

LESSON -2 p- BLOCK ELEMENTS – I

ANSWER THE FOLLOWING QUESTIONS:

1. Write a short note on anomalous properties of the first element of p-block.

- Small size of atom
- high electronegativity
- non availability of d-orbitals in their valence shell.

2. Describe briefly allotropism in p- block elements with specific reference to carbon.

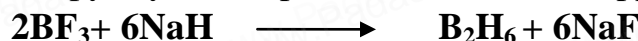
- ❖ Allotropy is the existence of an element in more than one form, having the *same chemical properties but different physical properties*.

The various forms of an element are called allotropes.

Examples: Carbon exists as diamond, graphite, graphene, fullerenes.

3. Boron does not react directly with hydrogen. Suggest one method to prepare diborane from BF_3 .

- ❖ Boron does not react directly with hydrogen.
- ❖ It forms a variety of hydrides called boranes.
- ❖ Treatment of gaseous boron trifluoride with sodium hydride around 450 K gives diborane.
- ❖ To prevent subsequent pyrolysis, the product diborane is trapped immediately.



4. Give the uses of Borax.

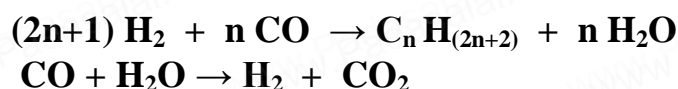
- i. It is used for the identification of coloured metal ions.
- ii. In the manufacture optical and borosilicate glass, enamels and glazes for pottery.
- iii. It is also used as a flux in metallurgy and also acts as a good preservative.

5. What is catenation ? describe briefly the catenation property of carbon.

- ❖ The atoms of some elements can link with one another through strong covalent bonds to form long chains or branches.
- ❖ This property is known as catenation.
- ❖ It is most common in carbon and quite significant in Si and S.
- ❖ **carbon has highest degree of catenation because:**
 - i) the valency of element is greater than or equal to two
 - (ii) element should have an ability to bond with itself
 - (iii) the self bond must be as strong as its bond with other elements
 - (iv) kinetic inertness of catenated compound towards other molecules.

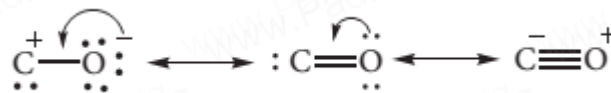
6. Write a note on Fischer Tropsch synthesis.

The Fischer-Tropsch process is a catalytic chemical reaction in which carbon monoxide (CO) and hydrogen (H_2) are converted into hydrocarbons of various molecular weights.

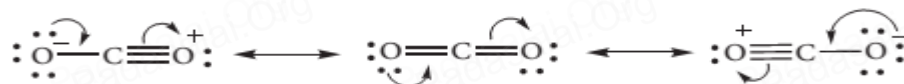


7. Give the structure of CO and CO₂.

CO: It has a linear structure. In CO, three electron pairs are shared between carbon and oxygen.



CO₂: Carbon dioxide has a linear structure with equal bond distance for the both C-O bonds. In this molecule there is one C-O sigma bond. In addition there is 3c-4e bond covering all the three atoms.

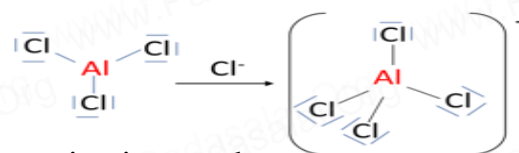


8. Give the uses of silicones.

- ❖ Silicones are used for low temperature lubrication and in vacuum pumps.
- ❖ They are used for making water proofing clothes.
- ❖ They are used as insulating material in electrical motor and other appliances.
- ❖ They are mixed with paints and enamels to make them resistant towards high temperature, sunlight, dampness and chemicals.

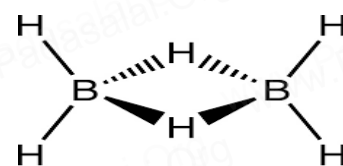
9. AlCl₃ behaves like a lewis acid. Substantiate this statement.

- ❖ The electric configuration of Al is $ns^2 np^1$.
- ❖ It has three electrons in its valence shell.
- ❖ It can form only three covalent bonds.
- ❖ There are only six electrons around Al and its octet remains incomplete.
- ❖ When one atom of Al combines with three chlorine atoms, its octet remains incomplete.
- ❖ AlCl₃ remains electron-deficient and acts as a Lewis acid
- ❖ In this reaction Cl⁻ ion is the electron donor, therefore it is a Lewis base, and AlCl₃ is the electron acceptor.



10. Describe the structure of diborane.

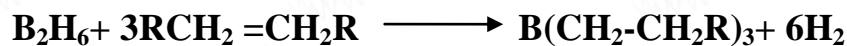
- ❖ Diborane is an electron deficient molecule.
- ❖ The structure of Diborane molecule consists of four hydrogen atoms and that of two boron atoms coming on the same plane.
- ❖ In between these planes, there are said to be two dividing atoms of hydrogen.
- ❖ The boron atom is known to be sp^3 hybridized and has four hybrid orbitals.
- ❖ From these four hybrid orbitals, three of the s orbitals have one electron each, and of which one is an empty orbital.
- ❖ The two electrons of the hybrid orbitals in each of the boron atoms form 2 bonds with the 1s hydrogen atoms.
- ❖ The two atoms of boron left with that of each unpaired electron orbital and empty orbital forms the two bridging (B-H-B) bonds with that of the two 1s hydrogen atoms, is also called as the banana bond.



Diborane

11. Write a short note on hydroboration.

- ❖ **Hydroboration** refers to the addition of a hydrogen-boron bond to C-C.
- ❖ It is highly used for anti Markovnikov addition.
- ❖ Diborane adds on to alkenes and alkynes in ether solvent at room temperature.



12. Give one example for each of the following

- (i) Icosogens : Boron (ii) Tetragen : Carbon
(iii) Pnictogen : Nitrogen (iv) Chalcogen: Oxygen

13. Write a note on metallic nature of p-block elements.

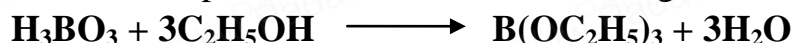
- ❖ The tendency of an element to form a cation by losing electrons is known as electropositive or metallic character.
- ❖ This character depends on the ionisation energy.
- ❖ Descending a group the ionisation energy decreases and hence the metallic character increases.
- ❖ p-block is the only one which contains metals, non-metals and metalloids.
- ❖ The common metal among p block elements are : aluminium ,gallium, indium and thallium(group 13), tin and lead (group 14) and bismuth (group 15).
- ❖ The common metalloids are silicon, Germanium, Arsenic, Antimony, and Tellurium.
- ❖ While all the remaining elements are non metals.

14. Complete the following reactions

- 1) $\text{B}(\text{OH})_3 + \text{NH}_3 \longrightarrow \text{BN} + 3\text{H}_2\text{O}$
- 2) $\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{SO}_4 + 5\text{H}_2\text{O} \longrightarrow \text{Na}_2\text{SO}_4 + 4\text{H}_3\text{BO}_3$
- 3) $\text{B}_2\text{H}_6 + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaBO}_2 + 4\text{H}_3\text{BO}_3$
- 4) $\text{B}_2\text{H}_6 + 6\text{CH}_3\text{OH} \longrightarrow 2\text{B}(\text{OCH}_3)_3 + 6\text{H}_2$
- 5) $4\text{BF}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{BO}_3 + 3\text{HBF}_4$
- 6) $\text{HCOOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{CO} + \text{H}_2\text{O} + \text{H}_2\text{SO}_4$
- 7) $2\text{SiCl}_4 + \text{NH}_3 \longrightarrow \text{Cl}_3\text{Si}-\text{NH}-\text{SiCl}_3$
- 8) $\text{SiCl}_4 + \text{C}_2\text{H}_5\text{OH} \longrightarrow \text{Si}(\text{OC}_2\text{H}_5)_4 + 2\text{Cl}_2$
- 9) $2\text{B} + 6\text{NaOH} \longrightarrow 2\text{Na}_3\text{BO}_3 + 3\text{H}_2$
- 10) $\text{H}_2\text{B}_4\text{O}_7 \longrightarrow 2\text{B}_2\text{O}_3 + \text{H}_2\text{O}$

15. How will you identify borate radical?

- ❖ Boric is heated with ethyl alcohol in presence of con. H_2SO_4 , an ester trialkyl borate is formed.
- ❖ The vapour of this ester burns with a green flame.



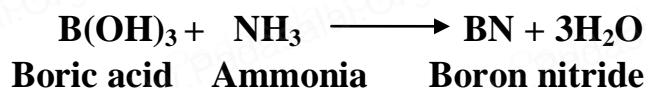
16. Write a note on zeolites.

- ❖ Zeolites are porous hydrated aluminosilicate minerals made from interlinked tetrahedra of Alumina(AlO_4) and Silica (SiO_4).
- ❖ In Zeolites the pore sizes are nearly uniform, allowing the crystal to act as a molecular sieve.
- ❖ Zeolite does not change its crystal structure even after undergoing dehydration.

- ❖ Its easy movement of water and ions within the structure make it suitable for various applications.
- ❖ This makes it possible to reverse dehydration and positive ion exchange (cation exchange).
- ❖ This is utilized for Water softening and purification processes, Catalysts.

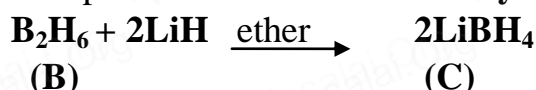
17. How will you convert boric acid to boron nitride?

Fusion of urea with $B(OH)_3$, in an atmosphere of ammonia at 800 - 1200 K gives boron nitride.



18. A hydride of 2nd period alkali metal (A) on reaction with compound of Boron (B) to give a reducing agent (C). Identify A, B and C.

- ❖ Hydride of 2nd period alkali metal (A) is **LiH (Lithium Hydride)**
- ❖ LiH reacts with compound of Boron (B) B_2H_6 to give reducing agent (C) Lithium boro hydride.
- ❖ Compound B is **Diborane**.
- ❖ Compound C is **Lithium boro hydride**.



19. A double salt which contains fourth period alkali metal (A) on heating at 500K gives (B).aqueous solution of (B) gives white precipitate with $BaCl_2$ and gives a red colour compound with alizarin. Identify A and B.

A double salt which contains fourth period alkali metal (A) is **Potash alum**.



(A) on heating at 500 K gives $K_2SO_4 \cdot Al_2(SO_4)_3$ (B) which is **burnt alum**.



20. CO is a reducing agent . justify with an example.

- ❖ CO is a strong reducing agent.
- ❖ It reduces metallic oxide into metals.
- ❖ Ex: $3CO + Fe_2O_3 \rightarrow 2Fe + 3CO_2$

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D-Block elements

1. What are transition metals? Give four examples.

The Metals whose atom have a partially filled d sub-shell, or which can give rise to cations with an incomplete d sub-shell is called transition metals. Ex. **Iron, Cobalt, Nickel, Copper.**

2. Explain the oxidation states of 3d series elements.

- ❖ Transition metals in 3d series exhibit two or more oxidation states.
- ❖ By losing electrons from $(n-1)d$ orbital and ns orbital as the energy difference between them is very small.
- ❖ The beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.
- ❖ The number of oxidation states increases with the number of electrons available.
- ❖ Sc has only one oxidation state +3; the middle element Mn has six different oxidation states from +2 to +7.
- ❖ The last element Cu shows +1 and +2 oxidation states only.

3. What are inner transition elements?

- ❖ Elements whose f orbital getting filled up by electrons are called **f block elements or inner transition elements.**
- ❖ These elements have electrons, (1 to 14) in the f orbital, (0 to 1) in the d orbital of the penultimate energy level and in the outermost orbital.

4. Justify the position of lanthanides and actinides in the periodic table.

- ❖ The actual position of Lanthanides in the periodic table is at group number 3 and period number 6.
- ❖ The sixth period after lanthanum, the electrons are preferentially filled in inner $4f$ sub shell.
- ❖ These fourteen elements following lanthanum show similar chemical properties.
- ❖ Therefore these elements are grouped together and placed at the bottom of the periodic table.
- ❖ Lanthanides have general electronic configuration $[\text{Xe}] 4f^{1-10} 5d^{0-1} 6s^2$
- ❖ The common oxidation state of lanthanides is +3.
- ❖ If we place these elements after Lanthanum in the periodic table below 4d series, the properties of the elements belongs to a group would be different and it would affect the proper structure of the periodic table.
- ❖ Hence a separate position is provided to the inner transition elements

5. What are actinides? Give three examples.

The fourteen elements following actinium starting from Thorium (Th) to Lawrentium (Lr) are called actinides. Ex: Thorium, Uranium, Neptunium

6. Why Gd^{3+} is colourless?

- ❖ The atomic no. of Gd is 64. Electronic configuration is $[\text{Xe}]4f^7 5d^1 6s^2$.
- ❖ In Gd^{3+} , there are 61 electrons. The electronic configuration will be $[\text{Xe}]4f^7 5d^0 6s^0$.
- ❖ Hence no electrons are there in outer d orbital. Due to this it is colourless.

7. Explain why compounds of Cu^{2+} are coloured but those of Zn^{2+} are colourless.

- ❖ Cu^{2+} has an unpaired electron and its configuration is $[\text{Ar}] 3d^9$.
- ❖ Unpaired electrons leads to paramagnetism.
- ❖ It allows d-d electron transition in the visible region, so the ion is coloured.
- ❖ Zn^{2+} has no paired electron and its configuration $[\text{Ar}] 3d^{10}$.
- ❖ Pairing electrons leads to diamagnetism. No d-d transition in it. So it is colourless

8. Describe the preparation of potassium dichromate.

- ❖ The reaction can be given as:
- ❖ $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$
- ❖ The solution of sodium chromate (Na_2CrO_4) is further purified with sulphuric acid to form a solution from which the crystals of orange coloured sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) can be extracted.
- ❖ $2\text{Na}_2\text{CrO}_4 + 2\text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O}$
- ❖ Now potassium dichromate can be obtained by reacting a solution of sodium dichromate with potassium chloride.
- ❖ $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$
- ❖ Thus we finally obtain the *orange crystals of potassium dichromate*.

9. What is lanthanide contraction and what are the effects of lanthanide contraction?

- ❖ The increase in atomic number from La To Lu, the number of electrons in the 4f orbital also increases.
- ❖ The 4f electrons have poor shielding effect.
- ❖ The attraction of the nucleus for the outermost electrons increases. This results in a steady decrease in the size of lanthanides with the increase in the atomic number.
- ❖ This is termed as lanthanide contraction.
- ❖ **Consequences:**
- ❖ Due to lanthanide contraction that there is variation in the basic strength of lanthanide hydroxides. Basic strength decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$.
- ❖ There is similarity in the properties of second and third transition series.
- ❖ Regular decrease in atomic radii.

11. What are interstitial compounds?

- ❖ Transition metal has a void in their crystal lattice structure.
- ❖ Small non-metallic atoms and molecules like hydrogen, boron, carbon etc can be trapped in the void during crystal structure formation.
- ❖ These are called interstitial compounds.
- ❖ They are neither ionic nor covalent and non-stoichiometric as in TiC , $\text{ZrH}_{1.92}$.

12. Calculate the number of unpaired electrons in Ti^{3+} , Mn^{2+} and calculate the spin only magnetic moment.

- ❖ $\text{Ti}^{3+} = 3d^1$; $n=1$ $\sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$
- ❖ $\text{Mn}^{2+} = 3d^5$; $n=5$ $\sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}$

13. Write the electronic configuration of Ce^{4+} and Co^{2+} .

❖ Electronic configuration of Ce^{4+} is $[Xe] 4f^0 5d^0 6s^0$

❖ Electronic configuration of Co^{2+} is $[Ar] 3d^7$

14. Explain briefly how +2 states becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

❖ On moving from Sc to Mn, the atomic number increases from 21 to 25. This means the number of electrons in the 3d-orbital also increases from 1 to 5.

Sc (+2) = d^1 , Ti (+2) = d^2 , V (+2) = d^3 , Cr (+2) = d^4 , Mn (+2) = d^5

❖ +2 oxidation state is attained by the loss of the **two** 4s electrons by these metals.

❖ Since the number of d electrons in (+2) state also increases from Ti^{+2} to Mn^{+2}

❖ The stability of +2 state increases as d-orbital is becoming more and more half-filled.

❖ Mn (+2) has d^5 electrons and it is half-filled d shell, which is highly stable.

15. Which is more stable? Fe^{3+} or Fe^{2+} explain.

❖ Fe^{3+} ion is **more stable** due to its half-filled 3d⁵ electron configuration and it has 5 unpaired electrons

❖ Fe^{2+} ion is partially filled d sub shell and it has 4 unpaired electrons.

❖ So Fe^{3+} is more stable than Fe^{2+} .

16. Explain the variation in $E^0 M^{3+} / M^{2+}$ 3d series.

❖ Transition metals in their high oxidation states tend to be oxidizing.

Reaction	Standard reduction potential (V)
$Ti^{3+} + e^- \longrightarrow Ti^{2+}$	-0.37
$V^{3+} + e^- \longrightarrow V^{2+}$	-0.26
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	-0.41
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	+1.51
$Fe^{3+} + 2e^- \longrightarrow Fe^{2+}$	+0.77
$Co^{3+} + 2e^- \longrightarrow Co^{2+}$	+1.81

❖ For example, Fe^{3+} is moderately a strong oxidant, and it oxidizes copper to Cu^{2+} ions.

❖ The negative values for titanium, vanadium and chromium indicate that the higher oxidation state is preferred.

❖ If we want to reduce such a stable Cr^{3+} ion, strong reducing agent which has high negative value for reduction potential like metallic zinc is required.

The high reduction potential of

Mn^{3+}/Mn^{2+} indicates Mn^{2+} is more stable than Mn^{3+} .

17. Compare lanthanides and actinides.

S.no	Lanthanoids	Actinoids
1.	Differentiating electron enters in 4f Orbital	Differentiating electron enters in 5f Orbital
2.	Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower
3.	They show less tendency to form Complexes	They show greater tendency to form Complexes
4.	Most of the lanthanoids are colourless	Most of the actinoids are coloured. For example. U^{3+} (red), U^{4+} (green), UO_2^{2+}

5.	They do not form oxo cations.	They do form oxo cations such as UO_2^{2+}
6.	Besides +3 oxidation states they show +2 and +4 oxidation states in few cases.	Besides +3 oxidation states they show higher oxidation states such as +4, +5, +6 and +7.

18. Explain why Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing.

- ❖ $\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+}$ E^0 value for $\text{Cr}^{3+}/\text{Cr}^{2+}$ is -0.41 V.
- ❖ Cr^{2+} is strongly reducing in nature. While acting as a reducing agent, it gets oxidized to Cr^{3+} .
- ❖ $\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}$ E^0 value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ is +1.57 V.
- ❖ Mn^{3+} acts as an oxidizing agent and gets reduced to Mn^{2+} .
- ❖ It has exactly half-filled d-orbital and has an extra-stability.

19. Compare the ionization enthalpies of first series of the transition elements.

- ❖ The first ionization enthalpies in each series increases gradually as we move from left to right.
- ❖ This is due to increase in nuclear charge corresponding to the filling of d electrons.
- ❖ The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular.
- ❖ The added electron enters (n-1) d orbital and the inner electrons act as a shield and decrease the effect of nuclear charge on valence ns electrons.
- ❖ Therefore, it leads to variation in the ionization energy values.

20. Actinide contraction is greater from element to element than the lanthanide contraction, why?

- ❖ In actinides, 5f orbitals are filled.
- ❖ Due to poor shielding effect of 5f, there will be increased nuclear charge on element to element of actinoid series.
- ❖ Hence, the size contraction in actinides is greater as compared to that in lanthanides.

21. Out of $\text{Lu}(\text{OH})_3$ and $\text{La}(\text{OH})_3$ which is more basic and why?

- ❖ Due to lanthanide contraction the size of lanthanide ions decreases from La^{3+} to Lu^{3+} .
- ❖ The covalent character of the hydroxides increases and the basic strength decreases.
- ❖ $\text{La}(\text{OH})_3$ is most basic and $\text{Lu}(\text{OH})_3$ is least basic.

22. Why europium (II) is more stable than Cerium (II)?

- ❖ Eu(II) has electronic configuration is $[\text{Xe}] 4f^7 5d^0$.
- ❖ Eu (II) has a half filled 4f subshell that provides it an extra stabilization energy.
- ❖ While in Ce(II) neither 4f subshell or 5d shell are not half filled.
- ❖ So Eu(II) is more stable than Ce(II)

23. Why do Zirconium and Hafnium exhibit similar properties?

- ❖ Zirconium and hafnium have very similar chemical behaviour, having closely similar radii due to lanthanide contraction
- ❖ Radius-dependent properties such as **lattice energies and stability constants of complexes** are also similar.
- ❖ Because of this similarity hafnium is found only in association with zirconium.

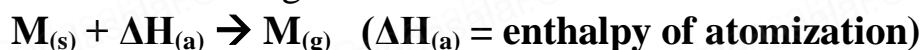
24. Which is stronger reducing agent Cr^{2+} or Fe^{2+} ?

- ❖ Cr^{2+} is a stronger reducing agent than Fe^{2+} .
- ❖ The standard electrode potential values $E^\circ(\text{Cr}^{3+}/\text{Cr}^{2+}) = -0.41 \text{ V}$ and
- ❖ $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}$.
- ❖ Cr^{2+} is easily oxidised to Cr^{3+} but Fe^{2+} cannot be as readily oxidised to Fe^{3+} .

25. The $E^\circ \text{M}^{2+}/\text{M}$ value for copper is positive. Suggest a possible reason for this.

The $E^\circ(\text{M}^{2+}/\text{M})$ value of a metal depends on the energy changes involved in the following:

1. Sublimation: The energy required for converting one mole of an atom from the solid state to the gaseous state.



2. Ionization: The energy required to take out electrons from one mole of atoms in the gaseous state.



3. Hydration: The energy released when one mole of ions are hydrated.



Now, copper has a high energy of atomization and low hydration energy. Hence, the $E^\circ(\text{M}^{2+}/\text{M})$ value for copper is positive.

26. Predict which of the following will be coloured in aqueous solution Ti^{2+} , V^{3+} , Sc^{4+} , Cu^+ , Sc^{3+} , Fe^{3+} , Ni^{2+} and Co^{3+}

Ionic State	Electronic configuration in ionic state
Ti^{3+}	$[\text{Ar}] 3d^1$
V^{3+}	$[\text{Ar}] 3d^2$
Cu^+	$[\text{Ar}] 3d^{10}$
Sc^{3+}	$[\text{Ar}]$
Mn^{2+}	$[\text{Ar}] 3d^5$
Fe^{3+}	$[\text{Ar}] 3d^5$
Co^{2+}	$[\text{Ar}] 3d^7$

❖ The ions which have the electrons in d-orbital and in which d-d transition is possible will be coloured. The ions in which d-orbitals are empty or completely filled will be colourless as no d-d transition is possible in those configurations

❖ It can be easily observed that only Sc^{3+} has an empty d-orbital and Cu^+ has completely filled d-orbitals.

❖ All other ions, except Sc^{3+} and Cu^+ , will be coloured in aqueous solution because of d -

d transitions.

27. Describe the variable oxidation state of 3d series elements.

- ❖ The variable oxidation states shown by the transition elements are due to the participation of outer ns and inner (n-1)d-electrons in bonding.

- ❖ Except scandium, the most common oxidation state shown by the elements of first transition series is +2. This oxidation state arises from the loss of two 4s electrons.
- ❖ This means that after scandium, d-orbitals become more stable than the s-orbital.

Elements	Outer electronic configuration	Oxidation states
Sc	3d ¹ 4s ²	+ 2, + 3
Ti	3d ² 4s ²	+ 2, + 3, + 4
V	3d ³ 4s ²	+ 2, + 3, + 4, + 5
Cr	3d ⁵ 4s ¹	+ 1, + 2, + 3, + 4, + 5, + 6
Mn	3d ⁵ 4s ²	+ 2, + 3, + 4, + 5, + 6, + 7
Fe	3d ⁶ 4s ²	+ 2, + 3, + 4, + 5, + 6
Co	3d ⁷ 4s ²	+ 2, + 3, + 4
Ni	3d ⁸ 4s ²	+ 2, + 3, + 4
Cu	3d ¹⁰ 4s ¹	+ 1, + 2
Zn	3d ¹⁰ 4s ²	+ 2

28. Which metal in the 3d series exhibits +1 oxidation state most frequently and why?

- ❖ Cu exhibits +1 oxidation state very frequently.
- ❖ It is because Cu (+1) has an electronic configuration of [Ar] 3d¹⁰ 4s¹.
- ❖ It can easily lose 4s¹ electron and it gives stable d¹⁰ configuration.

29. Why first ionization enthalpy of chromium is lower than that of zinc?

- ❖ The electronic configuration of Zn is Zn = Ar 3d¹⁰ 4s² and Cr is Ar 3d⁵ 4s¹.
- ❖ Ionisation enthalpy of Cr is lower than that of Zinc because in case of zinc first electron has to be removed from fulfilled orbital.
- ❖ The full filled electronic configuration is most stable so it requires high energy to remove electron from it.
- ❖ While in case of Chromium electron is easily removed from half filled orbital with less amount of energy.

30. Transition metals show high melting points why?

- ❖ Unpaired electrons and the empty or partially filled d-orbitals form covalent bonding in addition to the metallic bonding by s-electrons.
- ❖ Because of such strong bonding, d-block elements have high melting and boiling points than s and p block elements.
- ❖ This trend goes till d⁵ configuration and then decreases as more electrons get paired in the d-orbital.
- ❖ Cr, Mo and W possess the highest melting and boiling point in their series of elements.
- ❖ Manganese (Mn) and Technetium (Tc) have half-filled configuration resulting in weak metallic bonding and abnormally low melting and boiling points.
- ❖ Group 12, Zn, Cd and Hg have no unpaired d-electrons and hence no covalent bonding. Their melting and boiling point will be the lowest in their series.

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METALLURGY

ANSWER THE FOLLOWING QUESTIONS:

1. What is the difference between minerals and ores?

MINERAL	ORE
1. Naturally occurring substances of metals present in the earth's crust are called minerals	1. Minerals which can be used to obtain the metal profitably are called ores
2. All minerals are not ores	2. All ores are essentially minerals too
3. Ex: Clay is the mineral of Al	3. Bauxite are the main ore of Al

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

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

- ❖ Concentration of the ore
- ❖ Extraction of crude metal
- ❖ Refining of crude metal

3. What is the role of Limestone in the extraction of Iron from its oxide Fe_2O_3 ?

- ❖ Iron is extracted from its ore, haematite, in a blast furnace.
- ❖ The ore is fed into the top of the furnace along with coke and limestone.
- ❖ The limestone decomposes in the hot furnace, forming calcium oxide.
- ❖ This reacts with the sandy impurities (silicon dioxide) to form a slag.

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

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

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

- ❖ Coke is definitely the better reducing agent for the reduction of zinc oxide (ZnO) than carbon monoxide.
- ❖ The Gibbs free energy of formation becomes lower at temperatures above 1273 K, for CO_2 from C.
- ❖ In case of CO_2 from CO , the Gibbs free energy of formation is always higher than ZnO .
- ❖ Therefore, C is always considered better than CO for carrying out the reduction of Zn from ZnO at lower temperatures.

6. Describe a method for refining nickel.**Mond process for refining nickel:**

The impure nickel is heated in a stream of CO at around 350 K. The nickel reacts with the CO to form a highly volatile nickel tetracarbonyl. The solid impurities are left behind.



On heating the nickel tetracarbonyl around 460 K, the complex decomposes to give pure metal.

**7. Explain zone refining process with an example using the Ellingham diagram given below.**

- ❖ This method is based on the principle that impurities are more soluble in the molten state of metal (the melt) than in the solid state.
- ❖ In the process of zone refining, a circular mobile heater is fixed at one end of a rod of impure metal.
- ❖ As the heater moves, the molten zone of the rod also moves with it.
- ❖ As a result, pure metal crystallizes out of the melt and the impurities pass on to the adjacent molten zone.
- ❖ This process is repeated several times, which leads to the segregation of impurities at one end of the rod.
- ❖ Then, the end with the impurities is cutoff.
- ❖ Si, B, Ga, In can be purified by this process.

8. (A) Predict the conditions under which**(i) Aluminium might be expected to reduce magnesia.**

Above 1350°C, the standard Gibbs free energy of formation of Al₂O₃ from Al is less than that of MgO from Mg.

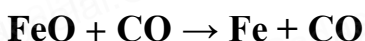
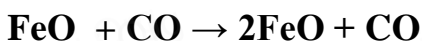
Therefore, above 1350°C, Al can reduce MgO.

(ii) Magnesium could reduce alumina.

Temperature below the point of intersection of Al₂O₃ and MgO curves, magnesium could reduce alumina. But the process will be uneconomical. MgO can Al₂O₃ reduce at any temperature below 1400°

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

In the production of iron from its oxide ore, the mixture of ore, coke and limestone is heated with a blast of air in furnace. Below 983K oxides of iron are reduced by carbon monoxide to iron.



Above 983K, FeO undergoes reduction by hot coke to iron. This region is called fusion zone

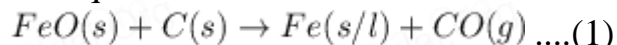


Thus carbon monoxide is more effective agent than carbon below 983K.

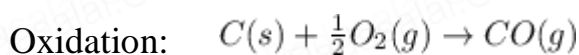
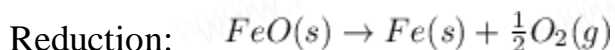
(C) it is possible to reduce Fe_2O_3 by coke at a temperature around 1200K .

The reducing agent used for reducing iron(III) oxide to iron is carbon monoxide and coke.

The equation for the reduction of iron oxide by coke, the reaction follows:



The two half reactions for the above reaction is given by the equations:



The net free energy change of the above reactions is:

$$\Delta G_{(\text{FeO}, \text{Fe})}^o + \Delta G_{(\text{C}, \text{CO})}^o = \Delta_r G^o$$

Below 1000 K, formation of FeO is more than the formation of Fe from CO. So, CO is the reducing agent for below 1000 K. As, above 1000 K, $\Delta_r G^o$ becomes negative and the reaction 1 becomes favourable.

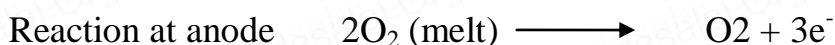
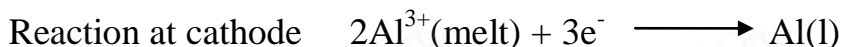
Hence, C is a better reducing agent than CO above 1000 K.

9. Give the uses of zinc.

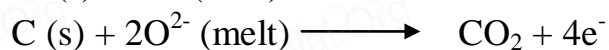
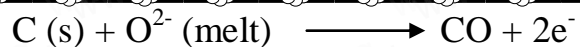
- ❖ It is used in galvanizing metals such as iron from corrosion
- ❖ It is used to produce die-castings in the automobile, electrical industries
- ❖ It is used in the manufacture of paints, rubber, cosmetics
- ❖ Brass an alloy of zinc is used in water valves as it is highly resistant to corrosion.

10. Explain the electrometallurgy of Aluminium.

- ❖ A fused mixture of purified alumina, and cryolite is taken in iron chamber.
- ❖ In this electrolysis, graphite is used as the anode and graphite-lined iron is used as the cathode. During the electrolysis, Al is liberated at the cathode, while CO and CO_2 are liberated at the anode.
- ❖ About 10% Calcium chloride is also added to the solution. Here CaCl_2 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.



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



Due to the above two reactions, anodes are slowly consumed during the electrolysis. The pure Al is formed at the cathode and settles at the bottom.

The net electrolysis reaction can be written as follows.



11. Explain the following terms with suitable examples.

(i) Gangue :

Sand, rock, and other impurities surrounding the mineral of interest in an ore .

An **example** of **gangue** is the rock surrounding a deposit of gold.

(ii) Slag:

Slag is waste matter separated from metal during smelting.

An **example** of **slag** is the iron and silica that is removed during copper and lead smelting

12. Give the basic requirement for vapour phase refining.

i) The metal should form a volatile compound with available reagent.

(ii) The volatile compound should be easily decomposable so that the recovery is easy.

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

(i) Silica in the extraction of copper.

During the roasting of pyrite ore, a mixture of FeO and Cu₂O is obtained.



The role of silica in the metallurgy of copper is to remove the iron oxide obtained during the process of roasting as 'slag'.

If the sulphide ore of copper contains iron, then silica (SiO₂) is added as flux before roasting.

Then, FeO combines with silica to form iron silicate, FeSiO₃ (slag).



(ii) Cryolite in the extraction of aluminium.

Cryolite (Na₃AlF₆) has two roles in the metallurgy of aluminium:

1. To decrease the melting point of the mixture from 2323 K to 1140 K.
2. To increase the electrical conductivity of Al₂O₃.

(iii) Iodine in the refining of Zirconium.

Zirconium metal is heated with **iodine** in an evacuated vapour to separate from impurities. This decomposes at 1800K to give a pure **Zirconium** metal and **iodine**.

Iodine is heated with **Zirconium** to form a volatile compound and decompose to give pure **zirconium**.

(iv) Sodium cyanide in froth floatation.

When a sulphide ore of a metal of interest contains other metal sulphides as impurities, depressing agents such as sodium cyanide, sodium carbonate etc are used to selectively prevent other metal sulphides from 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 $\text{Na}_2[\text{Zn}(\text{CN})_4]$ on the surface of zinc sulphide.

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

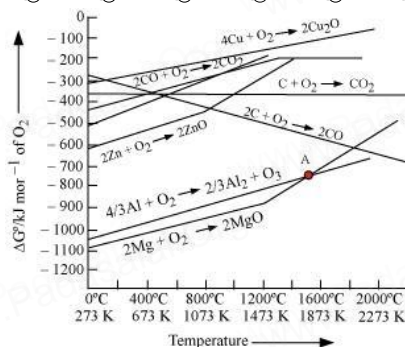
- ❖ It is carried out in an electrolytic cell containing aqueous solution of the salts of the metal
- ❖ The rods of impure metal are used as anode and thin strips of pure metal are used as cathode.
- ❖ The metal dissolves from the anode, pass into the solution while the same amount of metal ions from the solution will be deposited at the cathode.
- ❖ During electrolysis, the less electropositive impurities in the anode, settle down at the bottom and are removed as anode mud.

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
- ❖ Reaction at cathode: $2\text{Ag} (\text{s}) \longrightarrow \text{Ag}^+ (\text{aq}) + 1\text{e}^-$
- ❖ Reaction at anode: $\text{Ag}^+ (\text{aq}) + 1\text{e}^- \longrightarrow \text{Ag} (\text{s})$
- ❖ During electrolysis, at the anode the silver atoms lose electrons and enter the solution. The positively charged silver cations migrate towards the cathode and get discharged by gaining electrons and deposited on the cathode.

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

- ❖ Thermodynamic factor has a major role in selecting agent for a particular reaction. Only that reagent will be preferred which will lead to decrease in the free energy at a certain specific temperature.



❖ It can be observed from the above graph that a metal can reduce the oxide of other metals, if the standard free energy of formation $\Delta_f G^\circ$ of the oxide of the former is more negative than the latter.

❖ For example, since $\Delta_f G^\circ(\text{Al}, \text{Al}_2\text{O}_3)$ is more negative than $\Delta_f G^\circ(\text{Cu}, \text{Cu}_2\text{O})$, Al can reduce Cu_2O to Cu, but Cu cannot reduce Al_2O_3 .

❖ Similarly, Mg can reduce ZnO to Zn, but Zn cannot reduce MgO because $\Delta_f G^\circ(\text{Mg}, \text{MgO})$ is more negative than $\Delta_f G^\circ$

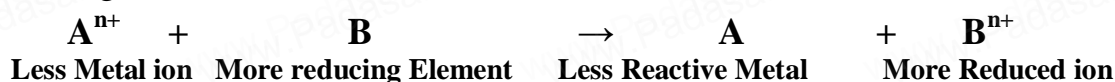
(Zn, ZnO).

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.

- ❖ The principles of metallurgy are effective in the reduction of metal ions to their respective metals in their solution (or) molten states.
- ❖ The reduction is carried out through electrolysis (or) using reducing elements. Such methods are based on electrochemical principles.
- ❖ $\Delta G^\circ = -nE^\circ F$
 n = Number of Electrons Gained
 E° = Electrode Potential of Redox Couple
- ❖ The value of E° for a metal depends on its reactivity. Thus, it differs from metal to metal. More reactive metals have high E° , whereas less reactive metals have low E° . It is difficult to reduce metals that have high E° .
- ❖ If the difference between the E° values of two metals is positive, then the value of ΔG° will be negative.
- ❖ Hence, the less reactive metal will come out of the solution and the more reactive metal will go into the solution.



Ex: The reduction of copper (II) to copper in the presence of iron.



In a simple electrolysis process, the positive ions always move towards the negative electrode called the cathode.

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SOLID STATE

ANSWER THE FOLLOWING QUESTIONS:

1. Define unit cell.

The smallest group of atoms or molecules whose repetition at regular intervals in three dimensional lattice of crystal is called unit cell.

2. Give any three characteristics of ionic crystals.

- ❖ Ionic solids have high melting points.
- ❖ These solids do not conduct electricity, because the ions are fixed in their lattice positions.
- ❖ They do conduct electricity in molten state (or) when dissolved in water because, the ions are free to move in the molten state or solution.

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.	They are anisotropic in nature	They are isotropic like liquids
4.	They have sharp melting points.	They soften over a range of temperature
5.	Definite heat of fusion	Heat fusion is not definite
6.	Ex. NaCl, Diamond	Ex. Glass, Rubber, Plastic

5. Explain briefly seven types of unit cell.

- ❖ A unit cell is characterised by the three edge lengths or lattice constants a , b and c and the angle between the edges α , β and γ .
- ❖ There are seven primitive crystal systems; cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic and rhombohedral.
- ❖ They differ in the arrangement of their crystallographic axes and angles.

S.NO	Crystal class	Axial distance	Axial angles	Possible Types	Examples
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, fcc, bcc	NaCl
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, bcc	SnO ₂
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, fcc, bcc, end centered	BaSO ₄
4.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ ; \gamma = 120^\circ$	Primitive	ZnO
5.	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Primitive	HgS
6.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ ; \beta \neq 90^\circ$	Primitive, end centered	Monoclinic Sulphur
7.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Primitive	H ₃ BO ₃

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

S.No	Hexagonal close packing	Cubic close packing.
1.	Tetrahedral voids of a second layer are covered by the spheres of the third layer.	Octahedral voids of a second layer are covered by the spheres of the third layer.
2.	The Spheres of the third layer are exactly aligned with those of first layer.	The Spheres of the third layer are not aligned with those of first layer(a) or second layer (b)
3.	The pattern is repeated in alternate layers as ABA arrangement	The stacking layers is continued as ABC ABC arrangement.
4.	This type of packing is known as hcp arrangement	This type of packing is known as ccp arrangement
5.	The coordination number of each sphere is 12 – six neighbouring spheres in its own layer, three spheres in the layer above and below.	The coordination number of each sphere is 12 – six neighbouring spheres in its own layer, three spheres in the layer above and below.

7. Distinguish tetrahedral and octahedral voids.

Tetrahedral voids	Octahedral voids
It is a vacant space among four spheres having tetrahedral arrangement	It is a void formed by 2 equilateral triangles with apices in opposite directions
There are 2 tetrahedral sites for each sphere	There is only 1 octahedral site for each sphere

8. What are point defects?

Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance. Point defects can be classified into three types :

(1) stoichiometric defects (2) impurity defects (3) non-stoichiometric defects

9. Explain Schottky defect.

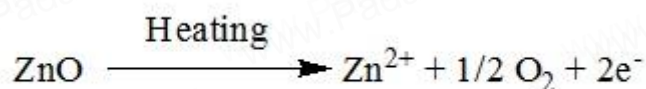
- ❖ Schottky defect occurs when oppositely charged atoms (cation and anion) leave their corresponding lattice sites and create a pair of Vacancy Defects.
- ❖ Since both cation and anion leave the lattice sites at the same time, so overall electrical neutrality of the crystal is maintained.
- ❖ Schottky defects occur in ionic crystals where the size of anion is almost same with the size of the cation. The atoms permanently leave the crystal.
- ❖ One Schottky defect leads to the formation of two vacancies.
- ❖ Two atoms reduce from the crystal for each Schottky defect.
- ❖ Due to vacancy formation, Schottky defect reduces density of the solid.
- ❖ In NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} . Thus, there is one Schottky defect per 10^{16} ions.
- ❖ For example, NaCl, KCl, CsCl and AgBr.

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

Metal excess defect:

- ❖ Metal excess defect due to anionic vacancies.

- ❖ This type of defect is exhibited by alkali halides like NaCl and KCl.
- ❖ Application of heat to NaCl in an atmosphere of sodium vapour results in deposition of the sodium atoms on the surface of the crystal.
- ❖ The sodium atoms lose electron to form Na^+
- ❖ The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl.
- ❖ The released electrons diffuse into the crystal and occupy anionic sites.
- ❖ The anionic sites occupied by unpaired electrons are called F-centres that imparts yellow colour to the crystals of NaCl due to the excitation of the electrons on absorption of energy from the visible light falling on the crystals.
- ❖ Metal excess defect due to the presence of extra cations at interstitial sites.
- ❖ Heating Zinc oxide that exists in white colour at room temperature loses oxygen and turns yellow.



- ❖ This results in excess of zinc in the crystal and its formula becomes Zn_{1+x}O .
- ❖ The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

Metal deficiency defect:

- ❖ Many solids possess less amount of the metal as compared to the stoichiometric proportion.
- ❖ For example, FeO is mostly found with a composition ranging from $\text{Fe}_{0.93}\text{O}$ to $\text{Fe}_{0.96}\text{O}$.
- ❖ In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+}

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

AAAA type:

- ❖ This can be obtained by repeating the AAAA type two dimensional arrangements 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.
- ❖ This is known as simple cubic arrangement
- ❖ In simple cubic packing, each sphere is in contact with 6 neighbouring spheres.
- ❖ Four in its own layer, one above and one below.
- ❖ The coordination number of the sphere in simple cubic arrangement is 6.

ABABA type:

- ❖ 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.

- ❖ 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.
- ❖ This is body centered cubic arrangement

ABC ABC type:

- ❖ The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids.
- ❖ When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called “C”
- ❖ Only when fourth layer is placed, its spheres are aligned with those of the first layer.
- ❖ This pattern of layers is often written as ABCABC.....
- ❖ This structure is called cubic close packed (ccp) or face-centered cubic (fcc) structure.
- ❖ Each sphere is in contact with twelve spheres.
- ❖ The coordination number is 12.

12. Why ionic crystals are hard and brittle?

The ionic compounds are very hard and brittle. In ionic compounds the ions are rigidly held in a lattice because the positive and negative ions are strongly attracted to each other and difficult to separate.

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

The second row can be placed in contact with the first row in such a way that the spheres of second row are exactly above the first row.

- ❖ The spheres of the two rows are aligned horizontally as well as vertically.
- ❖ Let the first row be ‘A’ type row and the second row is also of ‘A’ type due to its similarity with the first one.
- ❖ Similarly, we may place more rows to obtain AAA type of arrangement.
- ❖ Each sphere is in contact with four of its surrounding atom. Thus, the two dimensional coordination numbers is 4.

If the centers of these 4 immediate surrounding spheres are joined, a square is formed. Due to which this packing is known as square close packing in two dimension

14. What is meant by the term “coordination number”? What is the coordination number of atoms in a bcc structure?

Coordination number: - it is the total number of surrounding atoms of any constituent particle present in the crystal lattice.

The coordination number of atoms in a body-centred cubic structure is 8.