Effect.

Co. No.	**rC / rA**	**Shape of crystal**
2	0 to 0.155	Linear
3	0.155 to 0.255	Triangular
4	0.255 to 0.414	Tetrahedral
4	0.414 to 0.732	Square planar
6	0.414 to 0.732	Octahedral
8	0.732 to 1.000	Cubic or BCC

Lattice Energy / crystal Energy: -

Definition:-

1) It is amount of energy released when the number of gaseous cation & anion are condensed into crystal to form one mole of compound.

$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$, U = ΔH = - 411KJ/mol

Where ΔH=Heat of formation & U=Lattice energy. Negative sign means release of energy,

2) The energy required separates a mole of solid substance into gaseous ions. $NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$, ΔH = + 411 KJ/mol

The stability of ionic solid depends upon value of its lattice energy. Greater the lattice energy, more energy to separates ions & hence grater the stability.

Calculation of lattice Energy: -

1) Theoretical method: - using Born – Lande equation & Madelung constant.
2) Experimental method: - using Born – Haber cycle.

Theoretical method: - Born – Lande equation

Lattice energy (U) can be calculated for ionic solid by using the equation.

$$\boxed{U = -\frac{NA^2(Z^+)(Z^-)}{r} X \left(1 - \frac{1}{n}\right)}$$

Where, **N** = Avogadro's No. 6.023 x 10^{23} mol $^{-1}$, **A** = Madelung const, **Z^+** & **Z^-** = charge on cation & anion, **e** = charge on electron, **r** = distance between cation & anion, **n** = Born exponent constant.

The Madelung constant (Å): - NaCl – 1.7475, CsCl – 1.7627, Zinc blende – 1.6381,Wurtzite – 1.6410, Fluorite – 5.0388, Rutile – 4.816

Conclusion from Born – Lande Equation: -

1. The lattice energy is varies directly as product of charge on ions.
2. The lattice energy (U) varies inversely as internuclear distance.
3. The lattice energy (U) is depends upon type of crystal structure.

Experimental method: Born – Haber cycle

The formation of solid NaCl may takes place by combination of solid sodium& gaseous chlorine by two methods:-

Method (1) : - Direct combination

Combination of solid sodium metals & gaseous chlorine to form solid NaCl $\longrightarrow$

$Na(s) + ½ Cl_2(g) \longrightarrow NaCl(s)$, $ΔH_f = -411\ kJmol^{-1}$

Method (2): - Stepwise combination

Step –1: Sublimation of sodium

$Na(s) \longrightarrow Na(g)$, $S_{Na} = + 108.7\ KJmol^{-1}$

Energy is absorbed, called Heat of sublimation.

Step – 2: Dissociation of chlorine molecule

$½ Cl_2(g) \longrightarrow Cl(g)$, $½ D_{Cl_2} = + 121.4\ KJmol^{-1}$ Energy is absorbed, called Heat of Dissociation.

Step –3 : Formation of sodium ion

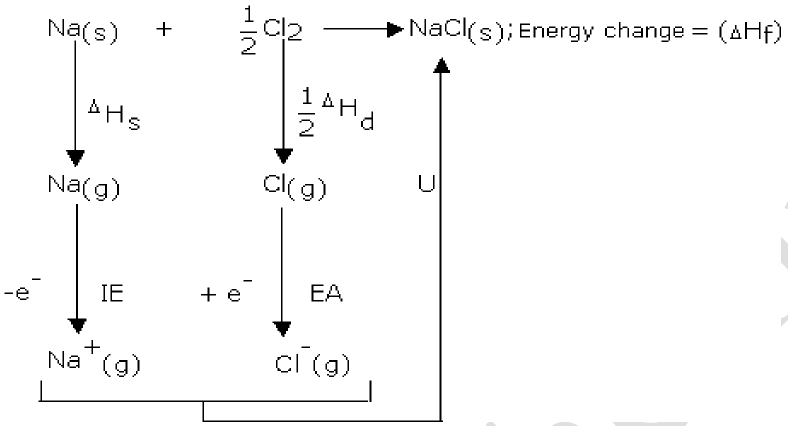
$Na(g) \longrightarrow Na^{+}(g) + e^{-}$, $I_{Na} = +502.0$ KJ mol^{-1}

Energy is absorbed, called Ionization err ray.

Step – 4 : Formation of chloride ion

$Cl(g) + e^{-} \longrightarrow Cl^{-}(g)$, $E_{Cl} = -354$ KJ mol^{-1} Energy is released, called Electron affinity.

Step – 5 : Formation of solid ionic Na^{+} Cl^{-} $Na^{+}(g) + Cl^{-}(g) \longrightarrow \longrightarrow Na^{+}Cl^{-}(s)$, $U_{NaCl} =$



According to Hess Law:-

It states that the enthalpy of reaction is the same whether the reaction takes place in one or several stapes.

Heat of formation: $\Delta Hf = S_{Na} + ½ D_{Cl2} + I_{Na} + E_{Cl} + U_{NaCl}$

$-411 = +108.7 + 121.4 + 502.0 - 354 + U_{Nacl}$

$U_{Nacl} = -411 - 108.7 - 121.4 - 502.0 + 354$

$= -788.96$ KJ mol^{-1}

Problem: 2. Calculate lattice energy of NaF from following data.

i) Heat of formation Hf = -569 KJ mol^{-1}

ii) Heat or Sublimation $S_{Na} = +100.4$ KJ mol^{-1}

iii) Heat of Ionization $I_{Na} = +493.7$ KJ mol^{-1}

iv) Heat of Dissociation ½ $D_{F2} = +153.0$ KJ mol^{-1}

v) Heat of Ionization E. $A._F$ = - 332.6 KJ mol **(U_{NaF}= -991.9 kJmol^{-1}**)

Problem: 3. Calculate lattices energy of NaI from Following

Hf = - 287.6 KJ mol^{-1}, S_{Na} = +108.7 KJ mol^{-1}, I_{Na} = 493.8 KJ mol^{-1}, ½D_{I2} = +106 KJ mol^{-1}, E.A. $_{I2}$ = - 305.9 KJ mol^{-1} **(U_{NaI}= - 690.8 kJmol^{-1}**)

Applications of Born Huber cycle: -

1) The Born Huber cycle is used to calculate any one of quantities in followingequation when all of other are known,

$$H_f = S + I + \frac{1}{2} D + E + U$$

2) The cycle can be used to find electron affinities of element for which direct experimental method is not available.
3) The cycle is useful as variation in stability of various ionic compounds.
4) It is also useful in knowing the nature of bonding i.e. Ionic or covalent bond incompound.
5) It can be used to explain why does metals fails to form stable ionic compoundsin low oxidation state example:- CaCl, MnCl, AlO, etc.

Defect structure:

The crystal may have some imperfections & such structure is called as defect structure. The defect structure is due to, (1) Ion vacancies in lattice, (2) Dislocation of ions - Interstitial position, (3) foreign ions or impurities in lattice, (4) non stoichiometric proportion of the ions.

A) Stoichiometric defect:

In perfect crystal definite arrangement of ions are at absolute zero temperature. But as temperature increases, same vacancies are created. There are two types of defect. In both defects, vacant sites are created which increases with increase in temperature.

1) Schottky defect:

It is due to vacancies in lattice, there is equal number of missing positive & negative ions in crystal lattice. Crystal remains neutral. It occurs when there is small difference in size of cation & anion. i.e. $r_c/r_a = 1$. example:- NaCl, KCl, NiO etc. It is found in strongly ionic compound with Coordination number 6.

2) Frankel defect:

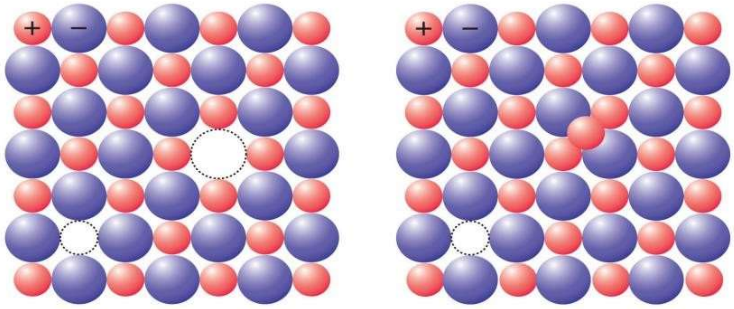
It is due to dislocation of ion in lattice. Usually positive ions (cation) occupy interstitials position rather than negative ion (anion) due to smaller size of cation. This defect occurs when there is large deference in size between cation & anions.

i.e. $r_c/r_a < 1$. It is found in covalent compounds with low Coordination number Example:- AgBr, AgI, ZnS, etc.

Difference between Schottky Defect and Frenkel Defect

Sr. No.	Schottky Defect	Frenkel Defect
1	Equal number of cations and anions are missing from the lattice sites.	A cation leaves the normal latticesite and occupies an interstitial site.

2	Found in highly ionic compounds with high coordination numbers and where the cations and anions are of similar size.	Found in ionic compounds with low coordination numbers and where the anions are much larger in size than cations.
3	Density of the solid decreases	Density of the solid remains the same.



(a) Schottky defect (b) Frenkel defect

Effect of Scottky & Frenkel Defect:

1) **Density:** - Lowers in density in Schottky, while no change in density in Frenkel defect.
2) **Electrical conductivity:** -Ionic crystal is weak conductor, but when defects in crystal electrical conductivity increases due to movement of ion from its lattice site to hole & new hole is created. Another ion close to this new hole move intoit. In this way holes migration takes place & conductivity in creases.
3) As number of holes increases in crystal lattice energy is less & hence stability of crystal is less.

B) Non – Stoichiometric Defect. :

In these compounds the ratio of action & anion differs from that indicated by ideal chemical formula. The crystal is electrically neutral. The crystal structure becomes irregular & this creates the defect eq. Scottky defect – NiO. (2) Frenkel defect - ZnO.

Solubility of Ionic solids:

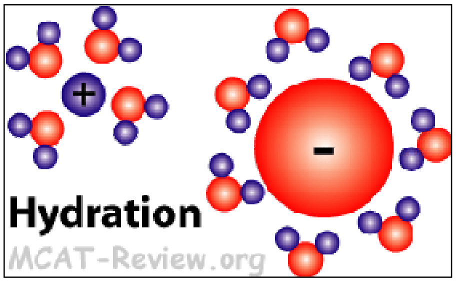
Ionic substances are soluble in polar solvent like water. The energy, which must be provide for separation & ion from crystal. This energy gain from solvent, when water is solvent, energy is termed as hydration energy.

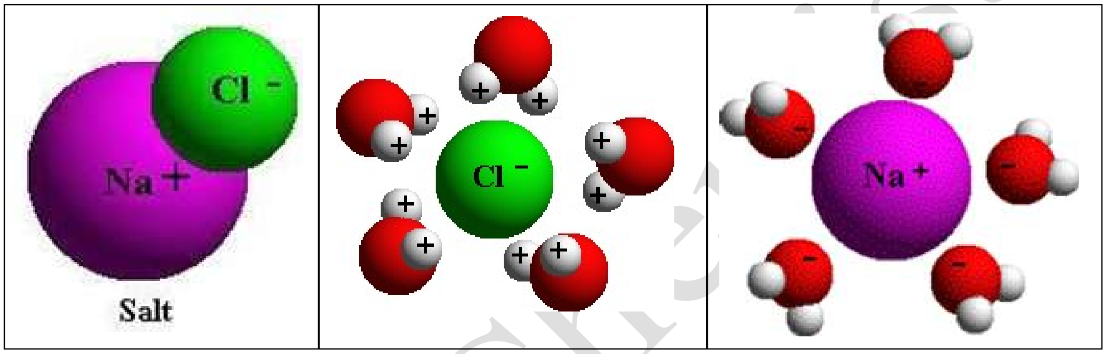
Anion, cation & salts are get hydrated in water. Metal ion interacts strongly with water molecule called **primary hydration sphere**. Negative oxygen end of H2O is towards cation (positive end). The Coordination number for Li$^+$, Na$^+$, K$^+$, is four (IV) i. e. four H2O molecules are in primary hydration sphere; while for Rb$^+$ & Cs$^+$ the Coordination number is six (VI). The water molecule in first sphere form H–bond to other water molecule through hydrogen gives **secondary sphere**.

Anions also can be hydrogen bonded to water with positive end of H2O i.e. H^+ ions.

If hydration energy is greater than lattice energy (**Exothermic**) the salt is soluble. While lattice energy is greater than hydration energy (**Endothermic**) it remains insoluble in water.

Interaction of cation & Anion with water molecule separate hydration of cation (Na^+) & Anion (Cl^-) gives NaCl dissolve in water.





Effect of Hydration Energy (Salvation energy):

1) Hydration energy & solubility increases with increase in value of dielectric constant.
2) With increase in size of cation & anion, solubility increases.
3) Lattice energy & hydration energy opposite to each other.
4) The solubility of ionic solid is low if the cation is strongly polarizing and the anion is easily polarizable.

Reference :

1. http://studymaterial.unipune.ac.in:8080/jspui/bitstream/123456789/6524/1/Ionic%20Solids%20%20TYBSC%20Navgire%20M.pdf

2. **Text book of Manali Publication**