"May God's guidance be with you during the Exam and may you be able to answer each question correctly. My prayers and Blessings are with you". - ACTC EMS

"Everything is chemistry, without chemistry Nothing"

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+2 CHEMISTRY MATERIAL & QBANK 2024-25

CLASS 12 VOLUME 1 & II **(WITH TEXT BOOK PAGE NUMBER)**

Unit 1: METALLURGY

Answer the following questions: BOOK BACK

1. What is the difference between minerals and ores? (S20, M22 2M, M24 5Mi)

Minerals	**Ores**
A naturally occurring substance obtained by mining which contain the metal in free state or in the form of compounds.	Minerals that contain ***high percentage metal***, from which it can be extracted ***conveniently*** and ***economically*** are called ores.
All minerals are not ores	All ores are Minerals
It contains a ***low* percentage of metal**	It contains a ***high* percentage of metals**
Ex: China clay **$Al_2O_3.2SiO_2.2H_2O$**	**Ex:** Hematite, Magnetite

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

The various steps involved in the extraction pure metals from their ores are

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

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

- In this extraction, a ***basic flux,*** quicklime (CaO) is used, since the gangue present in the ore is silica is which acidic in nature.
- The quicklime combines with it to form calcium silicate (slag).
  - $\underset{\textbf{Flux}}{CaO_{(s)}} + \underset{\textbf{Gangue}}{SiO_{2(s)}} \rightarrow \underset{\textbf{Slag}}{CaSiO_{3(s)}}$

4. Which type of ores can be concentrated by froth floatation method? Give two examples for such ores. (J20, M23 2M

- **Sulphide ores** can be concentrated by froth floatation method.
- **Example:** Galena (PbS) and Zinc blende (ZnS)

5. Describe a method for refining nickel. M22 5Mii

- **Mond process**

- **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.

$$Ni_{(s)} + 4\,CO_{(g)} \xrightarrow{350K} Ni(CO)_{4(g)}$$

On heating the nickel tetracarbonyl around 460 K, the complex decomposes and gives pure metal.

$$Ni(CO)_{4(g)} \xrightarrow{460K} Ni_{(s)} + 4\,CO_{(g)}$$

6. Explain zone refining process. PTA, M20, M23 5M

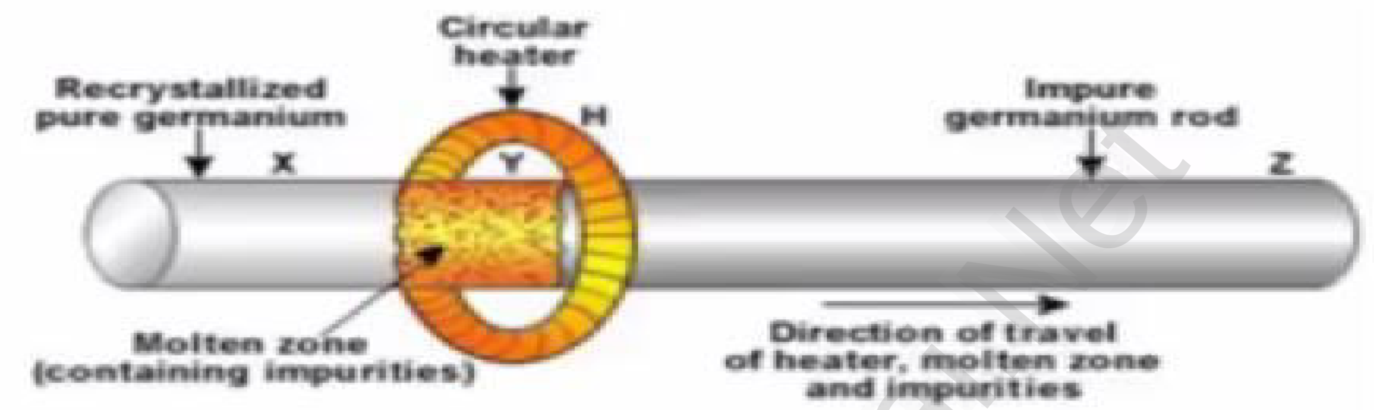
Principle:

- This method is based on the principles of **fractional crystallisation.**
- When an impure metal is melted and allowed to solidify, the impurities will prefer to be in the molten region. **i.e. impurities are more soluble** in the melt than in the **solid-state metal**.

Experiment:

- In this process the impure metal is taken in the form of a rod.
- One end of the rod is heated using a mobile induction heater which results in **melting of the metal** on that portion of the rod.
- When the heater is slowly moved to the other end the pure metal crystallizes while the **impurities will move** 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.

- The process is repeated several times by moving the heater in the same direction again and again to achieve the desired purity level.
- This process is carried out in an **inert gas atmosphere** to **prevent the oxidation of metals.**
  Ex: Elements such as Germanium (Ge), Silicon (Si) and Galium (Ga) that are used as semiconductor are refined using this process.



Zone refining of germanium metal.

7. (A) Predict the conditions under which

(i) Aluminium might be expected to reduce magnesia.

- From Ellingham diagram temperature above 1623K (1350°C), the stability of Al_2O_3 is higher than MgO.
- ΔG^o value for Al_2O_3 is less as compared to that of MgO above 1623K.
- So, Aluminium reduce MgO, gives the stable Al_2O_3 above 1623K.
- $MgO_{(s)} + 2Al_{(s)} \xrightarrow{above 1623K} Al_2O_3 + Mg_{(s)}$

ii) Magnesium could reduce alumina.

$$Al_2O_{3(s)} + 2Mg_{(s)} \xrightarrow{below 1623K} MgO_{(s)} + 2Al_{(s)}$$

Mg can reduce Al_2O_3 to Al below 1623K because ΔG^o value for Mg is less as compared to that of Al_2O_3. But above 1623K Mg could not 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) it is possible to reduce Fe_2O_3 by coke at a temperature around 1200K

Yes, the temperature around 1200K. **Carbon lines** below the iron line in Ellingham diagram. Hence we can use coke as a reducing agent.

Around 1200K ΔG° of formation of Fe_2O_3 has more negative value than ΔG° of formation of CO_2 from C.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO + heat$$

8. Give the uses of zinc.

(i) Metallic zinc is used in **Galvanising** metals such as iron and steel to protect them from rusting and corrosion.

(ii) It is used to produce **die-castings** in the automobile, electrical and hardware industries

(iii) **Zinc oxide** is used in the manufacture paints, rubber, cosmetics, plastics, inks, batteries, textiles and electrical equipment.

(iv) **Zinc sulphide** is used in making luminous paints, fluorescent lights and x-ray screens.

(v) **Brass an alloy of zinc** is used in water valves and communication equipment

9. Explain the electrometallurgy of Aluminium.

Hall-Herold process:

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

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

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

(iv) About 10% calcium chloride is also added to the solution. Here calcium chloride helps to lower the melting point of the mixture.

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

(vi) The chemical reactions involved in this process are as follows.

Ionisation of alumina $Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}$

Reaction at cathode $2Al^{3+}{}_{(melt)} + 6e^- \rightarrow 2Al_{(l)}$

Reaction at anode $6O^{2-}{}_{(melt)} \rightarrow 3O_2 + 12e^-$

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

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

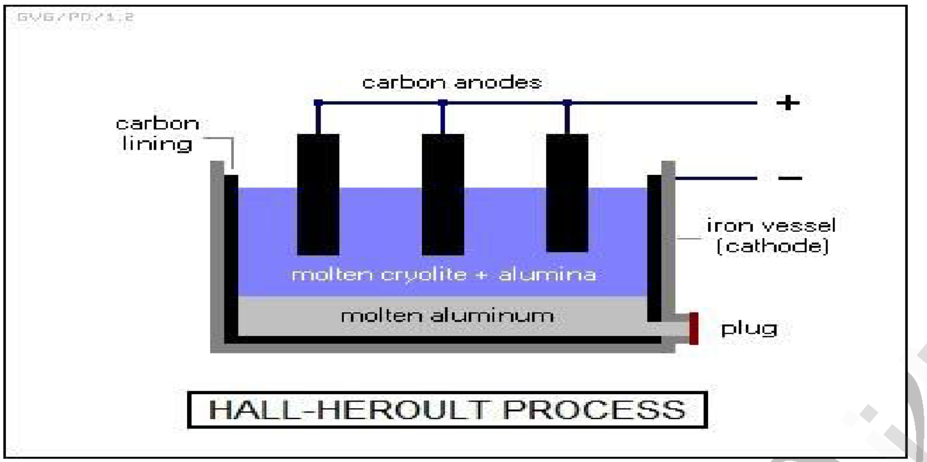
$$C_{(s)} + 2O^{2-} (melt)\ CO_2 + 4e^-$$

(viii) 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.

$$4Al^{3+}{}_{(melt)} + 6O^{2-}{}_{(melt)} + 3C_{(s)} \quad 4Al_{(l)} + 3CO_{2\,(g)}$$



10. Explain the following terms with suitable examples. I) gangue ii)slag (S20)

(i) Gangue: The rocky impurity associated with the ore is called gangue or matrix.

Example: silica (SiO_2) gangue present in the Fe_2O_3

(ii) slag: Slag is the fusible product formed when flux reacts with gangue during the extraction of metal.

- $CaO_{(s)} + SiO_{2(s)} \rightarrow CaSiO_{3(s)}$

Flux **Gangue** **Slag**

11. 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.

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

(i) Silica in the extraction of copper. M24 5Mii

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

$$FeO_{(s)} + SiO_{2(s)} \rightarrow FeSiO_{3(s)}$$

Flux **Gangue** **Slag**

(ii) Cryolite in the extraction of Aluminium.

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

- Aluminium is produced by the electrolytic reduction of fused alumina in the electrolytic cell. Alumina is not an electrolyte. So it is made as an electrolyte by dissolving it in the fused cryolite.
- The function of cryolite is to lower the fusion temperature. (melting point to 1173K)

(iii) Iodine in the refining of Zirconium.

- Zirconium 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.

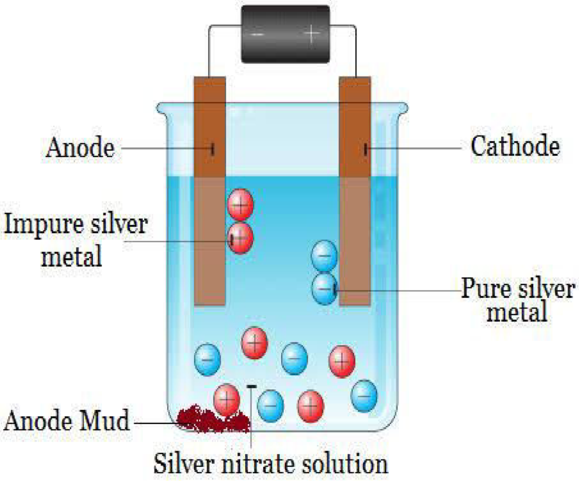
$$\underset{\textbf{(Impure)}}{Zr_{(s)} + 2I_{2(s)}} \xrightarrow{550K} \underset{\text{(volatile)}}{ZrI_4} \xrightarrow{1800K} \underset{\textbf{(Pure)}}{Zr_{(s)}} + 2I_{2(s)}$$

(iv) Sodium cyanide in froth floatation.

- Sulphide ores which are concentrated by the froth floatation process.
- Depressants are used to prevent certain type of particles from forming the froth.
- NaCN is used as a depressant to separate ZnS from PbS.
- It selectively prevents ZnS from coming to forth but allows PbS to come with forth. Because NaCN reacts with ZnS to form $Na_2[Zn(CN)_4]$.

13. Explain the principle of electrolytic refining with an example. J22 5M

- The crude metal is refined by electrolysis.
- It is carried out in an electrolytic cell containing aqueous solution of the salts of the metal of interest.
- The rods of **impure metal** are used as **anode** and **thin strips of pure metal** are used as **cathode.**
- The metal of interest 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 anode: $2Ag_{(s)} \rightarrow Ag^{+}_{(aq)} + 1e^{-}$

Reaction at cathode: $Ag^{+}_{(aq)} + 1e^{-} \rightarrow Ag_{(s)}$

- 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.
- Other metals such as copper, zinc etc., can also be refined by this process in a similar manner.

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

From the Ellingham diagram, it is clear that metals for which the standard free energy of formation ($\Delta_f G^\circ$) of their oxides is more is more negative can reduce the metal oxides for which the standard free energy of formation ($\Delta_f G^\circ$) of oxides is less negative.

Thermodynamic factor has a major role in selecting the reducing agent for a particular reaction. Only that regent will be preferred which will lead be decrease in the free energy (ΔG°) at a certain specific temperature.

E.g: Carbon reduce ZnO to Zn but not CO.

$ZnO + C \rightarrow Zn + CO$

$ZnO + CO \rightarrow Zn + CO_2$

In the first case, there is increase in the magnitude of ΔS° while in the second case, it almost remains the same. In other words, ΔG° will have more negative value in the first case, when C is the reducing agent then in the second case when CO acts as the reducing agent. Therefore, C is better reducing agent.

15. Give the limitations of Ellingham diagram. J23 3M

- Ellingham diagram is constructed based only on thermodynamic considerations.
- It gives information about the thermodynamic feasibility of a reaction.
- ***The interpretation of ΔG is based on the assumption that the reactants are in equilibrium with the product which is not always true.***

- *It does not tell anything about the rate of the reaction.*

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

- Electrochemical principles also find applications in metallurgical process.
- The reduction of oxides of active metals such as **sodium, potassium** etc., by carbon is thermodynamically not feasible.
- Such metals are extracted from their ores by using electrochemical methods.
- 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.
- Gibbs free energy change for the electrolysis process is given by the following expression $\Delta G° = -nFE°$

Where n - number of electrons involved in the reduction process,
F - the Faraday
E^0 - the electrode potential of the redox couple.

- If **E^0 is positive** then the **ΔG is negative** and the **reduction is spontaneous** and hence a redox reaction is planned in such a way that the e.m.f of the **net redox reaction is positive.**
- When a more reactive metal is added to the solution containing the relatively less reactive metal ions, the more reactive metal will go into the solution.
- For example,

$$Cu_{(s)} + 2Ag^{+}_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$

$$Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

Evaluate yourself 1

1. Write the equation for the extraction of silver by leaching with sodium cyanide and show that the leaching process is a redox reaction.

Answer : $\mathbf{4Ag_{(s)} + 8CN^-_{(aq)} + O_{2\,(g)} + 2H_2O_{(l)} \rightarrow 4[Ag(CN)_2]^-_{(aq)} + 4OH^-_{(aq)}}$

(Or) from silver ore to silver

$$4Ag_2S_{(s)} + 8CN^-_{(aq)} + O_{2\,(g)} + 2H_2O_{(l)} \rightarrow 4[Ag(CN)_2]^-_{(aq)} + 4OH^-_{(aq)} + 2S$$

$Zn_{(s)} + 2[Ag(CN)_2]^-_{(aq)} \rightarrow [Zn(CN)_4]^{2-}_{(aq)} + 2Ag_{(s)}$ (Or)

$$\mathbf{Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S}$$

Sodium argento cyanide (soluble)

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

Evaluate yourself 2 2. Magnesite (Magnesium carbonate) is calcined to obtain magnesia, which is used to make refractory bricks. Write the decomposition reaction.

Answer: $MgCO_3 \rightarrow MgO + CO_2$

Evaluate yourself 3

3. **Using Ellingham diagram indicate the lowest temperature at which ZnO can be reduced to Zinc metal by carbon. Write the overall reduction at this temperature.**

Ellingham diagram shows variation in standard Gibbs free energy change with temperature for the formation of oxide. The Ellingham diagram shows straight line upward slope with formation of oxide, but in case of ZnO there is sudden change. Ellingham diagram helps in the selecting suitable reducing agent.

By seeing the Ellingham diagram, the free energy formation ($\Delta_f G^\circ$) of CO from C becomes lower temperatures above 1120 K while that of CO_2 from C becomes lower above 1323 K than $\Delta_f G^\circ$ of ZnO. As $\Delta_f G^\circ$ of CO_2 from CO is always higher than that of ZnO. So C can reduce ZnO to Zn but not CO. Thus carbon is better reducing agent than CO for ZnO.

Evaluate yourself 4

4. Metallic sodium is extracted by the electrolysis of brine (aq. NaCl). After electrolysis the electrolytic solution becomes basic in nature. Write the possible electrode reactions.

Brine is a solution of sodium chloride (molten state).

The process of electrolysis involves using an electric current to bring about a chemical change and mark new chemicals.

In the electrolysis of brine, sodium ions migrate to the cathode, where electrons enter the melt and are reduced to sodium metal.

$Na^+ + e^- \rightarrow Na$ (at cathode)

Chloride ions migrate the other way toward the anode. They give up their electrons to the anode and are oxidised to chlorine gas.

$Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$ (at anode)

Overall Reaction: $2NaCl \rightarrow 2Na_{(s)} + Cl_{2(g)}$

For aqueous solution of NaCl: $H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$ (at cathode)

$Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$ (at anode)

Overall Reaction: $NaCl_{(aq)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)} + H_{2(g)} + \frac{1}{2} Cl_{2(g)}$

After electrolysis the electrolytic solution becomes basic in nature.

[Due to formation of hydroxide (OH^-) ion]

Important Questions

1. Difference between ore and mineral. (2) BB **(S20 2M, M22 2M, M24 5Mi**
2. Write the ores of copper, silver, Aluminium, Iron, zinc (3)
3. What are all the steps involves in metallurgical process?(2)
4. Write note on gravity separation. (3) **M22 5Mi**
5. Explain froth floatation.(6) **(A21) 5M**
6. Describe the underlying principle of forth floatation process. (4) **PTA 2M**
7. Give the depressing agents used in the froth floatation process and why we use depressing agents in that process? (OR)Role of depressing agent in froth floatation process? (4) **PTA2M**
8. Which type of ores can be concentrated by froth flotation method give two examples **(J20, M23 2M**
9. What are leaching process?(4)
10. Explain Cyanide leaching.(4) Explain how gold ore is leached by cyanide process. (4) **GM5Mi**
11. What is Cementation?(4)
12. What is Ammonia leaching.(4)
13. What is Acid leaching?(4) **J22 3M**
14. Explain magnetic separation.(6)
15. How will you manage sulphur dioxide produced during roasting process?(7)
16. Define the following terms (i) Roasting (6) (ii) Calcination (7) **PTA3M, M24 2M**
17. What is smelting? (8)
18. What is the role of quicklime in the extraction of iron from its oxide Fe_2O_3.(8) **(J20)** (BB)
    ANS: Used As Flux. **(Govt. key)**
19. What is Gangue?(3) Explain the following terms with suitable example. a)Gangue b) Slag.(BB) **PTA3M(S20)**
20. Explain extraction of copper from copper pyrites.(8) **PTA5M i**

21. What is the role of silica in the extraction of copper? (8) **M24 5Mii**
22. What is meant by blistered copper.(9)
23. Give one example for (i) Acidic flux (ii) Basic flux (8)
24. CO is reducing agent. Justify with an example. (8)& (LN 2 43) **PTA 2M**
25. Reduction by hydrogen, carbon, metal(9)
26. How Cr_2O_3 is reduced to Cr by Al powder? (10) **PTA 5M ii**
27. Explain Auto reduction.(10)
28. Define, observation, application & **Limitations of Ellingham diagram**. (13) **J23 3M**
29. Extraction of Aluminium-Hall -Herold process. (14)
30. Define refining process(15)
31. Write note on distillation. (15)
32. Write note on Liquation. (15) **J23 5Mii**
33. Explain electrolytic refining of silver. (16) **PTA5M ii** (Explain the principle of electrolytic refining with an example. **J22 5M)**
34. Explain zone refining process.(16) **M20 5M, M23 5M PTA 3M**
35. Explain Mond process. (Describe the method for refining of Nickel.) (16) **PTA5M ii**, **M22 5Mii, J23 5Mi.**
36. Explain Van-Arkel method. (17)
37. Application of Al, Zn, Fe, Cu & Au.

Unit 2: p-BLOCK ELEMENTS-I

Book evaluation Answer: page number: 55

Answer the following questions:

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

In p-block elements, the first member of each group differs from the other elements of the corresponding group.

1. ***Small size of the first member***

*2. **High ionisation enthalpy and high electronegativity***

3. Absence of d orbitals in their valance shell

Group 13:

- Boron is a ***metalloid*** while ***others are reactive metals.***
- **Boron** shows ***diagonal relationship*** with **silicon** of group 14.
- The ***oxides of boron and silicon*** are similar in their ***acidic nature.***

Group 14:

- **Carbon** is strictly a **nonmetal** while other elements are ***metalloids (silicon & germanium)*** or ***metals (tin & lead).***
- Carbon can form multiple bonds such as C=C, C=O etc... Carbon has a greater tendency to form a chain of bonds with itself or with other atoms which is known as **catenation.**
- Decrease in catenation property down the group (C>>Si>Ge≈Sn>Pb).

Group 15:

- Nitrogen can from multiple bonds (N=N, C=N, N=O etc...).
- ***Nitrogen is a diatomic gas*** unlike the other members of the group.

Group 16:

- ***Oxygen also exists as a diatomic gas*** in that group. Due to its ***high electronegativity it forms hydrogen bonds.***

Group 17:

- The first element of group 17, ***fluorine the most electronegative element.***
- It shows only -1 oxidation state.
- The fluorine also is the strongest oxidising agent and the most reactive element.

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

- Some elements exist in ***more than one crystalline*** or molecular forms in the ***same physical state.***
- This phenomenon is called allotropism (in greek *'allos'* means another and '*trope'* means change) and the different forms of an element are called allotropes.
    - **For example,** carbon exists as diamond and graphite.

Allotropes are the different forms of same element having different physical properties but almost similar chemical properties.

- Carbon exists in **two types of allotropic** forms.
- ***Crystalline forms*** - Graphite, Diamond, Graphene, Fullerenes and Carbon nanotubes.
- ***Amorphous forms (micro crystalline forms)*** – coal, charcoal, animal charcoal, lamp black

Graphite:

- **It** is the **most stable allotropic form of carbon** at normal temperature and pressure. **(**$\Delta_f H^\circ = 0$)
- It is **soft and conducts electricity.**
- It is composed of **flat two dimensional sheets** of carbon atoms.
- Each sheet is **a hexagonal net** of **sp^2 hybridised** carbon atoms with a C-C bond length of 1.41A° which is close to the C-C bond distance in benzene (1.40A°).
- Each carbon atom forms **three σ bonds** with three neighbouring carbon atoms using three of its valence electrons.
- The **fourth electron** present in the **unhybridised p orbital forms a π-bond.**
- These **π electrons are delocalised** over the entire sheet which is responsible for its electrical conductivity.
- The successive carbon sheets are held together by **weak van der Waals forces.** (weak forces)
- The distance between successive sheet is **3.40 A°.**

Uses of Graphite:

- It is used as a **lubricant in machinery** either on its own or as a **graphited oil.**
  - *For lining and marking electrodes of electric furnaces.*
  - *In making refractory crucibles*
  - *In making lead pencils.*
  - *As a moderator in nuclear reactor.*

Diamond

- **It** is **very hard.**
- The carbon atoms in diamond are **sp^3 hybridised.**
- Bonded to **four neighbouring carbon atoms by σ bonds.**
- C-C bond length of 1.54 A°.

- This results in a **tetrahedral arrangement** around each carbon atom that extends to the entire lattice.
- Since all four valance electrons of carbon are involved in bonding there is **no free electron for conductivity.**

Uses of diamond:

- It is used for sharpening hard tools, cutting glasses, making bores and rock drilling.
- It is used as a gem stone on account of reflection and refraction of light.
- Impure diamonds (black) are used in knives for cutting glass and rock borers.

Fullerenes:

- General formula $\mathbf{C_{2n}}$ (where $n \geq 30$)
- These allotropes are discrete molecules such as C_{32}, C_{50}, $\mathbf{C_{60}}$, $\mathbf{C_{70}}$, C_{76} etc..
- These molecules have **large cage like structures**.
- The C_{60} molecules have a **soccer ball** like structure and is called buckminster fullerene or buckyballs.
- It has a fused ring structure consists of **20 six membered rings** and **12 five membered rings.** (C_{70} 25 6Membered ring &12 5membered ring)
- Each carbon atom is **sp² hybridised** and
- **forms three σ bonds** with other three carbon atoms and the fourth electron remain free.
- **Free electron delocalised π bond** giving aromatic character to these molecules.
- The C-C bond distance is 1.44 A° and C=C distance 1.38 A°.

Carbon nanotubes

- It has graphite like tubes with fullerene ends.
- Along the axis, these nanotubes are stronger than steel and conduct electricity.
- These have many applications in nanoscale electronics, catalysis, polymers and medicine.

Graphene:

- It has a single planar sheet of **sp² hybridised** carbon atoms that are densely packed in a **honeycomb crystal lattice.**

3.Give the uses of Borax.

1. Borax is used for the identification of coloured metal ions.

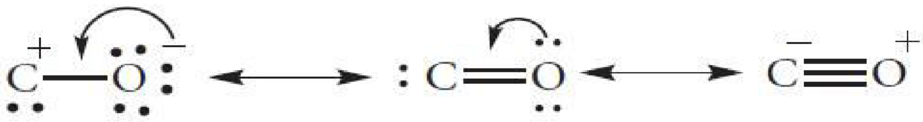
2. In the manufacture optical and borosilicate glass, enamels and glazes for pottery.

3. It is also used as a flux in metallurgy and also acts as a good preservative.

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

- **Catenation** is an ability of an element to ***form chain of atoms.***
- ***Carbon shares the property of catenation to maximum extent because it is small in size and can form pπ-pπ multiple bonds to itself.***

The following conditions are necessary for catenation:



(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.

(v) Carbon possesses all the above properties and forms a wide range of compounds with itself and with other elements such as H, O, N, S and halogens.

5. Write a note on Fisher tropsch synthesis.

The reaction of carbon monoxide with hydrogen at a pressure of less than 50 atm using metal catalysts at **500 - 700 K** yields saturated and unsaturated hydrocarbons.

$$nCO + (2n+1)H_2 \rightarrow C_nH_{(2n+2)} + nH_2O$$

Alkane (saturated hydrocarbon)

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$$

alkene (unsaturated hydrocarbon)

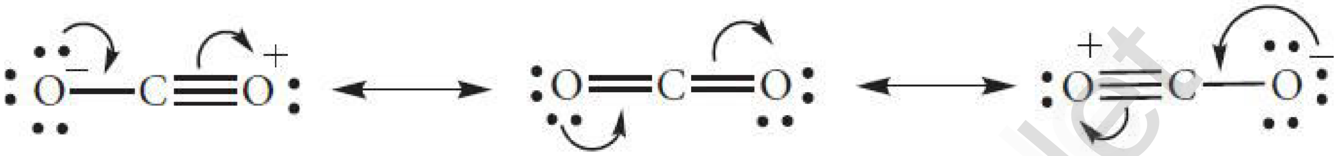
6. Give the structure of CO and CO_2.

Structure of CO :

- It has a linear structure.
- In carbon monoxide, three electron pairs are shared between carbon and oxygen.
- The C-O bond distance is 1.128Å.
- The structure can be considered as the resonance hybrid of the following two canonical forms.

Structure of CO_2

- Carbon dioxide has a **liner 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.



7. Give the uses of silicones.

1. Silicones are used for ***low temperature*** **lubrication** and in vacuum pumps, ***high temperature*** **oil baths** etc...

2. They are used for making **water proofing clothes.**

3. They are used as **insulting material** in electrical motor and other appliances.

4. They are mixed with **paints** and **enamels** to make them resistant towards high temperature, sunlight, dampness and chemicals.

Additional points:

- **Silicones** act as excellent insulators for electric motors and other appliances as they can withstand high temperatures.
- **Straight chain polymers** of 20 to 500 units are used as silicone fluids. They are water repellent because of the organic side group. These polymers are used in waterproofing textiles, as lubricants and as polish.
- **Silicone rubber** retain their elasticity even at low temperatures and resist chemical attack. They are mixed with paints to make them damp-resistant.
- **Silicone resins**, a cross-linked polymer used as non-stick coating for pans and are used in paints and varnish.
- **Silicone oils** are highly stable and non-volatile even on heating. Hence used for high temperature oil bath, high vacuum pump etc.

8. Describe the structure of diborane.

- In diborane two BH_2 units are linked by **two bridged hydrogens.** Therefore it has **eight B-H bonds.**
- Diborane has **only 12 valance electrons** (B 2x3 +6 H) and are not sufficient to form normal covalent bonds.

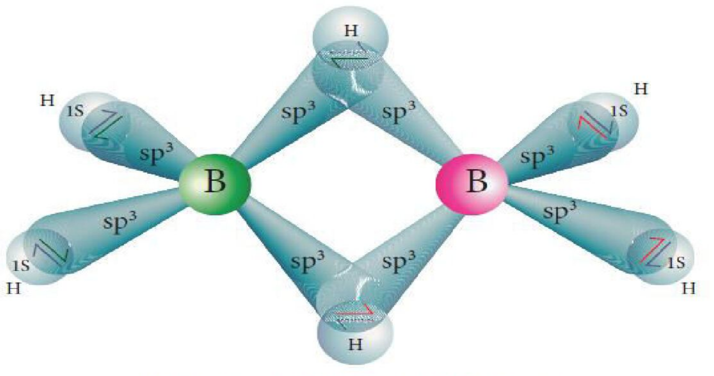
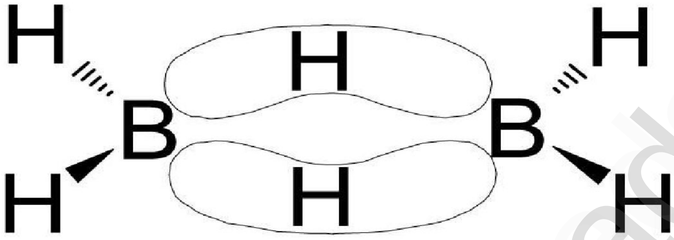
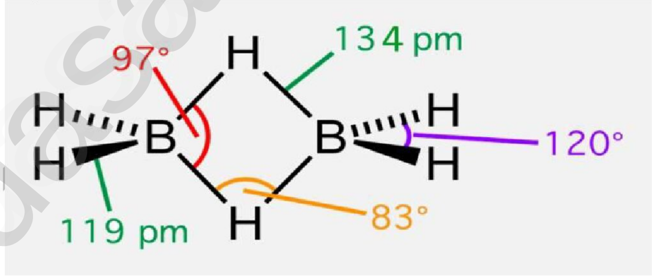


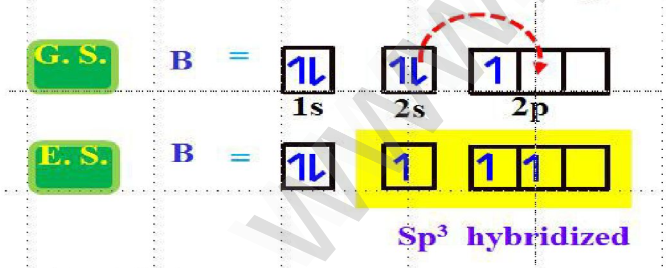
Figure 2. 3 Structure of diborane.

- The four terminal B-H bonds are **normal covalent bonds** (two centre - two electron bond or **$2c\text{-}2e^-$** bond).
- The remaining four electrons have to used for the bridged bonds. i.e. two three centred B-H-B bonds utilise two electrons each. Hence, these bonds are three centre- two electron bonds. **$(3c\text{-}2e^-)$**
- The bridging hydrogen atoms are in a plane.





- In diborne, the boron is **sp^3 hybridised.** Three of the four sp^3 hybridised orbitals contains single electron and the fourth orbital is empty.



- Two of the half-filled hybridised orbitals of each boron overlap with the two hydrogens to form four terminal 2c-2e bonds, leaving one empty and one half filled hybridised orbitals on each boron.
- The Three centre - two electron bonds, B-H-B bond formation involves overlapping the half-filled hybridised orbital of one boron, the empty hybridised orbital of the other boron and the half-filled 1s orbital of hydrogen.

9. Write a short note on hydroboration.

Diborane adds on to alkenes and alkynes in ether solvent at room temperature. This reaction is called hydroboration and is highly used in synthetic organic chemistry, especially for anti Markovnikov addition.

$$B_2H_6 + 6RCH{=}CHR \rightarrow 2B(RCH_2\text{-}CHR)_3$$

EXAMPLE:

$$B_2H_6 + 3CH_3\text{-}CH{=}CH_2 \rightarrow 2B(CH_3\text{-}CH_2CH_2)_3$$

$$2B(CH_3\text{-}CH_2CH_2)_3 + H_2O_2 \rightarrow CH_3\text{-}CH_2CH_2OH + B(OH)_3$$

10. Give one example for each of the following

(i) icosogens (ii) tetragen (iii) pnictogen (iv) chalcogen

(i) icosogens -Boron

(ii) tetragen - Carbon

(iii) pnictogen – Nitrogen

(iv) chalcogen - Oxygen

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

1. The tendency of an element to form a cation by loosing electron is known as ***electropositive*** or **metallic character.**
2. Metallic character depends on the ionisation energy.
3. ***Descending a group the ionisation energy decreases and hence the metallic character increases.***
4. In p-block, the elements present in lower left part are metals while the elements in the upper right part are nonmetals.

Group	***Metal***	***Metalloids***	***Non metal***
13	***Al, Ga, In, Tl, Nh***	***Boron***	
14	***Sn, Pb***	***Silicon, Germanium***	***Carbon***
15	***Bismuth***	***Arsenic, Antimony***	***N, P***
16	***Polonium***	***Tellurium***	***O, S, Se***
17	-	-	***F, Cl, Br, I, At, Ts***
18	-	-	***He, Ne, Ar, Kr, Xe, Rn, Og***

12. Complete the following reactions

a)	$B(OH)_3 + NH_3 \rightarrow$	**Ans:** $B(OH)_3 + NH_3 \xrightarrow{\Delta} BN + 3H_2O$ **Boron nitride**
b)	$Na_2B_4O_7 + H_2SO_4 + H_2O \rightarrow$	**Ans:** $Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$ **boricacid**
c)	$B_2H_6 + 2NaOH + 2H_2O \rightarrow$	**Ans:** $B_2H_6 + 2NaOH + 2H_2O \rightarrow 2NaBO_2 + 6H_2$ **Sodium metaborate**
d)	$B_2H_6 + CH_3OH \rightarrow$	**Ans:** $B_2H_6 + CH_3OH \rightarrow 2B(OCH_3)_3 + 6H_2$ **Trimethyl borate**
e)	$BF_3 + 3H_2O \rightarrow$	**Ans:** $4BF_3 + 3H_2O \rightarrow 4H_3BO_3 + 3H^+ + 3[BF_4]^-$ **Boric acid**
f)	$HCOOH + H_2SO_4 \rightarrow$	**Ans:** $HCOOH + H_2SO_4 \rightarrow CO + H_2O.H_2SO_4$
g)	$SiCl_4 + NH_3 \rightarrow$	**Ans:** $2SiCl_4 + NH_3 \xrightarrow[ether]{335K} Cl_3Si - NH - SiCl_3 + 2HCl$
h)	$SiCl_4 + C_2H_5OH \rightarrow$	**Ans:** $SiCl_4 + 4C_2H_5OH \rightarrow Si(OC_2H_5)_4 + 4HCl$
i)	$B + NaOH \rightarrow$	**Ans:** $B + NaOH \rightarrow 2Na_3BO_3 + 3H_2$
j)	$H_2B_4O_7 \rightarrow$	**Ans:** $H_2B_4O_7 \rightarrow 2B_2O_3 + H_2O$

13. How will you identify borate radical?

Flame Test: Borates on adding ethyl alcohol gives ethyl borate which when exposed to flame gives green colour flame. $H_3BO_3 + 3C_2H_5OH \xrightarrow{Conc\ H2SO4.} B(OC_2H_5)_3 + 3H_2O$

14. Write a note on zeolites.

- Zeolites are ***three-dimensional crystalline solids*** containing aluminium, silicon, and oxygen in their regular three-dimensional framework.
- They are hydrated sodium Alumino silicates with general formula $Na_2O.(Al_2O_3).x(SiO_2).yH_2O$ (x=2 to 10; y=2 to 6).
- Zeolites have porous structure in which the monovalent sodium ions and water molecules are loosely held.

i. The Si and Al atoms are tetrahedrally coordinated with each other through shared oxygen atoms.

ii. Zeolites are similar to clay minerals but they differ in their crystalline structure.

iii. Zeolites have a three dimensional crystalline structure looks like a honeycomb consisting of a network of interconnected tunnels and cages.

iv. Water molecules moves freely in and out of these pores but the zeolite framework remains rigid.

v. Another special aspect of this structure is that the pore/channel sizes are nearly uniform, allowing the crystal to act as a molecular sieve.

vi. The removal of permanent hardness of water using zeolites.

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

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

$$B(OH)_3 + NH_3 \xrightarrow{\Delta} BN + 3H_2O$$

16. 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.

(i) A hydride of **2nd period alkali metal (A)** is **LiH**

(ii) Compound of Boron (B) is **B_2H_6 diborane**

(iii) Reducing agent (C) is **$LiBH_4$.**

(iv) $2LiH + B_2H_6 \xrightarrow{Ether} 2LiBH_4$ (a strong reducing agent)

Compound	Formula	Name
A	LiH	Lithium hydride
B	B_2H_6	Diborane
C	$LiBH_4$	Lithium Boron hydride

17. 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 4th **period alkali metal (A)** is
- **$K_2SO_4Al_2(SO_4)_3.24H_2O \xrightarrow{500K} K_2SO_4Al_2(SO_4)_3 + 24H_2O$**
- ∴B is $K_2SO_4\ Al_2(SO_4)_3$ .This gives **white precipitate with $BaCl_2$.**
- $K_2SO_4Al_2(SO_4)_3$ gives red colour with Alizarin.

Compound	Formula	Name
A	**$K_2SO_4.Al_2(SO_4)_3.24H_2O$**	Potash alum

B	$K_2SO_4.Al_2(SO_4)_3$	***Burnt alum***

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

Thermodynamically CO_2 is more stable than CO, thus ***carbon monoxide has a relatively high tendency to be oxidized <u>it reduces the other substance</u>*** in the reaction.

Carbon monoxide acts as a strong reducing agent.

$$CO+Fe_2O_3 \rightarrow 2Fe+3CO_2$$

IMPORTANT QUESTION

1. Give one example for **Icosogens,** Tetragens, pnictogens, **chalcogens.** (28) **J23 2M**
2. What are the anomalous properties of the first elements of the p-block elements. (29) **S20 A21**
3. There is only a marginal difference in decrease in ionization enthalpy from Aluminium to Thallium – Explain why? (29)**M20 Compulsory 3 mark**
4. What is inert pair effect.(30) **M22 5Mi**
5. A hydride of 2nd period alkali metal (A) on reaction with compound of Boron (B) in the presence of ether to give a reducing agent (C). Identify A, B and C. **J20 2M Compulsory**
6. How will you identify borate radical? Write the reactions involved. (write ethyl borate test) (35) **PTA3M, GM2M, M23 5Mii**
7. How will you convert Boric acid to boron nitride?(35) **PTA2M, M24 2M**
8. Structure of Boric acid.(35)
9. What are the Uses of Boric acid. (35) **J22 3M, M22 5Mii, M24 5Mi**
10. How does Diborane react with H_2O & NaOH? (36)
11. Write a note on hydroboration. (37) **J23 5Mi**
12. Explain structure of diborane. (37) **M23 5Mi**
13. Write note on McAfee process (39)
14. Mention the uses of Aluminium chloride (39)
15. How to prepare potash alum & uses. (40) **J20, PTA 5M ii**
16. What is burnt alum.(40)
17. Occurrence of Group 14 (Carbon group) elements.(40)
18. What is catenation? Write the conditions for catenation property. (41) **J22 5M** Substantiate this statement. (41) **S20 2M** Write any two conditions for catenation. **M20 2M**

19. Write note on Fischer Tropsch synthesis. (44) M23 3M
20. Write note on structure & uses of CO & CO_2 (44, 45)
21. How does $SiCl_4$ react with alcohol & NH_3? (46)
22. Explain the preparation, uses of silicone. (47 & 48) M23 2M Uses
23. What are the types, properties of silicones. (47)
24. What are silicates?(48) **M24 5Mii**
25. Explain types of silicates. (48)

Lesson 3 p- block elements -II

1. What is inert pair effect?

In p-block elements, as we go down the group, two electrons present in the valence s-orbital (ns^2) become inert an are **not available for bonding**, (only p-orbital involves chemical bonding). This is called inert pair effect. **(Or) As per BOOK (page No 30)**

In heavier post transition metals, ***the outer s electrons (ns) have a tendency to remain inert and show reluctance to take part in the bonding, which is known as inert pair effect.***

2. **Chalcogens belongs to p-block. Give reason.**

- Chalcogens belongs to group 16 with a general electronic configuration of **ns^2np^4.**

  Since the ***last electron enters into p orbital,*** they belong to p block.

- Chalcogens are **ore forming elements**.
- Most of the ores are oxides and sulphide, therefore oxygen sulphur and other group 16 elements are called **Chalcogens.**
- In O, S, Se, Te and Po last electron enters to p-orbital.
- Therefore, Chalcogens belongs to p-block.

3. Explain why fluorine always exhibit an oxidation state of -1?

a. The electronic configuration of fluorine is $1s^2\ 2s^2\ 2p^5$.

b. To attain the noble gas configuration, it **gains one electron** an exhibits -1 oxidation state.

c. Fluorine is **most electronegative atom** so does not exhibit positive oxidation state.

d. Since it cannot expand its octet due **to non-availability of d-orbitals.**

4. Give the oxidation state of halogen in the following. a) OF_2 b) O_2F_2 c) Cl_2O_3 d) I_2O_4

a) OF_2 → -1 Oxidation state b) O_2F_2 → -1 Oxidation state

c) Cl_2O_3 → +3 Oxidation state d) I_2O_4 → **+4** Oxidation state

c)Cl_2O_3

$2x+3(-2) = 0$

$2x-6 = 0$

$2x = +6$ **$x = +3$** O.S of Cl is +3

d)I_2O_4

$2x+4(-2) = 0$

$2x-8 = 0$

$2x = +8$ **$x = +4$** O.S of I is **+4**

5. What are interhalogen compounds? Give examples.

Each halogen combines with other halogens to form a series of compounds known as inter halogen compounds. Ex: ClF, BrF, ClF_3. BrF_5. IF_7

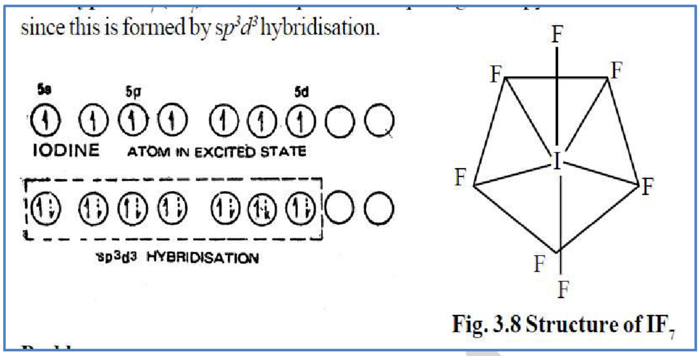


Fig. 3.8 Structure of IF_7

6. Why fluorine is more reactive than other halogens?

Fluorine is the most reactive element among halogens.

- This is due **to the minimum value of F-F bond dissociation energy.**
- **Fluorine is most electronegative** thus it is most reactive.

7. Give the uses of helium.

i. Helium and oxygen mixture is used **divers** in place of air oxygen mixture. This prevents the painful dangerous condition called bends.

ii. Helium is used to provide inert atmosphere in **electric arc welding of metals.**

iii. Helium has **lowest boiling point** hence used in **cryogenics.** (low temperatures science)

iv. It is much ***less dense than air*** and hence used for **filling air balloons.**

8. What is the hybridisation of iodine in IF_7? Give its structure.

- Hybridisation of iodine in IF_7 is **sp^3d^3** .
- Structure: **pentagonal bipyramidal.**

9. Give the balanced equation for the reaction between chlorine with cold NaOH and hot NaOH.

Chlorine reacts with cold (dilute) NaOH to give Sodium chloride and sodium hypochlorite are formed.

$$Cl_2 + 2NaOH \rightarrow \underset{\text{Sodium hypo chlorite}}{NaOCl} + NaCl + H_2O$$

Chlorine reacts with hot (concentrated) NaOH to give sodium chloride and sodium chlorate are formed.

$$3Cl_2 + 6NaOH \rightarrow NaClO_3 + 5NaCl + 3H_2O$$

10. How will you prepare chlorine in the laboratory?

- Chlorine is prepared by the action of conc. Sulphuric acid on sodium chloride in presence of manganese dioxide.

- **$4NaCl + MnO_2 + 4H_2SO_4 \rightarrow Cl_2 + MnCl_2 + 4NaHSO_4 + 2H_2O$**
- **$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$**

11. Give the uses of sulphuric acid.

- Sulphuric acid is used in the manufacture of fertilisers, ammonium sulphate and super phosphates and other chemicals such as hydrochloric acid, nitric acid etc.
- It is used as a drying agent and also used in the preparation of pigments, explosives etc.

12. Give a reason to support that sulphuric acid is a dehydrating agent.

Sulphuric acid is ***highly soluble in water*** and has ***strong affinity towards water*** and hence it can be used as a dehydrating agent. When dissolved in water it forms mono ($H_2SO_4.H_2O$) and di ($H_2SO_4.2H_2O$) hydrates and the reaction is ***exothermic.***

The dehydration property can also be illustrated by its reaction with organic compounds such as **sugar, oxalic acid and formic acid.**

$C_{12}H_{22}O_{11} + H_2SO_4 \rightarrow 2C + H_2SO_4.11H_2O$

(Sucrose)

$HCOOH + H_2SO_4 \rightarrow CO + H_2SO_4.H_2O$

(Formic Acid)

13. Write the reason for the anomalous behaviour of Nitrogen.

Nitrogen differ from other member of this group due to its

(i) Small size.

(ii) High electronegativity and High ionisation energy

(iii) Absence of “d" orbitals in their valence shell.

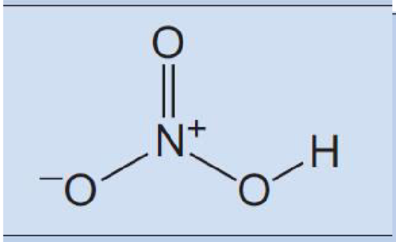
(iv) Chemically inert due to high bonding energy($225 calmol^{-1}$)

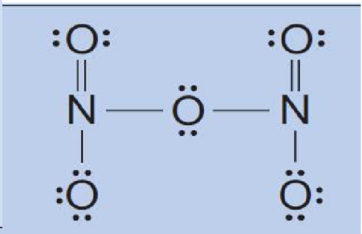
(v) Nitrogen exists as a **diatomic molecule(N_2)** with a **triple bond** ($N\equiv N$)between the two atoms. Consequently, its **bond enthalpy is very high.** On the contrary, phosphorous, arsenic and antimony form single bonds as P-P, As – As and Sb – Sb.

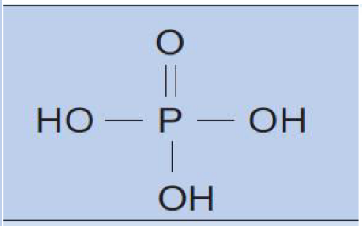
(vi) While Bismuth forms metallic bonds in elemental state however the single N-N bond is weaker than the single P-P bond because of high inter electronic repulsion of the non-bonding electrons, owing to the small bond length.

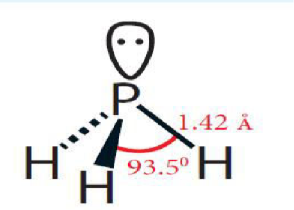
14. Write the molecular formula and structural formula for the following molecules.

a) Nitric acid b) dinitrogen pentoxide c) phosphoric acid d) phosphine









15. Give the uses of Argon.

(i) Argon prevents the oxidation of hot filament and prolongs the life in filament bulbs.

(ii) Mixed with 20.06% nitrogen and it is used in gas filled electric lamps.

(iii) It is also used in radio valves and tubes.

16. Write the valence shell electronic configuration of group-15 elements.

The general Valence shell electronic configuration of group 15 elements is **ns^2np^3.**

Nitrogen	**$2s^22p^3$.**	Phosphorus	**$3s^23p^3$.**		
Arsenic	**$4s^24p^3$.**	Antimony	**$5s^25p^3$.**	Bismuth	**$6s^26p^3$.**

17. Give two equations to illustrate the chemical behaviour of phosphine.

(i) Phosphine reacts ith halogens to give phosphorous penta halides

$PH_3 + 4Cl_2 \rightarrow PCl_5 + 3HCl$

(ii) Phosphine forms coordination compound with lewis acids such as boron trichloride.

$BCl_3 + PH_3 \rightarrow [Cl_3B \leftarrow : PH_3]$

(iii) phosphine precipitates some metal from their salt solutions.

$3AgNO_3 + PH_3 \rightarrow Ag_3P + 3HNO_3$

18. Give a reaction between nitric acid and a basic oxide.

Like other acids it reacts with bases and basic oxides to form salts and water

$ZnO + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2O$

$3FeO + 10HNO_3 \rightarrow 3Fe(NO_3)_3 + NO + 5H_2O$

19. What happens when PCl_5 is heated?

On heating phosphorous pentachloride, it decomposes into phosphorous trichloride and chlorine.

$PCl_{5(g)} \rightarrow PCl_{3(g)} + Cl_{2(g)}$

(Excess)

20. Suggest a reason why HF is a weak acid, whereas binary acids of the all-other halogens are strong acids.

- Because the **HF bond is so short**, it is **very strong** and therefore makes it **difficult for the bond to be broken**.

- In other words it **won't dissociate completely.**
- Stronger acids such as ***HCl and HBr have weaker bonds*** and are more likely to dissociate completely.
- Fluorine has the greatest affinity for hydrogen, due to the large electro negativity difference between them, forming HF which is associated due **to the hydrogen bonding.**
- Hydrofluoric acid is a weak acid whereas the other hydrohalic acid are strong acids.
  ……..H – F …… H – F……. H – F
- It takes tremendous amount of energy to break the strong H – F bond in water.

Alternatively, The hydrogen halides are extremely soluble in water due to the ionisation.

$$X + H_2O \rightarrow H_3O^+ + X^- \qquad (X = F, Cl, Br \text{ or } I)$$

Solutions of hydrogen halides are therefore acidic and known as hydrohalic acids. Hydrochloric, hydrobromic and hydroiodic acids are almost completely ionized an are therefore strong acids but HF a weak acid. For HF,

$$HF + H_2O \leftrightarrow H_3O^+ + F^-$$

$$HF + F^- \rightarrow HF_2^-$$

At high concentration, the equilibrium involves the removal of fluoride ions is important. Since it affects the dissociation of hydrogen fluoride, therefore it is a weak acid.

21. Deduce the oxidation number of oxygen in hypofluorous acid – HOF.

HOF

+1 +x -1=0

x=0

oxidation number of oxygen HOF=0

22. What type of hybridisation occur in a) BrF_5 b) BrF_3

Ans : a) BrF_5 – sp^3d^2 b) BrF_3 – sp^3d

23. Complete the following reactions.

1. **$4NaCl + MnO_2 + 4H_2SO_4$** $\rightarrow Cl_2 + MnCl_2 + 4NaHSO_4 + 2H_2O$
2. **$NaNO_2 + HCl$** $\rightarrow HNO_2 + NaCl$
3. **$P_4 + 3NaOH + 3H_2O$** $\rightarrow 3NaH_2PO_2 + PH_3 \uparrow$
4. **$3AgNO_3 + PH_3$** $\rightarrow Ag_3P + 3HNO_3$
5. **$4Mg + 8HNO_3$** $\rightarrow 4Mg(NO_3)_2 + 8H$

6. $2KClO_3 \xrightarrow{\Delta} 2\ KCl + 3O_2$

7. $Cu + 2H_2SO_4 \xrightarrow{\text{Hot con.}} CuSO_4 + SO_2 + 2H_2O$

8. $2Sb + 3Cl_2 \rightarrow 2SbCl_3$

9. $2HBr + H_2SO_4 \rightarrow 2H_2O + Br_2 + SO_2$

10. $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

11. $5XeO_6^{4-} + 2Mn^{2+} + 14H^+ \rightarrow 2MnO_4^- + 5XeO_3 + 7H_2O$

12. $2XeOF_4 + SiO_2 \rightarrow 2XeO_2F_2 + SiF_4$

13. $Xe + 2F_2 \xrightarrow{\text{Ni / 200 atm}} XeF_4$

IMPORTANT QUESTIONS

1. Occurrence of 15th group elements. (57)
2. Physical properties of 15th group elements. (57)
3. How will you prepare nitrogen from sodium azide and atmospheric air? (57)
4. N_2 is a chemically inert. Why? (58)
5. What are the uses of Nitrogen? (58)
6. Write note on Haber's process (58) **S20**
7. How is ammonia prepared in the laboratory? (58)
8. What is the reaction of Ammonia with Iron and copper salts? (60) **PTA5M ii**
9. Structure of Ammonia. (60)
10. Preparation of Nitric acid Oswald process. (61)
11. How is fuming nitric acid decompose on exposure? (61)
12. How does nitric acid act as nitrating agent? (62)
13. How does copper react with nitric acid? (63)
14. Give the uses of nitric acid (63)
15. Draw the structures of oxides of nitrogen (65)
16. Draw the structures of oxoacids of nitrogen (65) **M22 ONE MARK (hyponitrous acid)**
17. Explain Allotropy of phosphorus. (67)
18. How does phosphorous act as a reducing agent? (68) or

    Complete the reaction: $P_4 + NaOH + H_2O \rightarrow$ (68) **PTA 2MC**
19. How does phosphorous react with HNO_3? (68)
20. Uses of phosphorus. (68)

21. How is phosphine prepared? (68)

22. What is Holmes signal and uses? (70) **S20 5Mii**

23. Draw the structure of PH_3 (70) PCl_3 (71) P_2O_3 (P_4O_6) (71) P_4O_{10} (72)

24. Write the structure and basicity of following oxy acids. (72) **3M**

    i) hypo phosphoric acid ii) ortho phosphoric acid iii) pyro phosphoric acid

25. Occurrence of 16th group elements. (73)

26. Physical properties of 16th group elements. (73)

27. How is ozone estimated? (75) (Ozone (O_3) act as a powerful oxidizing agent why?**)**

28. Laboratory preparation of O_2. (74)

29. Laboratory Preparation of ozone (74)

30. Structure of ozone. (74)

31. How is ozone estimated?(75) (Ozone (O_3) act as a powerful oxidizing agent why?**) (75) PTA2M**

32. Uses of oxygen (75) **M22 5Mi**

33. Allotropic form of sulphur. (73)

34. Lab preparation of SO_2.(76)

35. SO_2 is an acidic or basic oxide. Why? (76)

36. Explain the bleaching action of Sulphur dioxide.(77) **A21 2M, J23 5Mii**

37. Write note on contact process. (77)

38. Structure of SO_2, Uses of SO_2.(77)

39. Manufacture of Sulphuric acid by contact process. (77)

40. Sulphuric acid is a dehydrating agent. Give example. (78) **J23 2M, M24 2M**

41. How does H_2SO_4 act as an oxidizing agent? (78, 79)

42. Sulphuric Acid is a dibasic acid. Prove it. (78) **J20 5Mii**

43. Give the uses of sulphuric acid. (80) **J24 3M**

44. How is sulphate radical/sulphuric acid detected? (80)

45. Draw the structure of oxoacids of sulphur. (80) Sulphurous acid, sulphuric acid, Marshall's acid **(M20)**, Caro's acid, Dithionic acid.

(Write the molecular formula and draw the structure of sulphurous acid and Marshall's acid.) **(M20 5Mi)**

46. Occurrence of 17th group elements. (81)

47.Physical properties of 17th group elements. (81)

48.Why fluorine is more reactive than other halogens? (BB98)**PTA1 2M & PTA3 5M i**

49.Manufacture of chlorine. (electrolytic process)(83)

50.How will you prepare chlorine in the laboratory? (82BB83) **2M**

51.Explain Deacon's process for manufacture of chlorine. (83) **J20 5Mii**

52.Physical properties of chlorine.(83)

53.Give the balanced equation for the reaction between chlorine with Cold NaOH and hot NaOH. (84) **S20**

54.Write about bleaching action of chlorine (85)

55.How will you prepare bleaching powder? (85) **M20 2M, M22 5Mii**

56.Uses of chlorine.(86)

57.How is aqua regia obtained? (86)

58.HF is not stored in glass bottles. Why? (88) **M20 5Mii**

59.What are interhalogen compound. Give two examples. (89) **GM5Mi A21, M22 3 mark**

60.What are the properties of interhalogen compounds.(89) **PTA5M, J22 5M**

61.Give reasons: ICl is more reactive than I_2. **PTA5M i**

62.Structure of interhalogen compounds AX, AX_3, AX_5,AX_7. (90)

63.What type of hybridisation is found in the following? (a) BrF (b)BrF_5 (c) BrF_3 d)IF_7(91) **(J20)3M, PTA 5M ii)**

64.Occurrence of 18th group elements.(91)

65.Physical properties of 18th group elements.(91)

66.How does XeF_6 react with NaOH? (92)

67.How does XeF_6 react with SiO_2? (92)

68.How does sodium per xenate act as strong oxidizing property? (92)

69.Uses of Helium(93) **GM 3M, S20,A21, PTA 3M, J23 3M, M24 3M**

70.Uses of Neon. (93)

71.Uses of Argon. (93) **PTA 3M J22 2M**

72.Uses of Krypton. (93)

73.Uses of Xenon. (93)

74.Uses of Radon. (93)

75.List any five compounds of xenon and mention the type of hybridization and structure of the compounds. (93) **PTA5M**

76.Find the oxidation state of halogen in the following compounds.BB 98 **M23 5Mi**

1) OF_2 2) I_2O_4

77. Complete the following reactions. BB 99 **M23 5Mii**

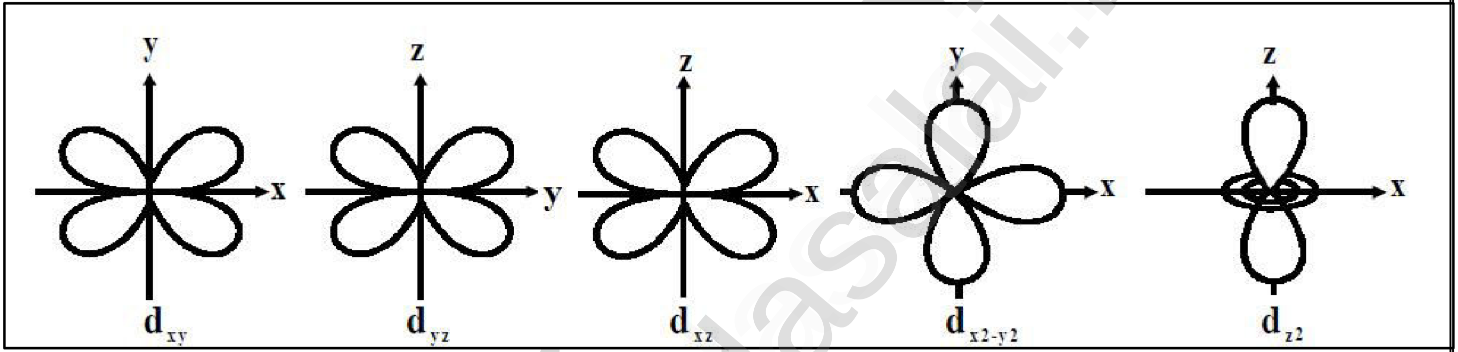
1) $P_4 + NaOH + H_2O \rightarrow$

2) $XeF_6 + H_2O \rightarrow$

3) $Cu + conc.H_2SO_4 \rightarrow$

ALL CHEMICAL EQUATION & Revise Book Back (Evaluation) Question Answer

UNIT 4 Transition and Inner transition elements



1. What are Transition metals. Give examples.

- Transition metal is an element whose atom has an ***incomplete d- subshell (orbital)*** in the neutral or cationic state.
- They occupy the central position of the periodic table, between s-block and p-block elements.
- Elements from ***group 3 to 11*** are called as Transition metals.
- **Example.** Gold, Silver, Iron, Platinum, etc…

2. Explain the Oxidation states of the 4d elements.

Yttrium to cadmium

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	+3, +4	+2 to +5	+2 to+6	+2 to +7	+2to +8	+2to +6	+2 to +4	+1 to+3	+2

3. What are inner transition elements.

- **f-block elements** are called inner transition elements.

Inner transition elements consist of two series

- **Lanthanoids** - 4f block elements
- **Actinoids** - 5f block elements

• Ce to Lu following La (Lanthanoids) **4f series** – 14 elements

• Th to Lr following Ac (Actinoids) **5f series** – 14 elements

4. Justify the position of Lanthanoids and actinoids in the Periodic table.

The position of Lanthanoides

- It presents in **3rd group and 6th period**

* After the Lanthanum, the electrons are preferentially filled in inner 4f sub shell.

* The 14 elements following Lanthanum show similar chemical properties.

* 14 elements are groups together and placed at the bottom of the periodic table.

This position can be justified as follows: -

* Lanthanides have general electronic configuration $\mathbf{[Xe]4f^{1-14}\,5d^{0-1}\,6s^2}$

* The common oxidation state of lanthanides +3

* All these elements have similar physical and chemical properties

The position of actinoides in the periodic table

- It presents in ***3rd group and 7th period***.

* The fourteen elements following actinium Th to Lr resemble in their physical and chemical properties.

* Actinoides have general electronic configuration $[Rn]5f^{2-14}6d^{0-2}\,7s^2$

* 14 elements are groups together and placed at the bottom of the periodic table.

5. What are Actinoides? Give three examples.

- ***5f- block elements*** are called actinoids.
- The 14 elements following Actinium from Th to Lr are called as Actinoides.
- Actinoides are those elements in which inner 5f sub shell in gradually filled up.
- Actinoides have general electronic configuration $[Rn]5f^{2-14}6d^{0-2}\,7s^2$
  - **Example**. Thorium (Th), Uranium(U), Plutonium(Pu).

6.**Give the preparation of Potassium dichromate**

Conversion of Chromate ore $FeO.Cr_2O_3$(Chromite Iron ore) to Sodium Chromate

Potassium dichromate is prepared from **chromite ore ($FeO.Cr_2O_3$)**. The ore is concentrated by **gravity separation.**

It is then mixed with excess sodium carbonate and lime and roasted in a reverbratory furnace.

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{900-1000°C} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2\uparrow$$

Chromite ore sodium chromate

Conversion of Sodium Chromate to Sodium Dichromate

The roasted mass is treated with water to separate soluble sodium chromate from insoluble iron oxide. The yellow solution of sodium chromate is treated with concentrated sulphuric acid which converts sodium chromate into sodium dichromate.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + H_2O + Na_2SO_4$$

Sodium chromate(Yellow) sodium dichromate (orange red)

Conversion of Sodium Dichromate to Potassium Dichromate

The saturated solution of sodium dichromate in water is mixed with KCl and then concentrated to get crystals of NaCl. It is filtered while hot and the filtrate is cooled to obtain $K_2Cr_2O_7$ crystals.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

7. Explain Lanthanide contraction and what are the effects of lanthanides contraction?

Definition:

As we move across 4f series, the atomic and ionic radii of lanthanoids show gradual ***decrease*** with increase in atomic number. This decrease in ionic size is called lanthanoid contraction.

Causes of Lanthanide contraction

- As we move from one element to another in 4f series (Ce to Lu) the ***nuclear charge increases*** by one unit and an additional electron is added into the same inner 4f sub shell (orbital).
- ***4f sub shell have a diffused shapes*** and therefore the ***shielding effect of 4f electrons*** relatively ***poor.***
- hence, with increase of nuclear charge, the valence shell is pulled slightly towards nucleus.
- As a result, the effective nuclear charge experienced by ***the 4f electrons increases and the size of Ln^{3+} ions decrease.***

(• Moving from Ce to Lu the nuclear charge increases.

• All the 14 electrons are added to the same 4f orbital.

• Poor shielding effect of the 4f electrons.

• Hence the attraction between the nucleus and the valance shell increases.)

Consequences of Lanthanide contraction

i) Basic nature

- As we from Ce^{3+} to Lu^{3+}, the basic character of Ln^{3+} ions decrease.
- Due to the decrease in the size of Ln^{3+} ions, the ionic character of Ln-OH bond decreases (covalent character increases) which results in the decrease in the basic nature.
- Since the order of size of Ln^{3+} ions are

$$Ce^{3+} > Pr^{3+} \ldots\ldots\ldots\ldots\ldots > Lu^{3+}$$

ii) **Similarities among lanthanoids:**

- There is regular decrease in their ionic radii.
- In the complete f-series only ***10pm decrease in atomic radii*** and ***20pm decrease in ionic radii*** are observed.
- Because of this very small change in radii of lanthanoids, their chemical properties are quite similar.
- The elements of second and third transition series resemble each other more closely than the elements of first and second transition series due to lanthanoid contraction.

For example: 4d series – Zr – Atomic radius 145pm

5d series - Hf – Atomic radius 144pm

iii) Regular decrease in their tendency to act as reducing agent, with increase in atomic number.

iv) Due to lanthanide contraction, these elements occur together in natural minerals and are difficult to separate.

8.Complete the following

a. $3MnO_4^{2-} + 4H^+ \rightarrow \mathbf{2MnO_4^- + MnO_2 + 2H_2O}$

$(2K_2MnO_4 + 4HCl \rightarrow \mathbf{2KMnO_4 + MnO_2 + 4KCl + 2H_2O})$

b. $C_6H_5CH_3 \xrightarrow{Acidified\ KMn04} \mathbf{C_6H_5COOH + 2MnO_2 + 2KOH}$

$(C_6H_5CH_3 \xrightarrow{Acidified\ KMn04} \mathbf{C_6H_5COOH})$

c. $MnO_4^- + 5Fe^{2+} \xrightarrow{8H+} \mathbf{Mn^{2+} + 5Fe^{3+} + 4H_2O}$

d. $2KMnO_4 \xrightarrow{\text{Red hot}}$ $\mathbf{K_2MnO_4 + MnO_2 + O_2}$

e. $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow$ $\mathbf{2Cr^{3+} + 3I_2 + 7H_2O}$

f. $Na_2Cr_2O_7 + 2KCl \rightarrow$ $\mathbf{K_2Cr_2O_7 + 2NaCl}$

9. What are interstitial compounds?

- When small atoms like Hydrogen, Boron, Carbon or Nitrogen are trapped in the interstitial holes in a metal lattice are called interstitial compounds.
- They are usually non-stoichiometric compounds.
- **Example:** TiC, $ZrH_{1.92}$, Mn_4N

The elements that occupy the metal lattice provide them new properties. **(MAY 2022)**

- (i) They are hard and show electrical land thermal conductivity.
- (ii) They have high melting points higher than those of pure metals.
- (iii) Transition metal hydrides are used as powerful reducing agents.
- (iv) Metallic carbides are chemically inert.

10.Calculate the number of unpaired electrons and Magnetic moment in Ti^{3+} and Mn^{2+}

Atomic Number of Ti =22

Electronic Configuration of Ti = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$

Electronic Configuration of Ti^{3+} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^1}$

Number of unpaired electrons = 1.

Spin only magnetic moment = $\sqrt{n(n+2)}$ = $\sqrt{1(1+2)} = \sqrt{3}$

= 1.732 BM

Atomic no of Mn = 25

Electronic Configuration of Mn = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$

Electronic Configuration of Mn^{2+} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^5}$

Number of unpaired electrons = 5.

Spin only magnetic moment = $\sqrt{n(n+2)}$ = $\sqrt{5(5+2)}$

= 5.92 BM.

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

- Ce atomic number 58 Ce^{+4} : [Xe] $4f^0\ 5d^0\ 6s^0$
- Co atomic number 27 Co^{+2} : [Ar] $4s^0\ 3d^7$

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

(i) It can be easily observed that **except Sc** all other metals possess +2 oxidation state.

(ii) Also, on moving from Sc to Mn, the atomic number increases from 21 to 25.

(iii) This means the number of electrons in the 3d – orbital also increases from 1 to 5.

$Sc^{+2} = d^1$ $Ti^{+2} = d^2$ $V^{+2} = d^3$ $Cr^{+2} = d^4$ $Mn^{+2} = d^5$

(iv) Oxidation state is attained by the ***loss of the two 4 electrons*** by these metals.

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

(vi) With the increase in the atomic number, the d-orbital becomes half-filled and they becomes more stable.

13. Which is more stable? Fe^{+2} or Fe^{+3}? Explain. (MAY 2022)

- Fe^{+2} : [Ar] $4s^0$ $3d^6$
- Fe^{+3} : [Ar] $4s^0$ $3d^5$
- Fe^{+3} is more stable. It is having ***half-filled stable $3d^5$*** electronic configuration.

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

- In transition series, as we move down from Ti to Zn, the standard reduction potential $E^0_{M^{2+}/M^{3+}}$ value is approaching towards less negative value and copper has a positive reduction potential i.e. elemental copper is more stable than Cu^{2+}.
- $E^0_{M^{2+}/M}$ value for manganese and zinc are more negative than regular trend. It is ***due to extra stability arises due to the half-filled d^5 configuration in Mn^{2+}*** and ***completely filled d^{10} configuration in Zn^{2+}*** .
- The **standard electrode potential** for the M^{3+}/M^{2+} indicates ***Mn^{2+} is more stable than Mn^{3+}***.
- The **high reduction potential** of Mn^{3+}/Mn^{2+} indicates ***Mn^{2+} is more stable than Mn^{3+}***.
- For Fe^{3+}/Fe^{2+} the reduction potential is 0.77V, and this low value indicates that both Fe^{3+} and Fe^{2+} can exist under normal condition.
- Mn^{3+} has a $3d^4$ configuration while that of Mn^{2+} is $3d^5$. The extra stability associated with a ***half-filled d orbital*** makes the reduction of ***Mn^{3+} very feasible.*** [E^0 =+1.51V]

15. Compare lanthanides and actinides.

	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 Ex.** U^{3+} (red), U^{4+} (green), UO_2^{2+} (Yellow)
5	They **do not** form oxo cations	They do form oxo cations such as UO_2^{2+}, NpO_2^{2+}
6	Besides **+3** oxidation states lanthanoids show **+2 and +4** oxidation states in few cases	Besides **+3** oxidation states actinoides, show higher oxidation states such as **+4, +5, + and +7.**

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

$E^0_{Cr^{3+}/Cr^{2+}}$ is -0.41V

$Cr^{2+} + 2e^- \rightarrow Cr \qquad E^0 = -0.91V$

If the standard electrode potential E^0 of a metal is **large and negative,** the ***metal is a powerful reducing agent because it loses electrons easily***.

$Mn \rightarrow Mn^{3+} + 3e^- \qquad Mn^{3+}\ [Ar]3d^4$

$Mn^{3+} + e^- \rightarrow Mn^{2+} \qquad E^0 = +1.51V$

If the standard electrode potential E^0 of a metal is **large and positive,** the ***metal is a powerful oxidising agent because it gains electrons easily.***

17. Compare the Ionization enthalpy of the first series Transition elements

- the minimum *amount of energy required to remove electron is called ionization energy.*
- Ionization energy of transition element is ***intermediate*** between those of s and p block elements.

- As we move from **left to right** in a transition metal series, the ionization enthalpy **increases** as expected. This is ***due to increase in nuclear charge corresponding to the filling of d electrons***.
- The first ionisation energy of 5d series of element are much higher than those of 3d and 4d series of elements.
- 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.

18. Actinoid contraction is greater from element to element than the lanthanoid contraction, why?

- Actinoid contraction is greater from element to element than the lanthanoid contraction, these ***5f orbitals have a poorer shielding effect*** than 4f orbitals in lanthanoids.
- Thus, the ***effective nuclear charge*** experienced by electrons in valence shells in case of actinoids is much more than, that experienced by lanthanoids.
- In actinoids, electrons are shielded by 5d, 4f, 4d and 3d whereas in lanthanoids, electrons are shielded by 4d, 4f only.
- Hence, ***the size contraction in actinoids is greater*** as compared to that in lanthanoids.
- So actinoids show greater contraction.

19. Out of $Lu(OH)_3$ and $La(OH)_3$ which is more basic and why?

- $La(OH)_3$ is more basic than $Lu(OH)_3$.
- As we move from Ce^{3+} to Lu^{3+} the basic character of Lu^{3+} ions decreases.
- Due to lanthanoid contraction the size of Lu^{3+} ions, the ionic character of Lu- OH bond decreases, covalent character increases which results in the decrease in the basicity.
- Therefore the basic character of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$

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

- Europium (II) is more stable than Cerium (II).
- Eu (Z=63) Electronic configuration –$[Xe]4f^7 5d^0 6s^2$

  Eu^{2+} Electronic configuration –$[Xe]4f^7 5d^0$

- Ce (Z=58) Electronic configuration –$[Xe]4f^2 5d^0\ 6s^2$

  Ce^{2+} Electronic configuration –$[Xe]4f^2 5d^0$
- Since Europium (II) has 4f half-filled subshells which provide more stability due to exchange energy.

21. Why do Zirconium and Hafnium exhibit similar properties?

- The elements of second and third transition series resemble each other more closely than the elements of first and second transition series due to ***lanthanoid contraction.***

For example: 4d series – Zr – Atomic radius 145pm

5d series - Hf – Atomic radius 144pm

- Zr and Hf exhibit similar properties due to lanthanoid contraction.
- Electrons present in f subshell have poor shielding due to which with the increasing atomic number or increasing effective nuclear charge, size gets constricted.
- Radius dependent properties such as lattice energy, solvation energy are similar.
- Thus lanthanoides contraction leads to formation of pair of elements and those known as chemical twins. Example: Zr-Hf.
- Hence size of hafnium and zirconium becomes almost equal.

22. Which is a strong reducing agent. Cr^{+2} or Fe^{+2}?

- Cr (Z=24) Electronic configuration –$[Ar]3d^5\ 4s^1$

  Cr^{2+} Electronic configuration –$[Ar]3d^4$
- Fe (Z=26) Electronic configuration –$[Ar]3d^6\ 4s^2$

  Fe^{2+} Electronic configuration –$[Ar]3d^6$

If standard electrode potential E^0 of a ***metal is large and negative, the metal is powerful reducing agent.***

$Cr^{2+} + 2e^- \rightarrow Cr \quad E^0 = -0.91V$

$Fe^{2+} + 2e^- \rightarrow Fe \quad E^0 = -0.44V.$

- The Std electrode potential of Cr^{+2} is –0.91V but for Fe^{+2} it is –0.44V.
- If the E^0 value is ***greater negative***, the metal is a powerful reducing agent.
- They will readily lose a electron.
- So Cr^{+2} is a strong reducing agent.

23. **The $E^0_{M^{2+}/M}$ value for copper is positive. Suggest a possible reason for this.**

- Copper has a positive reduction potential. Elemental copper is more stable than Cu^{2+}
- Cu^{2+} have a greater tendency to get reduced to elemental copper.

24. Describe the variable Oxidation states of the 3d elements.

- These elements have several (n – 1) d and ns electrons.
- The energy difference between the ns and the (n-1)d orbitals is very less. So they show variable oxidation state.
- At the beginning +3 is stable. Ex. Sc^{+3}
- At the end +2 is stable. Ex. Zn^{+2}
- Copper shows +1 and +2.
- Scandium show only +3.
- Manganese shows +2 to +7 oxidation state.
- Iron show +2 and +3 oxidation states.
- Mn^{+2} is more stable than Mn^{+3}. Because Mn^{+2} is having half-filled stable d^5 electronic configuration.

25. Which metal in the 3d series, which metal has +1 oxidation state, why?

- Copper show +1 oxidation state.
- Because by ***losing one electron it becomes a stable fully filled 3d^{10} configurations***.

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

- Cr(Z=24) Electronic configuration [Ar] $3d^5\ 4s^1$
- In the case of Cr, first electron has to be removed easily from 4s orbital to attain the more stable half-filled configuration. So Cr has lower ionisation enthalpy.
- Zn(Z=30) Electronic configuration [Ar] $3d^{10}\ 4s^2$
- Because in case of zinc first electron has to be removed from which fully filled orbital which is most stable so it require high energy to remove electron from it.

27. Transition metals show high melting points. why?

- The melting points of the transition metals are high due to **the 3d electrons being available for metallic bonding.**
- As we move from left to right along the transition metal series , melting point first increases as the ***number of unpaired d electrons available for metallic bonding increases***, reach a maximum value and then decreases, as the d electrons pair up and become less available for bonding.
- The maximum melting point at about the middle of transition metal series indicates ***that d^5 configuration is favourable for strong interatomic attraction.***

Important questions:

1. What are transition elements? Write two characteristics of the transition elements?(102) **PTA5Mi**
2. Classify the following elements into d-block and f-block elements: **(M20)**
   i) Tungsten ii) Ruthenium iii) promethium iv) Einsteinium
3. Transition metals show high melting points. Why? (103) **PTA 2MARK**
4. d-block elements have variable oxidation state. Why?(106) **PTA 2MARK**
5. Which is more stable Fe^{3+} or Fe^{2+}? Why? BB **M22 2M, M24 3M**
6. Which metal in the 3d series exhibits +1 oxidation state most frequently and why?(106-107) **S20 3MARK**

7. Explain why Cr^{3+} is strongly reducing while Mn^{3+} is strongly oxidizing? (108)**PTA5M i**
8. Sc^{3+}, V^{5+} are diamagnetic. Give reason. (110)
9. Calculate the magnetic moment of Ti^{3+}& V^{4+}. (110)
10. Calculate the number of unpaired electrons in Ti^{3+}, Mn^{2+} and calculate the spin only magnetic moment.(110) **A21, PTA 3MARK**
11. Most of the transition metals act as catalyst. Justify this statement.(110) **PTA 3M**
12. Explain the catalytic hydrogenation of alkene to alkane with equation. (110)
13. What is Zeigler – Natta catalyst? In which reaction it is used? Give equation.(110) **J22 2M**
14. Hume-Rothery rule. (110)
15. d-block elements readily form Alloy. Give reason.(111)
16. d-block elements formation of interstitial compounds (What are interstitial Compound)(111) (What are interstitial compounds? How they differ from the properties of its pure metals? Give an example)(111) **S20 2M, A21 2M, PTA 3M, J23 2M, J24 3M**
17. What are the properties of interstitial compounds? (111) **M22 3MARK**
18. d-block elements readily form complexes. Give reason. (111)
19. Describe preparation of potassium dichromate. (112)
20. How does potassium dichromate decompose on heating? (113)
21. Draw the structure of chromate, dichromate ions (113)
22. How does potassium dichromate act as oxidizing agent? (113)
23. Explain chromyl chloride test (114) **M20 3M**
24. Mention the uses of potassium dichromate (114)
25. How will you prepare potassium permanganate? (115)
26. Give the uses of potassium permanganate (118)
27. Justify the position of Lanthanoids and Actinoids in the periodic table.(BB)(118) **PTA5M i**
28. Electronic configuration of Lanthanoids. (120) Write down the electronic configuration of Gd(Z=64), Th(Z=90).
29. Oxidation state of Lanthanoids.(120)
30. Define, cause and consequences of Lanthanoid contraction.(121) **J20 5MARK, PTA 3M J23 5M, M24 5M**
31. Which is more basic among $Lu(OH)_3$ and $La(OH)_3$? Why?(BB) (121) PTA **2M, J24 2M**
32. Electronic configuration of actinoids.(122)

33. Oxidation state of actinoids.(123)

34. Differences between Lanthanoids and Actinoids. (123) **PTA 5MARK, J22 5M M23 3M**

5. COORDINATION CHEMISTRY

Answer the following questions: BOOK BACK

1. Write the IUPAC names for the following complexes.

i) **$Na_2[Ni(EDTA)]$** ➔ Sodium2,2',2'',2'''(ethane-1,2-diyldinitrilo)tetraacetatonickelate(II)

ii) **$[Ag(CN)_2]^-$** ➔ Dicyanidoargentate(I)ion

iii) **$[Co(en)_3]_2(SO_4)_3$** ➔ Tris(ethane -1,2 -diamine)cobalt(III)sulphate

iv) **$[Co(ONO)(NH_3)_5]^{2+}$** ➔ Pentaamminenitrito-κOcobalt(III) ion

v) **$[Pt(NH_3)_2Cl(NO_2)]$** ➔ Diamminechloridonitrito-κN platinum(II)

2. Write the formula for the following coordination compounds.

a) potassium hexacyanidoferrate(II) — **$K_4[Fe(CN)_6]$**

b) petacarbonyliron(0) — **$[Fe(CO)_5]$**

c) pentaamminenitrito-κNcobalt(III)ion — **$[Co(NH_3)_5(NO_2)]^{2+}$**

d) hexaamminecobalt(III)sulphate — **$[Co(NH_3)_6]_2(SO_4)_3$**

e) sodiumtetrafluoridodihydroxidochromate(III) — **$Na_3[CrF_4(OH)_2]$**

3. Arrange the following in order of increasing molar conductivity

i) $Mg[Cr(NH_3)(Cl)_5]$ ii) $[Cr(NH_3)_5Cl]_3[CoF_6]_2$ iii) $[Cr(NH_3)_3Cl_3]$

These complexes can ionize in solution as:

i) $Mg[Cr(NH_3)(Cl)_5] = Mg^{2+} + [Cr(NH_3)(Cl)_5]^{2-}$ **= 2 ions**

ii) $[Cr(NH_3)_5Cl]_3[CoF_6]_2 = [Cr(NH_3)_5Cl]^{2+} + [CoF_6]^{3-}$ **= 5 ions**

iii) $[Cr(NH_3)_3Cl_3]$ **= does not ionize**

As the number of ions in solution increases, their molar conductivity also increases.

$$[Cr(NH_3)_3Cl_3] < Mg[Cr(NH_3)(Cl)_5] < [Cr(NH_3)_5Cl]_3[CoF_6]_2$$

4. Give an example of coordination compound used in medicine and two examples of biologically important coordination compounds.

- Coordination compounds used in medicine **Cis-platin** (cis$[Pt(NH_3)_2Cl]$)is used as antitumor drug in cancer treatment.

- Ca- EDTA chelate is used in the treatment of lead and radioactive poisoning. That is for removing lead and radioactive metal ions from the body.

Examples of biologically important coordination compounds.

- Fe^{2+} Porphyrin complex present in RBC a important role in respiration.
- Mg^{2+} Porphyrin (corrin ring) complex present in chlorophyll plays a important role in photosynthesis.
- Co^{+} Porphyrin complex vitamin B_{12}.
- Many enzymes are known to be metal complexes, they regulate biological processes.

5. Based on VB theory explain why $[Cr(NH_3)_6]^{3+}$ is paramagnetic, while $[Ni(CN)_4]^{2-}$ is diamagnetic.

Complex	**$[Cr(NH_3)_6]^{3+}$**
Central metal ion and its electronic configuration	Cr^{3+} : $3d^3\,4s^0$
Outer orbitals of metal atom/ion	↑ ↑ ↑ ☐ ☐ ☐ ☐ ☐ ☐ ☐ $3d^3$ 4s 4p
Nature of ligand	NH_3 is weak field ligand. So no pairing of 3d electron in the metal.
Outer orbital of metal atom/ion in presence of ligand	↑ ↑ ↑ ☐ ☐ ☐ ☐ ☐ ☐ ☐ $3d^3$ 4s 4p
Hybridisation	(Coordination number - 6) d^2sp^3
Hybridised orbitals of the metal atom in the complex	↑ ↑ ↑ ☐ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ $3d^3$ $d^2\,sp^3$ Hybridised orbitals
Geometry	Octahedral
Magnetic property	No of unpaired electron = 3 Hence paramagnetic
Magnetic moment	$\mu_s = \sqrt{n(n+2)} = \sqrt{3(3+2)} = 3.872$ BM

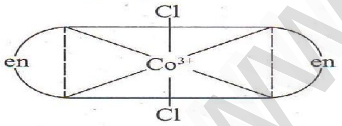
Complex	**$[Ni(CN)_4]^{2-}$**
Central metal ion and its electronic	Ni^{2+} : $3d^8\,4s^0$

configuration	
Outer orbitals of metal atom/ion	[↑↓][↑↓][↑↓][↑↓][↑↓][ ][↑↓][ ][ ][ ][ ] $3d^8$ $4s^2$ 4p
Nature of ligand	Strong field ligand causes the pairing of 3d electrons in the metal
Outer orbital of metal atom/ion in presence of ligand	[↑↓][↑↓][↑↓][↑↓][ ][ ][ ][ ][ ][ ][ ] $3d^8$ $4s^0$ $4p^0$
Hybridisation	(Coordination number – 4) Hybridisation – dsp^2
Hybridised orbitals of the metal atom in the complex	[↑↓][↑↓][↑↓][↑↓][ ][↑↓][↑↓][↑↓][↑↓][ ][ ] $3d^8$ dsp^2 $4p_z^0$ Hybridised orbitals
Geometry	Square planner
Magnetic property	No of unpaired electron = 0 Hence diamagnetic
Magnetic moment	$\mu_s = \sqrt{n(n+2)} = 0$

6. **Draw all possible geometrical isomers of the complex $[Co(en)_2Cl_2]^+$ and identify the optically active isomer.**

(*i*) Cis - $[Co(en)_2Cl_2]^+$

(*ii*) Trans $[Co(en)_2Cl_2]^+$



The coordination complex $[Co(en)_2Cl_2]^+$ has three isomers two optically active cis forms and the optically inactive trans form.

(Structure of optically active two cis form)

7. **$[Ti(H_2O)_6]^{3+}$ is coloured, while $[Sc(H_2O)_6]^{3+}$ is colourless- explain.** *(MARCH2020)*

Ti Z= 22 : $3d^2$ $4s^2$

Ti^{3+} : $3d^1$ $4s^0$.

- $[Ti(H_2O)_6]^{3+}$ Ti^{3+} has the outer electronic configuration **$3d^1$.**

- **d-d transition is possible** by absorption of energy from the visible light and produce purple colour.
- $[Ti(H_2O)_6]^{3+}$has **one unpaired electron** so it is coloured.

Sc (Z=21) : $3d^1\ 4s^2$

Sc^{3+} :$3d^0\ 4s^0$.

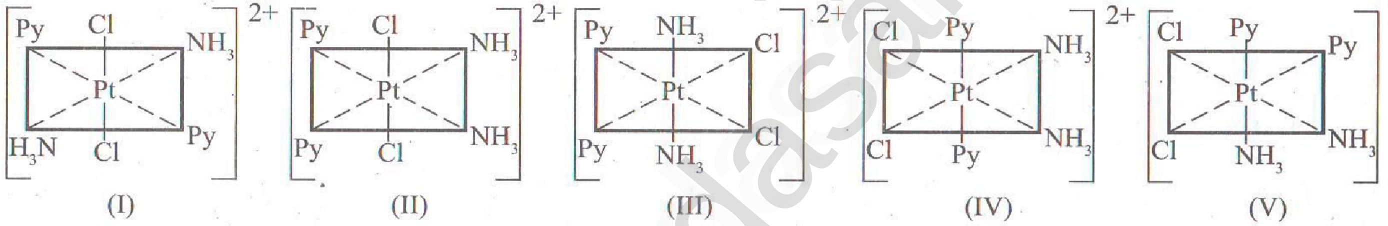
- Sc^{3+} has the outer electronic configuration **$3d^0$.**
- **d-d transition is not possible** and it is colourless.
- $[Sc(H_2O)_6]^{3+}$ has no unpaired electron so it is colourless.

8. Give an example for complex of the type $[Ma_2b_2c_2]$ where a, b, c are monodentate ligands and give the possible isomers.

The octahedral complexes of $[Ma_2b_2c_2]$ type can exist in **five geometrical isomers**.

(Where a, b, c are the complex monodentate).

$[Pt(NH_3)_2Cl_2(py)_2]^{2+}$



9. Give one test to differentiate $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$.

- $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers.
- When these isomers are dissolved in water, they ionize to give different ions in solution which react differently with different reagents.

Ex 1: Barium Chloride test

$[Co(NH_3)_5Cl]SO_4 + BaCl_2 \rightarrow$ **$BaSO_4\downarrow$ (White precipitate)**

$[Co(NH_3)_5SO_4]Cl + BaCl_2 \rightarrow$ No reaction

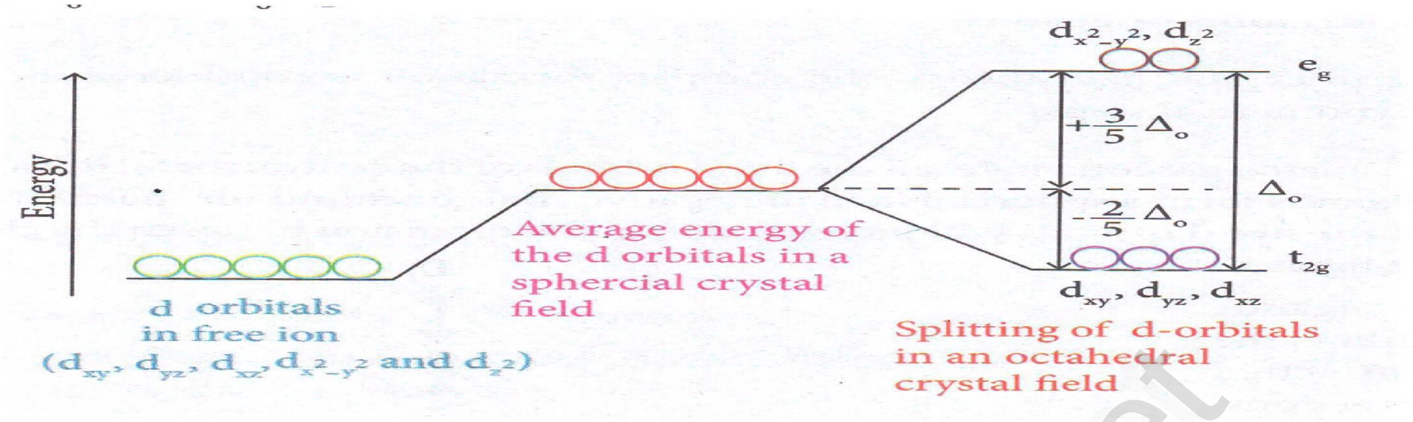
Ex 2 : Silver nitrate test

$[Co(NH_3)_5SO_4]Cl + AgNO_3 \rightarrow$ **$AgCl\downarrow$ (Curdy White precipitate)**

$[Co(NH_3)_5Cl]SO_4 + AgNO_3 \rightarrow$ No reaction

10. In an octahedral crystal field, draw the figure to show splitting of d orbitals.

During crystal field splitting in octahedral field, in order to maintain the average energy of the orbitals (bary centre) constant, the energy of the orbitals $d_{x^2-y^2}$ and dz^2 (e_g orbitals) will increase by 3/5 Δo and of the other three orbitals d_{xy}, d_{yz} and d_{zx}(t_{2g} orbitals) decrease by 2/5Δo. Here, Δo= crystal field spitting energy.



11. What is linkage isomerism? Explain with an example.

- Linkage isomers arises when an **ambidentate ligand** (NO_2^-, ONO^-, SCN^-, NCS^-, CN^-,NC^-) is bonded to the central metal atom/ion through either of its two different donor atoms.
- Ambidentate ligands are capable of coordinating in more than one way.

$[Co(NH_3)_5(NO_2)]^{2+}$ $[Co(NH_3)_5(ONO)]^{2+}$

Ex: $[Co(NH_3)_5(NO_2)]Cl_2$ Pentaamminenitrito-kNcobalt(III)chloride(N –attached)-yellow colour

$[Co(NH_3)_5ONO]Cl_2$ Pentaamminenitrito -kOcobalt(III)chloride (O –attached) –red colour

12. Classify the following ligand based on the number of donor atoms.

a) NH_3	-	monodentate	(N- Donar atom)
b) en	-	bidentate	(2N- Donar atom)
c) ox^{2-}	-	bidentate	(2O- Donar atom)
d) pyridine	-	monodentate	(N- Donar atom)

13. Give the difference between double salts and coordination compounds.

	Double salts	Co-ordination compound
1	They **lose their identity** in solution.	They **don't completely lose** their identity in solution.
2	Their properties are essentially the **same** as those of its constituent compounds.	Their properties are **different** from their constituents.
3	Completely dissociate into its **ions** in water.	**Do not** dissociate into its ions in water.

4	In double salts the metal atom/ion exhibit **normal valency**	The metal ion exhibits two types of valencies – **Primary and secondary.**
	Example: Mohr's salt (Ferrous ammonium sulphate $FeSO_4.(NH_4)_2SO_4.6H_2O$), Potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$	**Example**: $K_4[Fe(CN)_6]$
5	Give simple ions when added to water.	**Do not** give simple ions.
6	It can be **easily analyzed** by determining the ions present in the aqueous solution.	It **cannot** be easily analyzed by determining the ions present in the aqueous solution.

14. Write the postulates of Werner's theory.

1. Most of the elements exhibit, **two types of valence** (linkage) namely **primary valence** and **secondary valence** and each element tend to satisfy both the valences.
   - Primary valence is referred as the **oxidation state** of the metal atom.
   - Secondary valence as the **coordination number.**

For example, $CoCl_3.6NH_3$ according to Werner, the primary and secondary valences of cobalt are 3 and 6 respectively.

2. The **primary valence of a metal ion is positive** in most of the cases and zero in certain cases. They are always **satisfied by negative ions.**

   For example, the complex $CoCl_3.6NH_3$, The primary valence of Co is +3 and is satisfied by $3Cl^-$ ions.

3. The **secondary valence is satisfied by negative ions, neutral molecules, positive ions** or the combination of these.

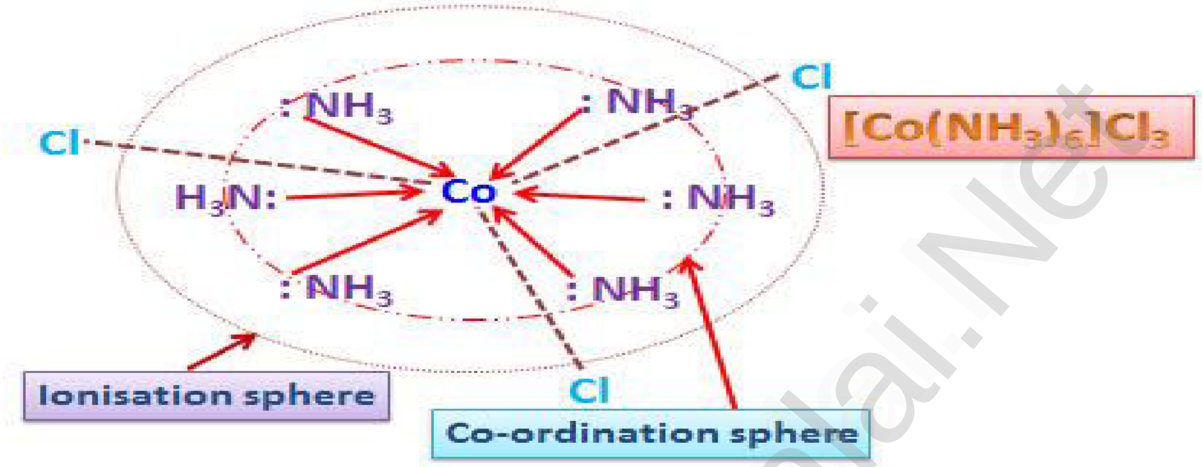
   The molecules or ion that satisfies secondary valencies are called ligands.

   For example,
   - $CoCl_3.6NH_3$ the secondary valence of cobalt is 6 and is satisfied by six neutral ammonia molecules,
   - $CoCl_3.5NH_3$ the secondary valence of cobalt is satisfied by five neutral ammonia molecules and a Cl^- ion.

4. According to Werner, there are **two spheres** of attraction around a metal atom/ion in a complex.

The **inner sphere is known as coordination sphere** and the groups present in this sphere are firmly attached to the metal.

The **outer sphere is called ionisation sphere.** The groups present in this sphere are loosely bound to the central metal ion and hence can be separated into ions upon dissolving the complex in a suitable solvent.



5. The **primary valences are non-directional** while the ***secondary valences are directional.*** The geometry of the complex is determined by the spatial arrangement of the groups which satisfy the secondary valence.

   For example, if a metal ion has a **secondary valence of six**, it has an **octahedral** geometry. If the **secondary valence is 4**, it has either **tetrahedral or square planar geometry.**

   The following table illustrates the Werner's postulates.

Complex	**formula**	**Groups satisfy the secondary valence(non-ionaisable, inner coordination sphere)**	**No. of ionisable Cl ions in the complex (outer coordination sphere)**	**No. of moles of AgCl formed = no. of moles of ionisable Cl^-**
$CoCl_3.6NH_3$	$[Co(NH_3)_6]Cl_3$	$6NH_3$	3 Cl^-	3 AgCl
$CoCl_3.5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	$5NH_3$ & 1 Cl^-	2 Cl^-	2 AgCl
Trans$CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	$4NH_3$ & 2 Cl^-	1 Cl^-	1 AgCl
Cis $CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	$4NH_3$ & 2 Cl^-	1 Cl^-	1 AgCl

Limitations of Werner's theory:

Even though, Werner's theory was able to explain a number of properties of coordination compounds, **it does not explain their colour and the magnetic properties.**

15. Why tetrahedral complexes do not exhibit geometrical isomerism.

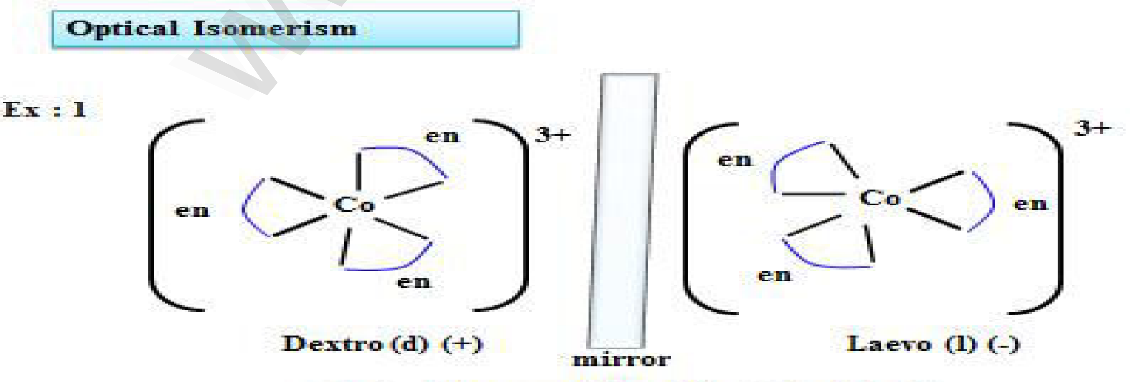
In tetrahedral geometry

- The relative positions of donor atoms of ligands attached with central metal atom are same with respect to each other.
- All the four ligands are adjacent or equidistant to one another.
- It has plane of symmetry.

Therefore, Tetrahedral complexes do not show geometrical isomerism.

16. Explain optical isomerism in coordination compounds with an example.

- The compounds which do not have a plane of symmetry show optical isomerism.
- Coordination compounds which possess chirality exhibit optical isomerism.
- The optically active isomers have non-superimposable mirror images or which cannot be superimposed on one another and the molecules which cannot be superimposed are **chiral.**
- The pair of two optically active isomers which are mirror images of each other are called **enantiomers.**
- **Dextro rotatory(+)**: The isomer which rotate the plane polarised light to the clockwise (right) is called 'd' (dextro rotatory).
- **Leavo rotatory(-):** The isomer which rotates the plane polarised light to the anticlockwise (left) is called 'l' (leavo rotatory).
- An equimolar mixture of dextro (d) and leavo (l) rotatory isomers is called **racemic mixture.**
- Optical isomerism is commonly shown by the octahedral complexes involving didentate ligands.
- **Ex:** $[Co(en)_3]^{3+}$



Optical isomers (d and l) of $[Co(en)_3]^{3+}$

17. What are hydrate isomers? Explain with an example.

- The exchange of free solvent molecules such as water, ammonia, alcohol etc.. in the crystal lattice with a ligand in the coordination entity will give different isomers.
- These type of isomers are called solvate isomers.
- If the solvent molecule is water, then these isomers are called hydrate isomers.
- **For example,** the complex with chemical formula $CrCl_3.6H_2O$ has three hydrate isomers as shown below.

$[Cr(H_2O)_6]Cl_3$	a **violet colour** compound and gives ***three chloride ions*** in solution
$[Cr(H_2O)_5Cl]Cl_2.H_2O$	a **pale green colour** compound and gives ***two chloride ions*** in solution
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$	**dark green colour** compound and gives ***one chloride ion*** in solution

18. What is crystal field splitting energy?

- After the crystal field splitting, the energy difference between the two levels (e_g and t_{2g}) is called crystal field splitting energy.
- In an octahedral complex, the d-orbitals of the central metal ion divide into two sets of different energies. The separation in energy is the crystal field splitting energy.

19. What is crystal field stabilization energy (CFSE) ?

The crystal field stabilisation energy is defined as the energy difference of electronic configurations in the ligand filed (E_{LF}) and the isotropic field/barycentre (E_{iso}).

$$\text{CFSE } (\Delta E_o) = \{E_{LF}\} - \{E_{iso}\} = \{[n_{t_{2g}}(-0.4)+n_{eg}(0.6)]\ \Delta_o + n_pP\} - \{n'_p\ P\}$$

Here, $n_{t_{2g}}$ is the number of electrons in t_{2g} orbitals; n_{eg} is number of electrons in e_g orbitals; n_p is number of electron pairs in the ligand field; n'_p is the number of electron pairs in the isotropic field (barycentre).

20. A solution of $[Ni(H_2O)_6]^{2+}$ is green, whereas a solution of $[Ni(CN)_4]^{2-}$ is colorless - Explain

$[Ni(H_2O)_6]^{2+}$,

↑↓	↑↓	↑↓	↑	↑

- Ni is in +2 oxidation state with the configuration **$3d^8$**. i.e., it has **two unpaired** electrons which **do not pair up** in the presence of **weak H_2O ligand.**
- Hence, it is coloured.
- The **d-d transition absorbs** red light and the complementary light emitted is **green.**

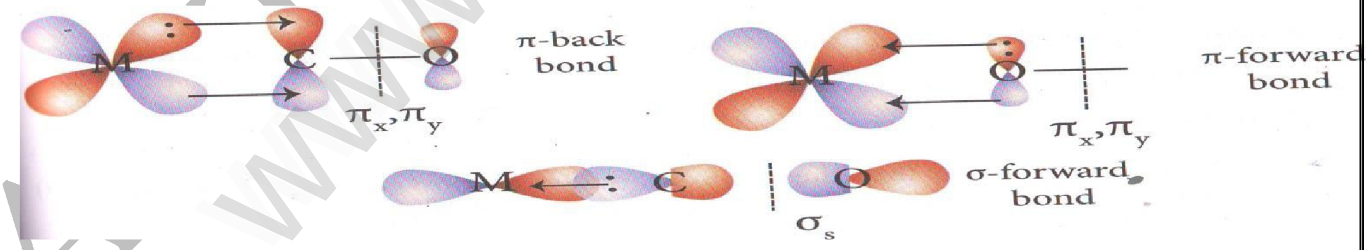
$[Ni(CN)_4]^{2-}$,

↑↓	↑↓	↑↓	↑↓	

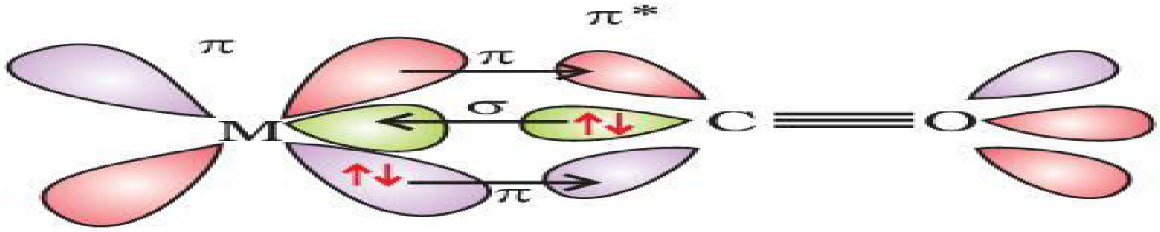
- Ni is again in +2 oxidation state with the configuration **$3d^8$**, but in the presence of strong CN^- ligand the two unpaired electrons in the 3d orbitals pair up.
- Hence **no d-d transition** is possible.
- Thus there is **no unpaired electron** present. Hence it is **colourless.**

21. Discuss briefly the nature of bonding in metal carbonyls.

- In metal carbonyls, the bond between metal atom and the carbonyl ligand consists of two components.
- The **first component** is an electron pair donation from the carbon atom of carbonyl ligand into a **vacant d-orbital** of central metal atom.
- This electron pair donation forms $M \xleftarrow{\sigma\ bond} CO$ sigma bond.
- This sigma bond formation increases the electron density in metal **d orbitals** and makes the metal **electron rich**.
- In order to compensate for this **increased electron density**, a filled metal **d-orbital interacts** with the **empty π* orbital** on the carbonyl ligand and transfers the added electron density **back to the ligand**.
- This second component is called **π-back bonding.**
- Thus in metal carbonyls, electron density moves from ligand to metal through sigma bonding and from metal to ligand through **pi bonding**,
- This synergic effect accounts for strong M ← CO bond in metal carbonyls.
  - This phenomenon is shown diagrammatically as follows.



- The metal-carbon bonds in metal carbonyls possess both σ and π-character.
- The M-C σ-bond is formed by the donation of lone pair of electrons of the carbonyl carbon into a vacant orbital of the metal.
- The M-C π-bond is formed by the donation of a pair of electrons from a filled d-orbital of metal into vacant antibonding π*orbital if carbon monoxide.
- The M-L bonding creates a synergic effect which strengthens the bond between CO and the metal.



Synergic bonding

22. What is the coordination entity formed when excess of liquid ammonia is added to an aqueous solution copper sulphate?

When excess of liquid ammonia is added to an aqueous solution of copper sulphate to give tetraamminecopper(II) sulphate.

$CuSO_4 \quad + \quad 4NH_3 \rightarrow \quad [Cu(NH_3)_4]SO_4$

(copper Sulphate) (Ammonia) tetraamminecopper(II) sulphate

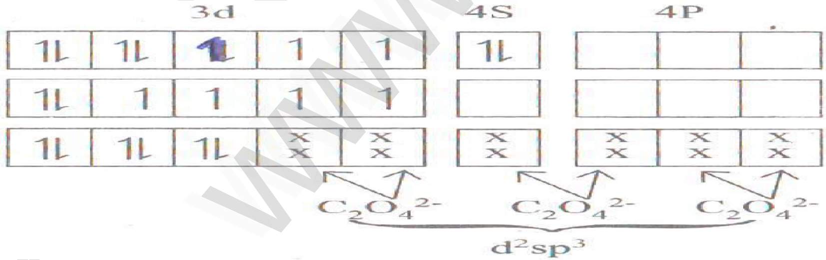
Therefore, the coordination entity is **$[Cu(NH_3)_4]^{2+}$**

23. On the basis of VB theory explain the nature of bonding in $[Co(C_2O_4)_3]^{3-}$.

- In the complex entity $[Co(C_2O_4)_3]^{3-}$, the Co is in +3 oxidation state.
- The outer electronic configuration of Co^{3+} is $3d^6$.
- The oxalato ligand is fairly **strong field ligand.**
- So it faces the 3d electrons in Co^{3+} to pair up and make two of the 3rd orbitals available for bonding.
- As a result, Co^{3+} shows d^2sp^3 hybridisation.

Electronic Configuration of Co atom

Electronic Configuration of Co^{3+} atom



Hybridisation and formation of $[Co(C_2O_4)_3]^{3-}$

- There is no unpaired electron in $[Co(C_2O_4)_3]^{3-}$.

  Thus $[Co(C_2O_4)_3]^{3-}$ is diamagnetic in nature.
- During the formation of $[Co(C_2O_4)_3]^{3-}$, two of the 3d-orbitals are used in bonding. Therefore it is a inner orbital (low spin) complex.

- The $[Co(C_2O_4)_3]^{3-}$ has the octahedral geometry.

24. What are the limitations of VB theory?

1. It does not explain the colour of the complex
2. It considers only the spin only magnetic moments and does not consider the other components of magnetic moments.
3. It does not provide a quantitative explanation as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal. For example, $[Fe(CN)_6]^{4-}$ is diamagnetic (low spin) whereas $[FeF_6]^{4-}$ is paramagnetic (high spin).

Extra points:

1. It does not distinguish between weak and strong ligands.
2. It does not give an extract explanation of thermodynamic or kinetic stabilities of coordination compounds.
3. It fails to explain relative energies of different shapes.
4. It fails to predict tetrahedral and square planar structures of some 4 coordinate complexes.
5. It is based on the number or assumptions.

25. Write the oxidation state, coordination number, nature of ligand, magnetic property and electronic configuration in octahedral crystal field for the complex $K_4[Mn(CN)_6]$.

Oxidation State	$K_4[Mn(CN)_6]$ $4(+1) + x + 6(-1) = 0$; **$x = +2$**
Coordination number	6
Nature of ligand	CN^- Monodentate ligand
Magnetic property	Mn – $3d^5\ 4s^2$ Mn^{2+} - $3d^5$ 3d $K_4[Mn(CN)_6]$ ↑↓ ↑↓ ↑ It has one unpaired electron. Therefore it is paramagnetic nature
Electronic configuration in octahedral crystal field	CN^- is strong field ligand therefore $t_{2g}^5\ e_g^0$

IMPORTANT QUESTIONS

1. Difference between double salt and coordination compounds.(131) **(A21, PTA 3M, M24 5Mi**
2. Explain Werner theory & limitation.(132) **(S20 5M, M22 5M)**
3. Write note on coordination entity.(133)
4. Define central metal ion (133) **M23 2M**
5. Write note on ligand (134)
6. Write the IUPAC ligand name for the following: a)$C_2O_4^{2-}$ b) H_2O c) Cl^- (137) **J22 3M**
7. Define coordination number.(134) **M22 2M**
8. Define oxidation number.(134)
9. Write note on coordination sphere.(134)
10. Write note on coordination polyhedron.(134)
11. In the complex $[Pt(NO_2)(H_2O)(NH_3)_2]Br$ identify the following i) central metal ion, ii) Ligand iii) coordination entity iv) oxidation number of the central metal ion. V) coordination number. **M23 3M**
12. In the complex $K_4[Mn(CN)_6]$ identify the following i) nature of Ligand ii) oxidation number of the central metal ion. iii) coordination number. **J23 3M**
13. Write the IUPAC name of the following: a) $[Ag(NH_3)_2]^+$ B) $[Co(NH_3)_5Cl]^{2+}$ **(M20 2M)**

    Write the following for the complex $[Ag(NH_3)_2]^+$. **M22 3M Compulsory**

    a)Ligand b) Central metal ion c) IUPAC Name.

    14. In the complex, $[Co(CN)_2Cl_2]Cl$, identify the following. **M24 3M Compulsory**

    i)IUPAC name ii)Central metal ion iii) Co-ordination number.

15. Write the IUPAC Name for the compound $Na_2[Ni(EDTA)]$ (140) **PTA5M i**
16. For the example $[Fe(en)_2Cl_2]Cl_2$, Identify **PTA5M i**

    1) Oxidation number of Fe, 2) Hybridization and shape

    3) Magnetic behavior, 4) Number of geometric isomers

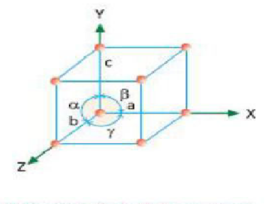
    5) Whether there may be optical isomer also? 6) IUPAC name

17. Explain types of complexes. (135)
18. Classification based on the net charge on the complex.(135)
19. Classification based on kind of ligands.(135)
20. Nomenclature of coordination compounds IUPAC Names(138-141)
21. Explain structural isomer. (coordination, Linkage **J24 3M,** ionization, solvate isomers) (142)

22. Write any two hydrate isomers of the complex with the molecular formula $CrCl_3.6H_2O$.(142)**M20 2M**
23. Explain Geometrical isomers (cis, trans isomer)(144,145)
24. Why tetrahedral complexes do not exhibit geometrical isomerism?(BB) (143)
25. Draw all possible geometrical isomers of the complex $[Co(en)_2Cl_2]^+$ and identify the optically active isomer. BBQ6 **J23 5M**
26. Define mer, fac isomer. (145)
27. Explain optical isomerism of coordination compounds with an example. (146)
28. Explain Valence Bond theory (VB Theory) & limitations. **(S20, J22 2M, PTA)**(149 &152)
29. Apply VB theory in $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$**(S20)**, $[Co(CN)_6]^{3-}$, $[Co(F)_6]^{3-}$**(M20)** (149-151)
30. Explain crystal field theory. (153)
31. In an Octahedral crystal field, draw the figure to show splitting of d orbitals (154) **J20 3M**
32. In a tetrahedral crystal field, draw the figure to show splitting of d orbitals (155)
33. Write note on spectrochemical series (156)
34. Calculate the CFSE value of $[Fe(H_2O)_6]^{3+}$ in high spin and low spin complexes. (157)
35. Calculate the CFSE value of $[Fe(CN)_6]^{3-}$ in high spin and low spin complexes. (158)
36. $[Sc(H_2O)_6]^{3+}$ is colourless – Explain. **M20 3M** (Explain about d-d transition) (159,160)
37. How are metal carbonyls classified based on the number of metal atom? (161)
38. How are metal carbonyls classified based on the structure? (161, 162)
39. Describe the nature of bonding in metallic carbonyls. (162) **M23 5M**
40. How can the stability of coordination complexes be interpreted? (163)
41. Define Labile, inert complexes. (163)
42. What is meant by stability constants? (163) significance of stability constants? (164)
43. Explain the importance and application of coordination compounds (166)
44. Give an example of Coordination compound used in medicine and a biologically important Coordination compound. (167) BB **M24 5Mii**
45. Mention the metal complexes and its metal ions are used in biological system (167) **S20 3M**
46. Give one test to differentiate $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$. **(BB) PTA 2M**

ALL IUPAC Name, Apply VB Theory & Revise Book Back (Evaluation) Question Answer

LESSON 6 SOLID STATE



Representation of dimensions of a unit cell

BOOK EVALUATION Answer the following questions:

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 and boiling 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***.
- They are **hard** as only strong external force can change the relative positions of ions.
- Ionic crystals are soluble in water and also in other polar solvents.
- Ionic crystal example: **NaCl**

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	Generally crystalline solids are anisotropic in nature	They are isotropic like liquids
4	They are true solids	They are considered as pseudo solids (or) super cooled liquids
5	Definite Heat of fusion	Heat of fusion is not definite
6	They have sharp melting points.	Gradually soften over a range of temperature and so can be moulded.
7	Examples: NaCl , diamond etc.,	Examples: Rubber, plastics, glass etc

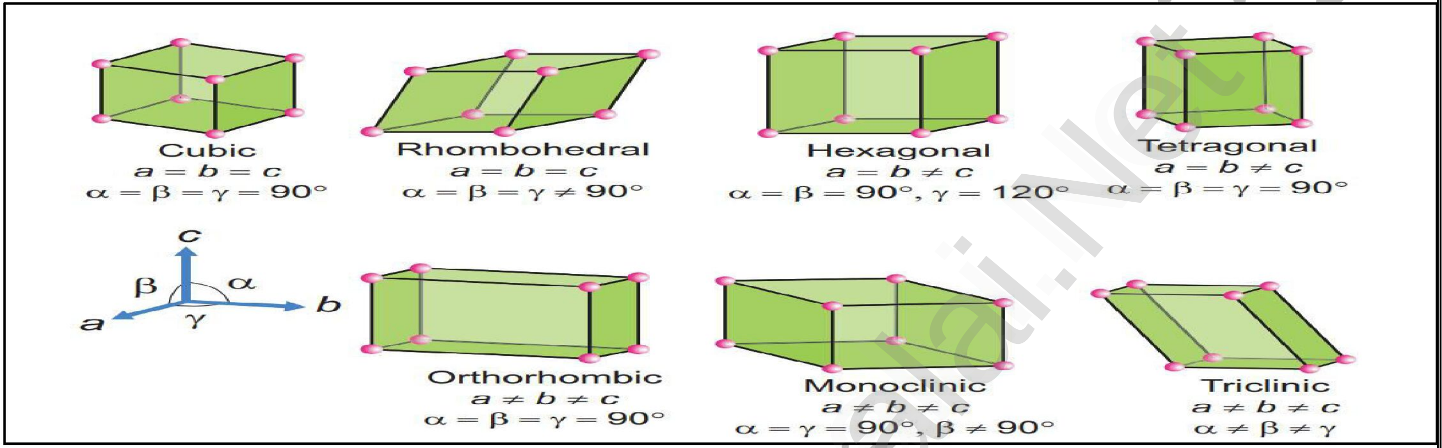
4. Classify the following solids. a) P_4 b) Brass c)diamond d) NaCl e) Iodine

a) P_4 - Molecular solid

b) Brass	-	Metallic solid
c) diamond	-	Covalent solid
d) NaCl	-	Ionic solid
e) Iodine	-	Molecular solid

5. Explain briefly seven types of unit cell.

Cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic and rhombohedral. They differ in the arrangement of their crystallographic axes and angles.



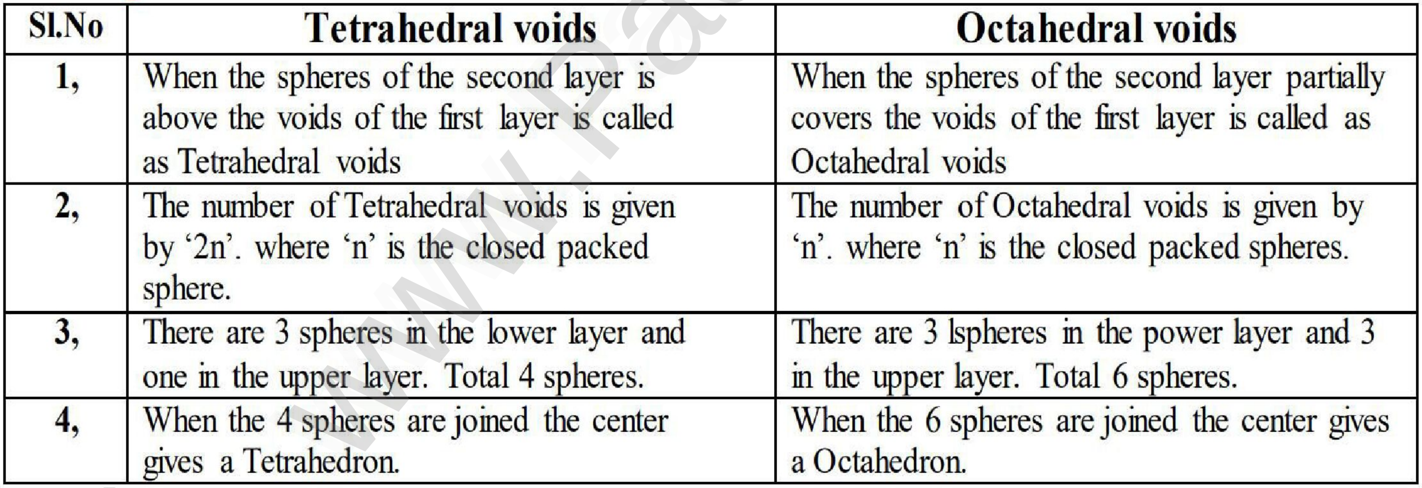
6. Distinguish between hexagonal close packing and cubic close packing.

Sl.No	Hexagonal close packing	cubic close packing
1.	The spheres can be arranged so as to fit into the depression in such a way that the thirdlayer is directly over a first layer (ABA arrangement)	In cubic close packing (ccp), the spheres of the fourth layer are present above the spheres of the first layer(ABC arrangement)
2.	This type is found in metals like Mg,Zn, etc.	This type is found in metals like Cu, Ag, etc.
3.	The unit cell of hexagonal close packing has 6 spheres.	The unit cell of cubic close packing has 4 spheres.
4.	The repeating unit of hexagonal close packing has two layers of spheres.	The repeating unit of hexagonal close packing has Threelayers of spheres.

Hexagonal Close packing	Cubic Close Packing
aba arrangement	abc arrangement
Hexagonal close packing is an arrangement of spheres in a lattice; there are ***two layers of spheres*** placed one on the other, forming tetrahedral and octahedral holes.	Cubic Close Packing is an arrangement of spheres in a lattice; there are ***three layers of spheres*** placed one on the other, covering all the octahedral holes by a third layer of spheres.
Holes	

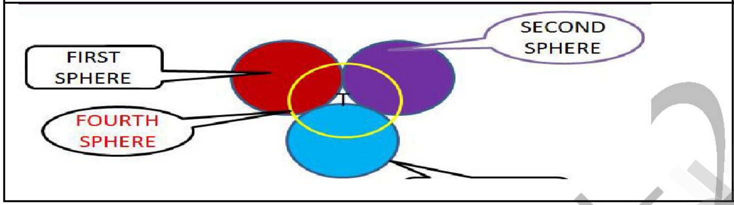
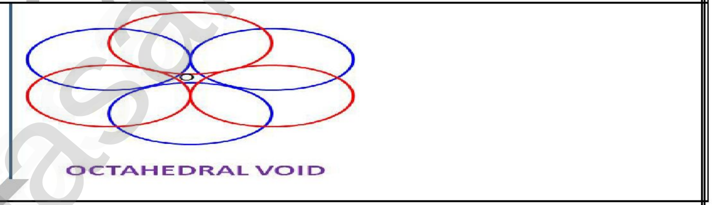
HCP has *tetrahedral* and *octahedral holes*.	CCP has *tetrahedral holes*, but the *octahedral holes are covered* by a layer of spheres.
Unit Cell	
The unit cell *contains 6 atoms*	The unit cell *contains 4 atoms*
HCP structure have *hexagonal unit cells*	CCP structures have *cubic unit cells.*
Repeating Unit	
The repeating unit of hcp has *two layers of spheres.*	The repeating unit of ccp has *three layers of spheres.*
Stacking Sequences of Layers	
HCP layers cycle between two equivalent shifted layers in an ABABAB sequence.	CCP layers cycle among three different layers in an ABCABC sequence
Volume of unit cells	
HCP units cells have a volume which can be calculated with the equation V=24 $\sqrt{2r^3}$ in which r =atomic randium	CCP units cells have a volume which can be calculated with the equation V = 8 $\sqrt{8r^3}$ in which r= atomic radius

7. Distinguish tetrahedral and octahedral voids.



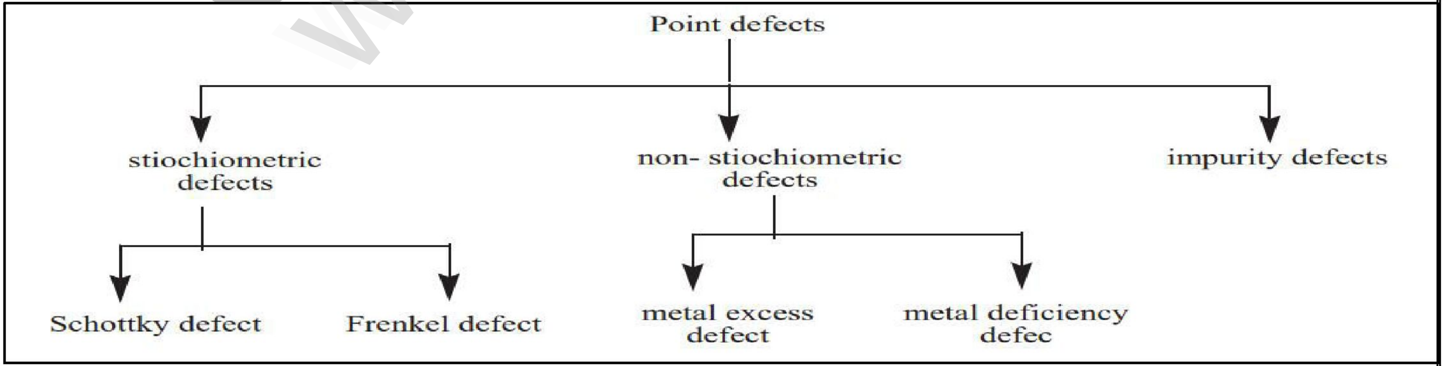
Sl.No	Tetrahedral voids	Octahedral voids
1,	When the spheres of the second layer is above the voids of the first layer is called as Tetrahedral voids	When the spheres of the second layer partially covers the voids of the first layer is called as Octahedral voids
2,	The number of Tetrahedral voids is given by '2n'. where 'n' is the closed packed sphere.	The number of Octahedral voids is given by 'n'. where 'n' is the closed packed spheres.
3,	There are 3 spheres in the lower layer and one in the upper layer. Total 4 spheres.	There are 3 lspheres in the power layer and 3 in the upper layer. Total 6 spheres.
4,	When the 4 spheres are joined the center gives a Tetrahedron.	When the 6 spheres are joined the center gives a Octahedron.

Tetrahedral void	Octahedral Void
Tetrahedral voids are unoccupied, *empty spaces present in substances having tetrahedral crystal systems.*	Octahedral voids are unoccupied, *empty spaces in substances having octahedral crystal systems.*

Crystal System	
Tetrahedral Voids can be found in substances having tetrahedral crystal systems.	Octahedral Voids can be found in substances having an octahedral arrangement in their crystal system.
Location in the Unit cell	
Tetrahedral Voids can be observed in ***edges of the unit cell.***	Octahedral Voids can be observed in the ***centre of the unit cell.***
Coordination Number	
The coordination number of the tetrahedral void is **four.**	The Coordination number of the octahedral void is **six.**
Number of Voids in the Crystal Lattice	
There are **two tetrahedral voids** per sphere in the crystal lattice.	There is **one octahedral void per sphere** in the crystal lattice.
	

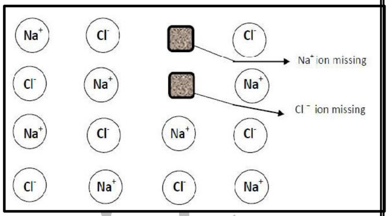
8. What are point defects?

- The irregularities or deviations from ideal arrangement around a point (or an atom) in a crystalline solid.
  - If the deviation occurs due to missing atoms, displaced atoms, or extra atoms the imperfection is named as a **point defect.**
  - Such defects arise due to imperfect packing during the original crystallization or they may arise from thermal vibrations of atoms at elevated temperatures.



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,** KCl, KBr, RbCl, CsCl, CsBr.
- Presence of large number of schottky defects in a crystal, **lowers its density.**
- **For example,** the theoretical density of vanadium monoxide (VO) calculated using the edge length of the unit cell is 6.5 g cm^{-3}, but the actual experimental density is 5.6g cm^{-3}.
- It indicates that there is approximately 14% Schottky defect in VO crystal.
- Schottky defect in VO crystal=calculated density – actual experimental density/calculated density x100

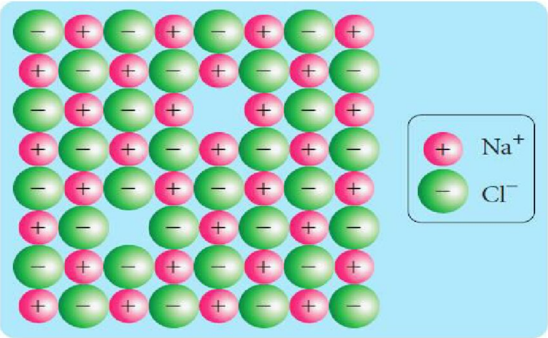
  =6.5-5.6/6.5x100

  =0.1384x100= **13.84%**
- Presence of Schottky defect in the crystal provides a simple way by which atoms or ions can move within the crystal lattice.

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.

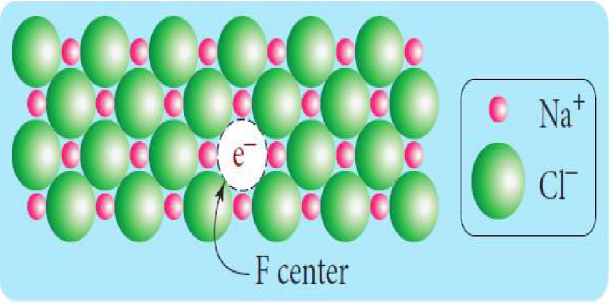
- Alkali metal halides NaCl, KCl show this type of defect.
- The electrical neutrality of the crystal can be maintained by the presence of anionic vacancies equal to the excess metal ions (or) by the presence of extra cation and electron present in interstitial position.
- **For example,** when NaCl crystals are heated in the presence of sodium vapour, Na^+ ions are formed and are deposited on the surface of the crystal.



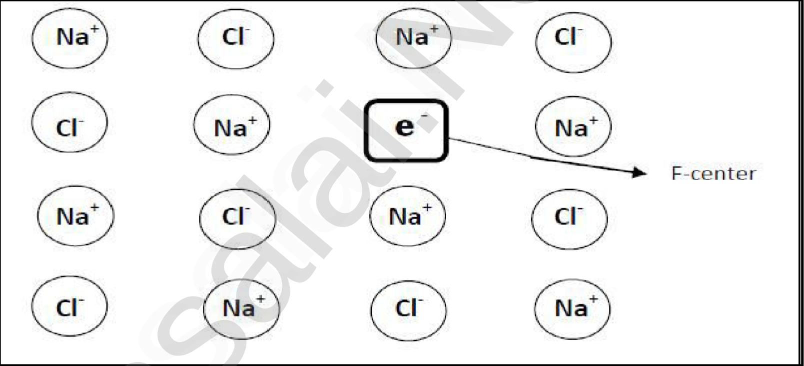
Schottky Defect

- Chloride ions (Cl^-) diffuse to the surface from the lattice point and combines with Na^+ ion. 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 $\mathbf{Na_{1+x}Cl}$.

- **(The anionic vacancies occupied by unpaired electrons are called F – Centre's (German word Farbenzenter for colour center))**
- **Excess of Lithium in LiCl crystal imparts (gives) pink color.**
- **Excess of potassium in KCl Crystal gives it lilac or violet color.**

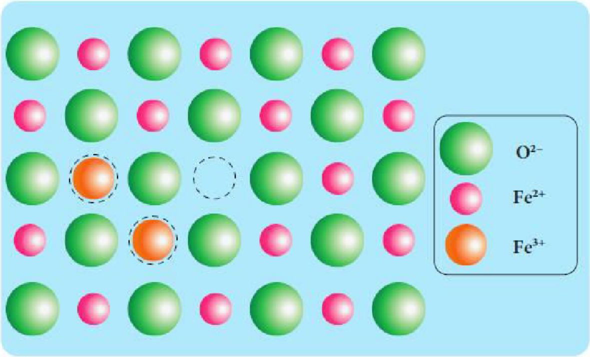


Metal Excess Defect

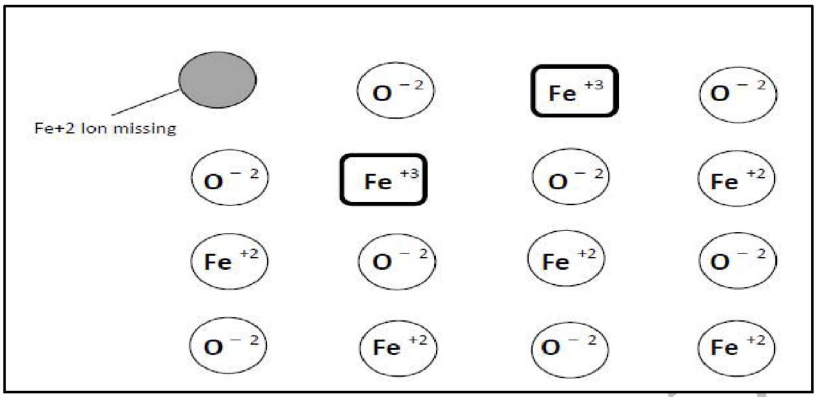


Metal deficiency defect:

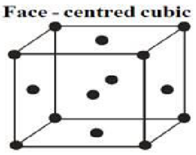
- Metal deficiency defect arises due to **the presence of less number of cations than the anions.**
- This defect is observed in a crystal in which, the **cations have variable oxidation states.**
- For example, in FeO crystal, some of the Fe^{2+} ions are missing from the crystal lattice.
- To maintain 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 Fe_xO. where x ranges from 0.93 to 0.98.



Metal Deficiency Defect



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



The atoms in the face centre is being shared by two unit cells each in the face centers makes (1/2) contribution to the unit cell.

Number of atoms in a 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. (refer book page 190)

(i) AAA… type:

i. Linear arrangement of spheres in one direction is repeated in two dimension i.e., more number of rows can be generated identical to the one dimensional arrangement such that all spheres of different rows align vertically as well as horizontally as shown in the fig.

ii. If we denote the first row as A type arrangement, then the above-mentioned packing is called AAA type, because all rows are identical as the first one.

iii. In this arrangement each sphere is in contact with four of its neighbours.

(ii) ABAB.. Type:

(i) In this type, the second row spheres are arranged in such a way that they fit in the depression of the first row as shown in the figure.

(ii) The second row is denoted as B type.

(iii) The third row is arranged similar to the first row A, and the fourth one is arranged similar to second one. i.e., the pattern is repeated as ABAB….In this arrangement each sphere is in contact with 6 of its neighbouring spheres.

(iv) On comparing these two arrangements (AAAA...type and ABAB….type) we found that the closest arrangement is ABAB…type.

(iii) ABC.. Type:

(i) Alternatively, the third layer may be placed over the second layer in such a way that all the spheres of the third layer fit in octahedral voids.

(ii) This arrangement of the third layer is different from other two layers (a) and (b), and hence, the third layer is designated (c).

(iii) If the stacking of layers is continued in abcabcabc… pattern, then the arrangement is called cubic close packed (ccp) structure.

13. Why ionic crystals are hard and brittle?

i. Ionic crystalline are hard because they are bound together by strong electrostatic attractive forces.

ii. To maximize the attractive force, cations are surrounded by as many anions as possible

iii. Ionic crystal is a presence of strong electrostatic forces of attraction in ionic solids which makes the ionic solids hard and there is also a non – directional nature in ionic crystals therefore, ionic bonds are brittle.

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

Packing efficiency:

Here, the spheres are touching along the leading diagonal of the cube as shown in the fig.

In ΔABC

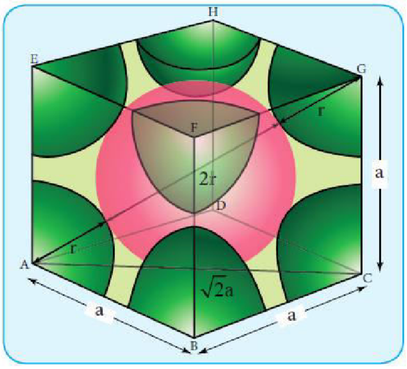
$$AC^2 = AB^2 + BC^2$$

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

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

In ACG

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



$$\therefore \text{Number of atoms in a bcc unit cell} = \left(\frac{N_c}{8}\right)+\left(\frac{N_b}{1}\right) = \left(\frac{8}{8}+\frac{1}{1}\right) = (1+1) = 2$$

$$AG = \sqrt{AC^2 + CG^2} = \sqrt{\left(\sqrt{2}a\right)^2 + a^2}$$

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

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

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

Volume of the sphere with radius 'r'

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

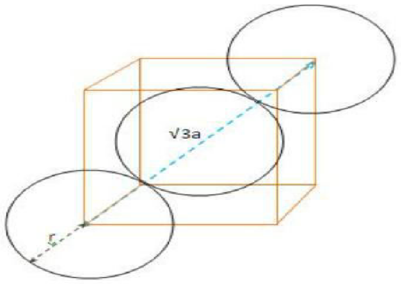
$$= \frac{\sqrt{3}}{16}\pi a^3$$

Number of spheres belong to a unit cell in **bcc arrangement** is equal to two and hence

The total volume of all spheres $= 2 \times \left(\frac{\sqrt{3}\pi a^3}{16}\right) = \frac{\sqrt{3}\pi a^3}{8}$

Packing fraction (efficiency) $= \frac{\text{Total volume occupied by spheres in a unit cell}}{\text{Volume of the Unit cell } (a^3)} \times 100$

$$\text{Packing fraction} = \frac{\left(\frac{\sqrt{3}\pi a^3}{8}\right)}{(a^3)} \times 100$$



$$= \frac{\sqrt{3}\pi}{8} \times 100 = \sqrt{3}\pi \times 12.5$$

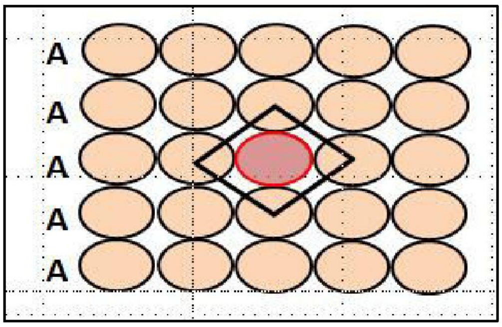
$$= 1.732 \times 3.14 \times 12.5$$

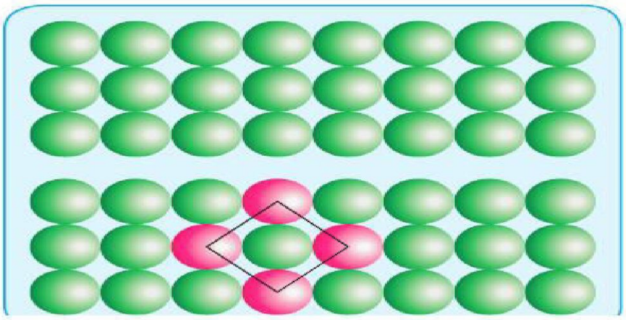
Packing Fraction = 68 %

i.e., 68% of the available volume is occupied. The available space is used more efficiently than in simple cubic packing.

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

- Linear arrangement of spheres in one direction is repeated in two dimension i.e., more number of rows can be generated identical to the one dimensional arrangement such that all spheres of different rows align vertically as well as horizontally.
- If we denote the first row as A type arrangement, then the above mentioned packing is called AAA type, because all rows are identical as the first one.
- In this arrangement each sphere is in contact with ***four of its neighbours.***
- Coordination number is 4.





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

(i) The number of nearest neighbours that surrounding a particle in a crystal is called the coordination number of that particle.

(ii) In a body – centered cubic structure coordination number of atoms is 8.

17. 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.

$\rho = \frac{nM}{a^3 N_A}$ $\rho = 7.2$ gcm^{-3}

$M = \frac{\rho a^3 N_A}{n}$ a = 288 pm = 288 × 10^{-10} cm

$N_A = 6.023 \times 10^{23}$ atom / mol

n = 2 atoms

$$\overset{3.6}{=} \frac{\cancel{7.2}\ \cancel{gcm}^{-3} \times (288 \times 10^{-10} \cancel{cm})^3 \times 6.023 \times 10^{23} \cancel{atoms}/mol}{\cancel{2}\ \cancel{atoms}}$$

$= 3.6 \times (288)^3 \times 10^{-30} \times 6.023 \times 10^{23}$

$= 3.6 \times (288)^3 \times 10^{-7} \times 6.023$ gmol^{-1}

= 51.78 gmol^{-1}

log 3.6 0.5563

3log 288 7.3782 3log 288 2.4594

log 10^{-7} $\bar{7}.0000$ + 3

6.023 0.7798 7.3782

1.7142

Antilog .7142 => 51.78

Number of atom present 208g of the element $= \frac{Mass}{Molar\ mass} \times N_A$

$= \frac{208g}{51.78 gmol^{-1}}$ x 6.023x10^{23}atoms mol^{-1}

= 24.18×10^{23}atom

log 208 2.3181

log 6.023 0.7798

3.0978

log 51.78 1.7142

1.3836

Antilog .3836 => 24.18

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

Radius (r) = 125 pm Since Aluminium crystallizes in fcc $4r = \sqrt{2}\ a$

$$a = 2\sqrt{2}\,r$$
$$= 2 \times 1.414 \times 125 \text{ pm}$$
$$= 353.4 \text{ pm}$$

(OR)

$4r = a\sqrt{2}$ r = 125 pm

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

$= \frac{2\times2\times125}{\sqrt{2}}$ $2 = \sqrt{2}\times\sqrt{2}$

$= \frac{\sqrt{2}\times\sqrt{2}\times2\times125}{\sqrt{2}} = \frac{\cancel{\sqrt{2}}\times\sqrt{2}\times250}{\cancel{\sqrt{2}}}$

$= 1.414 \times 250$

$a = 353.4\text{pm}$

log 1.414	0.1504
log 250	2.3979 (+)
	2.5483

Antilog .5483 => 353.4

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

Cation vacancies produced by NaCl= 10^{-2} mol

Since, 100 moles of NaCl produces cation vacancies after doping =10^{-2} mol

Therefore, 1 mole of NaCl will produce cation vacancies after doping.

$$= \frac{10^{-2}}{100} = \frac{10^{-2}}{10^{2}} = 10^{-4} \text{ moles of } SrCl_2$$

Total cationic vacancies, = 10^{-4} × Avogadro's number (N_A)

$= 10^{-4} \times 6.023 \times 10^{23}$ $= 6.023 \times 10^{19}$

The Concentration of cation (Sr^{2+}) vacancy = 6.023×10^{19}

So, that the concentration of cation vacancies created by $SrCl_2$ is 6.022×10^{19} per mol of NaCl

20. KF crystallizes in fcc structure like sodium chloride. calculate the distance between K^+ and F^- in KF.(Given : density of KF is 2.48 $g\ cm^{-3}$)

$\rho = \frac{nM}{a^3 N_A}$ n = 4 atoms

M = K+ F = 39+19

= 58 gmol^{-1}

$\rho = 2.48\text{gcm}^{-3}$

$N_A = 6.023 \times 10^{23}$atoms / mol

log 4	0.6021	2.3655
log 58	1.7634 (+)	1.1743 (–)
	2.3655	1.1912
log 2.48	0.3945	Antilog 0.1912 => 15.53
log 6.023	0.7798	

1.1743

$$a^3 = \frac{4\ \cancel{atoms} \times 58\ \cancel{g}\ \cancel{mol^{-1}}}{2.48\ \cancel{g}\ cm^{-3} \times 6.023 \times 10^{23}\ \cancel{atoms}\ \cancel{mol^{-1}}}$$

$a^3 = 15.15 \times 10^{-23}\ cm^3$

$= 155.3 \times 10^{-24}\ cm^3$

$= 155.3 \times (10^{-8})^3\ cm^3$

$a^3 = (5.374)^3 \times (10^{-8})^3\ cm^3 = 537.4 \times 10^{-10} cm$

a = 537.4 pm

$\sqrt[3]{155.3} = 155.3^{1/3}$

$\log 155.3^{1/3} = \frac{1}{3} \log 155.3$

$\log 155.3 = 2.1911 = \frac{2.1911}{3} = 0.7303$

Antilog 0.7303 => 5.374

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

$\rho = \frac{nM}{a^3 N_A}$ $\rho = 10 gcm^{-3}$

a = 100pm

$= 100 \times 10^{-10}$cm

$N_A = 6.023 \times 10^{23}$ atoms mol $^{-1}$

n = 4 atoms

$$= \frac{10\ g\ cm^{-3} \times (100 \times 10^{-10} cm)^3 \times 6.023 \times 10^{23}\ \cancel{atoms}\ mol^{-1}}{4\ atoms}$$

$$= \frac{10 \times 10^{6} \times 10^{-30} \times 6.023 \times 10^{23}}{4}$$

$= \frac{6.023}{4}$ gmol^{-1} = 1.505 gmol^{-1}

log 6.023 0.7798

log 4 0.6021

0.1777

Antilog 0.1777 => 1.505

Number of atoms present in 1g of crystal

$$= \frac{Mass}{Molar\ Mass} \times N_A$$

$$= \frac{1g \times 6.023\ atoms\ mol^{-1}}{1.505 gmol^{-1}}$$

= 4 atoms

log 6.023 0.7798

log 1.505 0.1775 (-)

0.6023

Antilog .6023 => 4.002

22. 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?

i. It is given that the atoms of x are present at the corners of the cube

∴ No. of atoms of x in one unit cell = $8 \times \frac{1}{8} = 1$

ii. It is also given that the atoms of y are present at the body centre

∴ No. of atoms of y in one unit cell = 1

Hence the formula of the compound is **XY**

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

In a body centered cubic lattic atom touch along the body diagonal of the cube. Thus $4r = \sqrt{3a}$

For BCC

$r = \frac{\sqrt{3}}{4} a$ $a = 4.3 \times 10^{-8}$

$r = \frac{\sqrt{3} \times 4.3 \times 10^{-8} cm}{4}$ $r = ?$

$= \frac{1.732 \times 4.3 \times 10^{-8} cm}{4}$

$= 1.862 \times 10^{-8}$ cm

r = 1.862Å

Radius of sodium atom 1.862Å

$\sqrt{3}$ log 3 $\frac{\cancel{0.4771}}{\cancel{2}}$ 0.2385

Antilog .2385 => 1.732

log 1.732 0.2385

log 4.3 0.6335 (+)

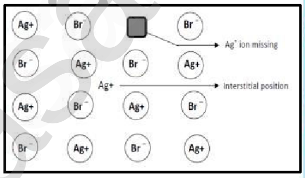
0.8720

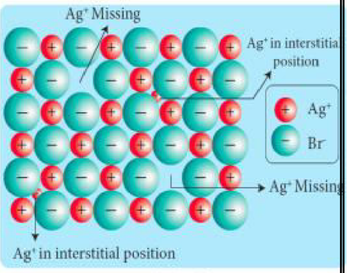
log 4 0.6021

0.2699

Antilog 0.2699 => 1.862

25. Write a note on Frenkel defect.





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 is shown by ionic solids in which cation and anion **differ in size.**
- This defect **does not affect the density** of the crystal.
- **For example ZnS, AgCl, AgBr** in this case, small Ag^+ ion leaves its normal site and occupies an interstitial position as shown in the figure.

Example

1. **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}?**

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

n = number of atom unit cell n = 2

M = Molar mass ($gmol^{-1}$)

a = Volume of the unit cell

N_A = Avagadro's number

M = 137.3$gmol^{-1}$

a = 508pm = 508×10^{-12}cm

log 2 0.3010 3log 508 2.7051

$a = 508 \times 10^{-10}$cm

$N_A = 6.023\times 10^{23}$cm atoms mol^{-1}

$$= \frac{2\ \cancel{atoms} \times 137.3 g\cancel{mol^{-1}}}{(508 \times 10^{-10} cm)^3 \times 6.023\times 10^{23} \cancel{atoms\ mol^{-1}}}$$

$$= \frac{2 \times 137.3 gcm^{-3}}{(508)^3 \times (10^{-10})^3 \times 6.023\times 10^{23}}$$

$$= \frac{2 \times 137.3}{(508)^3 \times 6.023\times 10^{-7}}$$

= 3.447 gcm^{-3}

= 3.45 gcm^{-3}

log 137.3   2.1377 (+)   3(+)

2.4387   8.1177

3log 508   8.1177   2.4387

log 6.023   0.7798   1.8975 (-)

log 10^{-7} $\bar{7}.0000$ 0.5412

1.8975   3.475

Antilog .5412 => 3.477   2

3.477

LESSON 6 SOLID STATE

1. Write General characteristics of solids. (177)
2. Difference between crystalline solids and Amorphous solids.(178)**PTA 3M, M22 5M J23 5M**
3. Define Isotropy and anisotropy.(178) **(S20)**
4. Explain ionic solids. (Introduction, NaCl diagram, Characteristics)(179) **PTA 5M i**
5. What are covalent solids? (179) **M22 2M**
6. Explain molecular solids. (179)
7. What are Metallic solids? (180)
8. Classify the following into covalent, molecular, ionic and metallic solids.**(A21) 3MARK C**
   (i) Diamond (ii) Brass (iii) NaCl (iv) Naphthalene (v) Glucose (vi) SiO_2
9. Define the terms crystal lattice and unit cell. (180) **PTA3M** Define unit cell. (180) **J22 2M**
10. What is meant by term "Coordination Number"? What is the Coordination Number of atoms in a bcc structure? (180) **A21 3MARK, M22 2M**
11. Define primitive& non-primitive unit cells? (181)
12. Explain briefly seven types of unit cell. (181)
13. Write note on SC. (183)
14. Write note on BCC. (183)
15. Sketch Face Centered cubic unit cell(FCC) and Calculate the number of atoms present in it. (184) **PTA3M M23 2M**
16. What is Bragg's equation? (184) **PTA 2M**

17. How will you calculate the density of the unit cell? (185)
18. 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}? (185)
19. An element has a face centered cubic unit cell with a length of 352.4 pm along an edge. The density of the element is 8.9 gcm^{-3}. How many atoms are present in 100 g of an element. (186)
20. What is packing efficiency? (187) **PTA 5M ii, J22 5Mi**
21. Calculate the Percentage efficiency of packing in case of simple cubic crystal?(187) **M24 5M**
22. Calculate the percentage efficiency of packing in body centered cubic system (188)**PTA3M**
23. What is void and its type? (190)
24. Note on radius ratio (192)
25. If the radius of the compound is between 0.155 – 0.225, find out the co-ordination number an structure of the compound. (192) **J20 5Mi**
26. If the no. of close packed sphere is 6, calculate the number of Octahedral voids and Tetrahedral voids generated. **(M20) 2MARK**

    ANS: Octahedral voids **(n)=6** Tetrahedral voids**(2n)=2x6=12**
27. Calculate the percentage efficiency of packing in face centered cubic system (192)
28. Outline the classification of point defects. (193) **PTA5M ii**
29. Explain Schottky defect **(GM5M, S20)**& Frenkel defect. **(M20, PTA3M, J22 5Mii)** (Stoichiometric defects) (193) **M23 5M** (Schottky, Frenkel defect)
30. Explain 'f' centers with a neat diagram.(194) **PTA5M ii**
31. Explain Metal excess defect, metal deficiency defect. (Non-Stoichiometric defects) (194)
32. Write note on Impurity defect. (195)
33. Aluminium crystallizes in a cubic close packed structure. Its metallic radius is 125pm. Calculate the edge length of unit cell. BB **M24 3M**
34. 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? (BB)**PTA 5M i**
35. An atom crystallizes in FCC crystal lattice and has a density of $10gcm^{-3}$ with unit cell edge length of 100pm. Calculate the number of atoms present in 1g of crystal. (BBQ$_{22}$201) **5M**

36. A face centred cubic solid of an element (atomic mass 60 $gmol^{-1}$) has a cube edge of 4A°. Calculate its density.(186) **GM3M**

37. What is piezoelectricity? (195)

ALL INSIDE PROBLEM & Revise Book Back (Evaluation) Question Answer

LESSON 7 CHEMICAL KINETICS

Answer the following questions:

1. **Define average rate and instantaneous rate.**

Average rate of chemical reaction

It may be defined as **the change in concentration of a reactant or product of a chemical reaction in a given interval of time.**

(It is defined as the change in concentration of the components of reactants over a finite time period.)

$$\text{Average rate of reaction} = \frac{\textit{Change in concentration of reactants or products}}{\textit{Time interval}}$$

Instantaneous rate of reaction

It may be defined as ***the rate of the reaction, at a particular instant during the reaction.***

Consider the reaction, R→P

Instantaneous reaction rate $= -\frac{d[R]}{dt} = \frac{d[P]}{dt}$ where, d[R] = small change in concentration.

dt = small change of time

AVERAGE RATE	INSTANTANEOUS RATE
Total change in concentration of reactant or product by the elapsed time	Change in concentration of reactant or product at particular instant of time
Denoted by $\Delta X/\Delta T$	Denoted by dx/dt.

2. Define rate law and rate constant.

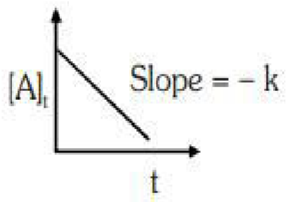
Rate Law: ***The expression in which reaction rate is given in terms of molar concentration of the reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical reaction.***

$xA + yB \rightarrow$ Products,

For a reaction rate law = $k[A]^m[B]^n$

k=rate constant

Rate Constant: When the concentration of reactants is unity, then the rate of reaction is known as rate constant. It is also called specific reaction rate.



3. Derive integrated rate law for a zero order reaction A→product

A reaction in which the rate is ***independent of the concentration*** of the reactant over a wide range of concentrations is called as zero order reactions. Such reactions are rare.

Let us consider the following hypothetical zero order reaction.

A → product

The rate law can be written as, Rate $\propto [A]^0$

$$\text{Rate} = k\,[A]^0$$

$$\frac{-d[A]}{dt} = k(1) \qquad (\therefore [A]^0 = 1)$$

$$-\,d[A] = k\,dt$$

Integrate the above equation between the limits of $[A_0]$ at zero time and [A] at some later time 't',

$$-\int_{[A_0]}^{[A]} d[A] = k \int_0^t dt$$

$$-\,(\,[A]\,)_{[A_0]}^{[A]} = k\,(t)_0^t$$

$$[A_0] - [A] = kt$$

$$k = \frac{[A_0] - [A]}{t} \quad \text{-----------(2)}$$

Equation (2) is in the form of a straight line y = mx + c

ie., $[A] = -kt + [A_0]$ ➔ $y = c + mx$

$$[A] = -kt + [A_0]$$

➔ $y = c + mx$

A plot of [A] vs time gives a straight line with a slope of –k and y- intercept of $[A_0]$.

4. Define half-life of a reaction. Show that for a first order reaction half-life is independent of initial concentration.

(i) The Half-life of a reaction is defined as ***the time required for the reactant concentration to one half its initial value.***

(ii) For first order reaction, the half- life is a constant i.e., it does not depend on the initial concentration. The rate constant for a first order reaction is given by

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]} \quad \text{at } t = t_{\frac{1}{2}} \;;\; [A] = \frac{[A_0]}{2}$$

$$k = \frac{2.303}{t_{\frac{1}{2}}}\log\frac{[A_0]}{\frac{[A_0]}{2}} \qquad k = \frac{2.303}{t_{\frac{1}{2}}}\log 2$$

$$k = \frac{2.303 \times 0.3010}{t_{\frac{1}{2}}} = \frac{0.6932}{t_{\frac{1}{2}}}$$

$$t_{\frac{1}{2}} = \frac{0.6932}{k}$$

5. What is an elementary reaction? Give the differences between order and molecularity of a reaction.

(i) Elementary reaction: Each and every single step in a reaction mechanism is called an elementary reaction.

(ii)

Order of a reaction	**Molecularity of a reaction**
It is the sum of the powers of concentration terms involved in the experimentally determined rate law.	It is the total number of reactant Species that are involved in an elementary step.
It can be zero (or) fractional (or) integer	It is always a whole number, cannot be zero or a fractional number.
It is assigned for an overall reaction	It is assigned for each elementary step of mechanism.

6. Explain the rate determining step with an example.

(i) The decomposition of hydrogen peroxide catalyzed by I^- .

$$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

(ii) It is experimentally found that the reaction is first order with respect to both H_2O_2 and I^-, which indicates that I^- is also involved in the reaction.

The mechanism involves the following steps.

Step:1

$H_2O_{2(aq)} + I^-_{(aq)} \rightarrow H_2O_{(l)} + OI^-_{(aq)}$ slow

Step : 2

$H_2O_{2(aq)} + OI^-_{(aq)} \rightarrow H_2O_{(l)} + I^-_{(aq)} + O_{2(g)}$ fast

Overall reaction is

$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2\,(g)}$

These two reactions are elementary reactions. Adding equ (1) and (2) gives the overall reaction. **Step 1 is the rate determining step,** since it involves both H_2O_2 and I^-, the overall reaction is bimolecular.

7. Describe the graphical representation of first order reaction.

Reaction whose rate depends on the reactant concentration raised to the first power is called a first order reaction. Let us consider the following Cl_2 first order reaction,

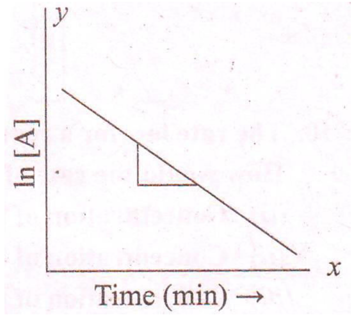
$A \rightarrow$ Product

Rate law can be expressed as Rate $\propto [A]^1$

Rate = k $[A]^1$

Where, k is the first order rate constant.

$\frac{-d[A]}{dt}$ = k $[A]^1$ ==> $\frac{-d[A]}{[A]}$ = k dt ---------- (1)



Integrate the above equation between the limits of time t = 0 and time equal to t, while the concentration varies from the initial concentration $[A_0]$ to [A] at the later time.

$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]} = k \int_0^t dt$$

$$(-\ln[A])_{[A_0]}^{[A]} = k(t)_0^1$$

$$-\ln[A] - (\ln[A_0]) = k\,(t - 0)$$

$$-\ln[A] - (\ln[A_0]) = kt$$

$$\ln\left(\frac{[A_0]}{[A]}\right) = kt \qquad \text{----------- (2)}$$

This equation is in natural logarithm. To convert it into usual logarithm with base 10, we have to multiply the term by 2.303.

$2.303 \log \left(\frac{[A_0]}{[A]}\right) = kt$

$k = \frac{2.303}{t} \log \left(\frac{[A_0]}{[A]}\right)$ ----------- (3)

Equation (2) can be written in the form

$y = mx + c$ as below

$\ln [A_0] - (\ln [A]) = kt$

$\ln [A] = (\ln [A_0]) - kt$

i. $y = c + mx$

If we follow the reaction by measuring the concentration of the reactants at regular time interval 't', a plot of ln[A] against 't' yields a straight line with a negative slpoe. From this, the rate constant is calculated.

8. Write the rate law for the following reactions.

(a) A reaction that is 3/2 order in x and zero order in y.

(b) A reaction that is second order in NO and first order in Br_2.

(a) Rate = $k\ [x]^{\frac{3}{2}}\ [y]^0$

(b) The reaction $2NO + Br_2 \rightarrow 2NOBr$ is second order in No and first order in Br_2

Rate = $k\ [NO]^2[Br_2]$

9. Explain the effect of catalyst on reaction rate with an example.

(i) ***A catalyst is substance which alters the rate of a reaction without itself undergoing any permanent chemical change.***

(ii) In the presence of a catalyst, ***the energy of activation is lowered and hence, greater number of molecules can cross the energy barrier and change over to products, thereby increasing the rate of the reaction.***

10. The rate law for a reaction of A, B and C has been found to be rate = $k[A]^2[B]\ [L]^{3/2}$. How would the rate of reaction change when

Rate = $k\ [A]^2[B][L]^{3/2}$ -------- (1)

(i) Concentration of [L] is quadrupled

When [L] = [4L]

Rate = $k\ [A]^2[B][4L]^{3/2}$

Rate = $8(k\ [A]^2[B][4L]^{3/2})$ -------- (2)

Comparing (1) and (2) ; rate is increased by 8 times.

(ii) Concentration of both [A] and [B] are doubled

When [A] = [2A] and [B] = [2B]

Rate = $k\,[2A]^2[2B][L]^{3/2}$

Rate = $8(k[A]^2[B][L]^{3/2})$ --------- (3)

Comparing (1) and (3); rate is increased by 8 times.

(iii) Concentration of [A] is halved

When [A] = $\left[\frac{A}{2}\right]$

Rate = $k\left[\frac{A}{2}\right]^2[B][L]^{3/2}$

Rate = $\frac{1}{4}(k[A]^2[B][L]^{3/2})$ --------- (4)

Comparing (1) and (4); rate is reduced to ¼ times.

(iv) Concentration of [A] is reduced to (1/3) and concentration of [L] is quadrupled.

When [A] = $\left[\frac{A}{3}\right]$ and [L] = [4L]

Rate = $k\left[\frac{A}{3}\right]^2[B][4L]^{3/2}$

Rate = $\left(\frac{8}{9}\right)(k[A]^2[B]\,[L]^{3/2})$ --------- (5)

Comparing (1) and (5); rate is reduced to $\frac{8}{9}$ times.

11. The rate of formation of a dimer in a second order reaction is 7.5×10^{-3} mol $L^{-1}s^{-1}$at 0.05 mol L^{-1} monomer concentration. Calculate the rate constant.

For second order reaction k = $\frac{Rate}{[A]^2}$ -------- (1)

Where k = rate constant of reaction

A = concentration of reactant or products using equation

$$k = \frac{7.5\times10^{-3}}{(0.05)^2} = \frac{75\times10^{-4}}{(5\times10^{-2})^2} = \frac{75\times10^{-4}}{(5\times10^{-4})} = 3\,mol^{-1}Ls^{-1}$$

12. For a reaction $x + y + z \rightarrow$ products the rate law is given by rate k = $[x]^{\frac{3}{2}}[y]^{\frac{1}{2}}$ what is the overall order of the reaction and what is the order of the reaction with respect to z.

rate k = $[x]^{\frac{3}{2}}[y]^{\frac{1}{2}}$

over all order = $\left(\frac{3}{2}+\frac{1}{2}\right) = 2$ i.e., **second order reaction.**

z=0 Since, the rate expression does not chain the concentration of **z, the reaction is zero order** with respect to z.

13. Explain briefly the collision theory of bimolecular reactions.

(i) Collision Theory was proposed independently by Max Trautz in 1916 and William Lewis in 1918. This theory is based on the kinetic theory of gases. According to this theory, chemical reactions occur as a result of collisions between the reacting molecules.

(ii) Let us understand this theory by considering the following reaction.

$$A_2(g) + B_2(g) \rightarrow 2AB(g)$$

(iii) If we consider that, the reaction between A2 and B2 molecules proceeds through collisions between them, then the rate would be proportional to the number of collisions per second.

(iv) Rate ∝ number of molecules colliding per litre per second (collision rate)

(v) The number of collisions is directly proportional to the concentration of both A_2 and B_2

Collision rate $\propto [A_2][B_2]$

Collision rate = $Z\,[A_2][B_2]$ Where, Z is a c onstant.

(vi) The collision rate in gases can be calculated from kinetic theory of gases.

For a gas at room temperature (298K) and 1 atm pressure, each molecule undergoes approximately 10^9 collisions per second, i.e., 1 collision in 10^{-9}second.

(vii) Thus, if every collision resulted in reaction, the reaction would be complete in 10^{-9} second. In actual practice this does not happen.

(viii) It implies that all collisions are not effective to lead to the reaction. In order to react, the colliding molecules must possess a minimum energy called activation energy.

(ix) The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.

(x) Fraction of effective collisions (f) is given by the following expression

$$f = e^{\frac{-E_a}{RT}}$$

(xi) To understand the magnitude of collision factor (f), Let us calculate the collision factor (f) for a reaction having activation energy of 100 kJ mol^{-1}at 300K.

$$f = e^{-\left(\frac{100\times 10^{3}\,J\,mol^{-1}}{8.314 Jk^{-1}\times mol^{-1}\times 300K}\right)}$$

$$f = e$$

$$f = e^{-40} \approx 4\times 10^{-18}$$

(xii) Thus, out of 1018 collisions only four collisions are sufficiently energetic to convert reactants to products.

(xiii) This fraction of collisions is further reduced due toorientation factor i.e., even if the reactant collide with sufficient energy, they will not react unless the orientation of the reactant molecules is suitable for the formation of the transition state.

(xiv) The figure illustrates the importance of proper alignment of molecules which leads to reaction.

(xv) The fraction of effective collisions (f) having proper orientation is given by the steric factor p.

$$\Rightarrow \text{Rate} = p \times e^{-\frac{E_a}{RT}} \times Z\,[A_2][B_2] \qquad \ldots\ldots\ldots\ldots(1)$$

As per the rate law,

$$\text{Rate} = k\,[A_2]\,[B_2] \qquad \ldots\ldots\ldots\ldots(2)$$

Where k is the rate constant

On comparing equation (1) and (2), the rate constant k is ‘

$$k = p\,Z\,e^{-\frac{E_a}{RT}}$$

14. Write Arrhenius equation and explains the terms involved.

The exact dependence of the rate of a chemical reaction o temperature is given by Arrhenius equation.

$$K = Ae^{\frac{-E_a}{RT}}$$

Where, A = Arrhenius factor or the frequency factor

T = Temperature

R = Gas constant

E_a = Activation Energy

15. The decomposition of Cl_2O_7 at 500K in the gas phase to Cl_2 and O_2 is a first order reaction. After 1 minute at 500K, the pressure of Cl_2O_7 falls from 0.08 to 0.04 atm. Calculate the rate constant in s^{-1}.

$$K = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{1\,min} \log \frac{[0.08]}{[0.04]}$$

$$k = 2.303 \log 2$$

$$k = 2.303 \times 0.3010$$

$$k = 0.6932\ min^{-1}$$

$$k = \left(\frac{0.6932}{60}\right) s^{-1}$$

$$k = 1.153 \times 10^{-2} s^{-1}.$$

16. Give two examples for zero order reaction.

1. photochemical reaction between H_2 and Cl_2.

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{hv} 2HCl_{(g)}$$

2. Decomposition of N_2O on hot platinum surface.

$$N_2O_{(g)} \rightleftharpoons \mathbf{N_{2(g)}} + \frac{1}{2}\mathbf{O_{2(g)}}$$

17. Explain pseudo first order reaction with an example.

A second order reaction ***can be altered to a first order reaction*** by ***taking one of the reactant in large excess,*** such reaction is called pseudo first order reaction.

(iii) Let us consider the acid hydrolysis of an ester,

$$\mathbf{CH_3COOCH_{3\,(aq)} + H_2O_{(l)} \xrightarrow{H^+} CH_3COOH_{(aq)} + CH_3OH_{(aq)}}$$

$$\mathbf{Rate = k\,[CH_3COOCH_3\,][H_2O]}$$

(iv) If the reaction is carried out with the *large excess of water*, there is **no significant change in the concentration of water during hydrolysis**. i.e.,concentration of water remains almost a constant.

(v) Now, we can define k $[H_2O]$ = k' ; Therefore the above rate equation becomes

$$\mathbf{Rate = k'\,[CH_3COOCH_3\,]}$$

(vi) Thus it follows first order kinetics.

18. Identify the order for the following reactions

(i) Rusting of Iron

(ii) Radioactive disintegration of $_{92}U^{238}$

(iii) 2A + 3B → products ; rate $= k\,[A]^{\frac{1}{2}}[B]^2$

(i) First order reaction

(ii) First order reaction

(iii) 2.5 order reaction (5/2)

19. A gas phase reaction has energy o activation 200 kJ mol^{-1}. If the frequency factor of the reaction is 1.6 ×10^{13} s^{-1}. Calculate the rate constant at 600 K.($e^{-40.09} = 3.8 \times 10^{-18}$)

$$K = Ae^{\frac{-E_a}{RT}}$$

$$k = 1.6 \times 10^{13}\ s^{-1}\ e^{-\left(\frac{200 \times 103\ J\ mol^{-1}}{8.314\ JK^{-1}mol^{-1} \times 600K}\right)}$$

$$k = 1.6 \times 10^{13}\ s^{-1}\ e^{-(40.1)}$$

$$k = 1.6 \times 10^{13}\ s^{-1} \times 3.8 \times 10^{-18}$$

$$k = 6.21 \times 10^{-5}\ s^{-1}$$

20. For the reaction $2x + y \rightarrow L$ find the rate law from the following data.

[x] (min)	[y] (min)	rate (M s^{-1})
0.2	0.02	0.15
0.4	0.02	0.30
0.4	0.08	1.20

Rate = $k[x]^n[y]^m$

$0.5 = k[0.2]^n[0.02]^m$ ....(1)

$0.30 = k[0.4]^n[0.02]^m$ ....(2)

$1.20 = k[0.4]^n[0.08]^m$ ....(3)

By dividing equation $\frac{(3)}{(2)}$

$$\frac{1.2}{0.3} = \frac{k[0.4]^n[0.08]^m}{k[0.4]^n[0.02]^m}$$

$$4 = \left(\frac{[0.08]}{[0.02]}\right)^m$$

$4 = (4)^m$ ∴ $m = 1$

By dividing equation $\frac{(2)}{(1)}$

$$\frac{0.30}{0.15} = \frac{k[0.4]^n[0.02]^m}{k[0.2]^n[0.02]^m}$$

$$2 = \left(\frac{[0.4]}{[0.2]}\right)^n$$

$2 = (2)^n \quad \therefore n = 1$

$\text{Rate} = k[x]^1[y]^1$

$\mathbf{0.5 = k[0.2]^1[0.02]^1}$

$\frac{0.15}{[0.2]^1[0.02]^1} = k$

$k = 37.5\,\text{mol}^{-1}\text{L s}^{-1}$

21. How do concentrations of the reactant influence the rate of reaction?

i. The ***rate of a reaction increases with the increase in the concentration of the reactants.***

ii. According to this theory, the rate of a reaction depends upon the number of collisions between the reacting molecules.

iii. Higher the concentration, greater is the possibility for collision and hence increase the rate.

22. How do nature of the reactant influence rate of reaction.

(i) The chemical reaction involves breaking of certain existing bonds of the reactant and forming new bonds which lead to the formation of product.

(ii) The net energy involved in this process is dependent on the nature of the reactant and hence the rates are different for different reactants.

23. The rate constant for a first order reaction is 1.54x 10^{-3} s^{-1}. Calculate its half life time.

$$t_{\frac{1}{2}} = \frac{0.693}{K} = \frac{0.693}{1.54 \times 10^{-3} sec^{-1}} = 450 \text{ seconds.}$$

24. The half- life of the homogeneous gaseous reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ which obeys first order kinetics is 8.0 minutes. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% of the initial value?

We know that, $k = \frac{0.693}{t_{\frac{1}{2}}}$

$k = \frac{0.693}{8.0}$ minutes = 0.087 minutes^{-1}

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]}$$

$$t = \frac{2.303}{0.087\, min^{-1}} \log \left(\frac{100}{1}\right)$$

$t = 52.93$ min

25. The time for half change in a first order decomposition of a substance A is 60 seconds. Calculate the rate constant. How much of A will be left after 180 seconds?

$t_{\frac{1}{2}} = 60$ min

Order of reaction = first order, so, for first order reaction,

We have $t_{\frac{1}{2}} = \frac{0.693}{k}$

$$K = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{60} = 0.01155\ s^{-1}$$

$$K = 0.0115\ s^{-1}$$

For time 3 mins (180 sec)

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$\therefore 0.01155 = \frac{2.303}{180} \log \frac{[100]}{[A]}$$

$$\frac{0.01155\ X 180}{2.303} = \log \frac{[100]}{[A]}$$

0.9207 = log 100 – log [A]

log [A] = log 100 – 0.9207

log [A] = 2 – 0.9207

log[A] = 1.0973

[A] = antilog of (1.0973)

[A] = 12.5%

26. A zero order reaction is 20% complete in 20 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?

(i) Let A = 100 M, $[A_0] – [A] = 20$ M,

For the zero order reaction

$$K = \left(\frac{[A_0] - [A]}{t}\right)$$

$$K = \left(\frac{20M}{20min}\right) = 1\ M\ min^{-1}$$

Rate constant for a reaction =1 M min^{-1}

(ii) To calculate the time for 80% of completion

K = 1 M min^{-1}, $[A_0]$=100M,

$[A_0]$ - [A] = 80M, t = ?

Therefore,

$$t = \left(\frac{[A_0] - [A]}{k}\right) = \left(\frac{80M}{1\,M\,min^{-1}}\right) = 80\text{min.}$$

27. The activation energy of a reaction is 225 k Cal mol^{-1} and the value of rate constant at 40°C is 1.8×10^{-5} s^{-1}. Calculate the frequency factor, A.

Here, we are given that

$E_0 = 22.5$ kcalmol^{-1} = 22500 cal mol^{-1}

T = 40° C = 40 + 273 = 313K

$K = 1.8 \times 10^{-5}\ s^{-1}$

Substituting the values in the equation

$$\log A = \log k + \left(\frac{E_a}{2.303\,RT}\right)$$

$$\log A = \log(1.8 \times 10^{-5}) + \left(\frac{22500}{2.303 \times 1.987 \times 313}\right)$$

log A = log (1.8) (-5) + (15.7089)

log A = 10.9642

A = antilog (10.9642)

$A = 9.208 \times 10^{10}$ collisions s^{-1}

28. Benzene diazonium chloride in aqueous solution decomposes according to the equation $C_6H_5N_2Cl \rightarrow C_6H_5Cl + N_2$. Starting with an initial concentration of 10 g L^{-1}, the volume of N_2 gas obtained at 50°C at different intervals of time was found to be as under:

t (min):	**6**	**12**	**18**	**24**	**30**	**∞**
Vol. of N_2(ml):	**19.3**	**32.6**	**41.3**	**46.5**	**50.4**	**58.3**

Show that the above reaction follows the first order kinetics. What is the value of the rate constant?

For a first order reaction

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_1}$$

In the present case, V_∞ = 58.3 ml.

The value of k at different time can be calculated as follows.

t(min)	V_1	$V_\infty - V_1$	$\frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_1}$

6	19.3	58.3 – 19.3 = 39.0	$k = \frac{2.303}{6} \log \left(\frac{58.3}{39}\right) = 0.0670 \text{ min}^{-1}$
12	32.6	58.3 – 32.6 = 25.7	$k = \frac{2.303}{12} \log \left(\frac{58.3}{25.7}\right) = 0.0683 \text{ min}^{-1}$
18	41.3	58.3 – 41.3 = 17.0	$k = \frac{2.303}{18} \log \left(\frac{58.3}{17}\right) = 0.0685 \text{ min}^{-1}$
24	46.5	58.3 – 46.5 = 11.8	$k = \frac{2.303}{24} \log \left(\frac{58.3}{11.8}\right) = 0.0666 \text{ min}^{-1}$

Since the value of k comes out to be nearly constant, the given reaction is of the first order. The mean value of k= 0.0676min^{-1}.

29. From the following data, show that the decomposition of hydrogen peroxide is a reaction of the first order:

t (min)	**0**	**10**	**20**
V (ml)	**46.1**	**29.8**	**19.3**

Where *t* is the time in minutes and V is the volume of standard KMnO$_4$ solution required for titrating the same volume of the reaction mixture.

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$k = \left(\frac{2.303}{t}\right) \log \left(\frac{V_0}{V_t}\right)$$

In the present case, V_0 = 46.1ml.

The value of k at each instant can be calculated as follows:

T(min)	V_t	$k = \left(\frac{2.303}{t}\right) \log \left(\frac{V_0}{V_t}\right)$
10	29.8	$k = \left(\frac{2.303}{10}\right) \log \left(\frac{46.1}{29.8}\right) = 0.0436 \text{ min}^{-1}$
20	19.3	$k = \left(\frac{2.303}{20}\right) \log \left(\frac{46.1}{19.3}\right) = 0.0435 \text{ min}^{-1}$

Thus, the value of k comes out to be nearly constant. Hence it is a reaction of the first order.

30. A first order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?

For the first order reaction

$$k = \left(\frac{2.303}{t}\right) \log \left(\frac{a}{a-x}\right)$$

when x = $\left(\frac{40}{100}\right)$ a = 0.4a

t = 50m

$$\therefore \mathbf{k} = \left(\frac{2.303}{50}\right) \log \left(\frac{a}{a-0.4a}\right)$$

$$k = \left(\frac{2.303}{50}\right) \log \left(\frac{1}{0.6}\right)$$

$k = 0.010216 min^{-1}$

t = ? when x = 0.8a

From above $k = 0.010216 min^{-1}$

$$\therefore \mathbf{t} = \left(\frac{2.303}{0.010216}\right) \log \left(\frac{a}{a-0.8a}\right)$$

$$\left(\frac{2.303}{0.010216}\right) \log \left(\frac{1}{0.2}\right) = 157.58min$$

The time at which the reaction will be 80% complete is **157.58 min.**

LESSON 7 CHEMICAL KINETICS

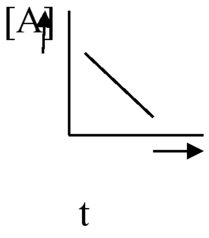
1. Define chemical kinetics. (205)
2. Define Rate of a chemical reaction. (205)
3. Write note on stoichiometry and rate of a reaction.(206)
4. Define average rate and instantaneous rate. (BB)207
5. Define rate law and rate constant. (BB)208
6. Give the difference between rate of a reaction and rate constant.(209) **PTA, A21, J23 3M**
7. What is an elementary reaction? (210)
8. Explain the rate determining step with an example. (210) **PTA 3M**
9. Define order and molecularity of a reaction. (210) **PTA 5Mi, J22 3M**
10. What is an order of a reaction? **M24 2M compulsory**
11. Give the differences between order and molecularity of a reaction. (210)

12. The rate of the reaction x + 2y → product is 4×10^{-3} mol $L^{-1}s^{-1}$, if [x] = [y] = 0.2M and rate constant at 400k is $2 \times 10^{-2}s^{-1}$, what is the overall order of the reaction?(211) **(J20) 2 MARK**
13. Derive integrated rate law for a first order reaction A → product.(212) **(PTA,M20) 5MARK**
14. Derive and describe the graphical representation of first order reaction.(212)
15. Give examples for the first order reaction. (213) **M22 2M**
16. Explain pseudo first order reaction with an example. (214)**GM3M**
17. Derive integrated rate law for a zero-order reaction A→product & Example (214) **A21 5M, J22 5M, J23 5M, M24 5Mi**
18. Give two examples for zero order reaction. (214) **M23 5Mi**
19. **Define half-life**-period **of reaction**. **J23 2M** Show that for a first order reaction half-life period is independent of initial concentration. (215) **PTA 5M I**
20. Calculate the half period for a zero order reaction.(215)**PTA 2M**
21. Explain about collision theory (217, 218)
22. Write Arrhenius equation and explains the terms involved. (220) **M22 3M, M24 3M**
23. Write the rate law for the following reactions. (BB)
    (a) A reaction that is 3/2 order in x and zero order in y.
    (b) A reaction that is second order in NO and first order in Br_2.
24. The rate constant for a first order reaction is 1.54×10^{-3} s^{-1}. Calculate its half life time.(BB 231) **(PTA, J20)**
25. Identify the order for the following reactions (BB)
    (i) Rusting of Iron
    (ii) Radioactive disintegration of $_{92}U^{238}$
    (iii) 2A + 3B → products ; rate $= k\,[A]^{\frac{1}{2}}[B]^2$
26. Derive Arrhenius equation to calculate activation energy from the rate constant k_1 and k_2 at temperature T_1 and T_2 respectively. (220,221) **PTA3MC**
27. What are the factors affecting the reaction rate? (222)
28. Explain the effect of catalyst on reaction rate with an example. (222) **S20 5Mi**

29. Powdered $CaCO_3$ reacts much faster with dilute HCl than with the same mass of $CaCO_3$ as marble. Give reason. **J20 3M COMPULSORY**

30. The rate of formation of dimer in a second order reaction is 7.5×10^{-3} mol $L^{-1}s^{-1}$ at 0.05 mol L^{-1} monomer concentration. Calculate the rate constant. (BB) **5M i**

31. For the general reaction A → B. Plot of concentration of A Vs time is given in the graph below. Answer the following Questions on the basis of this graph. (214) **PTA3M**



i) What is the order of the reaction?

ii) What is the slope of the curve?

iii) What is the Unit of rate constant?

32. a first order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete? (BBQ$_{30}$231) **GM5Mi**

33. Show that in case of first order reaction the time required for the completion of 99% is twice the time required for the completion of 90% of the reaction. **(217 ex 6 model) M23 3M COMPULSORY**

- **"NO PAIN, NO GAIN".**

Never Dreamed about success, Worked for it.

WISH U ALL THE BEST ACTC

"May God's guidance be with you during the Exam and may you be able to answer each question correctly. My prayers and Blessings are with you".- ACTC EMS

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