UNIT - 1 METALLURGY

Answer the following questions:

1. What is the difference between minerals and ores?

Minerals	Ores
A naturally occurring substance which contains metal in free state or in the form of compounds is called a **mineral**.	Minerals that contains a high percentage of metal, from which it can be extracted conveniently and economically are called **ores**.

2. What are the various steps involved in extraction of pure metals from their ores?

The extraction of a metal from its ore consists of the following metallurgical processes.

(i) Concentration of the ore (ii) Extraction of crude metal (iii) Refining of crude metal

3. What is the role of Limestone in the extraction of Iron from its oxide Fe $_2O_3$?

Limestone in the extraction of Iron from its oxide Fe $_2O_3$ is used as a flux.

$$\underset{\textbf{Flux}}{CaO\,(s)} + \underset{\textbf{Gangue}}{SiO2\,(s)} \longrightarrow \underset{\textbf{Slag}}{CaSiO3\,(s)}$$

4. Which type of ores can be concentrated by froth floatation method? Give two examples for such ores.

Sulphide ores can be concentrated by froth floatation method

Ex. Galena (PbS) and Zinc blende (ZnS)

5. Out of coke and CO, which is better reducing agent for the reduction of ZnO? Why?

(i) Above 1273 K The ΔG^o for the formation of $2C + O_2 \longrightarrow 2CO$ (g) is lower than the formation of ZnO on comparing the ΔG^o of formation of $2CO + O_2 \longrightarrow 2CO_2$ (g) it is higher than the ΔG^o of formation of ZnO.

(ii) Therefore C is always considered as better reducing agent than CO for the reduction of Zn from ZnO

(iii) In Ellingham diagram ΔG^o of ZnO is below the ΔG of formation of CO

6. Describe a method for refining nickel.

Mond process for refining nickel:

Principle: Impure metal is treated with a suitable reagent which can form a volatile compound with the metal.

Then the volatile compound is decomposed to give the pure metal.

Process: The impure nickel is heated with carbon monoxide at 350 K.

The nickel reacts with CO and forms a volatile nickel tetracarbonyl.

$$Ni\ (s) + 4\ CO\ (g) \longrightarrow Ni(CO)_4\ (g)$$

On heating the nickel tetracarbonyl around 460 K, the complex decomposes and gives pure metal. $Ni(CO)_4 \longrightarrow Ni\ (s) + 4\ CO\ (g)$

7. Explain zone refining process with an example

Method: Fractional Crystallisation.

Principle: . Impurities are more soluble in the melt than in the solid state metal.

Process:

- Impure metal is taken in the form of a rod.
- One end of the rod is heated using a mobile induction heater .
- The metal rod melts
- When the heater is slowly moved to the other end the pure metal crystallises
- The impurities moves on to the adjacent molten zone formed due to the movement of the heater.
- As the heater moves further away, the molten zone containing impurities also moves along with it.
- This process is repeated several times by moving the heater in the same direction again and again to get pure metal .
- It is carried out in an inert gas atmosphere to prevent the oxidation of metals .
- **Example** : Germanium (Ge), Silicon (Si) and Galium (Ga) are refined by this process.

8. (A) Predict the conditions under which

(i) Aluminium might be expected to reduce magnesia.

Above 1623K (1350°C) ΔG^o of formation of $4/3\ Al + O_2 \longrightarrow 2/3\ Al_2O_3$from Al is less than that of MgO from Mg . Therefore above 1623K , Al can reduce MgO.

(ii) Magnesium could reduce alumina.

Temperature below the point of intersection ΔG^o of formation of Al_2O_3 and MgO

that is below 1400°C Mg reduce Al_2O_3 (At the point of intersection $\Delta G^o = 0$)

(B) Carbon monoxide is more effective reducing agent than carbon below 983K but, above this temperature, the reverse is true –Explain.

Below 983K ΔG^o of formation of $2CO_{(g)} + O_{2\ (g)} \longrightarrow 2CO_{2\ (g)}$ is favoured due to more negative ΔG^o value Thus CO is a better reducing agent .

Above 983K ΔG^o of formation of $2C_{(s)} + O2_{(g)} \longrightarrow 2CO_{(g)}$ is favoured due to more negative ΔG^o value than the ΔG^o of formation of CO_2 . Thus C is a better reducing agent .

(c) it is possible to reduce Fe_2O_3 by coke at a temperature around 1200K

Around 1200K ΔG^o of formation of Fe_2O_3 has more negative value than ΔG^o of formation of CO_2 from C

9. Give the uses of zinc.

- Metallic zinc is used in **galvanising** metals such as iron and steel to protect them from rusting and corrosion.
- It is used to produce die-castings in the automobile, electrical and hardware industries
- Zinc oxide is used in the manufacture paints, rubber, cosmetics, plastics, inks, batteries, textiles and electrical equipment.
- Zinc sulphide is used in making luminous paints, fluorescent lights and x-ray screens.
- Brass an alloy of zinc is used in water valves and communication equipment

10. Explain the electrometallurgy of aluminium.

Hall-Herold process:

In this method, electrolysis is carried out in an iron tank lined with carbon which acts as a cathode.

The carbon blocks immersed in the electrolyte acts as a anode.

A 20% solution of alumina, obtained from the bauxite ore is mixed with molten cyrolite and is taken in the electrolysis chamber.

About 10% calcium chloride is also added to the solution.

Here calcium chloride helps to lower the melting point of the mixture.

The fused mixture is maintained at a temperature of above 1270 K.

The chemical reactions involved in this process are as follows.

Ionisaiton of alumina $Al_2O_3 \longrightarrow 2Al^{3+} + 3O^{2-}$

Reaction at cathode $2Al^{3+}$ (melt) + 3e- $\longrightarrow$ Al (l)

Reaction at anode $2O^{2-}$ (melt) $\longrightarrow$ O_2 + 3e-

Since carbon acts as anode the following reaction also takes place on it.

$$C\ (s) + O^{2-}\ (melt) \longrightarrow CO + 2e^-$$

$$C\ (s) + 2O^{2-}\ (melt) \longrightarrow CO_2 + 4e^-$$

Due to the above two reactions, anodes are slowly consumed during the electrolysis.

The pure aluminium is formed at the cathode and settles at the bottom.

The net electrolysis reaction can be written as follows.

$$4Al^{3+}\ (melt) + 6O^{2-}\ (melt) + 3C\ (s) \longrightarrow 4Al\ (l) + 3CO_2\ (g)$$

11. Explain the following terms with suitable examples.

(i) Gangue : Earthly waste substances occurring in ore eg. Silica

(ii) Slag : Waste matter separated from meta during smelting eg. $FeSiO_3$

(iii) Flux: The substance which is added in the ore to convert non-fusible gangue to fusible compound is called flux.

12. Give the basic requirement for vapour phase refining.

In this method, the metal is treated with a suitable reagent which can form a volatile compound with the metal. Then the volatile compound is decomposed to give the pure metal.

13. Describe the role of the following in the process mentioned.

(i) Silica in the extraction of copper.

Silica is an acidic flux It removes ferrous oxide as ferrous silicate (slag).

FeO(Gangue) + SiO_2(Flux) $\longrightarrow$ $FeSiO_3$(Slag)

(ii) Cryolite in the extraction of aluminium.

Cyrolite lowers the melting point of alumina and it increases the electrical conductivity .

(iii) Iodine in the refining of Zirconium.

Zr is heated in iodine vapours at about 550 K to form volatile ZrI_4. which is heated over tungsten filament at 1800K to get pure Zr.

$Zr\ (s) + 2I_2\ (s) \longrightarrow Zr\ I_4 \longrightarrow Zr\ (s) + 2I_2$

(Impure) (volatile) **(Pure)**

(iv) Sodium cyanide in froth floatation.

NaCN is used as a depressant. It selectively prevents ZnS from coming to froth but allows PbS to come with forth. Because NaCN reacts with ZnS to form $Na_2[Zn(CN)_4]$.

14. Explain the principle of electrolytic refining with an example.

Let us understand this process by considering electrolytic refining of silver as an example.

Cathode : Pure silver

Anode : Impure silver rods

Electrolyte : Acidified aqueous solution of silver nitrate.

When a current is passed through the electrodes the following reactions will take place

at anode $2Ag(s) \longrightarrow Ag^+(aq) + 1e^-$

at cathode $Ag^+(aq) + 1e^- \longrightarrow Ag(s)$

During electrolysis, silver atoms lose electrons and silver cations get electrons

15. The selection of reducing agent depends on the thermodynamic factor: Explain with an example.

The selection of reducing agent depends on the thermodynamic factor

- The reduction of metal oxide using reducing agent can occur if the free energy change is negative.
- The reducing reaction having large negative ΔG value is selected

Example

- Above1623K, Al has more negative ΔG° value than Mg
- Hence Al is used to reduce magnesia.
- Below 1623K, Mg has more negative ΔG° value than Al
- Hence Mg will be used to reduce Alumina.

16. Give the limitations of Ellingham diagram.

- Ellingham diagram is constructed based only on thermodynamic considerations.
- It gives information about the thermodynamic feasibility of a reaction.
- It does not tell anything about the rate of the reaction.
- It does not give any idea about the possibility of other reactions that might be taking place.
- The interpretation of ΔG is based on the assumption that the reactants are in equilibrium with the product which is not always true.

17. Write a short note on electrochemical principles of metallurgy.

In this technique, the metal salts are taken in a fused form or in solution form. The metal ion present can be reduced by treating it with some suitable reducing agent or by electrolysis.

18, Explain Froth flotation method

This method is commonly used to concentrate sulphide ores such as galena (PbS), zinc blende (ZnS)

Principle: Metallic ore particles are wetted by oil is separated from gangue.

In this method, the crushed ore is suspended in water and mixed with frothing agent such as pine oil, eucalyptus oil.

A small quantity of sodium ethyl xanthate which acts as a collector is also added.

A froth is generated by blowing air through this mixture.

The collector molecules attach to the ore particle and make them water repellent.

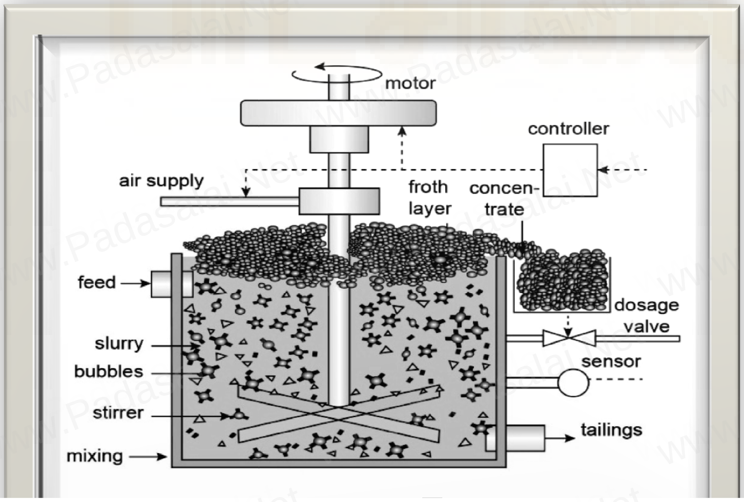
As a result, ore particles, wetted by the oil, rise to the surface along with the froth

The froth is skimmed off and dried to recover the concentrated ore.

The gangue particles wetted by water settle at the bottom.

When a sulphide ore of a metal contains other metal sulphides as impurities, depressing agents such as sodium cyanide or sodium carbonate are used to prevent other metal sulphides coming to the froth.

For example, when impurities such as ZnS is present in galena (PbS), sodium cyanide (NaCN) is added to depresses the flotation property of ZnS by forming a layer of zinc complex $Na_2[Zn(CN)_4]$ on the surface of zinc sulphide.



19. Explain Van-Arkel method for refining zirconium/titanium

Principle : It is based on the thermal decomposition of metallic compounds

Process :

Titanium and zirconium can be purified using this method.

The impure titanium metal is heated in an evacuated vessel with iodine at a temperature of 550 K to form the volatile titanium tetra-iodide.(TiI_4).

The impurities are left behind, as they do not react with iodine.

$$Ti\ (s) + 2I_2\ (s) \longrightarrow TiI_4\ (vapour)$$

The volatile titanium tetraiodide vapour is passed over a tungsten filament at a temperature aroud 1800 K.

The titanium tetraiodide is decomposed and pure titanium is deposited on the filament. The iodine is reused.

$$TiI_4\ (vapour) \longrightarrow Ti\ (s) + 2I_2\ (s)$$

20. What is Ellingham diagram?

The graphical representation of variation of the standard Gibbs free energy of reaction for the formation of various metal oxides with temperature is called Ellingham diagram

21. What are the applications of copper?

Copper is used for making coins and ornaments along with gold and other metals.

Copper and its alloys are used for making wires, water pipes and other electrical parts.

22. Explain electromagnetic separation method with example.

This method is applicable to ferromagnetic ores

Principle : It is based on the difference in the magnetic properties of the ore and the impurities.

Process: Tin stone can be separated from the wolframite impurities which is magnetic.

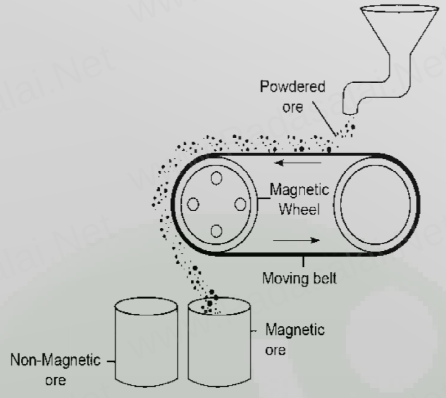
ores such as chromite, pyrolusite having magnetic property can be removed from the non magnetic siliceous impurities.

The crushed ore is poured on to an electromagnetic separator

It consisting of a belt moving over two rollers of which one is magnetic.

The magnetic part of the ore is attracted towards the magnet and falls as a heap close to the magnetic region

The nonmagnetic part falls away from it



Magnetic separation

23 .Distinguish between roasting and Calcination.

S. No.	Roasting	Calcination
	Ore is heated with excess of oxygen in a below the melting point of the metal.	Ore is strongly heated in the absence of air limited supply of air below the melting point of the metal
	It is applied for the conversion of sulphide ores into their oxides	It is applied for the conversion of carbonate ores into their oxides
	It removes impurities such as arsenic, sulphur and phosphorous by converting them into their volatile oxides	the water of crystallisation escapes as moisture.

24. Gravity separation or Hydraulic wash

Principle : The ore having high specific gravity is separated from the gangue

.Ore is crushed to a finely powdered form and treated with rapidly flowing current of water. During this process the lighter gangue particles are washed away by the running water.

This method is generally applied to concentrate the native ore such as gold and oxide ores such as hematite (Fe_2O_3), tin stone (SnO_2) etc

25. What is Metallurgy?

Metallurgy relate to the science and technology of metals.

www.Padasalai.Net

26. What is cementation?

Gold recovered by reacting the deoxygenated leached solution with zinc .Gold is reduced to its elemental state and the process is called **cementation**.

27. What is the Composition of copper matte?

Mixture of Cu_2S and FeS is called copper matte

28. Define the following terms; (i) Thermite, (ii) Ignitation powder, (iii) Cementation.

(i) Thermite: Mixture of oxide and Al in the ratio of 3:1 is called thermite.

(ii) Ignitation powder: BaO2+Mg powder acts as ignitation powder.

(iii) Cementation: Metal is reduced to its elemental state (zero oxidation sate) and process is called cementation.

20. State the principles of i. Leaching, ii. Smelting, iii. Distillation iv. Liquation v. Vapour **phase refining**

Principle: It is based on the solubility of the ore in a suitable solvent and the reactions in aqueous solution.

The crushed ore is allowed to dissolve in a suitable solvent, the metal present in the ore is converted to its soluble salt or complex while the gangue remains insoluble.

Smelting

In this method, a flux and a reducing agent such as carbon, carbon monoxide (or) aluminium is added to the concentrated ore and the mixture is melted by heating above the melting point of the metal is called smelting,

Distillation

In this method, the impure metal is heated to evaporate and the vapours are condensed to get pure metal.

Liquation

. The impure metal is placed on sloping hearth of a reverberatory furnace and it is heated just above the melting point of the metal in the absence of air, the molten pure metal flows down and the impurities are left behind. The molten metal is collected and solidified.

(v) Vapour phase refining:

The impure metal is converted into its volatile compound, which on heating is decomposed to pure metal.

21.Why does molten copper have blister appearance?

The metallic copper is solidified and it has blistered appearance due to evolution of SO_2 gas formed in this process. This copper is called blistered copper**.**

22.Write the name of the metal refined by each of the following processes:

(i) Distillation, (ii)Liquation, (iii) Electrolysis, (iv) Zone refining, (v) Van akral method

(i) Distillation- Zn and Hg (ii)Liquation- Sb, Pb,Hg, Bi (iii) Electrolysis- Ag,Cu,Zn (iv) Zone refining – Ge,Si,Ga (v) Van akral method-Ti,Zr.

UNIT 6 - SOLID STATE

1.Define unit cell.

A basic repeating structural unit of a crystalline solid is called a unit cell.

2. Give any three characteristics of ionic crystals.

- ✓ Ionic solids have high melting points.
- ✓ They do not conduct electricity.
- ✓ They conduct electricity in molten state (or) when dissolved in water
- ✓ They are hard

3. Differentiate crystalline solids and amorphous solids.

S.No	Crystalline solids	Amorphous solids
1	Long range orderly arrangement of constituents.	Short range, random arrangement of constituents.
2	Definite shape	Irregular shape
3	Anisotropic in nature	Isotropic in nature
4	They are true solids	They are pseudo solids (or) super cooled liquids
5	Definite Heat of fusion	Heat of fusion is not definite
6	They have sharp melting points.	They have sharp melting points.
7	Examples: NaCl , diamond etc.,	Examples: Rubber , plastics, glass etc

4. Distinguish between hexagonal close packing and cubic close packing.

S.NO	HEXAGONAL CLOSE PACKING	CUBIC CLOSE PACKING.
1	"ABA'' arrangement is known as the hexagonal close packed (hcp) arrangement.	"ABC'' arrangement is known as the hexagonal cubic close packing. (ccp) arrangement.
2	The spheres of the third layer is exactly aligned as first layer	The spheres of the third layer is not aligned with those of either the first or second layer.
3	The hexagonal close packing is based hexagonal unit cells with sides of equal length	The cubic close packing is based on the face centered cubic unit cell.
4	Tetrahedral voids of the second layer are covered by the sphere of the third layer	octahedral voids of the second layer are covered by the sphere of the third layer
5	hcp unit cells contain 6 atoms	ccp unit cells contain 4 atoms

5. Classify the following solids

a. P_4 - covalent solid b. Brass – Metallic solid c. diamond- covalent solid

d. NaCl – Ionic solid e. Iodine - Non polar molecular solid

6. Explain briefly seven types of unit cell.

There are seven primitive crystal systems 1. Cubic 2. Tetragonal 3.Orthorhombic 4. Hexagonal 5.Monoclinic 6. Triclinic and 7.Rhombohedral. They differ in the arrangement of their crystallographic axes and angles.

7. Distinguish tetrahedral and octahedral voids.

S.NO	TETRAHEDRAL VOIDS	OCTAHEDRAL VOIDS.
1	When a sphere of second layer (b) is above the void (x) of the first layer (a), tetrahedral void is formed.	When the voids (y) in the first layer (a) are partially covered by the spheres of layer (b), octahedral void is formed in (a)
2	If the number of close packed spheres be 'n' then, the number of tetrahedral voids generated is equal to 2n.	If the number of close packed spheres be 'n' then, the number of octahedral voids generated is equal to n
3	This constitutes four spheres – three in the lower (a) and one in the upper layer (b).	This constitutes six spheres – three in the lower layer (a) and three in the upper layer (b)
4	When the centers of these four spheres are joined, a tetrahedron is formed.	When the centers of these six spheres are joined, an octahedron is formed.

8. What are point defects?

Point defects are defects that occur only at or around a single lattice point of a crystal lattice

9. Explain Schottky defect.

Schottky defect arises due to the missing of equal number of cations and anions from the crystal lattice.

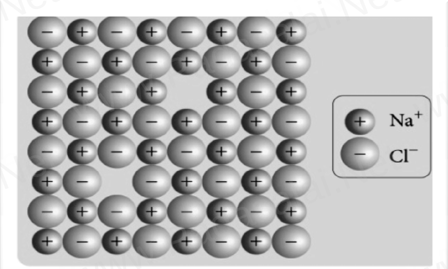
This effect does not change the stoichiometry of the crystal.

Ionic solids in which the cation and anion are of almost of similar size show schottky defect.

Example: NaCl.

Presence of large number of schottky defects in a crystal, lowers its density.

Presence of Schottky defect in the crystal provides movement of atoms or ions within the crystal lattice.

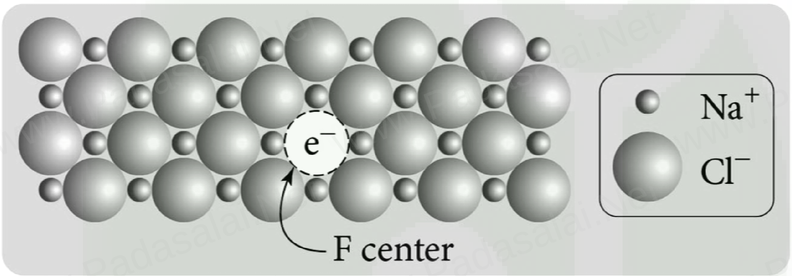


Schottky Defect

10. Write short note on metal excess and metal deficiency defect with an example.

Metal excess defect :

- Metal excess defect arises due to the presence of more number of metal ions as compared to anions.
- Alkali metal halides **NaCl, KCl** show this type of defect.
- The electrical neutrality of the crystal is maintained by the presence of electron present in interstitial position.
- For example, when **NaCl** crystals are heated in the presence of sodium vapour, Na+ ions are formed and are deposited on the surface of the crystal.
- Chloride ions (Cl-) diffuse to the surface from the lattice point and combines with Na+ ion.

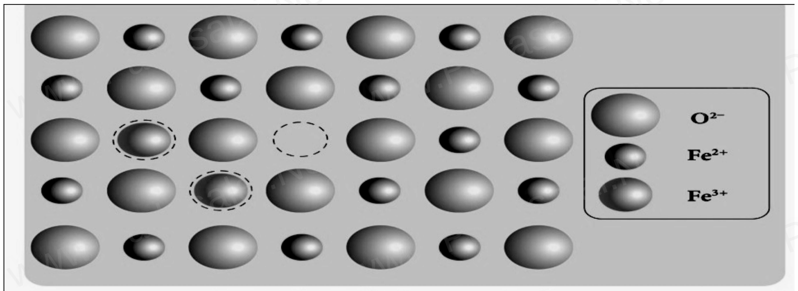


Metal Excess Defect

- The electron lost by the sodium vapour diffuse into the crystal lattice and occupies the vacancy created by the Cl- ions.
- Such anionic vacancies which are occupied by unpaired electrons are called **F centers.**
- Hence, the formula of NaCl which contains excess Na+ ions can be written as **Na Cl 1+ *x* .**

<u>Metal deficiency defect</u>

- Metal deficiency defect arises due to the presence of less number of cations than the anions.
- This defect is observed in a crystal in which, the cations have variable oxidation states.
- For example, in **FeO** crystal.
- Some of the Fe^{2+} ions are missing from the crystal lattice.



Metal Deficiency Defect

- To maintain the electrical neutrality, twice the number of other Fe^{2+} ions in the crystal is oxidized to Fe^{3+} ions.
- In such cases, overall number of Fe^{2+} and Fe^{3+} ions is less than the O^{2-} ions.
- It was experimentally found that the general formula of ferrous oxide is **FexO,** where x ranges from **0.93 to 0.98.**

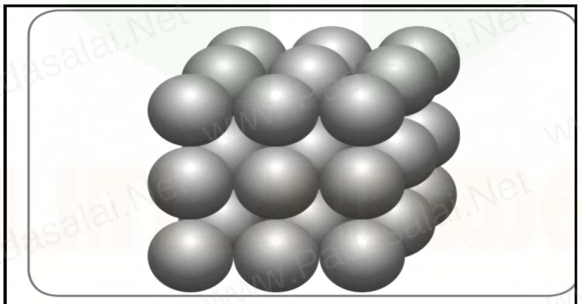
11. Calculate the number of atoms in a fcc unit cell.

No of atoms in fcc unit cell $= \frac{N_c}{8} + \frac{N_f}{2} = \frac{8}{8} + \frac{6}{2} = 1 + 3 = 4$

12. Explain AAAA and ABABA and ABCABC type of three dimensional packing with the help of neat diagram.

i. AAAA three dimensional packing

- It occurs in simple cubic arrangement
- This type of packing arrangements is obtained by repeating the AAAA type in three dimensions.
- Spheres in one layer sitting directly on the top of those in the previous layer so that all layers are identical.
- All spheres of different layers of crystal are perfectly aligned horizontally and also vertically,
- The unit cell of this arrangement is simple cubic
- In this each sphere is in contact with 6 neighbouring spheres
- Four in its own layer, one above and one below
- Hence the coordination number of the sphere in simple cubic arrangement is 6.



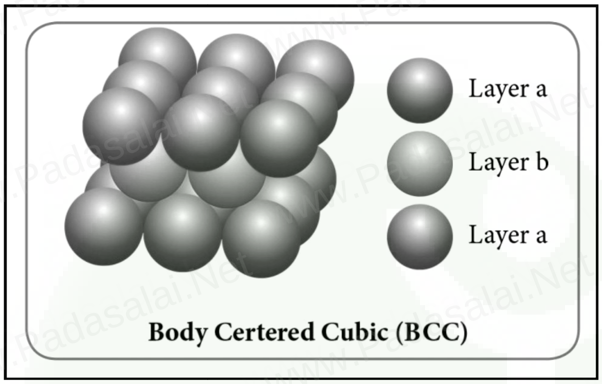
Simple Cubic (SC)

ii. ABABA three dimensional packing

- It occurs in body centered cubic arrangement

www.Padasalai.Net

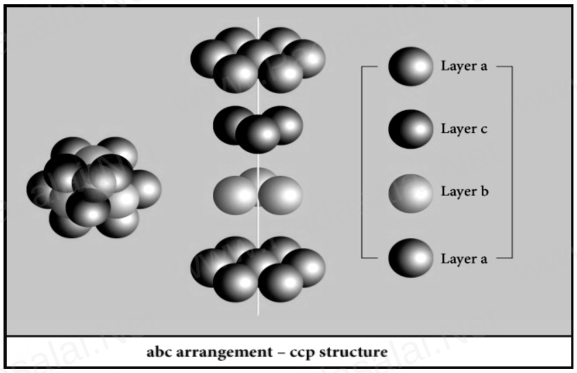
- In this arrangement, the spheres in the first layer (A type) are slightly separated and the second layer is formed by arranging the spheres in the depressions between the spheres in layer A as shown in figure.
- The third layer is a repeat of the first.
- This pattern ABABAB is repeated throughout the crystal.
- In this arrangement, each sphere has a coordination number of 8, four neighbors in the layer above and four in the layer below.



Body Certered Cubic (BCC)

iii. ABCABC three dimensional packing

- The **first layer 'a'**. formed by arranging the spheres as in the case of two dimensional arrangements
- The **second layer 'b'** is formed by placing the spheres in the depressions of the first layer
- A tetrahedral void **(x)** is formed in the second layer **(b)** a octahedral void **(y)** is formed. in the first layer **(a)**
- The third layer is placed over the second layer in such a way that all the spheres of the third layer fit in octahedral voids.
- This arrangement of the third layer is different from other two layers (a) and (b),
- hence, the third layer is designated (c).
- If the stacking of layers is continued in abcabcabc… pattern, then the arrangement is called cubic close packed (ccp) structure.
- In ccp arrangements, the coordination number of each sphere is 12 – six neighbouring spheres in its own layer, three spheres in the layer above and three sphere in the layer below.



abc arrangement – ccp structure

13. Why ionic crystals are hard and brittle?

- In ionic crystal cations and anions are bound together by strong electrostatic attractive forces.
- To maximize the attractive force, cations are surrounded by as many anions as possible and vice versa.

14. Calculate the percentage efficiency of packing in case of body centered cubic crystal.

In Δ ABC

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

$AC = \sqrt{AB^2 + BC^2}$

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

In Δ ACG

$AG^2 = AC^2 + CG^2$

In Δ AGC

$AG = \sqrt{AC^2 + CG^2}$

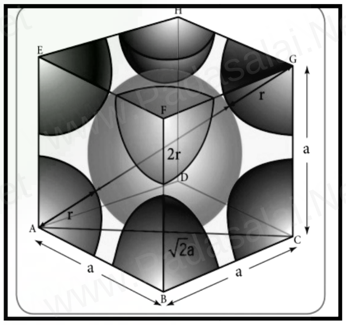
$AG = \sqrt{(\sqrt{2}\ a)^2 + a^2}$

$= \sqrt{2a^2 + a^2} = \sqrt{3\ a^2}$

$AG = \sqrt{3\ a^2}$

i.e. $\sqrt{3\ a^2} = 4r$

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



Volume of the sphere with radius **'r'** $= \frac{4}{3}\pi r^3$

$$= \frac{4}{3}\pi \left(\frac{\sqrt{3}}{4}\, a\right)^3$$

$$= \frac{4}{\cancel{3}} \times \frac{\cancel{\sqrt{3}} \times \cancel{\sqrt{3}} \times \sqrt{3}}{4 \times 4 \times 4}\, \pi a^3$$

$$= \frac{\sqrt{3}}{16}\, \pi a^3$$

No of spheresof of unit cell BCC = 2

Hence total volume of all spheres $= \cancel{2} \times \frac{\sqrt{3}\ \pi a^3}{\cancel{16}\ 8} = \frac{\sqrt{3}\ \pi a^3}{8}$

$$\text{packing fraction} = \frac{\text{Total volume occupied by spheres in unit cell}}{\text{volume of unit cell}} \times 100$$

$$= \frac{\frac{\sqrt{3}\ \pi a^3}{8}}{a^3} \times 100$$

$$= \sqrt{3}\ \pi \times 12.5$$

$$= 1.732 \times 3.14 \times 12.5$$

Percentage efficiency of packing in bcc = 68%

15. What is the two dimensional coordination number of a molecule in square close packed layer?

The two dimensional coordination number of a molecule in square close packed layeris 4 In this arrangement each sphere is in contact with four of its neighbours.

16. **Experiment shows that Nickel oxide has the formula Ni O 0.96 1.00 . What fraction of Nickel exists as of Ni^{2+} and Ni^{3+} ions?**

Formula Ni O 0.96 1.00

So ratio of Ni: O = 98: 100

Let the no of Ni^{2+} is = x

Let the no of Ni^{3+} is = 98 – x

Charge on Ni = charge on O

$3(98 - x) + 2x = 2(100)$

$294 - 3x + 2x = 200$

$-x = 200 - 294$

$x = 94$

$$\text{Percentage of } Ni^{+2} = \frac{\text{Atoms of } Ni^{+2}}{\text{Total no. of Ni}} \times 100$$

$$= \frac{94}{98} \times 100 = 96\ \%$$

$\text{Percentage of } Ni^{+3} = 100 - 96 = 4\%$

17. What is meant by the term "coordination number"? What is the coordination number of atoms in a bcc structure?

The neighbouring atoms surrounded by each atom is called coordination number. In the body centre, each atom is surrounded by eight nearest neighbours and coordination number is **8.**

18. An element has bcc structure with a cell edge of 288 pm. the density of the element is 7.2 gcm-3. how many atoms are present in 208g of the element.

Given

Edge of bcc (**a**) = 288pm = 288×10^{10} cm

Density7.2 gcm^{-3}

Mass of element : 208g

Volume of unit cell $a^3 = (288 \times 10^{-10}\ cm)^3 = 2.39 X 10^{-23}\ cm^3$

$$\text{Volume of 208g of element} = \frac{M}{D} = \frac{208\ g}{7.2\ gcm^{-3}} = 28.89\ cm^3$$

$$\text{No. of unit cells} = \frac{\text{Total volume}}{} = \frac{28.89\ cm^3}{} = 12.09 \times 10^{23}$$

www.Padasalai.Net

Volume of unit cell $2.39X10^{-23}$ cm^3

For a bcc umber of atoms per unit cell = 2

No of atoms present in 208g = No of atoms per unit cell x No of unit cell = 2 x 12.09 x 10^{23}

= 24,18 x 10^{23}

No of atoms present in 208g = **2.418 x 10^{24}**

19. Aluminium crystallizes in a cubic close packed structure. Its metallic radius is 125pm. calculate the edge length of unit cell.

Given : r = 125pm.

For ccp a = $2\sqrt{2}$ r

= 2 x 1.44 x 125 pm = 354 pm (approximate)

20. If NaCl is dopped with 10-^{2} mol percentage of strontium chloride, what is the concentration of cation vacancy?

Given

1 Cation of Sr^{2+} will create 1 cation vacancy in Nacl.

Number of cation vacancies created in the lattice of Nacl = to the number of divalent Sr^{2+} ions added.

Given Conetration of $SrCl_2 = 10^{-2}$ mol%

Concentration is in percentage so that take total 100 mol of solution

Number of moles of NaCl = 100 – moles of $SrCl_2$

Moles of $SrCl_2$ is very negligible as compare to total moles so

Number of moles of NaCl = 100

1 mol of NaCl is dopped with = $10^{-2}/100$ moles of $SrCl_2$

= 10^{-4} mol of $SrCl_2$

So cation vacancies per mole of NaCl =10^{-4} mol

1 mol = 6.022 x10^{23} particles

So

So cation vacancies per mole of NaCl = 10^{-4} x 6.022 x10^{23}

= 6.02 x10^{19}

So that, the concentration of cation vacancies created by $SrCl_2$ = **6.022 × 10^{19}**

21. KF crystallizes in fcc structure like sodium chloride. calculate the distance between K+ and F− in KF.(given : density of KF is 248 3 .*g cm*−3)

Step 1. Calculate the numbers of K+ and F- ions in a unit cell

Number of K^+ (Edge centre and in body centre) $= \frac{N_e}{4} + \frac{N_b}{1} = \frac{12}{4} + \frac{1}{1} = 4$

Number of F^- (Corner and in face cerntr) $= \frac{N_c}{8} + \frac{N_f}{2} = \frac{8}{8} + \frac{6}{2} = 4$

There are four K+ and four F- ions or four KF formula units (FU)

Step 2. Calculation of mass of a unit cell

Mass of 6.022×10^{23}FU $= 58.10$ g mol^{-1}

Mass of 4 FU $= \frac{58.10 \text{ g mol}^{-1} \text{ x } 4}{6.022\times10^{23}} = 3.86 \text{ x } 10^{22}$ g

Step 3. Calculation of volume of a unit cell

Density of KF is $= 2.48$ g cm$-^{3}$

∴ Volume of a unit cell $= \frac{M}{\mathbf{D}} = \frac{3.86 \text{ x } 10^{22} \text{ g}}{2.48 \text{ g } cm-^{3}} = 1.56 \text{ x } 10^{22}$ cm-^{3}

Step 4. Calculation of edge length of the unit cell

$V = 1^3$

∴ $1 = 3\sqrt{V} = 3\sqrt{1.56} \times 10^{-22}$ cm^3 $= 5.38\times10^{-8}$ cm $=$ **538 pm**

Step 5. Calculation of interionic distance

In NaCl unit cell, the edge length is twice the interionic distance.

∴ **Interionic distance** = 538 / 2 pm = **269 pm**

22. An atom crystallizes in fcc crystal lattice and has a density of 10 3 gcm^{-3} with unit cell edge length of 100pm. calculate the number of atoms present in 1 g of crystal.

Given:

Density $=10^{-3}$ gcm^{-3} a = 100 pm = 100 x 10 -^{10} cm Mass = 1g

No of atoms in Fcc unit cell = 4

Volume of unit cell $a^3 = (100 \text{ x } 10^{-10} \text{ cm})^3 = 10^{-24}$ gcm^{-3}

www.Padasalai.Net

$$\text{Volume of crystal} = \frac{M}{D} = \frac{1\text{g}}{10^{-3}\ \text{gcm}^{-3}} = 10^{3}\ \text{gcm}^{-3}$$

$$\text{No of unit cells in 1 g of crystal} = \frac{\text{Volume of crystal}}{\text{Volume of unit cell}} = \frac{10^{3}\ \text{gcm}^{-3}}{10^{-24}\ \text{gcm}^{-3}} = 10^{3} \text{ x } 10^{24}$$

$$= 10^{27}$$

No of atoms in each fcc unit cell = 4

Total no of atoms in 10^{27} unit cells = 4 x 10^{27}

No of atoms in 1 g of crystal = **4 x 10^{27}**

(OR)

$$\text{Total no of atoms 1 g of crystal} = \frac{Z \text{ x } M}{a^{3} \text{ x } d} = \frac{4 \text{ x } 1\text{ g}}{(100 \text{ x } 10^{-10}\text{ cm})^{3} \text{ x } 10^{-3}\ \text{gcm}^{-3}} = \frac{4}{10^{-24} \text{ x } 10^{-3}}$$

$$= \mathbf{4 \text{ x } 10^{27}}$$

23. Atoms X and Y form bcc crystalline structure. Atom X is present at the corners of the cube and Y is at the centre of the cube. What is the formula of the compound?

$$\text{No of corner (X) atoms} = \frac{Nc}{8} = \frac{8}{8} = 1$$

$$\text{No of body centre (Y) atoms} = \frac{Nb}{8} = \frac{1}{1} = 1$$

Formula of the compound = XY

24. Sodium metal crystallizes in bcc structure with the edge length of the unit cell 4.3 ×10^{-8} *cm*. calculate the radius of sodium atom.

Given: a = 4.3 ×10^{-8} *cm*.

$$\text{For BCC } r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \text{ x } 4.3\times10^{-8}\ cm. = \frac{1.732 \text{ x } 4.3\times10^{-8}}{4} = \mathbf{1.786 \text{ x } 10^{-8}\ \text{cm}}$$

25. Explain what happens when ZnO is heated?

ZnO is colourless at room temperature.

When it is heated, it becomes yellow in colour.

On heating, it loses oxygen and thereby forming free Zn2+ ions.

The excess Zn2+ ions move to interstitial sites and the electrons also occupy the interstitial positions.

26. Explain Frenkel defect.

Frenkel defect arises due to the dislocation of ions from its crystal lattice.

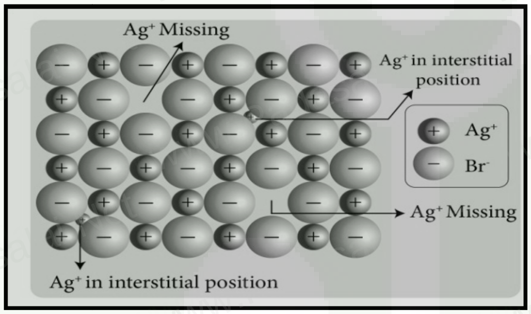
The ion which is missing from the lattice point occupies an interstitial position.

This defect occurs when cation and anion differ in size.

Unlike Schottky defect, this defect does not affect the density of the crystal.

For example AgBr

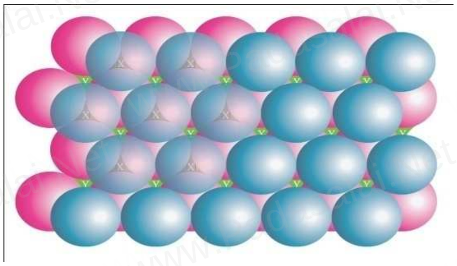
In this case, small Ag+ ion leaves its normal site and occupies an interstitial position as shown in the figure.



27. Explain hcp arrangement (ABABA)

It is a hexagonal closed packing arrangement

- The **first layer 'a'**. is formed by arranging the spheres as in the case of two dimensional arrangements.
- The **second layer 'b'** is formed by placing the spheres in the depressions of the first layer.
- The formation of second layer is obtained by placing the spheres on the depression **(x)** or **(y).**
- A tetrahedral void is formed. in the second layer **(b)** just above the void **(x)** of the first layer **(a)**
- This constitutes four spheres – three in the lower (a) and one in the upper layer (b).
- When the centers of these four spheres are joined, a tetrahedron is formed.
- At the same time, the voids (y) in the first layer (a) are partially covered by the spheres of layer (b), a octahedral void is formed in (a).
- This constitutes six spheres – three in the lower layer (a) and three in the upper layer (b).



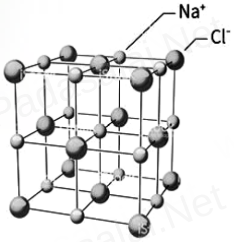
x – Tetrahedral void
y- Octahedral void

- When the centers of these six spheres are joined, an octahedron is formed. Simultaneously new tetrahedral voids (or holes) are also created by three spheres in second layer (b) and one sphere of first layer (a)
- The **third layer is** arranged as a first layer as shown in the figure. This "aba'' arrangement is known as the hexagonal close packed (hcp) arrangement.
- In this arrangement, the tetrahedral voids of the second layer are covered by the spheres of the third layer.
- In hcp arrangements, the coordination number of each sphere is 12 – six neighbouring spheres in its own layer, three spheres in the layer above and three sphere in the layer below.

28. How are crystalline solids classified?

i.Ionic solids ii. covalent solids iii. molecular solids iv. metallic solids

29. Explain Ionic solids.



- The structural units of an ionic crystal are cations and anions.
- They are bound together by strong electrostatic attractive forces.
- To maximize the attractive force, cations are surrounded by as many anions as possible and vice versa.
- Many Ionic solids are cubic close packed. Example: NaCl crystal.

30 . Explain covalent solids.

- In covalent solids, atoms are bound together in a three dimensional network by covalent bonds. Examples: Diamond, silicon carbide
- Such crystals are very hard, and have high melting point.
- They are poor thermal and electrical conductors.

31 . Explain molicular solids.

- In molecular solids, the constituents are neutral molecules.

www.Padasalai.Net

- They are held together by weak van der Waals forces.
- Molecular solids are soft and they do not conduct electricity.
- These molecular solids are further classified into three types.

i. Non polar molecular solids

In non polar molecular solids constituent molecules are held together by weak dispersion forces or London forces.

They have low melting points.

They are in liquids or gaseous state at room temperature.

Examples: **naphthalene and anthracene**

(ii) Polar molecular solids

The constituents molecules have polar covalent bonds.

They are held together by strong dipole-dipole interactions.

They have higher melting points than the non-polar molecular solids.

Examples are **solid CO_2 and solid NH_3**

iii. Hydrogen bonded molecular solids

The constituent molecules are held together by hydrogen bonds.

They are soft solids under room temperature.

Examples: **solid ice (H_2O), glucose, urea**

32 . Explain Metallic solids:

In metallic solids, the lattice points are occupied by positive metal ions and a cloud of electrons pervades the space.

They are hard, and have high melting point.

They possess excellent electrical and thermal conductivity.

They possess bright lustre.

Examples: Metals and metal alloys Cu, Cu- Zn alloy

33. Calculate the number of atoms in ecc and bcc unit cell.

No of atoms in ecc unit cell $= \frac{N_c}{8} + \frac{N_e}{2} = \frac{8}{8} + \frac{12}{4} = 1 + 3 = 4$

$$N_c \quad + \quad N_b \qquad 8 \qquad 1$$

No of atoms in bcc unit cell $= \frac{}{8} \quad \frac{}{2} = \frac{}{8} + \frac{}{1} = 1 + 1 = 2$

34. Barium has a body centered cubic unit cell with a length of 508pm along an edge. What is the density of barium in g cm^{-3}?

Solution:

$$\rho = \frac{nM}{a^3 N_A}$$

Given:

$n = 2$ $M = 137.3\ \text{gmol}^{-1}$ $a = 508\text{pm} = 5.08 \text{ X } 10^{-8}\text{cm}$

$$\rho = \frac{2 \text{ atoms} \times 137.3 \text{ g mol}^{-1}}{(5.08 \times 10^{-8} \text{ cm})^3 \times (6.023 \times 10^{-8} \text{ atoms mol}^{-1})} = \frac{274.6}{131.10 \text{ x } 10^{-24} \text{ x } 6.023 \text{ x } 10^{23}}$$

$$= \frac{274.6}{131.10 \text{ x } 6.023 \text{ x } 10^{-1}} = \frac{274.6 \text{ x } 10}{789.6} = 0.347 \text{ x } 10 = \mathbf{3.47\ g\ cm^{-3}}$$

35. Calculate the percentage efficiency of packing in case of Sc cubic crystal.

Consider a cube with an edge length = ‘a’.

Volume of the cube with edge length a is $= a \times a \times a = a^3$

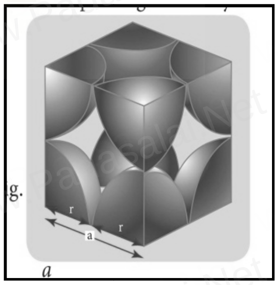
Let ‘r’ is the radius of the sphere. From the figure, $a = 2r = r = \frac{a}{2}$

Volume of the sphere with radius **‘r’** $= \frac{4}{3}\pi r^3$

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

$$= \frac{4}{3}\pi \text{ x } \frac{a^3}{8}$$

$$= \frac{\pi a^3}{6}$$



No of spheres of of unit cell SC = 1

$$\text{Hence volume of sphere} = 1 \times \frac{\pi a^3}{6}$$

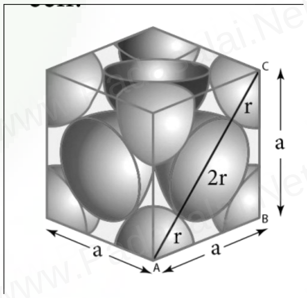
$$\text{packing fraction} = \frac{\text{Total volume occupied by spheres in unit cell}}{\text{volume of unit cell}} \times 100$$

$$= \frac{\frac{\pi a^3}{6}}{a^3} \times 100 = \frac{100\,\pi}{6}$$

$$= \frac{100 \times 3.14}{6} = \mathbf{52.3}\ \%$$

Percentage efficiency of packing in SC = 52.3%

36. Calculate the percentage efficiency of packing in case of face centered cubic crystal.



From the figure

$AC = 4r$

$4r = a\sqrt{2}$

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

In Δ ABC

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

$AC = \sqrt{AB^2 + BC^2}$

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

$$\text{Volume of the sphere with radius 'r'} = \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi\ (\sqrt{2}\ a / 4)^3$$

$$= \frac{\overset{3}{\cancel{4}}}{3}\,\pi \times \frac{\cancel{2}\sqrt{2}\;a^3}{\underset{2}{\cancel{4}\times\cancel{4}}\times 4}$$

$$= \frac{\sqrt{2}\;\pi\,a^3}{24}$$

No of spheres of unit cell FCC = 4

$$\text{Hence total volume of all spheres} = \cancel{4} \times \frac{2\sqrt{2}\;a^3}{\underset{6}{\cancel{24}}} = \frac{2\sqrt{2}\;a^3}{6}$$

$$\text{Packing efficiency} = \frac{\text{Total volume occupied by spheres in unit cell}}{\text{volume of unit cell}} \times 100$$

$$= \frac{\dfrac{2\sqrt{2}\;a^3}{6}}{a^3} \times 100$$

$$= \frac{\sqrt{2}\;\pi \times 100}{6}$$

$$= \frac{1.414 \times 3.14 \times 100}{6}$$

Percentage efficiency of packing in fcc = 74. %

37. Write note on Impurity defect:

- Due to the presence of impurity ions in ionic solids causes vacancies in the crystal lattice of the host.
- For example, addition of $CdCl_2$ to silver chloride yields solid solutions where the divalent cation Cd^{2+} occupies the position of Ag+.
- This disturbs the electrical neutrality of the crystal.
- In order to maintain the same, proportional number of Ag+ ions leaves the lattice.

- This produces a cation vacancy in the lattice, such kind of crystal defects are called impurity defects.

Dr. C. Aruljosephraj
P.G. Assistant in Chemistry,
St. Joseph's Hr. Sec. School,
Manjakuppam,
Cuddalore – 607 001
9865480887