12TH STANDARD

CHEMISTRY – VOL – I

QUESTION AND ANSWERS

PREPARED BY

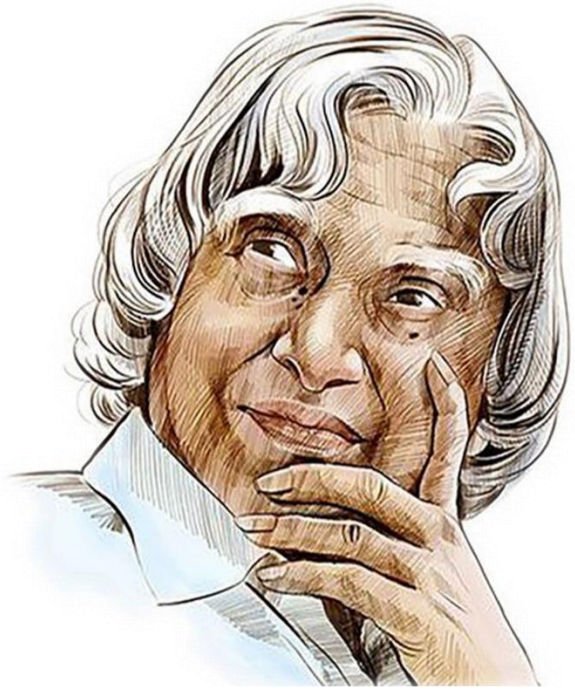
MR. S.JOHNSON., M.SC., M.SC., B.ED.,

JJ TUITION CENTRE

INJAMBAKKAM,

CHENNAI – 600115

CONTACT: +91 99410 65270



“YOU CANNOT CHANGE YOUR FUTURE, BUT YOU CAN CHANGE YOUR HABITS, AND SURELY YOUR HABITS WILL CHANGE YOUR FUTURE”

- Dr. A.P.J. ABDUL KALAM

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UNIT – 1 – METALLURGY

II. Answer the following questions: [QY-23, APR-24]

1. What is the difference between minerals and ores? [QY19,SEP20,FMT,HY,FRT,MAY22]

Minerals	Ores
A naturally occurring substance obtained by mining which contains the metal in free state or in the form of compounds.	Ore contains a high percentage of metal, from which it can be extracted conveniently and economically.
They have definite crystalline structure	They do not have definite crystalline structure
All minerals are not ores	All ores are Minerals
It contains a low percentage of metal	It contains a high percentage of metals
Ex: Mineral of Al is bauxite and china clay	**Ex:** Ore of Al is bauxite

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

The extraction of pure metals from the concentrated ores is carried out in two steps:

- Conversion of the ore into oxides of the metal of interest.
- Reduction of the metal oxides to elemental metals.

3. What is the role of Limestone in the extraction of Iron from its oxide Fe_2O_3? [SEP-20, FRT-22, FUT-23, QY-24]

In the extraction of iron, a basic flux limestone is used. Limestone decomposes to form CaO which reacts with silica gangue present in the iron ore is acidic in nature to form calcium silicate (slag).

$$\underset{\text{Flux}}{CaO\ (s)} + \underset{\text{Gangue}}{SiO_2\ (s)} \longrightarrow \underset{\text{Slag}}{CaSiO_3\ (s)}$$

4. Which type of ores can be concentrated by froth floatation method? Give two examples for such ores. [SEP-20, FRT-22, MAR-23, QY-24, MAR-25]

- Sulphide ores can be concentrated by the froth floatation method.
- (Eg) Galena (PbS), Zinc blende (ZnS).

5. Describe a method for refining nickel. (or) How is Ni purified by Mond process? (or) Explain the purification of Nickel.[PTA3,FMT,HY,FRT,MAY22,FUT23,HY23,MAR25]

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

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

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

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

6. Explain zone refining process with an example.[PTA-6, MAR20, FMT-22, FRT, MAR, JUN-23, FUT-23, QY-24, SRT-25]

- This method is based on the principle of fractional crystallization. The impure metal is melted and allowed to solidify, the impurities will prefer to remain in the molten region, ie; impurities are more soluble in the melt than in the solid-state metal.
- 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, melting the metal on that portion of the rod.

- When the heater is slowly moved to the other end pure metal crystallizes while 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.
- This 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.
- Germanium, Silicon, and gallium which are used as semiconductors are refined by this process.

7. Using the Ellingham diagram, (A) Predict the conditions under which (i) Aluminium might be expected to reduce magnesia. (ii) Magnesium could reduce alumina.
(B) It is possible to reduce Fe_2O_3 by coke at a temperature around 1200 K.

(A) (i) Ellingham diagram for the formation of Al_2O_3 and MgO intersects around 1600K.
- Above this temperature aluminium lines lies below the magnesium line.
- Hence we can use aluminium to reduce magnesia above 1600K.

(ii) In Ellingham diagram below 1600K magnesium line lies below aluminium line.
- Hence, below 1600K magnesium can reduce alumina.

(B) In Ellingham diagram above 1000K carbon line below the iron line.
- Hence, it is possible to reduce Fe_2O_3 by coke at a temperature around 1200K.

8. Give the uses of zinc. [PTA-4, FUT-24]
- Metallic zinc is used in galvanising metals such as iron and steel structures to protect them from rusting and corrosion.
- Zinc is also used to produce die-castings in the automobile, electrical and hardware industries.
- Zinc oxide is used in the manufacture of many products such as paints, rubber, cosmetics, pharmaceuticals, plastics, inks, batteries, textiles arid electrical equipment.
- Zinc sulphide is used in making luminous paints, fluorescent lights and x-ray screens.
- Brass an alloy of zinc is used in water valves and communication equipment as it is highly resistant to corrosion.

9. Explain the electrometallurgy of aluminium. [GMQP-19, FMT-22, SRT, HY-24]

Cathode : Iron tank lined with carbon **Anode** : Carbon blocks

Electrolytes: 20% solution of alumina, obtained from the bauxite ore is mixed with molten cryolite and is taken in the electrolysis chamber. About 10%, calcium chloride is also added to the solution. Here calcium chloride helps to lower the melting point of the mixture.

Temperature : Above 1270 K.

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) + $3e^- \rightarrow Al_{(l)}$

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

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

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

- Due to the above two reactions, anodes are slowly consumed during the electrolysis.
- The pure aluminium is formed at the cathode and settles at the bottom.
- The net electrolysis reaction can be written as follows:

$$4Al^{3+}\ (melt) + 6O^{2-}\ (melt) + 3C_{(s)} \rightarrow 4A_{(l)} + 3CO_{2(g)}$$

10. Explain the following terms with suitable examples. [PTA-2, SEP-20, FRT-22]

(i) Gangue (ii) Slag

(i) Gange: The non-metallic impurities, rocky materials and siliceous matter, associated with the ore is called gangue. **Example:** SiO_2 is the gangue present in the iron ore.

(ii) Slag: Slag is the fusible product formed when flux reacts with gangue during the extraction of metal. **Example:** $CaO_{(s)} + SiO_2 \longrightarrow CaSiO_3$

Flux *Gangue* *Slag*

11. Give the basic requirement for vapour phase refining. [HY-24]

The two requirements for vapour phase refining are:

- The metal should form a volatile compound with a suitable reagent.
- 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. (or) What is the role of silica in extraction of copper? [FMT-22, APR-24] (ii) Cryolite is the extraction of aluminium. [QY-19,MAR25] (iii) Iodine in the refining of Zirconium. [QY-19,FRT,MAR25] (iv) Sodium cyanide in froth floatation. [FMT-22]

(i) The role of silica in the extraction of copper is to remove the iron oxide obtained during the process of roasting as slag. If the sulphide ore of copper contains iron, the silica (SiO_2) is added as flux before roasting. Then, FeO combines with silica to form iron silicate, $FeSiO_3$ (Slag).

(ii) Cryolite reduces the melting point of Al_2O_3 and increases its 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.

(iii) Zirconium crude metal is heated with iodine in an evacuated vapour to separate from impurities and this decomposes at 1800 K to give a pure zirconium metal and iodine. Initially, iodine is heated with zirconium to form a volatile compound.

(iv) Sulphide ores are concentrated by the froth floatation process. Depressants are used to prevent a certain types of particles from forming the froth. NaCN act as a depressant to separate ZnS from PbS.

13. Explain the principle of electrolytic refining with an example. (or) How is silver purified by electrolytic refining process? [HY-19, FRT,JULY-22, QY-23]

- Electrolytic refining is carried out in an electrolytic cell

Cathode : Thin strips of pure metal **Anode** : Impure metal

Electrolyte : Acidified aqueous solution of salt of the metal.

- 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 $Ag(s) \longrightarrow Ag^{+}(aq) + 1e^{-}$

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

- 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.

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 (ΔfG0) of their oxides is more negative can reduce the metal oxides for which the standard free energy of formation (ΔfG0) of oxides is less negative.
- The thermodynamic factor has a major role in selecting the reducing agent for a particular reaction. Only that reagent will be preferred which will lead to a decrease in the free energy (AG°) at a certain specific temperature. E.g – Carbon reduce ZnO to Zn but not CO.

$ZnO + C \rightarrow Zn + CO$ .....(1) $ZnO + CO \rightarrow Zn + CO_2$ .....(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 a better reducing agent.

15.Give the limitations of Ellingham diagram. [HY-22, FRT-23, JUN-23, HY-23, FUT-24]

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

16.Write a short note on electrochemical principles of metallurgy. [QY-23]

- 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

$$\Delta G^\circ = -nFE^\circ$$

- Where n is number of electrons involved in the reduction process, F is the Faraday and E° is the electrode potential of the redox couple.
- If E° 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, $Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$

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

EVALUATE YOURSELF

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

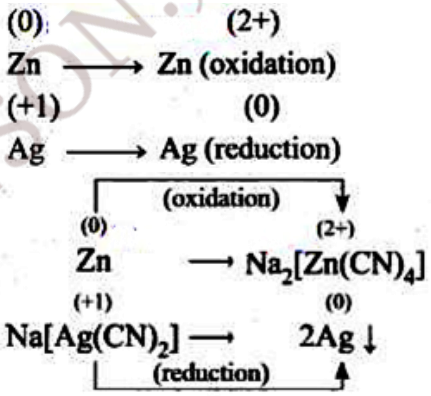
The crushed ore of argentite (Ag_2S) is leached with sodium cyanide solution. This reaction forms sodium Argento cyanide $Na[Ag(CN)_2]$

Step 1: $Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$

The solution of sodium Argento cyanide combines with zinc dust and forms sodium tetra cyano zincate and precipitated silver.

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

In the step 2, redox reaction take place.



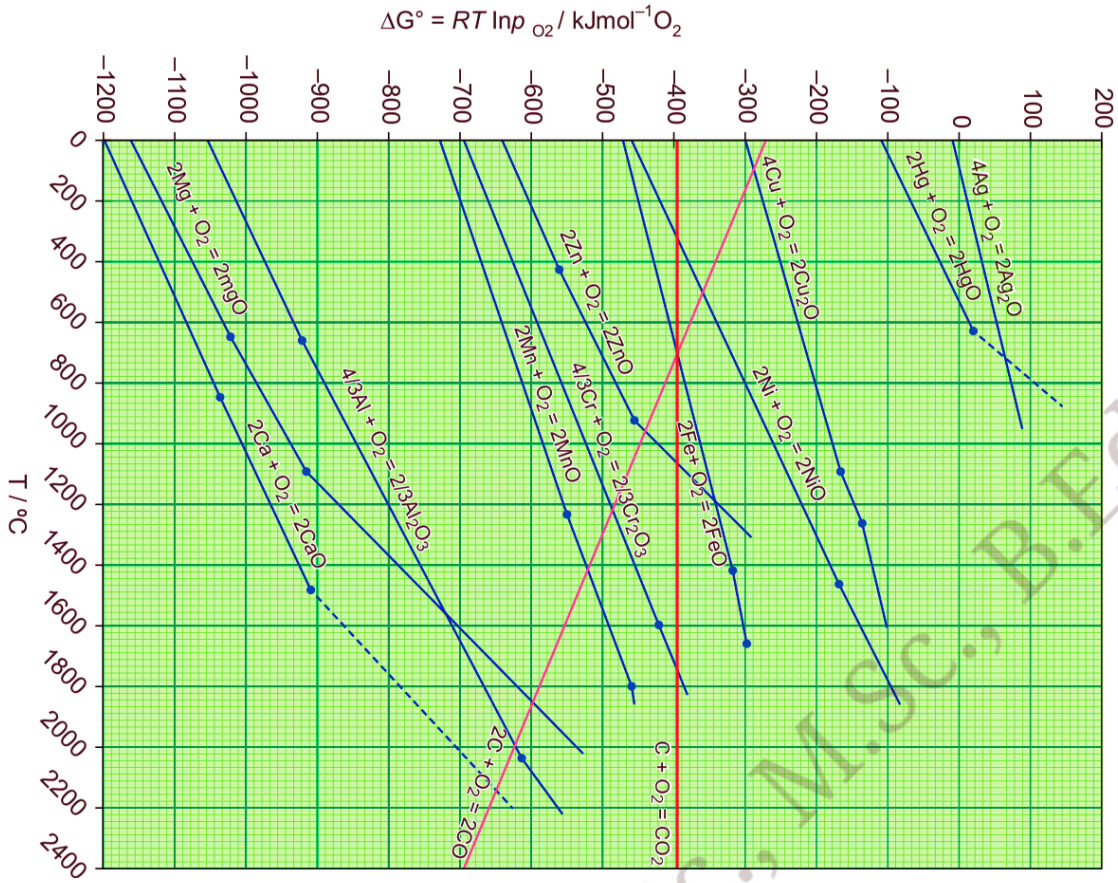
2. Magnesite (Magnesium carbonate) is calcined to obtain magnesia, which is used to make refractory bricks. Write the decomposition reaction.

Magnesite is a carbonate of magnesium. Magnesite when heated at 800°C to 1000°C at the CO_2 content in it is driven off. The residue so obtained is known as calcined magnesite.

$$MgCO_3 \rightarrow MgO + CO_2\uparrow$$

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

Ellingham diagram for the formation of ZnO and CO intersects around 1200K. Below this temperature the carbon line lies above zinc line. Hence ZnO is more stable than CO so the reduction is thermodynamically not feasible at this temperature range.



However above 1200K carbon line lies below the zinc line, hence carbon can be used as a reducing agent above 1200K.

$2Zn + O_2 \rightarrow 2ZnO$ (1) $2C + O_2 \rightarrow 2CO$ (2)

Reversing (1) and adding with equation (2)

$2ZnO \rightarrow 2Zn + O_2$ $2CO \rightarrow 2C + O_2$ $2ZnO + 2C \rightarrow 2Zn + 2CO$

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

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

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

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

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

For aqueous solution of NaCl:

$H_2O + 2e^- \rightarrow \frac{1}{2}H_2\uparrow + OH^-$ (at cathode) $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ (at anode)

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

After electrolysis the electrolytic solution becomes basic in nature. [Due to formation of hydroxide (OH^-) ion].

GOVERNMENT EXAM QUESTION PAPER

1. Oxides like Ag_2O and HgO undergo self-reduction. Why? [QY-19]

Decomposition temperature of Ag_2O and HgO are 600 and 700K respectively.

These oxides are unstable at moderate temperatures undergo self reduction.

2. Name the collector and depressing agent used in froth flotation process. [HY-19]

- Sodium ethyl xanthate acts as a collector.
- Sodium cyanide, Sodium carbonate are used as depressing agents in froth flotation process.

3. How is metal purified by distillation method? Give example. [FRT-22]

This method is employed for low boiling volatile metals like zinc (boiling point 1180 K) and mercury (630 K). In this method, the impure metal is heated to evaporate and the vapours are condensed to get pure metal.

4. Explain how gold ore is leached by cyanide process. [GMQ19,FMT22,FUT23,FRT25]

- Gold is usually found in native state.
- The leaching process is intended to concentrate the gold metal.

$$4Au\,(s) + 8CN^-\,(aq) + O_2\,(g) + 2H_2O\,(l) \longrightarrow 4[Au(CN)_2]^-\,(aq) + 4OH^-(aq)$$

$$Zn\,(s) + 2[Au(CN)_2]^-\,(aq) \longrightarrow [Zn(CN)_4]^{-2}(aq) + 2Au\,(s)$$

- In this reaction, gold is reduced to its elemental state and the process is called cementation.

5. Write a note on gravity separation method. [FRT-22, MAY-22, SRT-25]

- Gravity separation method, the ore having high specific gravity is separated from the gangue that has low specific gravity by simply washing with running water.
- Ore is crushed to a finely powdered form and treated with rapidly flowing current of water.
- During this process the lighter gangue particles are washed away by the running water.
- This method is generally applied to concentrate the native ore such as gold and oxide ores such as haematite (Fe_2O_3), tin stone (SnO_2)

6. How is acid leaching done for the sulphide ores? (or) Explain Acid Leaching with an example. [JULY-22, HY-23, FUT-24]

- Leaching of sulphide ores such as ZnS, PbS etc., can be done by treating them with hot aqueous sulphuric acid.

$$2ZnS\,(s) + 2H_2SO_4\,(aq) + O_2(g) \longrightarrow 2ZnSO_4\,(aq) + 2S\,(s) + 2\,H_2O$$

- In this process the insoluble sulphide is converted into soluble sulphate and elemental sulphur.

7. In metallurgy roasting of ore is done below its melting points whereas smelting is done above its melting point. Why? [QY-19, FRT-25]

Roasting: Roasting is the method the sulphide ore is converted into oxide ore below its melting only it exist in solid.

Smelting: Smelting is a chemical substance that forms an easily fusible slag with gangue.

8. What are the main observation of Ellingham diagram? [QY-19]

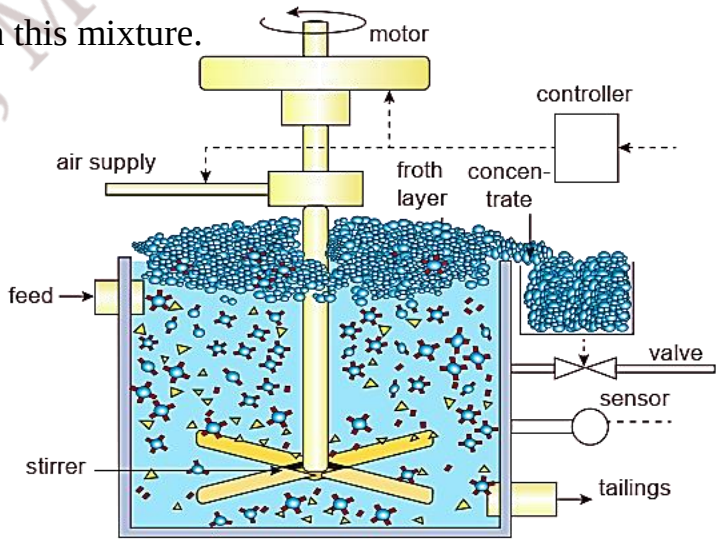
- For most of the metal oxide formation, the slope is positive. It can be explained as follows. Oxygen gas is consumed during the formation of metal oxides which results in the decrease

in randomness. Hence, ΔS becomes negative and it makes the term, TΔS positive in the straight line equation.

- The graph for the formation of carbon monoxide is a straight line with negative slope. In this case ΔS is positive as 2 moles of CO gas is formed by the consumption of one mole of oxygen gas. It indicates that CO is more stable at higher temperature.
- As the temperature increases, generally ΔG value for the formation of the metal oxide become less negative and becomes zero at a particular temperature. Below this temperature, ΔG is negative and the oxide is stable and above this temperature ΔG is positive. This general trend suggests that metal oxides become less stable at higher temperature and their decomposition becomes easier.
- There is a sudden change in the slope at a particular temperature for some metal oxides like MgO, HgO. This is due to the phase transition (melting or evaporation).

9. Explain froth flotation, with diagram. [JUL-21, FRT-23, SRT-24, FRT-25]

- Froth flotation method is commonly used to concentrate sulphide ores such as galena (PbS), zinc blende (ZnS) etc...
- In this method, the metallic ore particles which are preferentially wetted by oil can be separated from gangue.
- In this method, the crushed ore is suspended in water and mixed with frothing agent such as pine oil, eucalyptus oil etc.
- A small quantity of sodium ethyl xanthate which acts as a collector is also added.
- A froth is generated by blowing air through this mixture.
- The collector molecules attach to the ore particle and make them water repellent.
- As a result, ore particles, wetted by the oil, rise to the surface along with the froth.
- The froth is skimmed off and dried to recover the concentrated ore.
- The gangue particles that are preferentially wetted by water settle at the bottom.



10. What is auto reduction? [HY-22, FRT-22, FRT-23]

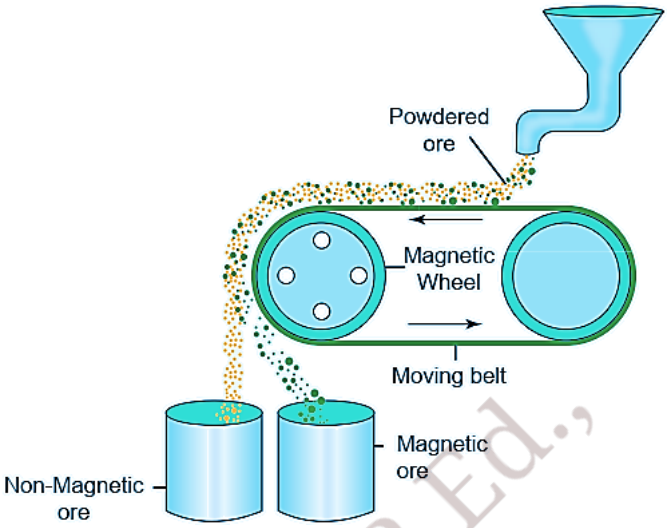
Simple roasting of some of the ores give the crude metal. In such cases, the use of reducing agents is not necessary. For example, mercury is obtained by roasting of its ore cinnabar (HgS)

$$HgS\,(s) + O_2\,(g) \longrightarrow Hg\,(l) + SO_2\uparrow$$

11. How are ores concentrated by magnetic separation method? [HY,FRT-22]

- Magnetic separation method is applicable to ferromagnetic ores and it is based on the difference in the magnetic properties of the ore and the impurities.
- For example tin stone can be separated from the wolframite impurities which is magnetic.

- Similarly, ores such as chromite, pyrolusite having magnetic property can be removed from the non magnetic siliceous impurities. The crushed ore is poured on to an electromagnetic separator consisting of a belt moving over two rollers of which one is magnetic.
- The magnetic part of the ore is attracted towards the magnet and falls as a heap close to the magnetic region while the nonmagnetic part falls away from it as shown in the figure



12. What is chemical leaching? [FRT-22]

- This method is based on the solubility of the ore in a suitable solvent and the reactions in aqueous solution.
- In this method, the crushed ore is allowed to dissolve in a suitable solvent, the metal present in the ore is converted to its soluble salt or complex while the gangue remains insoluble.

13. What type of oxidation process is employed for $CaCO_3$? Explain it. (or) What is Calcination? [FMT-22, APR-24]

Calcination is the process in which the concentrated carbonate ore is strongly heated in the absence of air. During calcination of carbonate ore, carbon dioxide is expelled

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

14. What are uses of Aluminium? [FMT-22, FRT-23]

- Many heat exchangers/sinks and our day to day cooking vessels are made of aluminium.
- It is used as wraps (aluminium foils) and is used in packing materials for food items,
- Aluminium is not very strong, However , its alloys with copper, manganese, magnesium and silicon are light weight and strong and they are used in design of aeroplanes and other forms of transport.
- As Aluminium shows high resistance to corrosion, it is used in the design of chemical reactors, medical equipments, refrigeration units and gas pipelines.
- Aluminium is a good electrical conductor and cheap, hence used in electrical overhead electric cables with steel core for strength.

15. In Ellingham diagram, the slope is positive for most of the metal oxide formation. Justify. [FMT-22]

Oxygen gas is consumed during the formation of metal oxides which results in the decrease in randomness. Hence, ΔS becomes negative and it makes the term, $T\Delta S$ positive in the straight line equation. So, most of the metal oxide formation in Ellingham diagram, the slope is positive.

16. Write about the liquation process. [JUN-23]

Liquation is a metallurgical technique to separate metals from an ore, metal or alloy. This is done by heating the material until one of the constituents starts melting and the other remains solid. The liquid melt is drained away from the other and collected. Earlier, it was used to

extract antimony minerals from ore. It is also used to remove lead containing silver from copper.

17. Explain Van-Arkel method for refining Titanium. (or) Explain how Zr and Ti are refined by Van-Arkel method. [HY-22, FRT-23, FUT-24]

- This method is based on the thermal decomposition of metal compounds which lead to the formation of pure metals. Titanium and zirconium can be purified using this method.
- For example, the impure titanium metal is heated in an evacuated vessel with iodine at a temperature of 550 K to form the volatile titanium tetra-iodide.(TiI_4). The impurities are left behind, as they do not react with iodine. $Ti\,(s) + 2I_2\,(s) \xrightarrow[\Delta]{550K} TiI_4\,(vapour)$
- The volatile titanium tetraiodide vapour is passed over a tungsten filament at a temperature aroud 1800 K. The titanium tetraiodide is decomposed and pure titanium is deposited on the filament. The iodine is reused. $TiI_4\,(vapour) \xrightarrow[\Delta]{1800\,K} Ti\,(s) + 2I_2\,(s)$

Zirconium: $Zr\,(impure) + 2I_2 \xrightarrow{523\,K} ZrI_4$ $\qquad$ $ZrI_4 \xrightarrow{1800K} Zr\,(pure) + 2I_2$

18. Write any four refining methods of crude metal. [FRT-23]

Distillation, Liquation, Electrolytic refining, Zone Refining, Vapour phase method (Mond process for refining nickel, Van-Arkel method for refining zirconium/titanium)

19. What is meant by cementation? [FRT-22, SRT-25]

Gold can be recovered by reacting the deoxygenated leached solution with zinc. In this process the gold is reduced to its elemental state (zero oxidation sate) and the process is called **cementation**. $Zn\,(s) + 2[Au(CN)_2]^-\,(aq) \longrightarrow [Zn(CN)_4]^{-2}(aq) + 2Au\,(s)$

20. What is Roasting? Given an example. [FRT-24]

Roasting is the method, usually applied for the conversion of sulphide ores into their oxides. In this method, the concentrated ore is oxidised by heating it with excess of oxygen in a suitable furnace below the melting point of the metal.

$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2\uparrow$ $\qquad$ $2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2\uparrow$

21. What is blister copper? [FRT-24]

The copper sulphide is oxidised to its oxide which is subsequently converted to metallic copper as shown below.

$$2Cu_2S\,(l,s) + 3O_2\,(g) \longrightarrow 2Cu_2O\,(l,s) + 2SO_2\,(g)$$
$$2Cu_2O\,(l) + Cu_2S\,(l) \longrightarrow 6Cu\,(l) + SO_2\,(g)$$

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

22. Explain Aluminothermic process. [FRT-24]

Metallic oxides such as Cr_2O_3 can be reduced by an aluminothermic process. In this process, the metal oxide is mixed with aluminium powder and placed in a fire clay crucible. To initiate the reduction process,

$$Cr_2O_3 + 2Al \xrightarrow{\Delta} 2Cr + Al_2O_3$$

UNIT – 2 – P-BLOCK ELRMENTS - I

II. Answer the following questions:

1. Write a short note on anamolous properties of the first element of p-block. [SEP-20, AUG-21]

In p-block elements the first member of each group differs from the other elements of the corresponding group. The following factors are responsible for this anomalous behaviour.

- Small size of the first member.
- High ionisation enthalpy and high electronegativity.
- Absence of d-orbitals in their valance shell.

The first member of the group-13, boron is a metalloid while others are reactive metals. Moreover, boron shows diagonal relationship with silicon of group -14. The oxides of boron and silicon are similar in their acidic nature.

2. Describe briefly allotropism in p- block elements with specific reference to carbon. [FMT-22]

Some elements exist in more than one crystalline or molecular forms in the same physical state. This phenomenon is called allotropism. Most common allotropes of carbon are,

Graphite, Diamond, Fullerenes, Carbon nanotubes, Graphene.

3. Give the uses of Borax. [HY-19, AUG-21, HY-23, QY24, SRT,MAR-25]

- Used for the identification of coloured metal ions (Borax bead test)
- Manufacture of optical and borosilicate glass, enamels and glazes for pottery.
- Flux in metallurgy.
- Good preservative.

4. What is catenation? Describe briefly the catenation property of carbon. [MAR, SEP20, JUL,SEP-22, FUT,HY-23,24]

Catenation is an ability of an element to form a chain of atoms. The conditions for catenation are

- The valency of the element is greater than or equal to two. The element should have the ability to bond with itself. The self-bond must be as strong as its bond with other elements.
- Kinetic inertness of catenated compound towards other molecules.
- Carbon possesses all the above properties and shows catenation.
- Carbon 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. [PTA-4, QY-22,24 MAR-23]

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.

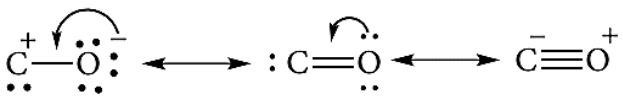
$$nCO + (2n+1)H_2 \longrightarrow C_nH_{(2n+2)} + nH_2O$$

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

6. Give the structure of CO and CO_2. [QY-24]

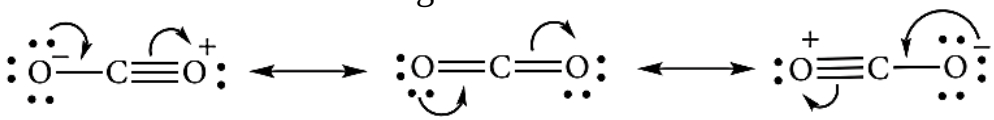
Structure of CO:

- 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 linear structure with equal bond distance for the both C-O bonds.
- In this molecule there is two C-O sigma bond.
- In addition there is 3c-4e bond covering all the three atoms.

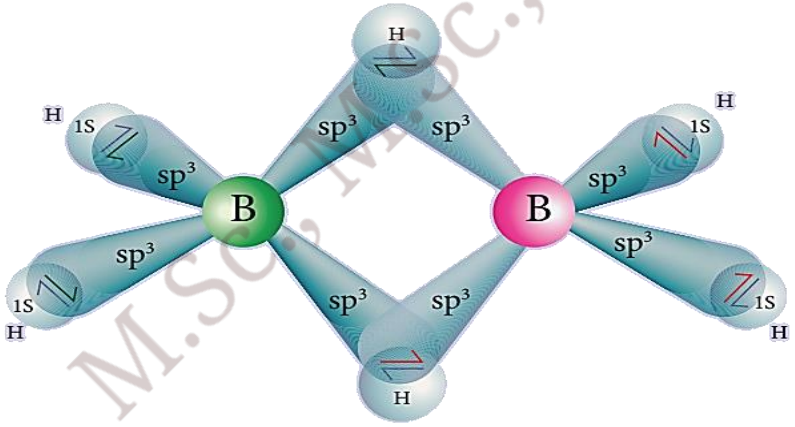


7. Give the uses of silicones. [FMT-22, HY-22, MAR-23, FUT-23,24, HY24, FRT25]

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

8. Describe the structure of diborane. [PTA-3, FMT-22, MAR-23, FUT-23,24]

- In diborane two BH_2 units are linked by two bridged hydrogens.
- Therefore, it has eight B-H bonds.
- However, diborane has only 12 valance electrons and are not sufficient to form normal covalent bonds.
- The four terminal B-H bonds are normal covalent bonds (two centre – two electron bond or 2c-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. The bridging hydrogen atoms are in a plane as shown in the figure. In dibome, 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. [JUN-23, FRT-24, FUT-24, FRT-25]

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

$$B_2H_6 + 3RCH = CHR \rightarrow B(CH_2 - CH_2R)_3 + 6H_2$$ **[SRT,JUN-23]**

10. Give one example for each of the following: icosogens, tetragen, prictogen, chalcogen

1. Icosogens:	2. Tetragen:	3. Prictogen:	4. Chalcogen:
Boron	Carbon	Oxygen	Fluorine
Aluminium	Silicon	Sulfur	Chlorine
Gallium	Germanium	Selenium	Bromine

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

- The tendency of an element to form a cation by loosing electrons is known as an electropositive or metallic character. This character depends on the ionisation energy.
- Generally on descending a group the ionisation energy decreases and hence the metallic character increases.
- In p-block, the elements present in lower left part are metals while the elements in the upper right part are non-metals.

GROUP	METALS	NON-METALS	METALLOIDS
13	Al, Ga, In, Tl	-	B
14	Sn, Pb	C	Si, Ge
15	Bi	N, P	As, Sb
16	Po	O, S, Se	Te
17	-	F, Cl, Br, I, At	-
18	-	He, Ne, Ar, Kr, Xe, Rn	-

12. Complete the following reactions:

(a) $B(OH)_3 + NH_3 \rightarrow$ **[HY-22, SRT25]**
(b) $Na_2B_4O_7 + H_2SO_4 + H_2O \rightarrow$
(c) $B_2H_6 + 2NaOH + 2H_2O \rightarrow$
(d) $B_2H_6 + CH_3OH \rightarrow$
(e) $BF_3 + 9H_2O \rightarrow$ **[FRT-25]**
(f) $HCOOH + H_2SO_4 \rightarrow$
(g) $SiCl_4 + NH_3 \rightarrow$ **[QY-19]**
(h) $SiCl_4 + C_2H_5OH \rightarrow$
(i) $B + NaOH \rightarrow$ **[QY-19]**
(j) $H_2B_4O_7 \xrightarrow{\text{Redhot}}$ **[HY-22, SRT25]**

(a) $B(OH)_3 + NH_3 \xrightarrow{\Delta} \underset{\text{(Boron nitride)}}{BN} + 3H_2O$

(b) $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4\underset{\text{(Boric acid)}}{H_3BO_3} + 2Na_2SO_4$

(c) $B_2H_6 + 2NaOH + 2H_2O \longrightarrow \underset{\text{(Sodiummeteborate)}}{4NaBO_2} + 6H_2$

(d) $B_2H_6 + 6CH_3OH \longrightarrow \underset{\text{(Trimethyl borate)}}{2B(OCH_3)_3} + 6H_2$

(e) $4BF_3 + 9H_2O \longrightarrow \underset{\text{(Boric acid)}}{4H_3BO_3} + 3H^+ + 3[BF_4]^-$

(f) $HCOOH + H_2SO_4 \longrightarrow \underset{\text{(Carbon monoxide)}}{CO} + H_2O + H_2SO_4$

(g) $SiCl_4 + NH_3 \xrightarrow[\text{ether}]{330\ K} \underset{\text{(Chlorosizalanes)}}{Cl_3Si - NH - SiCl_3}$

(h) $SiCl_4 + C_2H_5OH \longrightarrow \underset{\text{(Tetraethoxy silane)}}{Si(OC_2H_5)_4} + 2Cl_2$

(i) $2B + 6NaOH \longrightarrow \underset{\text{(Sodium borate)}}{2Na_3BO_3} + H_2O$

(j) $H_2B_4O_7 \xrightarrow{\text{Red hot}} \underset{\text{(Boric anhydride)}}{2B_2O_3} + H_2O$

13. How will you identify borate radical?(or) Write ethyl borate test. [PTA-5, GMQ, QY-19, HY-22, MAR-23, FUT-24, MAR-25]

- When boric acid or borate salt is heated with ethyl alcohol in presence of concentrated H_2SO_4, an ester triethyl borate is formed.
- The Vapour of this ester burns with a green edged flame and this reaction is used to identify the presence of borate.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow[H_2SO_4]{\text{Conc.}} B(OC_2H_5)_3 + 3H_2O$$

14. Write a note on zeolites. (OR) What are Zeolites? [PTA-2, QY-19,24, SRT-24]

- 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,
  $Na_2O.(Al_2O_3).\boldsymbol{x}(SiO_2)\boldsymbol{y}(H_2O)$ ($\boldsymbol{x}$ = 2 to 10; $\boldsymbol{y}$ = 2 to 6)
- Zeolites have the porous structure in which the monovalent sodium ions and water molecules are loosely held.
- The Si and Al atoms are tetrahedrally coordinated with each other through shared oxygen atoms.
- Zeolites are similar to clay minerals but they differ in their crystalline structure.
- Zeolites structure looks like a honeycomb consisting of a network of interconnected tunnels and cages.
- Water molecules moves freely in and out of these pores but the zeolite framework remains rigid.
- Another special aspect of this structure is that the pore/channel sizes are nearly uniform, allowing the crystal to act as a molecular sieve.
- The removal of permanent hardness of the water can be done using zeolites.

15. How will you convert boric acid to boron nitride? [PTA-3, QY,HY-23, MAR-24]

Fusion of urea with boric acid $B(OH)_3$, in an atmosphere of ammonia at 800 – 1200 K 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. [PTA-1, JUL-20, SRT-23]

- A hydride of 2nd period alkali metal (A) is lithium hydride (LiH).
- Lithium hydride (A) reacts with diborane (B) to give lithium borohydride (C) which is acts as a reducing agent.

$$B_2H_6 + 2LiH \xrightarrow{\text{Ether}} 2LiBH_4$$

(A) Lithium hydride – LiH, **(B)** Diborane – B_2H_6, **(C)** Lithium borohydride – $LiBH_4$

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 fourth-period alkali metal (A) is potash alum
  $K_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$
- On heating potash alum (A) 500K give anhydrous potash alum (or) burnt alum (B).

$$K_2SO_4.Al_2(SO_4)_3.24\,H_2O \xrightarrow{500\,K} K_2SO_4.Al_2(SO_4)_3 + 24\,H_2O$$

- Aqueous solution of burnt alum, has sulphates ion, potassium ion and aluminium ion. Sulphate ion reacts with $BaCl_2$ to form white precipitate of Barium Sulphate

$$(SO_4)_2 + BaCl_2 \rightarrow BaSO_4 + 2Cl^-$$

- Aluminium ion reacts with alizarin solution to give a red colour compound.

18. CO is a reducing agent. Justify with an example. [PTA-6, FMT-22, SRT-24]

- CO_2 Thermodynamically, CO_2 is much more stable than CO, thus carbon monoxide has a relatively high tendency to be oxidised to form carbon di oxide. As it is oxidised it reduces the other substance in the reaction.
- When CO is used to reduce a metal oxide, it gets oxidized to form CO_2

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

EVALUATE YOURSELF

1. Why group 18 elements are called inert gases? Write the general electronic configuration of group 18 elements.

- The group-18 consists of 6 elements, helium, neon, argon, krypton, xenon and radon. All these are gases have completely filled s and p orbitals, hence they are more stable and have least reactivity.
- Therefore group-18 elements are called inert gases. ns^2np^6 is the general electronic configuration of group elements.

GOVERNMENT EXAM QUESTION PAPER

1. How is Potash Alum prepared? What happens when it is heated to 500K? (or) Write the preparation of potash alum? [HY-19, JUN-20, QY-22, HY-24]

The alunite the alum stone is the naturally occurring form and it is $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$. When alum stone is treated with excess of sulphuric acid, the aluminium hydroxide is converted to aluminium sulphate. A calculated quantity of potassium sulphate is added and the solution is crystallised to generate potash alum. It is purified by recrystallisation.

$$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3 + 6H_2SO_4 \longrightarrow K_2SO_4 + 3Al_2(SO_4)_3 + 12\,H_2O$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24\,H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24\,H_2O$$

Potash alum is heating at 500 K loses water of hydration and swells up. The swollen mass is known as **burnt alum**.

$$K_2SO_4.Al_2(SO_4)_3.24\,H_2O \xrightarrow{500\ K} K_2SO_4.Al_2(SO_4)_3 + 24\,H_2O$$

2. Although Graphite and Diamond are allotropes of carbon, graphite is soft whereas diamond is hard. Why? [QY-19]

- Carbon alone forms the familiar substances graphite and diamond. Both graphite and diamond are made only of carbon atoms.
- Graphite is very soft and slippery while Diamond is the hardest substance.
- While there are strong covalent bonds between carbon atoms in each layer, there are only weak forces between layers. This allows layers of carbon to slide over each other in graphite.
- On the other hand, in diamonds, each carbon atom is the same distance from each of its neighboring carbon atoms. they are bonded by strong covalent bonds
- Diamond is hard because it has four carbon atoms which form a strong covalent bond in tetrahedral structure whereas graphite is arranged in layer form through weak wander walls force hence is slippery in nature.

For example:

1. The slippery nature of graphite is attributed to the pencil lead.
2. The hardness of a diamond is used to drill, grind or cut materials.
3. Graphite is a good conductor because of the free electrons present in it

3. Give the uses of Potash alum. [QY-19, QY-23, FRT-25]

- It is used for purification of water. It is also used for water proofing and textiles
- It is used in dyeing, paper and leather tanning industries
- It is employed as a styptic agent to arrest bleeding.

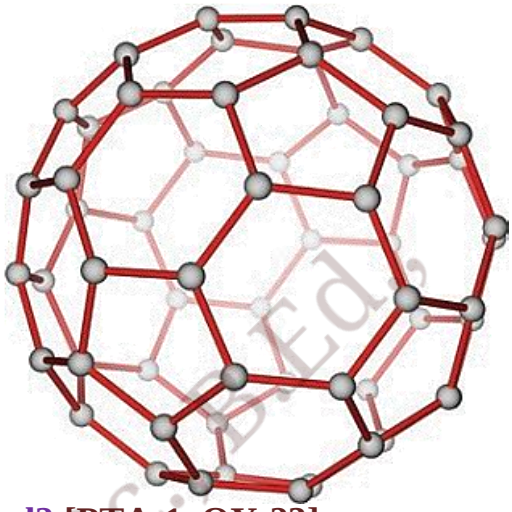
4. There is only a marginal difference in decrease in ionisation enthalpy from Aluminium to Thallium – Explain why? [MAR-20]

The reason for decrease in ionisation enthalpy from Aluminium to Thallium is due to the presence of inner d and f-electrons which has poor shielding effect compared to s and p-electrons.

5. What are the uses of boric acid? [MAY,JULY-22, SRT-24, MAR-24]

- Boric acid is used in the manufacture of pottery glases, enamels and pigments.
- It is used as an antiseptic and as an eye lotion.
- It is also used as a food preservative.

6. What are fullerenes? [FMT-22]



Fullerenes are newly synthesised allotropes of carbon. Unlike graphite and diamond, these allotropes are discrete molecules such as C_{32}, C_{50}, C_{60}, C_{70}, C_{76} etc., these molecules have cage like structures as shown in the figure. The C60 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. Each carbon atom is sp^2 hybridised and forms three σ bonds & a delocalised π bond giving aromatic character to these molecules. The C-C bond distance is 1.44 Å and C=C distance 1.38 Å.

7. Which is known as Inorganic benzene? How it is prepared? [PTA-1, QY-23]

Borozole or **Borazine** is known as Inorganic benzene. When treated with excess ammonia at low temperatures diborane gives diboranediammonate. On heating at higher temperatures it gives inorganic benzene (borazole).

$$3B_2H_6 + 6NH_3 \xrightarrow{-153\ K} 3(B_2H_6.2NH_3)\ (or)\ 3[BH_2(NH_3)_2]^+[BH_4]^-$$

$$3B_2H_6 + 2NH_3 \xrightarrow[\text{Clossed vessel}]{\text{High temp}} 2B_3N_3H_6 + 12H_2$$

(Borazole or Borazine - Inorganic benzene)

8. What are amphiboles? Give example. [PTA-1,]

Double chain silicates (or amphiboles): These silicates contains $[Si_4O_{11}]_n^{6n-}$ ions. In these silicates there are two different types of tetrahedra : (i) Those sharing 3 vertices (ii) those sharing only 2 vertices.

Examples:

1) **Asbestos:** These are fibrous and non-combustible silicates. Therefore they are used for thermal insulation material, brake linings, construction material and filters. Asbestos being carcinogenic silicates, their applications are restricted.

9. How does boric acid reacts with NaOH?

It reacts with sodium hydroxide to form sodium metaborate and sodium tetraborate.

$$H_3BO_3 + NaOH \rightarrow NaBO_2 + 2H_2O$$

$$4H_3BO_3 + 2NaOH \rightarrow Na_2B_4O_7 + 7H_2O$$

10. What happens when Boric acid is heated? [QY-23]

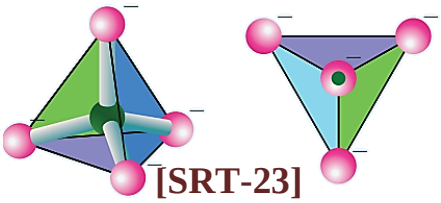
Boric acid when heated at 373 K gives metaboric acid and at 413 K, it gives tetraboric acid. When heated at red hot, it gives boric anhydride which is a glassy mass.

$$4H_3BO_3 \xrightarrow{373\ K} 4HBO_2 + 4H_2O$$

$$4HBO_2 \xrightarrow{413\ K} H_2B_4O_7 + H_2O$$

$$H_2B_4O_7 \xrightarrow{\text{Red hot}} 2B_2O_3 + H_2O$$

11.Write about orthosilicates. [FRT-24]



The simplest silicates which contain discrete $[SiO_4]^{4-}$ tetrahedral units are called **ortho silicates** or **neso silicates**.

12.$AlCl_3$ is more stable where as $TlCl_3$ is highly unstable. Why? [SRT-23]
(or) What is Inert Pair Effect? [QY-24]

- Aluminium (III) chloride is stable whereas thallium (III) chloride is highly unstable and disproportionates to thallium (I) chloride and chlorine gas.
- This shows that in thallium the stable lower oxidation state corresponds to the loss of *np* electrons only and not *ns* electrons.
- Thus 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.

13.What are Silicates? [MAR-24]

The mineral which contains silicon and oxygen in tetrahedral $[SiO_4]^{4-}$ units linked together in different patterns are called silicates. Nearly 95 % of the earth crust is composed of silicate minerals and silica. The glass and ceramic industries are based on the chemistry silicates.

How will you prepare chlorine in the laboratory?

14.Write about McAfee process. [FRT-24]

Aluminium chloride is obtained by heating a mixture of alumina and coke in a current of chlorine.

$$2Al_2O_3 + 3C + 6Cl_2 \longrightarrow 4AlCl_3 + 3CO_2$$

On industrial scale it is prepared by chlorinating aluminium around 1000 K

$$2Al + 3Cl_2 \xrightarrow{1000\ K} 2AlCl_3$$

15.What is water gas equilibrium? [FMT-22]

The equilibrium involved in the reaction between carbon dioxide and hydrogen, has many industrial applications is called water gas equilibrium. $CO_2 + H_2 \rightleftharpoons CO + H_2O$

16.What is the action of heat on Borax? [SAT-22]

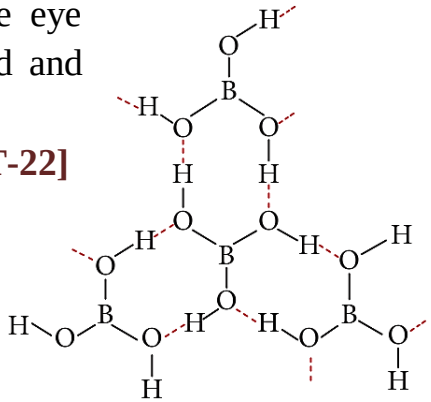
On heating it forms a transparent borax beads.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$$

17.Mention the uses of boron. [SAT-22]

- Boron has the capacity to absorb neutrons. Hence, its isotope $^{10}B_5$ is used as moderator in nuclear reactors.
- Amorphous boron is used as a rocket fuel igniter. Boron is essential for the cell walls of plants.
- Compounds of boron have many applications. For example eye drops, antiseptics, washing powders etc., contains boric acid and borax. In the manufacture of Pyrex glass, boric oxide is used.

18.Draw the structure of Boric acid and mention its uses [SAT-22]



- Boric acid is used in the manufacture of pottery glases, enamels and pigments.
- It is used as an antiseptic and as an eye lotion.
- It is also used as a food preservative.

19.How is dibonane prepared?

Diborane can also be obtained in small quantities by the reaction of iodine with sodium borohydride in diglyme.

$$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$$

On heating magnesium boride with HCl a mixture of volatile boranes are obtained.

$$2Mg_3B_2 + 12HCl \longrightarrow 6MgCl_2 + B_4H_{10} + H_2$$

$$B_4H_{10} + H_2 \longrightarrow 2B_2H_6$$

UNIT – 3 – P-BLOCK ELRMENTS - II

II. Answer the following questions:

1. What is inert pair effect? [QY-19, MAY-22, QY,HY-22, QY-23]

In p-block elements, as we go down the group, two electrons present in the valence s-orbital become inert and are not available for bonding (only p-orbital involves chemical bonding). This is called inert pair effect. This effect is also observed in groups 14, 15 and 16.

2. Chalcogens belongs to p-block. Give reason. [SRT-22]

- Chalcogens are ore forming elements.
- Most of the ores are oxides and sulphides, 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.
- Chalcogens general electronic configuration is ns^2np^4.

3. Explain why fluorine always exhibit an oxidation state of -1? [FUT-23]

- The electronic configuration of Fluorine is $1s^2$, $2s^2$, $2p_x^2$, $2p_y^2$, $2p_z^1$.
- Fluorine the most electronegative element than other halogens and cannot exhibit any positive oxidation state.
- Fluorine does not have d-orbital while other halogens have d-orbitals.
- Therefore fluorine always exhibit an oxidation state of-1 and others in halogen family shows +1, +3, +5 and +7 oxidation states.

4. Give the oxidation state of halogen in the following. [FRT25]

(i) OF_2 [MAR-23] (ii) O_2F_2 (iii) Cl_2O_3 [SRT-23] (iv) I_2O_4 [SRT,MAR-23]

(i) OF_2	(ii) O_2F_2	(iii) Cl_2O_3	(iv) I_2O_4
$+2 + 2(x) = 0$	$2(+1) + 2x = 0$	$2(x) + 3(-2) = 0$	$2(x) + 4(-2) = 0$
$+2 = -2x$	$2x = -2$	$2x = +6$	$2x = +8$
$2x = -2$ $x = -1$	$x = -1$	$x = +3$	$x = +4$

5. What are interhalogen compounds? Give examples. [GMQ,HY-19, AUG-21, MAY-22, QY-22, QY-23, MAR-25]

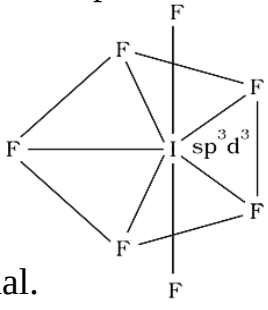
Each halogen combines with other halogens to form a series of compounds called interhalogen compounds. For example, ClF, BrF_3, ClF_3, BrF_5, IF_7.

6. Why fluorine is more reactive than other halogens? [PTA-1&3, QY-19,SRT25]

Fluorine is the most reactive element among halogen. This is due to the minimum value of F – F bond dissociation energy. Hence fluorine is more reactive than other halogens.

7. Give the uses of helium. [PTA-2, GMQ, QY-19, SEP-20, AUG-21, SRT-22, QY-22, QY,JUN-23, MAR-24]

- Helium and oxygen mixture is used by divers in place of air oxygen mixture. This prevents the painful dangerous condition called bends.
- Helium is used to provide inert atmosphere in electric arc welding of metals
- Helium has lowest boiling point hence used in cryogenics (low temperature science).
- It is much less denser 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 of IF_7 is pentagonal bi-pyramidal.

9. Give the balanced equation for the reaction between chlorine with cold NaOH and hot NaOH. [SEP-20]

- Reaction between chlorine with cold NaOH: $Cl_2 + H_2O \rightarrow HCl + HOCl$

$HCl + NaOH \rightarrow NaCl + H_2O$ $HOCl + NaOH \rightarrow NaOCl + H_2O$

Overall reaction $Cl_2 + 2NaOH \longrightarrow \underset{\text{sodium hypo chlorite}}{NaOCl} + NaCl + H_2O$

Chlorine reacts with cold NaOH to give sodium chloride and sodium hypochlorite.

- Reaction between chlorine with hot NaOH: $Cl_2 + H_2O \rightarrow HCl + HOCl$

$HCl + NaOH \rightarrow NaCl + H_2O$ $HOCl + NaOH \rightarrow NaOCl + H_2O$

$3NaOCl \rightarrow NaClO_3 + 2NaCl$

Overall reaction $3Cl_2 + 6NaOH \longrightarrow \underset{\text{sodium chlorate}}{NaClO_3} + 5NaCl + 3H_2O$

Chlorine reacts with hot NaOH to give sodium chlorate and sodium chloride.

10. How will you prepare chlorine in the laboratory? [PTA-2, FUT-23]

- Chlorine is prepared by the action of cone, sulphuric acid on chlorides in presence of manganese dioxide. $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow Cl_2 + MnCl_2 + 4NaHSO_4 + 2H_2O$
- It can also be prepared by oxidising hydrochloric acid using various oxidising agents such as manganese dioxide, lead dioxide, potassium permanganate or dichromate.

$PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2$ $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl + 8H_2O + 5Cl_2$

$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

- When bleaching powder is treated with mineral acids chlorine is liberated

$CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$ $CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$

11. Give the uses of sulphuric acid. [FRT25]

- 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. Prove that sulphuric acid is a dehydrating agent (or) Give a reason to support that sulphuric acid is a dehydrating agent. [PTA1,QY,HY19, HY22, JUN, QY23, MAR24]

- Sulphuric acid is highly soluble in water. It has strong affinity towards water
- 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 HCOOH.

$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2SO_4 \longrightarrow 12C + H_2SO_4.11H_2O$

$\underset{\text{Formic acid}}{HCOOH} + H_2SO_4 \longrightarrow CO + H_2SO_4.H_2O$

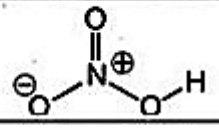
$\underset{\text{Oxalic acid}}{(COOH)_2} + H_2SO_4 \longrightarrow CO + CO_2 + H_2SO_4.H_2O$

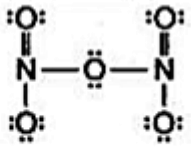
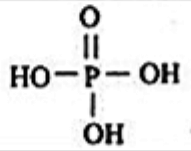
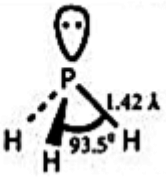
13. Write the reason for the anamolous behaviour of Nitrogen.

- Due to its small size, high electro negativity, high ionisation enthalpy and absence of d-orbitals. Nitrogen exists a diatomic molecule with triple bond between the two atoms whereas other elements form single bond in the elemental state.
- N, has a unique ability to form $p\pi - p\pi$ multiple bond whereas the heavier members of this group (15) do not form $p\pi - p\pi$ bond, because their atomic orbitals are so large and diffused that they cannot have effective overlapping.
- N cannot form $d\pi - p\pi$ bond due to the absence of d – orbitals whereas other elements can.

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

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

	Molecule	Molecular formula	Structure
a.	Nitric acid	HNO_3	

b.	Dinitorgen pentaoxide	N_2O_5	
c.	Phosphoric acid	H_3PO_4	
d.	Phosphine	PH_3	

15. Give the uses of argon. [PTA-2, JULY-22]

- Mixed with 20.06% nitrogen and it is used in gas filled electric lamps.
- It is also used in radio valves and tubes.
- Argon prevents the oxidation of hot filament and prolongs the life in filament bulbs.

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

General electronic configuration of group 15 elements are ns^2np^3.

- Nitrogen – [He] $2s^2\ 2p^3$ Phosphorous – [Ne] $3s^2\ 3p^3$ Arsenic – [Ar] $3d^{10}\ 4s^2\ 4p^3$
- Antimony – [Kr] $4d^{10}\ 5s^2\ 5p^3$ Bismuth – [Ne] $4f^{14}\ 5s^{10}\ 6s^2\ 6p^3$

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

- Phosphine reacts with halogens to give phosphorous penta halides.

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

- Phosphine forms coordination compound with lewis acids such as boron trichloride.

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

- 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. [FUT-23]

Nitric acid 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? [MAR-25]

On heating phosphorous pentachloride, it decomposes into phosphorus trichloride and chlorine. $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$

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

- 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 are strong acids. …….H-F…..H-F…..H-F……
- Due to hydrogen bonding in HF, it cannot be completely ionised and therefore they are weak acids. But other hydrohalic acids are completely ionised and so are strong acids.

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

- In case of O – F bond is HOF, fluorine is most electronegative element. So its oxidation number is -1.
- Thereby oxidation number of O is +1. Similarly in case of O – H bond is HOF. O is highly electronegative than H. So its oxidation number is -1 and oxidation number of H is +1.
- So, Net oxidation of oxygen is $+1 + x - 1 = 0$. Oxidation number of O in HOF is zero.

22. What type of hybridisation occur in (i) BrF_5 (ii) BrF_3 [SEP-20]

(i) BrF_5 : BrF_5 is a AX_5 type. Therefore is has sp^3d^2 hybridisation. Hence, it has square pyramidal shape.

(ii) BrF_3 : BrF_3 is a AX_3 type. Therefore it has sp^3d hybridisation. Hence, it has T-shape.

23. Complete the following reactions.

1. **$NaCl + MnO_2 + H_2SO_4 \longrightarrow$**

   $4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow Cl_2 + MnCl_2 + 4\,NaHSO_4 + 2H_2O$

2. **$NaNO_2 + HCl \longrightarrow$**

   $NaNO_2 + HCl \longrightarrow NaCl + HNO_2$

3. **$IO_3^- + I^- + H^+ \longrightarrow$**

   $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$

4. **$I_2 + S_2O_3^{2-} \longrightarrow$**

   $I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$

5. **$P_4 + NaOH + H_2O \longrightarrow$ [MAR-23, SRT-25]**

   $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3\uparrow$

6. **$AgNO_3 + PH_3 \longrightarrow$ [FUT-23]**

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

7. **$Mg + HNO_3 \longrightarrow$**

   $4Mg + 10HNO_3 \longrightarrow 4\,Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$

8. **$KClO_3 \xrightarrow{\Delta}$ [FUT-23]**

   $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$

9. **Cu + Hot Conc.$H_2SO_4 \longrightarrow$ [MAR, FUT-23]**

   $Cu + \text{Hot Conc.}2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2\uparrow$

10. **$Sb + Cl_2 \longrightarrow$**

    $2Sb + 3Cl_2 \longrightarrow 2SbCl_3$

11. **$HBr + H_2SO_4 \longrightarrow$**

    $2HBr + H_2SO_4 \longrightarrow 2SO_2 + 2H_2O + Br_2$

12. **$XeF_6 + H_2O \longrightarrow$ [MAR-23]**

    $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

13. **$XeO_6^{4-} + Mn^{2+} + H^+ \longrightarrow$**

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

14. **$XeOF_4 + SiO_2 \longrightarrow$**

    $2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$

15. **$Xe + F_2 \xrightarrow[400°C]{Ni\ /\ 200\ atm}$**

    $Xe + 3F_2 \xrightarrow[400°C]{Ni\ /\ 200\ atm} XeF_6$

EVALUATE YOURSELF

1. Write the products formed in the reaction of nitric acid (both dilute and concentrated) with zinc.

(*i*) Zinc with Conc. HNO_3:

$4Zn + 10HNO_3 \longrightarrow \underset{\text{(Zinc nitrate)}}{4Zn(NO_3)_2} + \underset{\text{(Ammonium nitrate)}}{NH_4NO_3} + 3H_2O$

(*ii*) **Zinc with Dil. HNO_3:**

$$4Zn + 10HNO_3 \longrightarrow \underset{\text{(Zinc nitrate)}}{4Zn(NO_3)_2} + \underset{\text{(Nitrous oxide)}}{N_2O} + 5H_2O$$

GOVERNMENT EXAM QUESTION PAPER

1. What are the properties of inter halogen compounds? [PTA-2, QY-19, JUL-22]

Properties of inter halogen compounds:

- The central atom will be the larger one.
- It can be formed only between two halogen and not more than two halogens.
- Fluorine can't act as a central metal atom being the smallest one.
- Due to high electronegativity with small size fluorine helps the central atom to attain high coordination number.
- They can undergo the auto ionization.
- They are strong oxidising agents included.

$$2ICl \rightleftharpoons I^+ + ICl_2^- \qquad 2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$$

2. How is pure phosphine prepared from phosphorous acid? [GMQ-19, HY-22]

Phosphine is prepared in pure form by heating phosphorous acid.

$$\underset{\text{Phosphorous acid}}{4H_3PO_3} \xrightarrow{\Delta} \underset{\text{Ortho phosphoric acid}}{3H_3PO_4} + \underset{\text{Phosphine}}{PH_3}\uparrow$$

3. How is bleaching powder prepared? [MAR-20, MAY-22]

Bleaching powder is produced by passing chlorine gas through dry slaked lime (calcium hydroxide). $Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$

4. SO_2 – is a reducing agent. Prove it. [SRT-22]

- SO_2 – It can readily be oxidised, it acts as a reducing agent. It reduces chlorine into hydrochloric acid. $SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$
- It also reduces potassium permanganate and dichromate to Mn^{2+}

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

5. What is the reaction of ammonia on Cu^{2+} solution? [SRT-22]

Ammonia reacts with metallic salts to forming complexes

$$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$$

Tetraamminecopper(II)ion (a coordination complex)

6. What are the uses of oxygen? [MAY-22]

- Oxygen is used up by living beings in respiration process.
- It is used for burning of fuels.
- In industry it is used for cutting, welding and melting metals.
- It is used in water treatment and chemical combustion.

7. Explain the bleaching action of Chlorine? [QY-19, FRT25]

Oxidising and bleaching action: Chlorine is a strong oxidising and bleaching agent because of the nascent oxygen.

$$H_2O + Cl_2 \longrightarrow HCl + \underset{\text{Hypo chlorous acid}}{HOCl}$$

$$HOCl \longrightarrow HCl + (O)$$

Colouring matter + Nascent oxygen → Colourless oxidation product

The bleaching of chlorine is permanent. It oxidises ferrous salts to ferric, sulphites to sulphates and hydrogen sulphide to sulphur.

$$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$$

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

$$2FeSO_4 + H_2SO_4 + HOCl \longrightarrow Fe_2(SO_4)_3 + HCl + H_2O$$

overall reaction $2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$

$Cl_2 + H_2O \longrightarrow HCl + HOCl$

$Na_2SO_3 + HOCl \longrightarrow Na_2SO_4 + HCl$

overall reaction $Na_2SO_3 + H_2O + Cl_2 \longrightarrow Na_2SO_4 + 2HCl$

$Cl_2 + H_2S \longrightarrow 2HCl + S$

8. Why HF cannot be stores in glass bottles? [MAR-20]

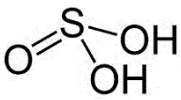
Moist hydrofluoric acid (not dry) rapidly react with silica and glass.

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

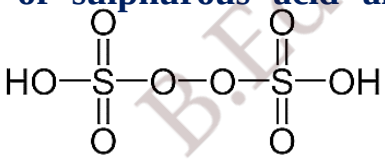
$$Na_2SiO_3 + 6HF \rightarrow Na_2SiF_6 + 3H_2O$$

9. Write the molecular formula and draw the structure of sulphurous acid and Marshall's acid. [MAR-20]

(i) Sulphurous acid (H_2SO_3)



(ii) Marshall's acid or Peroxodisulphuric acid ($H_2S_2O_8$)



10. Write a short note on Holmes Signal. [SEP-20, HY-22]

- In a ship, a pierced container with a mixture of calcium carbide and calcium phosphide, liberates phosphine and acetylene when thrown into sea.
- The liberated phosphine catches fire and ignites acetylene.
- These burning gases serves as a signal to the approaching ships.
- This is known as **Holmes signal**.

11. Explain the bleaching action of Sulphur dioxide. [AUG-21, JUN-23, MAR-25]

In presence of water, sulphur dioxide bleaches coloured wool, silk, sponges and straw into colourless due to its reducing property. $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2(H)$

$$\underset{\text{Coloured}}{X} + 2(H) \longrightarrow \underset{\text{Colourless}}{XH_2}$$

However, the bleached product (colourless) is allowed to stand in air, it is reoxidised by atmospheric oxygen to its original colour. Hence bleaching action of sulphur dioxide is temporary.

Uses: Sulphur dioxide is used in bleaching hair, silk, wool etc...

- It can be used for disinfecting crops and plants in agriculture.

Structure of sulphur dioxide: In sulphur dioxide, sulphur atom undergoes sp2 hybridisation. A double bond arises between S and O is due pπ – dπ overlapping.

12. Complete the following reactions. [SRT-22]

(i) NH_3 (excess) + Cl_2 → ?

(ii) NH_3 + Cl_2 (excess) → ?

(i) With excess ammonia $2\,NH_3 + 3\,Cl_2 \longrightarrow N_2 + 6\,HCl$

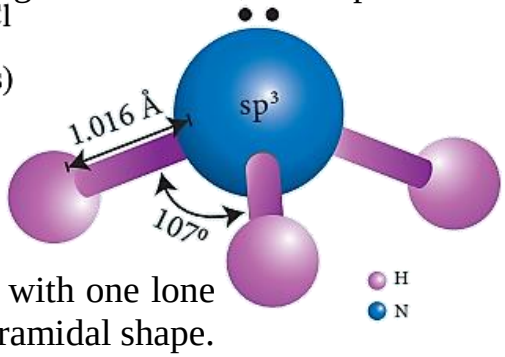
$6\,HCl + 6\,NH_3 \longrightarrow 6\,NH_4Cl$

(ii) With excess of chlorine ammonia reacts to give nitrogen trichloride, an explosive substance. $2NH_3 + 6Cl_2 \longrightarrow 2NCl_3 + 6\,HCl$

$2NH_3(g) + HCl(g) \longrightarrow NH_4Cl\,(s)$

13. Explain the structure of ammonia. [SRT-22]

- Ammonia molecule is pyramidal in shape N-H bond distance is 1.016 Å and H-H bond distance is 1.645 Å with a bond angle 107°.
- The structure of ammonia may be regarded as a tetrahedral with one lone pair of electrons in one tetrahedral position hence it has a pyramidal shape.



14.Show that phosphine act as a reducing agent. [QY-23]

Phosphine shows reducing agent in the reaction with some metal compounds. For example, Phosphine reacts with $AgNO_3$ to reduce and produce precipitates of Ag_3P (silver phosphide).

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

15.Powdered $CaCO_3$ reacts much faster with dilute HCl than with the same mass of $CaCO_3$ as marble. Give reason. [SEP-20]

For a given mass of react and when a particle decrease, surface are increases, Increase in surface area of the reactant leads to more collisions per litre per second and hence the rate of reaction also increases. $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2$

16.Explain the Deacons's process for manufacture of chlorine [SEP-20]

In this process a mixture of air and hydrochloric acid is passed up a chamber containing a number of shelves, pumice stones soaked in cuprous chloride are placed. Hot gases at about 723K are passed through a jacket that surrounds the chamber.

$$4HCl + O_2 \xrightarrow[Cu_2Cl_2]{400^0C} 2H_2O + 2Cl_2\uparrow$$

The chlorine obtained by this method is dilute and is employed for the manufacture of bleaching powder. The catalysed reaction is given below

$$2Cu_2Cl_2 + O_2 \longrightarrow \underset{\text{Cuprous oxy chloride}}{2Cu_2OCl_2} \qquad Cu_2OCl_2 + 2HCl \longrightarrow \underset{\text{Cupric chloride}}{2CuCl_2} + H_2O$$

$$2CuCl_2 \longrightarrow \underset{\text{Cuprous chloride}}{Cu_2Cl_2} + Cl_2$$

17.Sulphuric acid dibasic acid prove it [SEP-20]

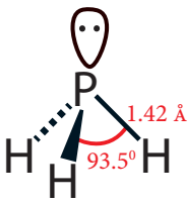
It is a strong dibasic acid. Hence it forms two types of salts sulphates and bisulphates.

$$H_2SO_4 + NaOH \longrightarrow \underset{\text{sodium bisulphate}}{NaHSO_4} + H_2O \qquad H_2SO_4 + 2NaOH \longrightarrow \underset{\text{sodium sulphate}}{Na_2SO_4} + 2H_2O$$

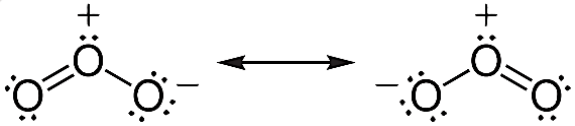
$$H_2SO_4 + 2NH_3 \longrightarrow \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4}$$

18.Explain the structure of Phosphine. [SRT-25]

- In phosphine, phosphorus shows sp^3 hybridisation.
- Three orbitals are occupied by bond pair and fourth corner is occupied by lone pair of electrons.
- Hence, bond angle is reduced to 93.5°.
- Phosphine has a pyramidal shape.



19.Draw the structure of Ozone? [FRT-25]



20.Write the reason for the anomalous behaviour of nitrogen. [SRT-25]

- Small size of the first member (nitrogen)
- High ionisation enthalpy and high electronegativity
- Absence of d orbitals in their valance shell

II. Answer the following questions:

1. What are transition metals? Give four examples.

The metallic elements that have incompletely filled d or f subshell in the neutral or cationic state are called transition metals.

Examples: Copper, Iron, Cobalt, Nickel.

2. Explain the oxidation states of 4d series elements.

- The oxidation states of 4d metals vary from +3 for Y and La to +8 for Ru and Os.
- The highest oxidation state of 4d and elements are found in their compounds with the higher electronegative elements like O, F and Cl.

Example:

- RuO_4, OsO_4 and WCl_6.
- Generally in going down a group, a stability of the higher oxidation state increases while that of lower oxidation state decreases.
- It is evident from the Frost diagram (ΔG_0 vs oxidation number) as shown below,For titanium,vanadium and chromium, the most thermodynamically stable oxidation state is +3.

3. What are inner transition elements? [SUT-24]

- The elements in which the extra electron enters (n-2)f orbitals are called f-block elements.
- These elements are also called as inner transition elements because they form a transition series within the transition elements.
- As the f orbitals lie inner to the penultimate shell, therefore these elements having partially filled f orbitals, are also called inner transition elements.
- In the inner transition elements there are two series of elements.
  - ❖ Lanthanoids (Previously called lanthanides)
  - ❖ Actinoids (Previously called actinides)

4. Justify the position of lanthanides and actinides in the periodic table. (or) Describe the position of f-block elements in the periodic table. [PTA–1, SRT-22, SUT-24]

Lanthanides:

- The actual position of lanthanides in the periodic table is at group number 3 and period number 6. In the sixth period, the electrons are perferentially filled in inner 4f-sub shell.
- The 14 elements following lanthanum (Ce to Lu) show similar chemical properties. Hence they are grouped together and placed at the bottom of the periodic table.
- This position is justified as follows: Lanthanoids have general electronic configuration [Xe] $4f^{1-14}\ 5d^{0-1}\ 6s^2$. The common oxidation state of lanthanoids is +3. All these elements have similar physical and chemical properties.

Actinides:

- Similarly the 14 elements following actinium (Th to Lr) resemble in their physical and chemical properties.
- If we place these elements after Lanthanum in the periodic table below 4d series and actinides below 5d series, the properties of the elements belongs to a group would be different and it would affect the proper structure of the periodic table. Hence a separate position is provided to the inner transition elements at the bottom of the periodic table.
  - ❖ Actinoids have general electronic configuration [Rn] $5f^{0-14}\ 6d^{0-2}\ 7s^2$
  - ❖ The common oxidation state of actinoids is +3
  - ❖ In addition to that actinoids show variable oxidation states such as +2 , +3 , +4 ,+5,+6 and +7.

5. What are actinoids? Give three examples.

- Similarly the 14 elements following actinium (Th to Lr) are called actinoids.
- Similer to lanthanoids, hence a separate position is provided to the inner transition elements at the bottom of the periodic table.
- Actinoids have general electronic configuration [Rn] $5f^{0-14}$ $6d^{0-2}$ $7s^2$

Example: Actinium (**Ac**), Thorium (**Th**), Protactinium (**Pa**), Uranium (**U**), Neptunium (**Np**), Plutonium (**Pu**), Americium (**Am**), Curium (**Cm**), Berkelium (**Bk**), Californium (**Cf**), Einstenium (**Es**), Fermium (**Fm**), Mendelevium (**Md**), Nobelium (**No**) and Lawrentium (**Lr**)

6. Describe the preparation of potassium dichromate.[PTA2, SRT,QY23,HY24, MAR25]

- **Important Ore:** $K_2Cr_2O_7$ is prepared from chromite–Iron ore, or Chromite ore.
- **Concentration method:** The ore is converted by gravity separation
- Conversion of chromite iron ore into sodium chromate.

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \xrightarrow{900 - 1000^0C} 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2\uparrow$$

- Conversion of sodium chromate into sodium dichromate:

$$\underset{\text{sodium chromate (yellow)}}{2\,Na_2CrO_4} + H_2SO_4 \longrightarrow \underset{\text{sodium dichromate (orange red)}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

- Conversion of sodium dichromate into potassium dichromate :

$$\underset{\text{sodium dichromate (orange red)}}{Na_2Cr_2O_7} + 2KCl \longrightarrow \underset{\text{potassium dichromate (orange red)}}{K_2Cr_2O_7} + 2NaCl$$

7. What is lanthanide constraction and what are the effects of lanthanide contraction? [PTA-3, SEP-20, JUN-23, QY-23, MAR,SUT-24]

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

Consequences of lanthanoid contraction:

1. Basicity differences:

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 basicity.

2. Similarities among lanthanoids:

In the complete f - series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed. because of this very small change in radii of lanthanoids, their chemical properties are quite similar.

The elements of the second and third transition series resemble each other more closely than the elements of the first and second transition series.

8. Complete the following

a. $MnO_4^{2-} + H^+ \longrightarrow ?$

$$\underset{\text{Manganate ion}}{3MnO_4^{2-}} + \underset{\text{Acid medium}}{4H^+} \longrightarrow \underset{\text{Permanganate ion}}{2MnO_4^-} + \underset{\text{Manganese dioxide}}{MnO_2} + 2H_2O$$

b. $C_6H_5CH_3 \xrightarrow[KMnO_4]{\text{acidified}} ?$

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[\text{(Oxidation)}]{\text{acidified } KMnO_4} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

c. $MnO_4^- + Fe^{2+} \longrightarrow ?$

$2MnO_4^- + 10\,Fe^{2+} + 16\,H^+ \longrightarrow 2Mn^{2+} + 10\,Fe^{3+} + 8H_2O$

Permanganate ion — Ferrous ion — (Oxidation) — Ferric ion

d. $KMnO_4 \xrightarrow[\text{Red hot}]{\Delta} ?$ **[JUN-25]**

$2KMnO_4 \xrightarrow[\text{Red hot}]{\Delta} K_2MnO_4 + MnO_2 + O_2$

Potassium Permanganate — Potassium Manganate — Manganese dioxide

e. $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow ?$

$Cr_2O_7^{2-} + 6\,I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

Iodide ion — (Oxidation) — Iodine

f. $Na_2Cr_2O_7 + KCl \longrightarrow ?$

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

Sodium dichromate — Potassium dichromate

9. What are interstitial compounds? [PTA-1, SEP-20, AUG-21, QY,MAY-22, JUN,SUT-23, QY-23, SRT,QY-24]

- An interstitial compound or alloy is a compound that is formed when small atoms like hydrogen, boron, carbon or nitrogen are trapped in the interstitial holes in a metal lattice.
- They are usually non-stoichiometric compounds. Transition metals form a number of interstitial compounds such as TiC, $ZrH_{1.92}$, Mn_4N etc.
- The elements that occupy the metal lattice provide them new properties.

10. Calculate the number of unpaired electrons in Ti^{3+}, Mn^{2+} and calculate the spin only magnetic moment. [PTA-6, AUG-21, SUT-24]

Ti (Z = 22). Electronic configuration [Ar] $3d^2\ 4s^2$

Ti^{3+} – Electronic configuration [Ar] $3d^1$

So, the number of unpaired electrons in Ti^{3+} is equal to 1.

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

$$\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.732\ BM$$

Mn (Z = 25). Electronic configuration [Ar] $3d^5\ 4s^2$

Mn^{2+} – Electronic configuration [Ar] $3d^5$

So, the number of unpaired electrons in Mn^{2+} is 5.

Spin only magnetic moment $\mu_s = \sqrt{n(n+2)}$ $\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.92\ BM$

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

Ce (Z = 58) → $Ce^{4+} + 4e^-$

Ce^{4+} – $Is^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$

$C_O{}^{2+}$ – $Is^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$.

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.

- It can be easily observed that except Sc all other metals possess +2 oxidation state.
- Also, on moving from Sc to Mn, the atomic number increases from 21 to 25.
- This means the number of electrons in the 3d – orbital also increases from 1 to 5.

  $Sc^{2+} = d^1$ $Ti^{2+} = d^2$ $V^{2+} = d^3$ $Cr^{2+} = d^4$ $Mn^{2+} = d^5$
- +2 oxidation state is attained by the loss of the two 4s electrons by these metals.
- Since the number of d electrons in (+2) state also increases from Ti2+ to Mn2+ the stability of +2 state increases.
- As a result d- orbital is becoming more and more half-filled which is highly stable.

13. Which is more stable? Fe^{3+} or Fe^{2+} – explain. [QY19, MAY,QY22, SUT,QY23, MAR24]

Fe (Z = 26) $Fe \rightarrow Fe^{2+} + 2e^-$ $Fe \rightarrow Fe^{3+} + 3e^-$

- Fe^{2+} [Number of electrons 24] Electronic configuration = $[Ar]3d^6$
- Partially filled d-subshell is less stable.
- Fe^{3+} [Number of electrons 23] Electronic configuration = $[Ar]3d^5$
- Among Fe^{3+} and Fe^{2+}, Fe^{3+} is more stable due to half filled d-orbital. This can be explained by Aufbau principle. Half filled and completely filled d-orbitals are more stable than partially filled d-orbitals. So Fe^{3+} is more stable than Fe^{2+}.

14. Explain the variation in $E^0_{M2+/M3+}$ 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+} half cell gives the relative stability between M^{3+} and M^{2+}.
- 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 0.77 V, and this low value indicates that both Fe^{3+} and Fe^{2+} can exist under normal condition.
- Mn^{3+} has a $3d^2$ configuration while that of Mn^{2+} is $3d^5$. The extra stability associated with a half filled d sub-shell makes the reduction of Mn^{3+} very feasible [E° = +1.51 V]

15. Compare lanthanides and actinides. [PTA-4, QY,HY-19, JUL-22, QY,HY22, MAR-23, SUT,QY-23, QY-24, JUN-25]

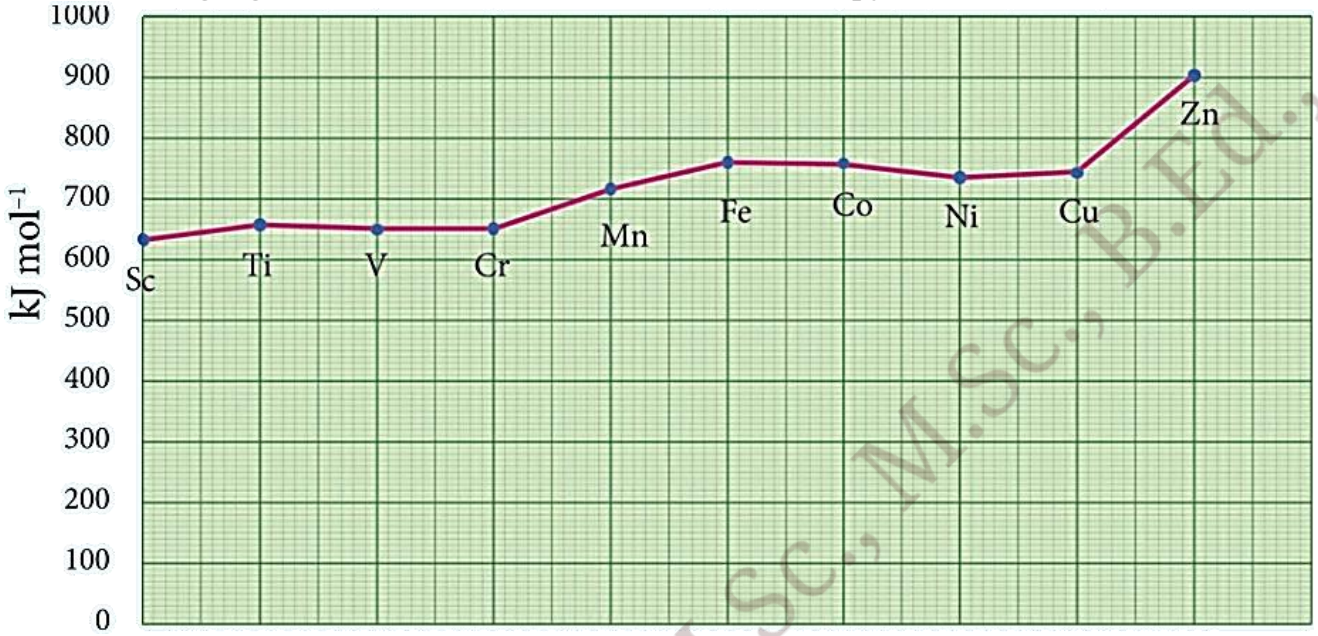
S. NO.	LANTHANOIDS	ACTINOIDS
1	Differentiating electron enters in 4f orbital	Differentiating electron eneters in 5f orbital
2	Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower
3	They show less tendency to form complexes	They show greater tendency to form complexes
4	Most of the lanthanoids are colourless	Most of the actinoids are coloured. For example. U^{3+} (red), U^{4+} (green) , UO_2^{2+} (yellow)
5	They do not form oxo cations	They do form oxo cations such as UO_2^{2+}, NpO_2^{2+} etc
6	Besides +3 oxidation states lanthanoids show +2 and +4 oxidation states in few cases.	Besides +3 oxidation states actinoids show higher oxidation states such as +4, +5, +6 and +7.

16. Explain why Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing. [PTA-5]

- Cr^{2+} is strong reducing while Mn^{3+} is strongly oxidising.
- E° value for Cr^{3+}/Cr^{2+} is negative (-0.41 V). If the standard electrode potential E° of a metal is large and negative, the metal is a powerful reducing agent because it loses electrons easily.
- E° value for Mn^{3+}/Mn^{2+} is positive (+ 1.51 V)
- If the standard electrode potential E° of a metal is large and positive, the metal is a powerful oxidising agent because it gains electrons easily.

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

- 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 following figure show the trends in ionisation enthalpy of transition elements.



- Transition metals have smaller atomic radii and higher nuclear charger which increase the ionisation energy when compound to alkali metals.
- 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-l)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.
- The ionisation enthalpy values can be used to predict the thermodynamic stability of their compounds. Let us compare the ionisation energy required to form Ni^{2+} and Pt^{2+} ions.
- For Nickel, IE + IE = 737 + 1753 = 2490 $kJmol^{-1}$
- For Platinum, IE + IE = 864 + 1791 = 2655 $kJmol^{-1}$
- Since, the energy required to form Ni^{2+} is less than that of Pt^{2+}, Ni(II) compounds are thermodynamically more stable than Pt(II) compounds.

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

- Actinoid contraction is greater from element to element than lanthanoid contraction. The 5f orbitals in Actinoids have a very poorer shielding effect than 4f orbitals in lanthanoids.
- Thus, the effective nuclear charge experienced by electron 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.

19. Out of $LU(OH)_3$ and $La(OH)_3$ which is more basic and why? [PTA-2, SUT-24]

- $La(OH)_3$ 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 lanthanoid ions decreases regularly with increase in atomic size.
- Due to the decrease in 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.
- So actinoid show greater contraction.

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

- Eu^{2+} Electronic configuration – [Xe] $4f^7\ 5d^0\ 6s^0$
- Ce^{2+} Electronic configuration – [Xe] $4f^1\ 5d^1\ 6s^0$
- In Eu(II), 4f subshell a half filled and 5d subshell is empty.
- According to Aufbau principle, half filled and completely filled d (or) f orbitals are more stable than partially filled f orbitals.
- Hence Eu^{2+} [Xe] $4f^7\ 5d^0\ 6s^0$ is more stable than Ce^{2+} [Xe] $4f^1\ 5d^0\ 6s^0$

21. Why do zirconium and Hafnium exhibit similar properties? [MAR-25]

- 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.
- Thus size of hafnium and zirconium becomes almost equal, and hence both have similar properties.

22. Which is stronger reducing agent Cr^{2+} or Fe^{2+}? [SRT-22]
[$E^0_{Cr2+/Cr}$ = -0.91V, $E^0_{Fe2+/Fe}$ = -0.44V]

Reason: Cr^{2+} is a stronger reducing agent than Fe^{2+}.

- This can be explained on the basis of the standard electrode potential values. ($E^0_{Cr2+/Cr}$ = -0.91V) and ($E^0_{Fe2+/Fe}$ = -0.44V)
- Thus Cr^{2+} is easily oxidised to Cr^{3+} but Fe^{2+} cannot oxidised to Fe^{3+}.
- Cr^{2+} standard electrode potential values is more negative value.

23. The $E^0_{M2+/M}$ value for copper is positive. Suggest a possible reason for this.

$E^0_{(M2+/M)}$ value for copper metal is the sum of enthalpy changes taking place in the steps given below.

$$M_{(s)} + \Delta_a H^0 \rightarrow M^+_{(g)}$$
($\Delta_a H^0$ = Standard enthalpy of atomisation)
$$M^+_{(g)} + \Delta_i H^0 \rightarrow M^{2+}_{(g)}$$
($\Delta_i H^0$ = Standard ionisation enthalpy)
$$M^{2+}_{(g)} + \Delta_{hyd} H^0_{aq} \rightarrow M^{2+}_{(aq)}$$
($\Delta_{hyd} H^0$ = Standard hydration enthalpy)

Copper has a high enthalpy of atomisation (energy absorbed), but low enthalpy of hydration (energy released)
Thus $E^0_{(Cu2+/Cu)}$ is positive.

24. Describe the variable oxidation state of 3d series elements. [AUG-21]

- The first transition metal Scandium exhibits only +3 oxidation state, but all other transition elements exhibit variable oxidation states by loosing electrons from (n-l)d orbital and ns orbital as the energy difference between them is very small.
- At the beginning of the 3d series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.

- The number of oxidation states increases with the number of electrons available, and it decreases as the number of paired electrons increases. For example, in the 3d series, first element Sc has only one oxidation state +3 the middle element Mn has six different oxidation states from +2 to +7. The last element Cu shows +1 and +2 oxidation states only.
- Mn^{2+} ($3d^5$) is more stable than Mn^{4+} ($3d^3$) is due to half filled stable configuration.

25. Which metal in the 3d series exhibits +1 oxidation state most frequently and why? [SEP-20]

- Cu is the only metal in the first transition series (2d series) which exhibits only +1 oxidation state most frequently.
- It is unique in 3d series having a stable +1 oxidation state. This is because the Electronic configuration of Cu (Z = 29) is [Ar] $3d^{10}$ $4s^1$ and after losing one electron it acquires a stable $3d^{10}$ configuration.
- So copper element only can have +1 oxidation state.

26. Why first ionization enthalpy of chromium is lower than that of zinc? [SRT-22]

- The 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 ionization enthalpy.
- But in the case of Zinc (Z = 30), electronic configuration [Ar] $3d^{10}$ $4s^2$.
- The first electron has to be removed from the most stable fully filled electronic configuration becomes difficult and it requires more energy.

27. Transition metals show high melting points why? [PTA-6, QY-24]

- 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 inceases, reach a maximum value and then decreases, as the d electrons pair up and become less available for bonding.
- For example, in the first series the melting point inceases from Scandium (m.pt 1814K) to a maximum of 2183K for vanadium, which is close to 2180K for chromium. However, manganese in 3d series and Tc in 4d series have low melting point. The maximum melting point at about the middle of transition metal series indicates that d5 configuration is favourable for strong interatomic attraction.

ELEMENTS EVALUATE YOURSELF

1. Compare the stability of Ni^{4+} and Pt^{4+} from their ionisation enthalpy values

IE	Ni	Pt
I	737	864
II	1753	1791
III	3395	2800
IV	5297	4150

- The value of the ionisation enthalpies can be used in estimating the relative stability of various transition metal compounds (or ions).
- Formation of Pt^{4+} requires lesser energy as compared to the formation of Ni^{4+}
- Pt^{4+} compounds are stable than Ni^{4+} compounds because the energy needed to remove 4 electrons in Pt is less than that of Ni.

2. Why iron is more stable in +3 oxidation state than in +2 and the reverse is true for Manganese?

- Fe (Z = 26). Electronic configuration [Ar] $3d^6$ $4s^2$
- Fe → Fe^{3+} + $3e^-$ Fe^{3+} Electronic configuration [Ar] $3d^5$. If d' orbital is half filled, it is more stable than . Fe^{2+} where it is [Ar] $3d^6$.
- Mn (Z = 25). Electronic configuration [Ar] $3d^5$ $4s^2$
- Mn → Mn^{2+} + $2e^-$ By the loss of $2e^-$, Mn^{2+} is more stable due to half filled configuration. Mn → Mn^{3+} + $3e^-$. Mn^{3+} Electronic configuration [Ar] $3d^4$ 4s°.
- Among this Fe^{3+} is more stable than Fe^{2+} and the Mn^{2+} is more stable than Mn^{3+}.

GOVERNMENT EXAM QUESTION PAPER

1. Classify the following elements into d-block and f-block elements: [MAR-20]

a) Tungstan b) Ruthenium c) Promethium d) Einsteinium

a) Tungstan - d block
b) Ruthenium - d block
c) Promethium - f block
d) Einsteinium - f block

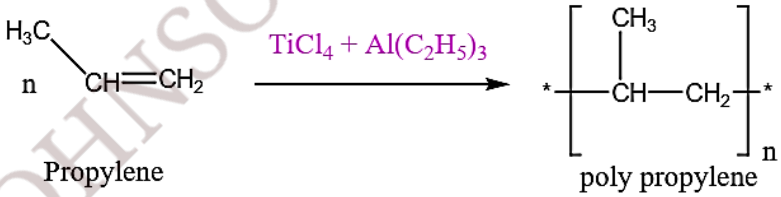
2. Why do transition metals form Coordination Compound? (or) Do transition elements form complex co-ordinate compounds? (or) Why do d-block elements readily form coordination compounds? [QY-19, SRT-22]

- Transition elements have a tendency to form coordination compounds with a species that has an ability to donate an electron pair to form a coordinate covalent bond.
- Transition metal ions are small and highly charged and they have vacant low energy orbitals to accept an electron pair donated by other groups. Due to these properties, transition metals form large number of complexes.

Ex: $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$, etc..

3. What is Zeigler – Natta catalyst? Give its use. [JUL-22]

A mixture of $TiCl_4$ and trialkyl aluminium is used for polymerization.



Propylene — poly propylene

Uses: It is used for polymerisation.

4. What is chromyl chloride test? Give equations. (or) Write the Chromyl chloride test. [GMQ-19, MAR-20, SUT,QY-23, HY-24]

- When potassium dichromate is heated with any chloride salt in the presence of Conc.H_2SO_4, orange red vapours of chromyl chloride (CrO_2Cl_2) is evolved.
- This reaction is used to confirm the presence of chloride ion in inorganic qualitative analysis.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + \underset{\text{Chromyl chloride}}{2CrO_2Cl_2}\uparrow + 3H_2O$$

- The chromyl chloride vapours are dissolved in sodium hydroxide solution and then acidified with acetic acid and treated with lead acetate. A yellow precipitate of lead chromate is obtained.

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow \underset{\substack{\text{Leadchromate}\\(\text{Yellowprecipitate})}}{PbCrO_4}\downarrow + 2CH_3COONa$$

5. Explain the preparation of potassium permanganate from pyrolusite. (or) Explain the preparation of $KMnO_4$. [GMQ-19]

Potassium permanganate is prepared from pyrolusite (MnO_2) ore. The preparation involves the following steps.

Conversion of MnO_2 to potassium manganate: Powdered ore is fused with KOH in the presence of air or oxidising agents like KNO_3 or $KClO_3$. A green coloured potassium manganate is formed.

$$2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\substack{\textit{potassium manganate}\\ \textit{(Green)}}}{2K_2MnO_4} + 2H_2O$$

Oxidation of potassium manganate to potassium permanganate: Potassium manganate thus obtained can be oxidised in two ways, either by chemical oxidation or electrolytic oxidation.

Chemical oxidation: In this method potassium manganate is treated with ozone (O_3) or chlorine to get potassium permanganate.

$$2MnO_4^{2-} + O_3 + H_2O \longrightarrow 2MnO_4^- + 2OH^- + O_2$$

$$2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^- + 2Cl^-$$

Electrolytic oxidation: In this method aqueous solution of potassium manganate is electrolyzed in the presence of little alkali.

$$K_2MnO_4 \rightleftharpoons 2K^+ + MnO_4^{2-}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

Manganate ions are converted into permanganate ions at anode.

$$\underset{\textit{Green}}{2MnO_4^{2-}} \rightleftharpoons \underset{\textit{purple}}{2MnO_4^-} + 2e^-$$

$H_2$is liberated at the cathode.

$$2H^+ + 2e^- \longrightarrow H_2 \uparrow$$

The purple coloured solution is concentrated by evaporation and forms crystals of potassium permanganate on cooling.

6. Give brief account on the Oxidation State of Lanthanoids. [SRT-22]

- The common oxidation state of lanthanoids is +3. In addition to that some of the lanthanoids also show either +2 or +4 oxidation states.
- Gd^{3+} and Lu^{3+} ions have extra stability, it is due to the fact that they have exactly half filled and completely filled f-orbitals respectively.their electronic c onfigurations are

  Gd^{3+} : $[Xe]4f^7$ $\qquad\qquad$ Lu^{3+} : $[Xe]4f^{14}$
- Similarly Cerium and terbium attain $4f^0$ and $4f^7$ configurations respectively in the +4 oxidation states. Eu^{2+} and Yb^{2+} ions have exactly half filled and completely filled f orbitals respectively.
- The stability of different oxidation states has an impact on the properties of these elements. The following table shows the different oxidation states of lanthanoids.

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		+2		+2	+2						+2	+2	
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4					+4	+4					

7. Write the properties of interstitial compound. [MAY-22]

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

8. Calculate the equivalent weight of $KMnO_4$ in the following reactions. [QY-19]

a) $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

b) $2MnO_4^- + 10Fe^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O$

a) Equivalent weight of $KMnO_4$ in neutral medium $= \frac{Molecular\ weight\ of\ KMnO4}{no.of\ moles\ of\ electrons\ transferred}$

$= \frac{158}{3} = 52.67$

b) Equivalent weight of $KMnO_4$ in neutral medium $= \frac{Molecular\ weight\ of\ KMnO4}{no.of\ moles\ of\ electrons\ transferred}$

$= \frac{158}{5} = 31.6$

9. (i) The first ionisation energy of Chromium is less than that of Zinc. Why? [SRT-22]

(ii) Why do 3d series transition elements possess variable oxidation states?

(i) Cr – $[Ar]3d^5 4s^2$ Zn – $[Ar]3d^{10}4s^2$

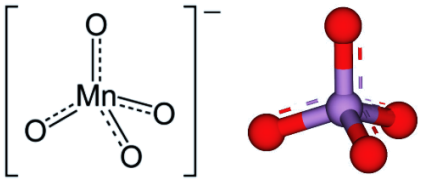
Ionisation energy Cr is lower than that of zinc first electron has to be remove from full filled orbital and full filled electronic configuration is more stable than half filled so it require high energy to remove electron from it.

(ii) The first transition metal Scandium exhibits only +3 oxidation state, but all other transition elements exhibit variable oxidation states by loosing electrons from (n-1)d orbital and ns orbital as the energy difference between them is very small. At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.

The number of oxidation states increases with the number of electrons available, and it decreases as the number of paired electrons increases. Hence, the first and last elements show less number of oxidation states and the middle elements with more number of oxidation states. For example, the first element Sc has only one oxidation state +3; the middle element Mn has six different oxidation states from +2 to +7. The last element Cu shows +1 and +2 oxidation states only.

10. Explain the structure of permanganate ion. [HY-22]

Permanganate ion has tetrahedral geometry in which the central Mn^{7+} is sp^3 hybridised.



11. Give the conditions for the formation of alloys by Hume-Rothery rule. [SUT-23]

- According to Hume-Rothery rule to form a substitute alloy the difference between the atomic radii of solvent and solute is less than 15%.
- Both the solvent and solute must have the same crystal structure and valence and their electro negativity difference must be close to zero.
- Transition metals satisfying these mentioned conditions form a number of alloys among themselves, since their atomic sizes are similar and one metal atom can be easily replaced by another metal atom from its crystal lattice to form an alloy.

12. What are the causes of lanthanide contraction? [SRT-24]

- In f-block elements, the positive charge on the nucleus rises by one unit, and one additional electron enters the same 4f subshell, as the atomic number increases.

- Electrons in the 4f subshell poorly shield each another. Shielding is less in a 4f subshell than in a d subshell.
- As the nuclear charge increases, the valence shell is drawn closer to the nucleus. Hence, as a result contraction takes place.

13. Which metal in the 3d series exhibits + 1 oxidation State most frequently and why? [SEP-20]

- The first transition metal copper exhibits only only +1 oxidation state
- It is unique in 3d series having a stable +1 oxidation state
- Cu (Z =29) Electronic configuration is [Ar] $3d^{10}$ $4S^{1}$
- So cupper elements only can have +1 oxidation state

14. Explain the Catalytic properties of Transition Elements. [SUT-24]

- The chemical industries manufacture a number of products such as polymers, flavours, drugs etc.,
- Most of the manufacturing processes have adverse effect on the environment so there is an interest for eco-friendly alternatives.
- In this context, catalyst based manufacturing processes are advantageous, as they require low energy, minimize waste production and enhance the conversion of reactants to products.
- Many industrial processes use transition metals or their compounds as catalysts. Transition metal has energetically available d orbitals that can accept electrons from reactant molecule or metal can form bond with reactant molecule using its d electrons.
- For example, in the catalytic hydrogenation of an alkene, the alkene bonds to an active site by using its π electrons with an empty d orbital of the catalyst.

UNIT – 5 – COORDINATION CHEMISTRY

II. Answer the following questions:

1. Write the IUPAC names for the following complexes.

(i) $Na_2[Ni(EDTA)]$ [QY-19, SMT-22] (ii) $[Ag(CN)_2]^-$ (iii) $[Co(en)_3]_2(SO_4)_3$ [QY-19]

(iv) $[Co(ONO)(NH_3)_5]^{2+}$ (v) $[Pt(NH_3)_2Cl(NO)_2]$ [QY-19]

(i) Sodium 2,2',2'',2'''-(ethane-1,2-diyldinitrilo tetraacetato)nickelate (II)

(ii) Dicyanidoargentate (I) ion (iii) Tris(ethane-1,2-diamine)cobalt(III)sulphate

(iv) Pentaamminenitrito-kO cobalt(III)ion (v) Diamminechloridonitrito-kN platinum(II)

2. Write the formula for the following coordination compounds.

a) potassiumhexacyanidoferrate(II) [FRT24] b) pentacarbonyliron(0) [FRT-24]

c) pentamminenitrito-kN cobalt(III)ion d) hexaamminecobalt(III)sulphate [FRT24]

e) sodiumtetrafluridodihydroxidochromate(III)

a) $K_4[Fe(CN)_6]$ b) $[Fe(CO)_5]$ c) $[Co(NH_3)_5(NO_2)]^{2+}$

d) $[Co(NH_3)_6]_2(SO_4)_3$ e) $Na_3[CrF_4(OH)_2]$

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) $[Cr(NH_3)_3Cl_3]$

Molar conductivity increases as the number of ions 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.

- Cis-platin is used as an 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.
- A red blood corpuscles (RBC) is composed of heme group, which is Fe^{2+}- Porphyrin complex.it plays an important role in carrying oxygen from lungs to tissues and carbon dioxide from tissues to lungs.
- Chlorophyll, a green pigment present in green plants and algae, is a coordination complex containing Mg^{2+} as central metal ion surrounded by a modified Porphyrin ligand called corrin ring. It plays an important role in photosynthesis, by which plants converts CO_2 and water into carbohydrates and oxygen.
- Vitamin B_{12}(cyanocobalamine) is the only vitamin consist of metal ion. It is a coordination complex in which the central metal ion is Co^+ surrounded by Porphyrin like ligand.
- Many enzymes are known to be metal complexes, they regulate biological processes. For example, Carboxypeptidase is a protease enzyme that hydrolytic enzyme important in digestion, contains a zinc ion coordinated to the protein.

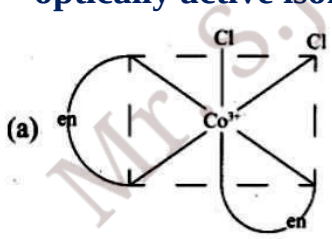
5. Based on VB theory explain why $[Cr(NH_3)_6]^{3+}$ is paramagnetic, while $[Ni(CN)_4]^{2-}$ is diamagnetic. [AUG-21]

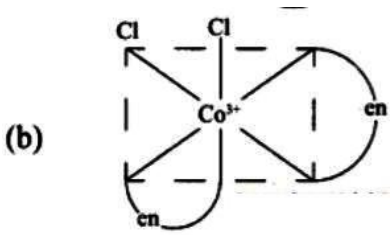
Complex	**$[Cr(NH_3)_6]^{3+}$**
Central metal ion and its electronic configuration	Cr^{3+} : $3d^3\ 4s^0$
Outer orbitals of metal atom/ion	↑ ↑ ↑ ☐ ☐ ☐ ☐ ☐ ☐ $3d^3$ 4s 4p
Nature of ligand	NH_3 is weak field ligand. So no pairing of 3d electrons in the metal.

Outer orbital of metal atom/ion in presence of ligand	↑ ↑ ↑ ☐ ☐ ☐ ☐ ☐ ☐ $3d^3$ 4s 4p
Hybridisation	Coordination number – 6 Hybridisation – d^2sp^3
Hybridised orbitals of the metal atom in the complex	↑ ↑ ↑ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ $3d^3$ d^2sp^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**

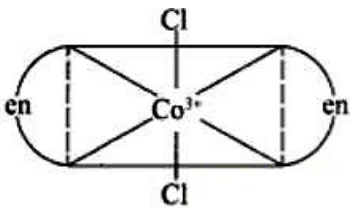
Complex	**$[Ni(CN)_4]^{4-}$**
Central metal ion and its electronic configuration	Ni^{2+} : $3d^8\ 4s^0$
Outer orbitals of metal atom/ion	↑↓ ↑↓ ↑↓ ↑ ↑ ☐ ☐ ☐ ☐ $3d^8$ 4s 4p
Nature of ligand	CN is strong field ligand causes the pairing of 3d electrons in the metal.
Outer orbital of metal atom/ion in presence of ligand	↑↓ ↑↓ ↑↓ ↑↓ ☐ ☐ ☐ ☐ ☐ $3d^8$ 4s 4p
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 planar
Magnetic property	No of unpaired electron = 0, Hence diamagnetic
Magnetic moment	$\mu_s = \sqrt{n(n+2)} = \sqrt{0(0+2)} =$ **0**

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





Two cis $[Co(en)_2Cl_2]^+$ isomers **(optically active)**



One trans $[Co(en)_2Cl_2]^+$ isomers **(optically inactive)**

7. $[Ti(H_2O)_6]^{3+}$ is coloured, while $[Sc(H_2O)_6]^{3+}$ is colourless – explain. [MAR-20, JUN-25]

Ti : **$3d^2\ 4s^2$** ∴ Ti^{3+} : **$3d^1\ 4s^0$**

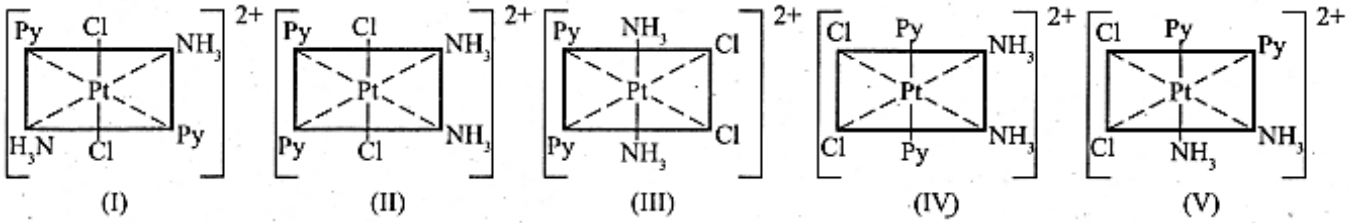
$[Ti(H_2O)_6]^{3+}$ has one unpaired electron so it is coloured.

Sc : **$3d^1\ 4s^2$** ∴ Sc^{3+} : **$3d^0\ 4s^0$**

$[Sc(H_2O)_6]^{3+}$ has no unpaired e^- 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. The five geometrical isomers for the complex ion $[PtCl_2(NH_3)_2(py)_2]^{2+}$ are shown below.



9. Give one test to differentiate $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$. [QY-19]

$[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionization isomers.

When these isomers are dissolved in water, they ionise to give different ions in solution which react differently with different reagents.

$[Co(NH_3)_5Cl]SO_4 \rightarrow [Co(NH_3)_5Cl]^{2+} + SO_4^{2-}$

$[Co(NH_3)_5SO_4]Cl \rightarrow [Co(NH_3)_5SO_4]^{+} + Cl^{-}$

For Ex.1: Barium Chloride test

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

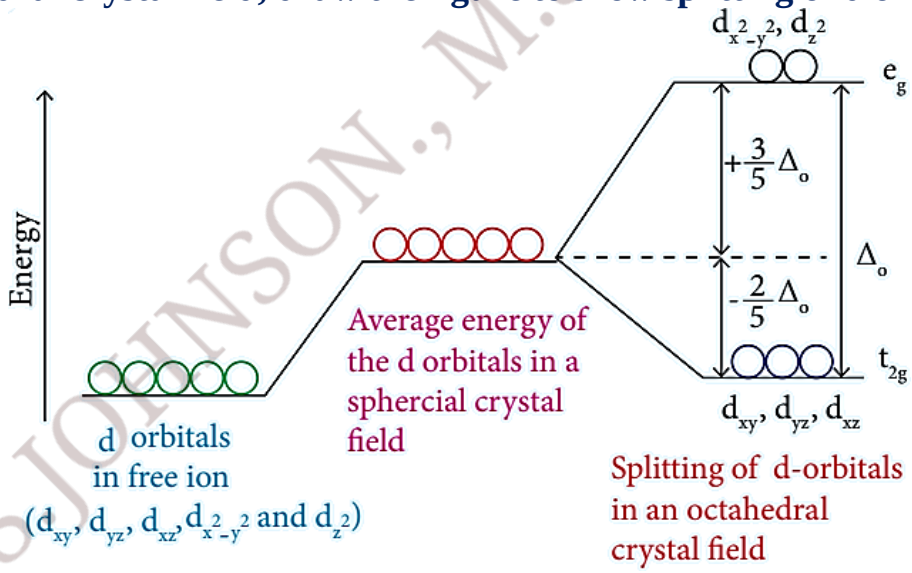
$[Co(NH_3)_5SO_4]Cl + BaCl_2 \rightarrow$ No reaction

For Ex.2: Silver nitrate test

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

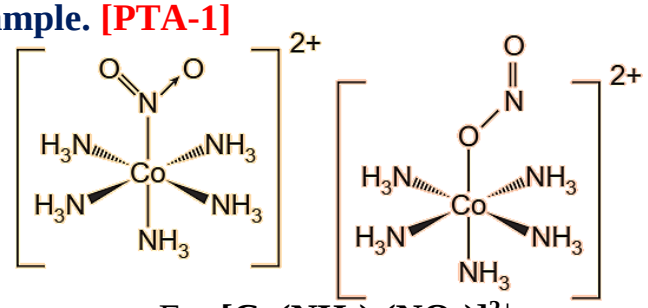
$[Co(NH_3)_5SO_4]Cl + AgNO_3 \rightarrow AgCl\downarrow$ **(Curdy White precipitate)**

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



11.What is linkage isomerism? Explain with an example. [PTA-1]

This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms. In the below mentioned examples, the nitrite ion is bound to the central metal ion Co^{3+} through a nitrogen atom in one complex, and through oxygen atom in other complex.



Ex: **$[Co(NH_3)_5(NO_2)]^{2+}$**

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

a) NH_3 b) en c) ox^{2-} d) pyridine

a) NH_3 - monodentate (N-Donor atom) b) en - bidentate (2N-Donor atom)

c) ox^{2-} - bidentate (2O-Donor atom) d) pyridine - monodentate (N-Donor atom)

13. Give the difference between double salts & coordination compounds. [AUG21, MAR24]

	Double salts	Co-ordination compound
1	Double salts contain two simple salt in equimolar proportion.	The simple salts from which they are formed may or may not be in equimolar proportion.
2	These exist only in solid state and dissociate into consistent species in their solutions	They retain their identity in solid as well as in solution state.
3	They lose their identity in dissolved state	They do not lose their identity in dissolved state
4	Their properties essential the same as those of constituent species.	Their properties different from their constituents for ***ex:*** $K_4[Fe(CN)_6]$ does not show the test of the Fe^{2+} and CN^- ions.
5	In double salts the metal atom/ion exhibit normal valency	The metal ion exhibits two types of valencies – Primary and secondary

14. Write the postulates of Werner's theory. [SEP-20, MAY-22, MAR-25]

- Most of the elements exhibit, two types of valence namely primary valence and secondary valence and each element tend to satisfy both the valences. In modern terminology, the primary valence is referred as the oxidation state of the metal atom and the secondary valence as the coordination number. **For example**, according to Werner, the primary and secondary valences of cobalt are 3 and 6 respectively.
- 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** in the complex $CoCl_3.6NH_3$, The primary valence of Co is +3 and is satisfied by $3Cl^-$ ions.
- The secondary valence is satisfi ed by negative ions, neutral molecules, positive ions or the combination of these.

  For example, in $CoCl_3.6NH_3$ the secondary valence of cobalt is 6 and is satisfied by six neutral ammonia molecules, whereas in $CoCl_3.5NH_3$ the secondary valence of cobalt is satisfied by five neutral ammonia molecules and a Cl^- ion.
- 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.
- The primary valences are non-directional while the secondary valences are directional. The geometry of the complex is determined by the special 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	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^-
$CoCl_3.6NH_3$	$6NH_3$	$3Cl^-$	3AgCl
$CoCl_3.5NH_3$	$5NH_3$ & Cl^-	$2Cl^-$	2AgCl
$CoCl_3.4NH_3$	$4NH_3$ & $2Cl^-$	Cl^-	AgCl
$CoCl_3.3NH_3$	$3NH_3$ & $3Cl^-$	-	-

15.Why tetrahedral complexes do not exhibit geometrical isomerism? [SRT-23]

Tetrahedral complexes do not show geometrical isomerism because

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

16.Explain optical isomerism in coordination compounds with an example. [JUN-25]

Coordination compounds which possess chairality exhibit optical isomerism similar to organic compounds. The pair of two optically active isomers which are mirror images of each other are called enantiomers. Their solutions rotate the plane of the plane polarised light either clockwise or anticlockwise and the corresponding isomers are called 'd' (dextro rotatory) and 'l' (levo rotatory) forms respectively. The octahedral complexes of type $[M(xx)_3]^{n\pm}$, $[M(xx)_2AB]^{n\pm}$ and $[M(xx)_2B_2]^{n\pm}$ exhibit optical isomerism.

Examples: The optical isomers of $[Co(en)_3]^{3+}$ are shown in figure (1) and The coordination complex $[CoCl_2(en)_2]^+$ has three isomers, two optically active cis forms and one optically inactive trans form. These structures are shown in figure (2)

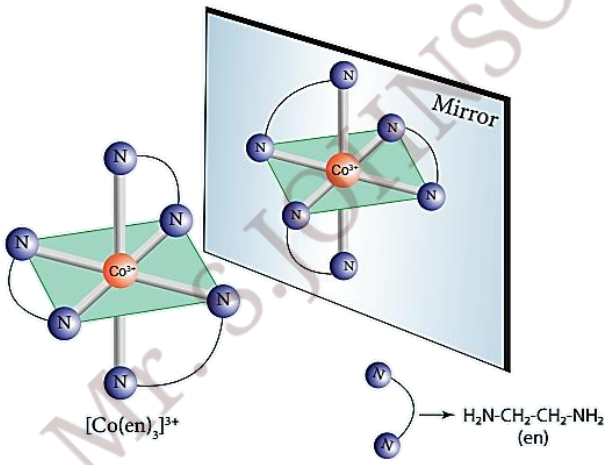


Figure (1) – Optical isomer

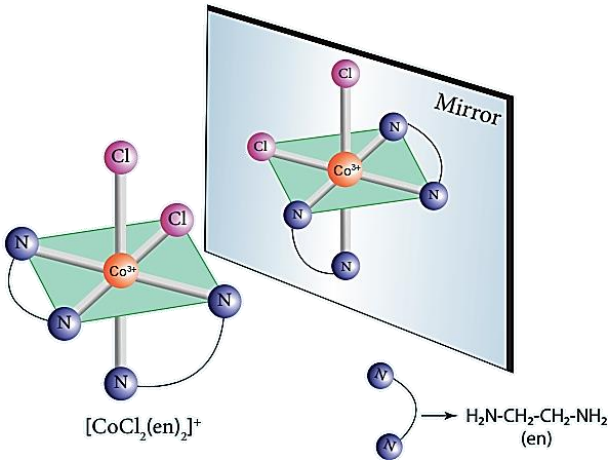


Figure (2) – Optical isomer

17.What are hydrate isomers? Explain with an example. [MAR-20, MAR-25]

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 2 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? [HY-22]

- The orbitals lying along the axes dx^2-y^2 and dz^2 orbitals will experience strong repulsion and raise in energy to a greater extent than the orbitals with lobes directed between the axes (d_{xy}, d_{yz} and d_{zx}). Thus the degenerate d orbitals now split into two sets and the process is called crystal field splitting.
- 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 field (E_{LF}) and the isotropic field/barycentre (E_{iso}).

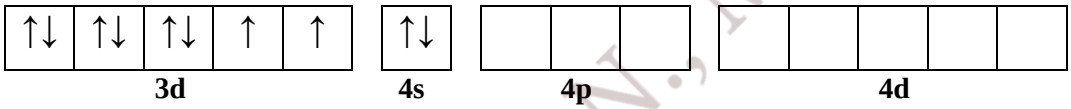
CFSE (ΔE_o) = $\{E_{LF}\}$ - $\{E_{iso}\}$ = $\{[n_{t_{2g}}(-0.4) + n_{e_g}(0.6)]\ \Delta_o + n_pP\}$ - $\{n'_pP\}$

Here, $n_{t_{2g}}$ is the number of electrons in t_{2g} orbitals; n_{e_g} 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).

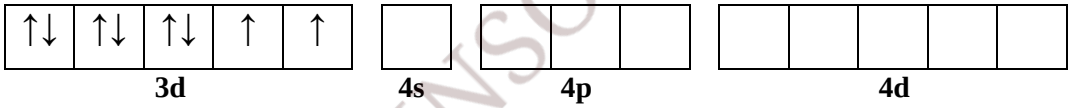
20.A solution of $[Ni(H_2O)_6]^{2+}$ is green, whereas a solution of $[Ni(CN)_4]^{2-}$ is colourless – Explain.

Complex I: $[Ni(H_2O)_6]^{2+}$ The outer electronic configuration of Ni is $3d^8\ 4s^2$

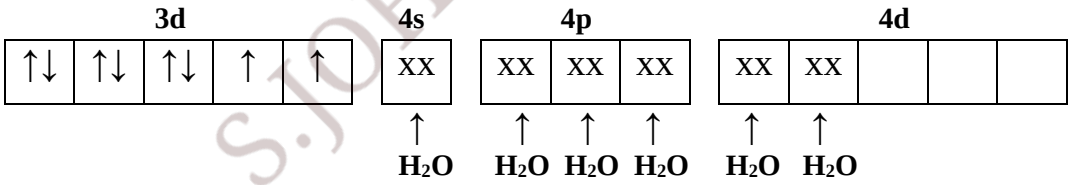
Ni atom



Ni^{2+} ion $3d^8\ 4s^0$



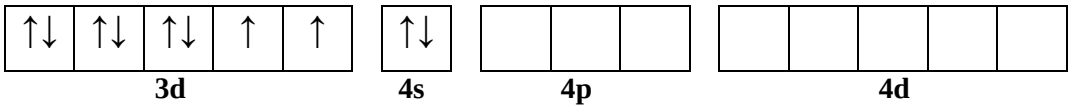
Ni in $[Ni(H_2O)_6]^{2+}$ H_2O is weak field ligand so pairing does occur.



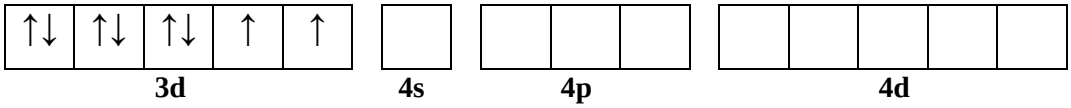
Hybridisation is sp^3d^2. Two unpaired electrons so coloured and paramagnetic in nature.

Complex II: $[Ni(CN)_4]^{2-}$ The outer electronic configuration of Ni is $3d^8\ 4s^2$

Ni atom



Ni^{2+} ion $3d^8\ 4s^0$



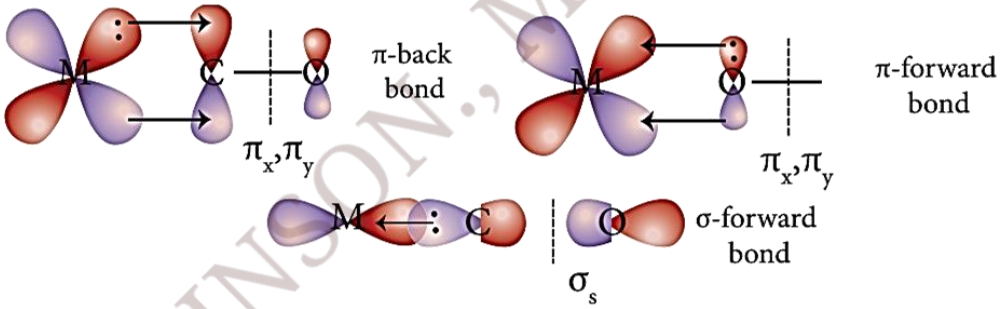
Ni in $[Ni(CN)_4]^{2-}$ CN is strong field ligand so pairing occur.

3d					4s	4p		4d				
↑↓	↑↓	↑↓	↑↓	xx	xx	xx	xx					
				↑ CN⁻	↑ CN⁻	↑ CN⁻	↑ CN⁻					

Hybridisation is dsp^2. No unpaired electrons so colourless and diamagnetic in nature.

21.Discuss briefly the nature of bonding in metal carbonyls. [SRT-23]

- 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.



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

The coordination complex formed when excess of liquid ammonia is added to an aqueous solution of copper sulphate is $[Cu(NH_3)_4]SO_4$ – Tetraamminecopper(II)sulphate

$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$ **(Tetraamminecopper(II)sulphate)**

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

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

$[Co(C_2O_4)_3]^{3-}$ Outer electronic configuration – $3d^7\ 4s^2$

Co in Ground State

3d					4s	4p			4d				
↑↓	↑↓	↑	↑	↑	↑↓								

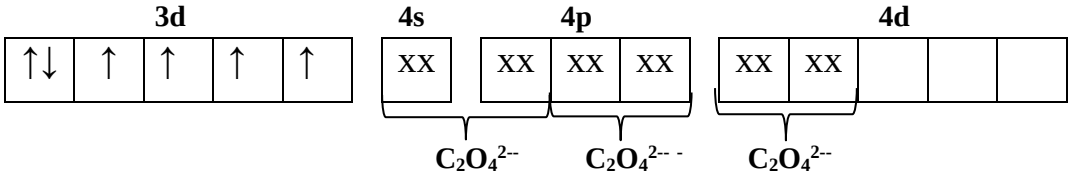
Cobalt exists in +3 oxidation state in the given complex.

Co^{3+} in existed state

3d					4s	4p			4d				
↑↓	↑	↑	↑	↑									

Oxalate is a weak field ligand. So no pairing of 3d orbitals occurs.

Co^{3+} in $[Co(C_2O_4)_3]^{3-}$



Hybridisation is **sp^3d^2**

Geometry: **octahedral**

Magnetic character: Since it has 4 unpaired electron. The complex is **paramagnetic**.

24. What are the limitation of VB theory? [QY,HY-19, AUG-21, SMT-22, JUL-22, HY-24]

- It does not explain the colour of the complex
- It considers only the spin only magnetic moments and does not consider the other components of magnetic moments.
- 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).

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

- $K_4[Mn(CN)_6]$ – Potassium hexacyanomanganate(II)
- Oxidation state of manganese

$$4(+1) + x + 6(-1) = 0$$
$$4 + x - 6 = 0$$
$$x - 2 = 0$$
$$\boldsymbol{x = 2}$$

∴ Oxidation state of Manganese is **+2**

- Coordination number = **6**
- CN- is a strong field ligand
- Paramagnetic (one unpaired) monodentate
- Magnetic moment $\mu_s = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} =$ **1.732 BM**
- Electronic configuration = d^{5+} : $t_{2g}^5\ e_g^0$

Evaluate Yourself

1. When a coordination compound $CrCl_3.4H_2O$ is mixed with silver nitrate solution, one mole of silver chloride is precipitated per mole of the compound. There are no free solvent molecules in that compound. Assign the secondary valence to the metal and write the structural formula of the compound.

- When a coordination compound $CrCl_3.4H_2O$ is mixed with silver nitrate solution, one mole of silver chloride is precipitated per mole of the compound. This shows $CrCl_3.4H_2O$ complex compound contains one Cl^- counter ion.
- There are no free solvent molecules in $CrCl_3.4H_2O$ compound, this shows water molecules are coordinated with a central metal ion.
- Therefore, the coordination complex is $[CrCl_3.4H_2O]Cl$ Secondary value of the central metal ion is $2Cl^-$ and $4H_2O$. Hence coordination number is 6.
- Werner's structure of $[CrCl_2.(H_2O)_4]Cl$

2. In the complex, $[Pt(NO_2)(H_2O)(NH_3)_2]Br$, identify the following

a) Central metal atom/ion
b) Ligands(s) and their types
c) Coordination entity
d) Oxidation number of the central metal ion
e) Coordination number

a) Central metal ion – Pt^{2+}
b) Ligands and their types – NO_2 – Negative monodendate ligand, H_2O and NH_3 – neutral monodendate ligand
c) Coordination entity – $[Pt(NO_2)(H_2O(NH_3)_2]^{3+}$
d) Oxidation number of the central metal ion
– x + 1(-1) + 1(0) + 1(0) = + 1 ⇒ x – 1 = + 1 ⇒ **x = + 2**
e) Coordination number – **4**

3. Write the IUPAC name for the following compounds.

a) $K_2[Fe(CN)_3(Cl)_2(NH_3)]$
b) $[Cr(CN)_2(H_2O)]$ $[CO(ox)_2(en)]$
c) $[Cu(NH_3)_2Cl_2]$
d) $[Cr(NH_3)_3(NC)_2(H_2O)]^+$
e) $[Fe(CN)_6]^{4-}$

a) Potassium amminedichloridotricyanidoferrate (III)
b) Tetraaquadicyanidochromium (II) mono(ethylene diamine) dioxalato cobalate (IV)
c) Diamminedichloro copper (II)
d) Triammineaquodicyanido – kN Chromium (III)ion
e) Hexacyanidoferrate (II) ion

4. Give the structure for the following compounds.

a) diamminesilver (I) dicyanidoargentate(I)
b) Pentaammine nitrito-kN-cobalt (III) ion
c) hexafluorido cobaltate (III) ion
d) dichloridobis(ethylenediamine) Cobalt (III) sulphate
e) Tetracarbonylnickel (0)

a) $[Ag(NH_3)_2]$ $[Ag(CN)_2]$
b) $[Co(NH_3)_5NO_2]^{2+}$
c) $[CoF_6]^{3-}$
d) $[Co(en)_2Cl_2]_2SO_4$
e) $[Ni(CO)_4]$

5. A solution of $[Co(NH_3)_4I_2]Cl$ when treated with $AgNO_3$ gives a white precipitate. What should be the formula of isomer of the dissolved complex that gives yellow precipitate with $AgNO_3$. What are the above isomers called?

- A solution of $[Co(NH_3)_4I_2]Cl$ when treated with $AgNO_3$ gives a white precipitate, because Cl^- ion is counter ion.
- Formula of isomer of the dissolved complex that gives yellow precipitate with $AgNO_3$ is, $[Co(NH_3)_4Cl\ I]I$ because I^- is counter ion
- $[Co(NH_3)_4I_2]Cl$ and $[Co(NH_3)_4Cl\ I]I$ both are ionisation isomers.

6. Three compounds A, B and C have empirical formula $CrCl_3.6H_2O$. they are kept in a container with a dehydrating agent and they lost water and attaining constant weight as shown below.

Compound	Initial weight of the compound (in g)	Constant weight after dehydration (in g)
A	4	3.46
B	0.5	0.466
C	3	3

Compound A: $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ Compound B: $[Cr(H_2O)_5Cl]Cl_2.H_2O$

Compound C: $[Cr(H_2O)_3Cl_3].3H_2O$

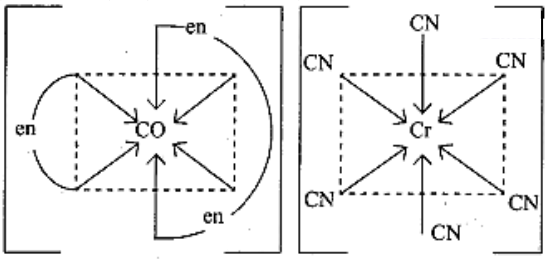
7. Indicate the possible type of isomerism for the following complexes and draw their isomers

i) $[Co(en)_3][Cr(CN)_6]$ [JUN-25]

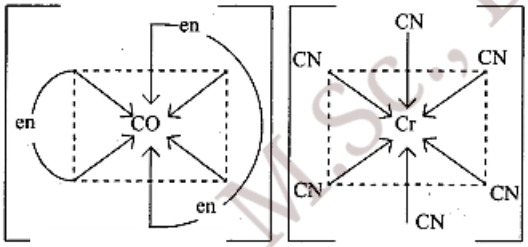
ii) $[Co(NH_3)_5(NO_2)]^{2+}$ [JUN-25]

iii) $[Pt(NH_3)_3(NO_2)]Cl$

i) $[CO(en)_3][Cr(CN)_6]$ – Exhibits coordination isomerism

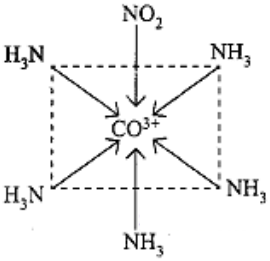


(a) $[Co(en)_3][Cr(CN)_6]$

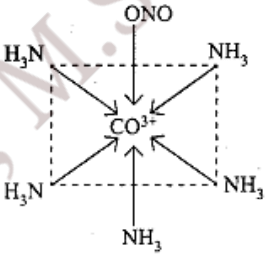


(b) $[Cr(en)_3][Co(CN)_6]$

ii) $[Co(NH_3)_5(NO_2)]^{2+}$ – Exhibits linkage isomerism

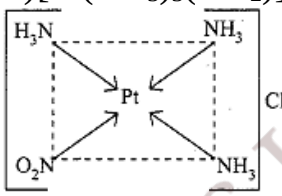


(a) $[Co(NH_3)_5(NO_2)]^{2+}$ – N attached



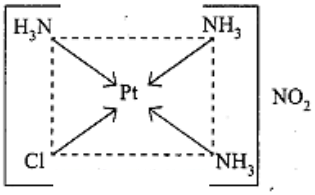
(b) $[Co(NH_3)_5(ONO)]^{2+}$ – O attached

iii)$[Pt(NH_3)_3(NO_2)]Cl$ – Exhibits ionisation isomerism



Here Cl^- is counter ion

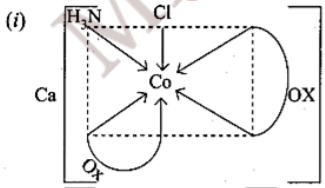
(a) $[Pt(NH_3)_3(NO_2)]Cl$

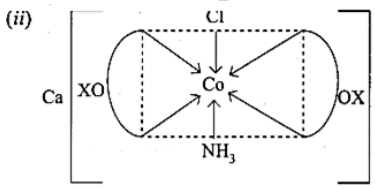


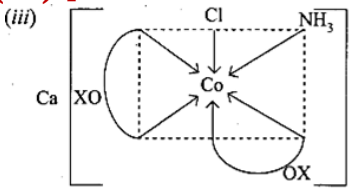
Here NO_2^- is counter ion

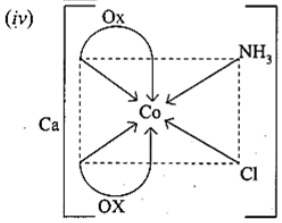
(b) $[Pt(NH_3)_3Cl]NO_2$

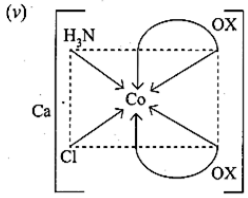
8. Draw all possible stereo isomers of a complex $Ca[Co(NH_3)Cl(ox)_2]$







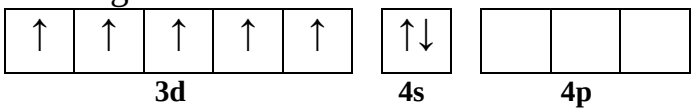




9. The spin only magnetic moment of Tetrachloridomanganate(II)ion is 5.9 BM. On the basis of VBT, predict the type of hybridisation and geometry of the compound.

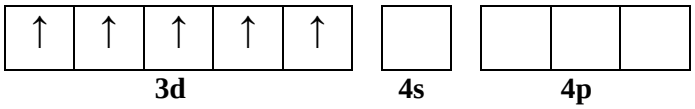
$[MnCl_4]^{2-}$ Electronic configuration of Mn (z=25) is $3d^5\ 4s^2$

Mn is ground state



Manganese exists in +2 oxidation state in the given complex.

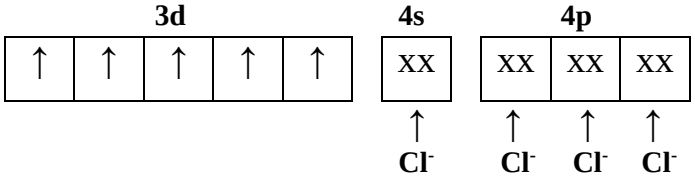
Mn^{2+} in existed state



Mn^{2+} in the complex $[MnCl_4]^{2-}$

Cl^- is weak field ligand so no pairing occurs. It has 5 unpaired electrons. Hence paramagnetic.

Magnetic moment, $\mu_s = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} =$ **5.9 BM**



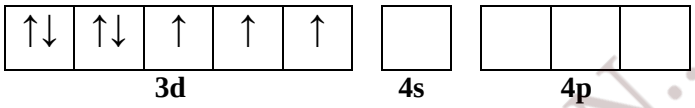
∴ Hybridisation is sp^3. So the geometry of the complex is tetrahedral.

10.Predict the number of unpaired electrons in $[CoCl_4]^{2-}$ ion on the basis of VBT.

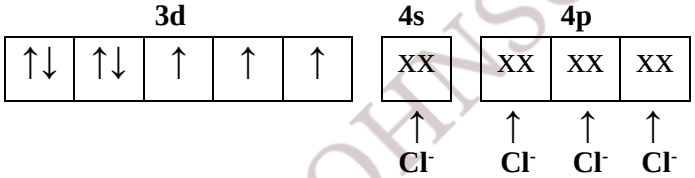
Central metal atom and its outer electronic configuration: Co: $3d^7\ 4s^2$

Coblat exists in +2 oxidation state in the given complex.

Co^{2+} in existed state



Nature of ligand: Cl^- is weak field ligand so no pairing occurs. Hybridise orbitals of the Co^{2+} in the complex $[CoCl_4]^{2-}$



Unpaired electrons: 3

11.A metal complex having composition $Co(en)_2Cl_2Br$ has been isolated in two forms A and B. (B) reacted with silver nitrate to give a white precipitate readily soluble in ammonium hydroxide. Whereas A gives a pale yellow precipitate. Write the formula of A and B. state the hybridization of Co in each and calculate their spin only magnetic moment.

Compound A - pale yellow precipitate - counter ion Br^-	Compound B - white precipitate - counter ion Cl^-
$[Co(en)_2Cl_2]Br$	$[Co(en)_2Cl\ Br]Cl$

12.The mean pairing energy and octahedral field splitting energy of $[Mn(CN)_6]^{3-}$ are 28,800 cm^{-1} and 38500 cm^{-1} respectively. Whether this complex is stable in low spin or high spin?

Mean pairing energy = 28,800 cm^{-1} Octahedral field splitting energy = 38,500 cm^{-1}

$[Mn(CN)_6]^{3-}$ Mn = $3d^5\ 4s^2$ $Mn^{3+} = 3d^4$

High Spin Complex	Low Spin Complex
Electronic Configuration of isotropic fields d^6 ⇅ ↑ ↑ ↑ ↑ Number of paired electrons(n_p^1) = .1 ∴ E_{iso} = 1	
Ligand field electronic configuration : $t_{2g}^4\ e_g^2$ CFSC = {[4(0.4)+2(0.6)]Δ_o+1p}–{1} = {–1.6+1.2]Δ_o+p}–{1} = (–0.4 Δ_o +p) –{1} = (– 0.4 × 13000) + 21,000 –1 = –5200 + 21000 –1 = 15799 cm^{-1}	Ligand field electronic configuration : $t_{2g}^6\ e_g^0$ CFSC = {[6(–0.4)+0(0.6)]Δ_o+3p}–{1} = –2.4Δ_o+3p–1 = (–2.4 × 13000) + (3×21000) –1 = – 31200 + 63000 –1 = 31799 cm^{-1}
High positive CFSE, value indicates that high spin complex is favoured.	High positive CFSE, value indicates that low spin complex is not favourable one.

13.Draw energy level diagram and indicate the number of electrons in each level for the complex $[Cu(H_2O)_6]^{2+}$. Whether the complex is paramangnetic or diamagnetic?

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

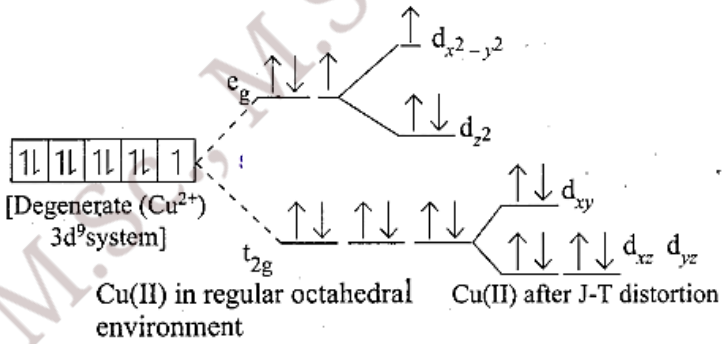
Central metal ion is Cu^{2+}

Electronic Configuration is $2d^9\ 4s^0$

$nt_{2g} = 6e^-$

$ne_g = 3e^-$

Since one unpaired electron is present, the complex is paramagnetic and C,N is 6 the geometry is Octahedral.



14.For the $[CoF_6]^{3-}$ ion the mean pairing energy is found to be 21000 cm^{-1}. The magnitude of Δ_0 is 13000 cm^{-1}. Calculate the crystal field stabilization energy for this complex ion corresponding to low spin and high spin states.

Mean pairing energy = 21,000cm^{-1} Δ_0 = 13000 cm^{-1}.

$[CoF_6]^{3-}$, Co = $3d^7\ 4s^2$; Co^{3+} = $3d^6$

High Spin Complex	Low Spin Complex
Electronic Configuration of isotropic fields d4 ↑ ↑ ↑ ↑ ☐ Number of paired electrons(n_p^1) = 0 ∴ E_{iso} = 0	
Ligand field electronic configuration : $t_{2g}^3\ e_g^1$ CFSE = {[3(–0.4)+1(0.6)]Δ_o+ 0 × p}–{0} = [–1.2+0.6]Δ_o = (–0.6) Δ_o = – 0.6 x 38,500 = –23100 cm^{-1}	Ligand field electronic configuration : $t_{2g}^4\ e_g^0$ CFSE = {[4(–0.4)+0(0.6)]Δ_o+2p}–{0} = [–1.6]Δ_o+2p = (–1.6 × 38,500) + (2 × 28,800) = – 61600 + 57600 = – 4000 cm^{-1}

GOVERNMENT EXAM QUESTION PAPER

1. What are Ionisation isomers? Give an example? [GMQ-19, HY-24]

Ionisation isomers arises when an ionisable counter ion (simple ion) itself can act as a ligand. The exchange of such counter ions with one or more ligands in the coordination entity will

result in ionisation isomers. Its will give different ions in solution. For example, $[Pt(en)_2Cl_2]Br_2$ and $[Pt(en)_2Br_2]Cl_2$.

2. Define Co-ordination number. [MAY-22]

The number of ligand donor atoms bonded to a central metal ion in a complex is called the coordination number of the metal. In other words, the coordination number is equal to the number of σ-bonds between ligands and the central atom.

3. In the complex $[Co(C_2O_4)_3]^{3-}$, mention the (i) Hybridisation (ii) Nature of ligand (iii) Geometry. [HY-19]

i) Hybridisation : sp^3d^2 ii) Nature of ligand : Oxalato is a negative weak field ligand (oxalate anion is a bidentate ligand) iii) Geometry : Octahedral

4. Arrange the following ligands in the ascending order on the basis of crystal field splitting power H_2O, CO, Br^-, CN^- [HY-19]

Spectrochemical series: $Br^- < H_2O < CN^- < CO$

5. Mention the metal complexes and its metal ions are used in biological system. [SEP20] (or) Give an example of Coordination compound used in medicine and a biologically important Coordination compound. [MAR-24]

- A red blood corpuscles (RBC) is composed of heme group, which is Fe^{2+}- Porphyrin complex. It plays an important role in carrying oxygen from lungs to tissues and carbon dioxide from tissues to lungs.
- Chlorophyll, a green pigment present in green plants and algae, is a coordination complex containing Mg^{2+} as central metal ion surrounded by a modified Porphyrin ligand called corrin ring. It plays an important role in photosynthesis, by which plants converts CO_2 and water into carbohydrates and oxygen.
- Vitamin B_{12}(cyanocobalamine) is the only vitamin consist of metal ion. It is a coordination complex in which the central metal ion is Co^+ surrounded by Porphyrin like ligand.
- Many enzymes are known to be metal complexes, they regulate biological processes. For example, Carboxypeptidase is a protease enzyme that hydrolytic enzyme important in digestion, contains a zinc ion coordinated to the protein.
- Many complexes are used as medicines for the treatment of various diseases. For example, (1) **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. (2) **Cis-platin** is used as an antitumor drug in cancer treatment.

6. Write the following for the complex $[Ag(NH_3)_2]^+$. [MAY-22]
(i) Ligand (ii) Central Metal ion (iii) IUPAC name

i) Ligand – NH_3 ii) Central Metal ion – Ag^+ iii) IUPAC name – diaminesilver(I)ion

7. Write the IUPAC ligand for the following: (i) $C_2O_4^{2-}$ (ii) H_2O (iii) Cl^- [JUL-22]

i) Oxalato ii) Aqua iii) Chlorido

8. Write the IUPAC name of the following:
i) $[Ag(NH_3)_2]^+$ ii) $[Co(NH_3)_5Cl]^{2+}$ [MAR-20]

i) Diamminesilver(I)ion ii) Pentaamminechloridocobalt(III)ion

9. Calculate the magnetic moment and magnetic property of $[CoF_6]^{3-}$ [MAR-20]

Magnetic moment of $[CoF_6]^{3-}$ $\mu_s = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} =$ **4.89 BM**

Magnetic property of $[CoF_6]^{3-}$ = No. of unpaired electrons = **4.** Hence **paramagnetic**.

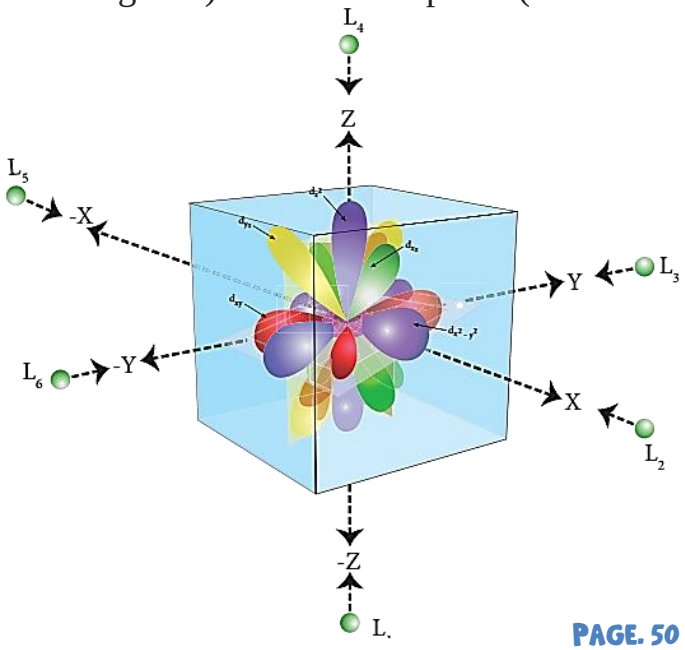
10.Explain $[Fe(CN)_6]^{3-}$ is paramagnetic, using Crystal Field theory. [GMQ-19]

High Spin Complex	Low Spin Complex
Electronic configuration in isotropic field : d5  No. of paired electrons (n'p) = 0; Therefore, E_{iso} = 0	
Ligand field: Electronic configuration : $t^3_{2g}\ e^2_g$ CFSE = {[3(-0.4)+2 (0.6)] Δ_o + 0 × P} - {0} = 0	Ligand field: Electronic configuration : $t^5_{2g}\ e^0_g$ CFSE = {[5(-0.4)+0 (0.6)] Δ_o + 2 × P} - {0} = -2 Δ_o + 2P = (-2 ×35000) + (2× 30000) = -10000 cm^{-1} Negative CFSE value indicates that low spin complex is favoured
Nature of the complex	Low spin (Spin paired)
Electronic configuration of central metal ion	$t^5_{2g}\ e^0_g$
Magnetic property	No. of unparied electrons = 1; Hence paramagnetic
Magnetic moment (Using spin only formula)	$\mu_s = \sqrt{n(n+2)} = \sqrt{1(1+2)}$ = $\sqrt{3}$ = **1.732 BM**

11.Write the postulates of Crystal Field theory. [QY-19]

Valence bond theory helps us to visualise the bonding in complexes. However, it has limitations as mentioned above. Hence Crystal Field Theory to explain some of the properties like colour, magnetic behaviour etc., This theory was originally used to explain the nature of bonding in ionic crystals. Later on, it is used to explain the properties of transition metals and their complexes. The salient features of this theory are as follows.

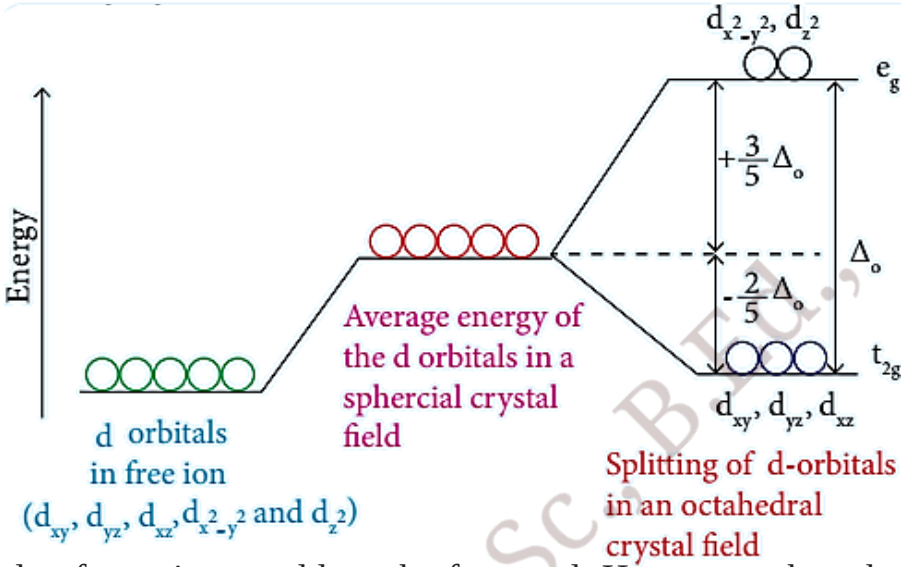
- Crystal Field Theory (CFT) assumes that the bond between the ligand and the central metal atom is purely ionic. i.e. the bond is formed due to the electrostatic attraction between the electron rich ligand and the electron deficient metal.
- In the coordination compounds, the central metal atom/ion and the ligands are considered as point charges (in case of charged metal ions or ligands) or electric dipoles (in case of metal atoms or neutral ligands).
- According to crystal field theory, the complex formation is considered as the following series of hypothetical steps.



Step 1: In an isolated gaseous state, all the five d orbitals of the central metal ion are degenerate. Initially, the ligands form a spherical field of negative charge around the metal. In this field, the energies of all the five d orbitals will increase due to the repulsion between the electrons of the metal and the ligand.

Step 2: The ligands are approaching the metal atom in actual bond directions. To illustrate this let us consider an octahedral field, in which the central metal ion is located at the origin and the six ligands are coming from the +x, -x, +y, -y, +z and -z directions as shown below.

As shown in the figure, the orbitals lying along the axes dx^2-y^2 and dz^2 orbitals will experience strong repulsion and raise in energy to a greater extent than the orbitals with lobes directed between the axes (d_{xy}, d_{yz} and d_{zx}). Thus the degenerate d orbitals now split into two sets and the process is called crystal field splitting.



Step 3: Up to this point the complex formation would not be favoured. However, when the ligands approach further, there will be an attraction between the negatively charged electron and the positively charged metal ion, that results in a net decrease in energy. This decrease in energy is the driving force for the complex formation.

Crystal field splitting in octahedral complexes:

During crystal field splitting in octahedral field, in order to maintain the average energy of the orbitals (barycentre) constant, the energy of the orbitals dx^2-y^2 and dz^2 (represented as e_g orbitals) will increase by $3/5\Delta_o$ while that of the other three orbitals d_{xy}, d_{yz} and d_{zx} (represented as t_{2g} orbitals) decrease by $2/5\Delta_o$. Here, Δ_o represents the crystal field splitting energy in the octahedral field.

12.Give the main assumptions of Valence Bond Theory? [HY-22, HY-23,24]

- The ligand → metal bond in a coordination complex is covalent in nature. It is formed by sharing of electrons (provided by the ligands) between the central metal atom and the ligand.
- Each ligand should have at least one filled orbital containing a lone pair of electrons.
- In order to accommodate the electron pairs donated by the ligands, the central metal ion present in a complex provides required number (coordination number) of vacant orbitals.
- These vacant orbitals of central metal atom undergo hybridisation, the process of mixing of atomic orbitals of comparable energy to form equal number of new orbitals called hybridised orbitals with same energy.
- The vacant hybridised orbitals of the central metal ion, linearly overlap with filled orbitals of the ligands to form coordinate covalent sigma bonds between the metal and the ligand.
- The hybridised orbitals are directional and their orientation in space gives a definite geometry to the complex ion.

Coordination number	Hybridisation	Geometry	Examples
2	sp	Linear	$[CuCl_2]^-$, $[Ag(CN)_2]^-$

3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$[Ni(CO)_4]$, $[NiCl_4]^{2-}$
4	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$
5	dsp^3 ($d_{x^2-y^2}$ orbital is involved)	Trigonal bipyramidal	$Fe(CO)_5$
6	d^2sp^3 (d_{z^2} and $d_{x^2-y^2}$ orbitals of inner shell are involved)	Octahedral	$[Ti(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{2-}$, $[Fe(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$ (Inner orbital complexes)
6	sp^3d^2 (d_{z^2} and $d_{x^2-y^2}$ orbitals of the outer shell are involved)	Octahedral	$[FeF_6]^{4-}$,$[CoF_6]^{4-}$, $[Fe(H_2O)_6]^{2+}$ (Outer orbital complexes)

- In the octahedral complexes, if the *(n-1)d* orbitals are involved in hybridisation, then they are called inner orbital complexes or low spin complexes or spin paired complexes. If the *nd* orbitals are involved in hybridisation, then such complexes are called outer orbital or high spin or spin free complexes. Here n represents the principal quantum number of the outermost shell.
- The complexes containing a central metal atom with unpaired electron(s) are paramagnetic. If all the electrons are paired, then the complexes will be diamagnetic.
- Ligands such as CO, CN^-, en, and NH_3 present in the complexes cause pairing of electrons present in the central metal atom. Such ligands are called strong field ligands.
- Greater the overlapping between the ligand orbitals and the hybridised metal orbital, greater is the bond strength.

13. What is facial isomer? [SMT-22]

Octahedral complex of the type $[MA_3B_3]^{n\pm}$ also shows geometrical isomerism.

If the three similar ligands (A) are present in the corners of one triangular face of the octahedron and the other three ligands (B) are present in the opposing triangular face, then the isomer is referred as a facial isomer (fac isomer).

14. How will you differentiate primary and secondary valencies? [SMT-22]

- Most of the elements exhibit, two types of valence namely primary valence and secondary valence and each element tend to satisfy both the valences. The primary valence is referred as the oxidation state of the metal atom and the secondary valence as the coordination number.

  For example, **$[Co(NH_3)_6]Cl_3$** – according to Werner, the primary and secondary valences of cobalt are 3 and 6 respectively.
- 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.

- The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these (No. of ligand).

15. In the complex, ~~$[Co(CN)_2Cl_2]Cl$~~ $[Co(en)_2Cl_2]Cl$, identify the following, i) IUPAC name, ii) Central metal ion and iii) Co-ordination number [MAR-24]

i) Dichloridobis(ethane-1,2-diamine)cobalt(III)chloride ii) Co^{3+} iii) 6

16. Mention any three applications of coordination complexes? [SRT-24]

- Phthalo blue – a bright blue pigment is a complex of Copper (II) ion and it is used in printing ink and in the packaging industry.
- Purification of Nickel by Mond's process involves formation $[Ni(CO)_4]$, which Yields 99.5% pure Nickel on decomposition.
- EDTA is used as a chelating ligand for the separation of lanthanides, in softening of hard water and also in removing lead poisoning.
- Coordination complexes are used in the extraction of silver and gold from their ores by forming soluble cyano complex. These cyano complexes are reduced by zinc to yield metals. This process is called as Mac-Arthur –Forrest cyanide process.
- Some metal ions are estimated more accurately by complex formation. For example, Ni^{2+} ions present in Nickel chloride solution is estimated accurately for forming an insoluble complex called $[Ni(DMG)_2]$.
- Many of the complexes are used as catalysts in organic and inorganic reactions. For example,

(i) Wilkinson's catalyst – $[(PPh_3)_3\ RhCl]$ is used for hydrogenation of alkenes.

(ii) Ziegler-Natta catalyst - $[TiCl_4] + Al(C_2H_5)_3$ is used in the polymerization of ethene.

- In order to get a fine and uniform deposit of superior metals (Ag, Au, Pt etc.,) over base metals, Coordination complexes $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ etc., are used in electrolytic bath.
- Many complexes are used as medicines for the treatment of various diseases. For example,

(1) 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.

(2) Cis-platin is used as an antitumor drug in cancer treatment.

- In photography, when the developed film is washed with sodium thio sulphate solution (hypo), the negative film gets fixed. Undecomposed AgBr forms a soluble complex called sodiumdithiosulphatoargentate(I) which can be easily removed by washing the film with water.

$$AgBr + 2\,Na_2S_2O_3 \longrightarrow Na_3\left[Ag\left(S_2O_3\right)_2\right] + 2\,NaBr$$

17. In the complex, $[Co(NH_3)_4Cl_2]Cl$, mention i) Ligands, ii) Central Metal atom/ion and iii) Co-ordination number [SRT-24]

i) NH_3 – neutral ligand, Cl – negative ligand ii) Co^{3+} iii) 6

18. For the complex, $[Cu(NH_3)_4]SO_4$, mention i) Nature of the complex, ii) Shape of the complex and iii) IUPAC name [HY-23]

i) Its entity is $[Cu(NH_3)_4]^{2+}$. So, its **cationic complex** ii) Co-ordination number is 6. **Square planar** iii) **Tetraamminecopper(II)sulphate**

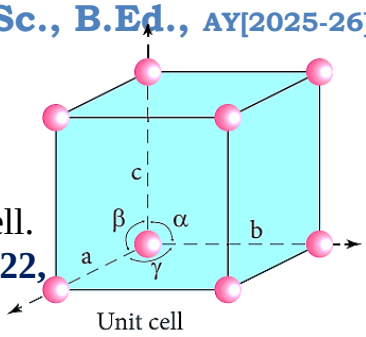
19.Calculate CFSE value for the $[Fe(H_2O)_6]^{3+}$ complex. [SRT-23]

High Spin Complex	Low Spin Complex
Electronic configuration in isotropic field : d5  No. of paired electrons (n'p) = 0; Therefore, E_{iso} = 0	
Ligand field: Electronic configuration : $t^3_{2g}\ e^2_g$ CFSE = {[3(-0.4)+2 (0.6)] Δ_o + 0 × P} - {0} = 0	Ligand field: Electronic configuration : $t^5_{2g}\ e^0_g$ CFSE = {[5(-0.4)+0 (0.6)] Δ_o + 2 × P} - {0} = -2 Δ_o + 2P = (-2 ×14000) + (2× 30000) = 32000 cm^{-1} High positive CFSE value indicates that low spin complex is not a favourable one.
Nature of the complex	High spin (Spin free)
Electronic configuration of central metal ion	$t^5_{2g}\ e^2_g$
Magnetic property	No. of unparied electrons = 5; Hence paramagnetic
Magnetic moment (Using spin only formula)	$\mu_s = \sqrt{n(n+2)} = \sqrt{5(5+2)}$ $= \sqrt{35}$ = **5.916 BM**

20.Define the term central atom in co-ordination compounds. [MAR-23]

The central atom/ion is the one that occupies the central position in a coordination entity and binds other atoms or groups of atoms (ligands) to itself, through a coordinate covalent bond. For example, in $K_4[Fe(CN)_6]$, the central metal ion is Fe^{2+}.

UNIT – 6 – SOLID STATE



Unit cell

II. Answer the following questions:

1. Define unit cell. [AUG-21, FRT,JUL-22, QY-23]

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

2. Give any three characteristics of ionic crystals. [PTA1,QY,FRT22, FUT23]

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

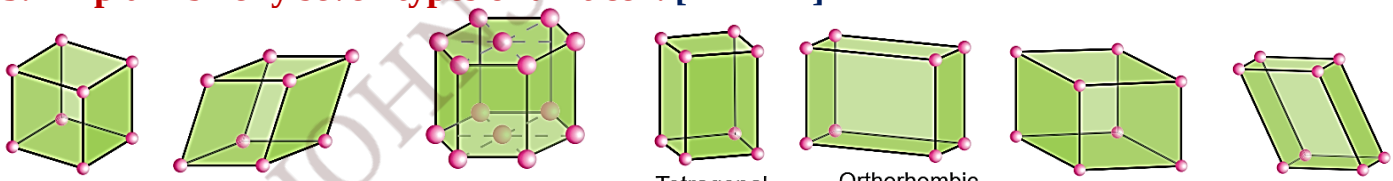
3. Differentiate crystalline solids & amorphous solids.[PTA1,HY,MAY,FMT-22, FUT,HY,SRT-23, FUT-24]

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. P_4, Brass Diamond NaCI iodine

P_4 – Molecular solid, Brass – Metallic solid, Diamond – Covalent solid, NaCl – Ionic solid, Iodine – Molecular solid

5. Explain briefly seven types of unit cell. [FRT-22]



Cubic – NaCl, **Tetragonal** – TiO_2, **Orthorhombic** – $BaSO_4$, **Hexagonal** – ZnO, **Monoclinic** – $PbCrO_4$, **Triclinic** – H_3BO_3, **Rhombohedral** – Cinnabar Cubic

6. Distinguish between hexagonal close packing and cubic close packing. [FRT-25]

HEXAGONAL CLOSE-PACKING	CUBIC CLOSE PACKING
aba arrangement	abc arrangement
The spheres of the third layer are exactly aligned with those of the first layer	The spheres of the third layer are not aligned with those of the first layer or second layer.
The hexagonal close packing is based on hexagonal unit cells with sides of equal length.	The cubic close packing is based on the face centered cubic unit cell.

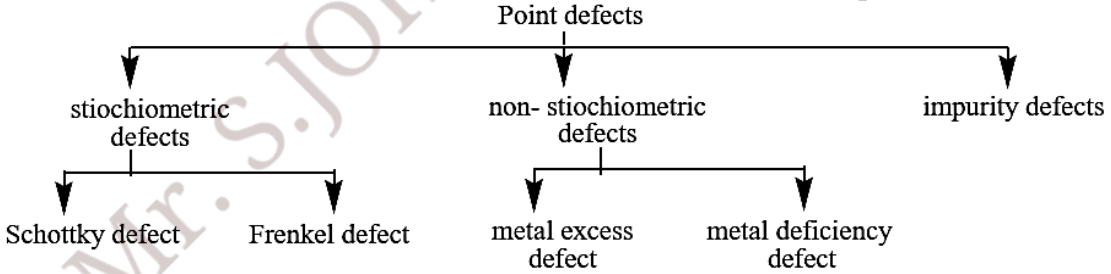
Tetrahedral voids of the second layer may be covered by the spheres of the third layer	Third layer may be placed above the second layer in a manner such that its sphere cover the octahedral voids
The unit cell of hexagonal close packing has 6 spheres	The unit cell of cubic close packing has 4 spheres
This type is found in metals like Mg, Zn	This type is found in metals like Cu, Ag

7. Distinguish tetrahedral and octahedral voids. [HY-22, QY-23,24, MAR-25]

TETRAHEDRAL VOID	OCTAHEDRAL VOID
A single triangular void in a crystal is surrounded by four (4) spheres and is called a tetrahedral void	A double triangular void like c is surrounded by six(6) spheres and is called an octahedral void
A sphere of second layer is above the void of the first layer, a tetrahedral void is formed	The voids in the first layer are partially covered by the spheres of layer now such a void is called an octahedral void
This constitutes four spheres, three in the lower and one in upper layer. When the centres of these four spheres are joined a tetrahedron is formed	This constitutes six spheres, three in the lower layer and three in the upper layer. When the centers of these six spheres are joined an octahedron is formed
The radius of the sphere which can be accommodated in an octahedral hole without disturbing the structure should not exceed 0.414 times that of the structure forming sphere	The sphere, which can be placed in a tetrahedral hole without disturbing the close-packed structure should not have a radius larger than 0.225 times the radius of the sphere-forming the structure
Radius of an tetrahedral void rR = 0.225	Radius of a octahedral void rR = 0.414
The coordination number is 4.	The coordination number is 6.

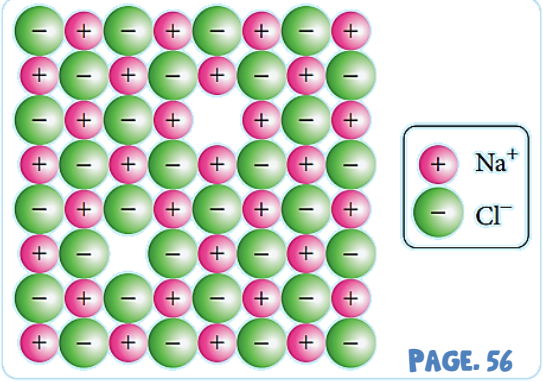
8. What are point defects? (OR) How are point defects classified? [FRT-22, FUT-23]

- 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 crystallisation or they may arise from thermal vibrations of atoms at elevated temperatures.



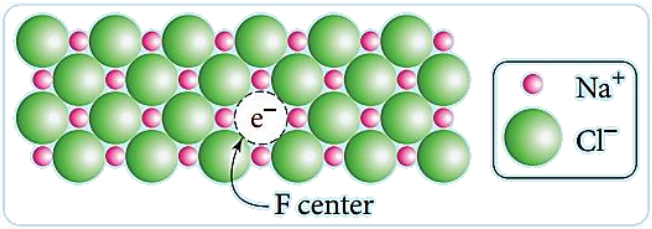
9. Explain Schottky defect. [GMQ,QY19,SEP20,FRT22,FUT,QY23,SRT,FUT24,SRT25]

- The schottky defect arises due to the missing of an 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 similar size show Schottky defect. Example: NaCl.
- Presence of large number of schottky defects in crystal, lowers its density.



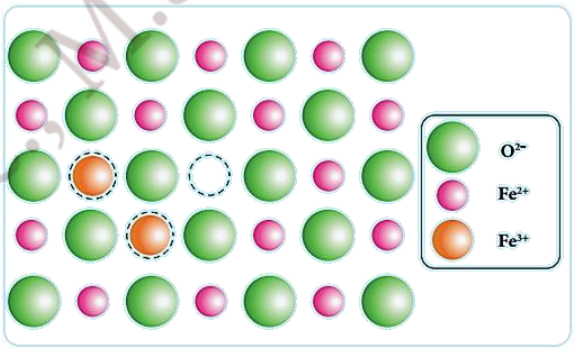
10. Write short note on metal excess and metal deficiency defect with an example. [QY24]

Metal excess defect: [MAR-25]



- 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.
- 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 $Na_{1+x}Cl$.

Metal deficiency defect: [SRT-25]



- 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 electrical neutrality, twice the number of other Fe^{2+} ions in the crystal is oxidized to Fe^{3+} ions.
- In such cases, the 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.

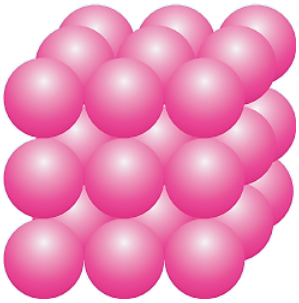
11. Calculate the number of atoms in a fcc unit cell. [HY-19, FMT,FRT-22, QY-24, SRT25]

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

$\therefore$ Number of atoms in a fcc unit cell $= \frac{N_c}{8} + \frac{N_f}{2} = \frac{8}{8} + \frac{6}{2} = 1 + 3 = 4.$

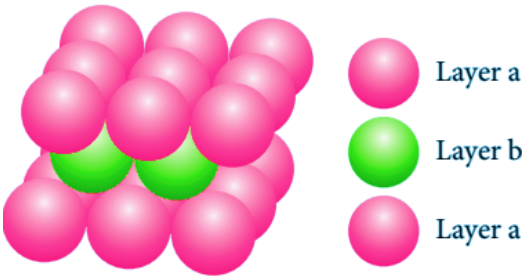
12. Explain AAAA and ABABA and ABCABC type of three-dimensional packing with the help of a neat diagram.

AAAA type of three-dimensional packing



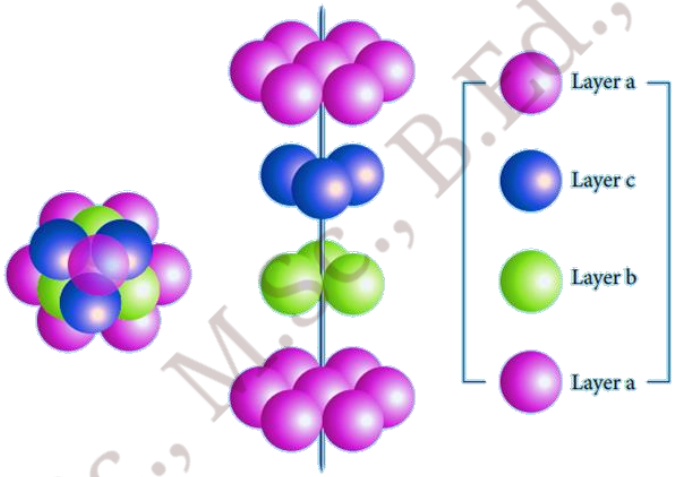
- This type of three-dimensional packing arrangement.
- This can be obtained by repeating the AAAA type two dimensional arrangements in three dimensions.
- Spheres in one layer sitting directly on the top of those in the previous layer so that all layers are identical.
- All spheres of different layers of crystal are perfectly aligned horizontally and also vertically
- Each spheres is in contact with 6 neighbouring spheres – four in its own layer, one above and one below it.
- Hence the coordination number of the sphere in simple cubic arrangement is 6.

ABABA type of three-dimensional packing:



- This is body centred cubic arrangement.
- The spheres in the first layer (A type) are slightly separated and the second layer is formed by arranging the spheres in the depressions between the spheres in layer A.
- The third layer is a repeat of the first.
- This pattern ABABAB is repeated throughout the crystal.
- Each sphere has a coordination number of 8, four neighbours in the layer above and four in the layer below.

ABCABC type of three-dimensional packing:



- This is face centred cubic arrangement.
- The first layer is formed by arranging the spheres as in the case of two dimensional ABAB arrangements.
- This is layer A. Second layer is formed by placing the spheres in the depressions of the first layer. This is layer B.
- There are two voids x and y.
- If void y in the first layer (A) are partially covered by the spheres of layer (B), it is an octahedral void.
- The third layer (C) may be placed over the second layer (B) in such a way that all the spheres of the third layer fit in octahedral voids.
- This third layer (C) is different from the other two layers (A) and (B).
- This is called cubic closed packed (ccp) structure.
- The coordination number is 12. Voids – The empty spaces between the three-dimensional layers are known as voids. There are two types of common voids possible. They are tetrahedral and octahedral voids.

13. Why ionic crystals are hard and brittle? [FUT-24, FRT-25]

- Ionic crystalline are hard because they are bound together by strong electrostatic attractive forces.
- To maximize the attractive force, cations are surrounded by as many anions as possible and vice versa.
- The electrostatic repulsion can be enough to split or disorient completely the lattice infrastructure. Thus imparts the brittle character.

14. Calculate the percentage efficiency of packing in the case of a body-centered cubic crystal. Packing efficiency. [QY-19, FRT,HY-24]

In body-centered cubic arrangement the spheres are touching along the leading diagonal of the cube as shown in the,

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 ΔACG

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

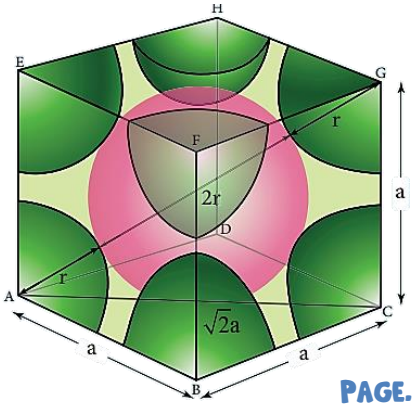
$$AG = \sqrt{AC^2 + CG^2}$$

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

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

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

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



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

∴ Volume of the sphere with radius 'r'

$$= \frac{4}{3}\pi r^3$$

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

$$= \frac{\sqrt{3}}{16}\pi a^3 \quad ...(1)$$

Number of spheres belong to a unit cell in bee arrangement is equal to two and hence the total volume of all spheres

$$= 2 \times \left(\frac{\sqrt{3}\,\pi\,a^3}{16}\right) = \frac{\sqrt{3}\,\pi\,a^3}{8}$$

Dividing (2) by (3)

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

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

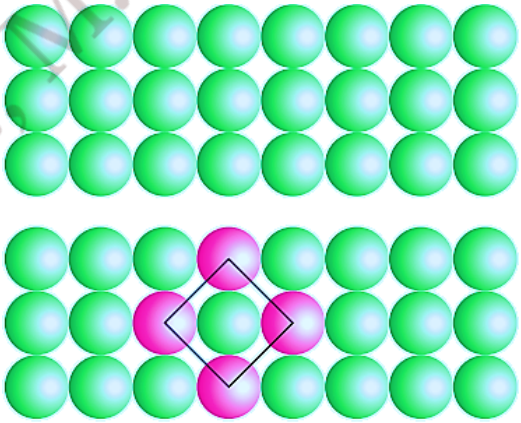
$$= \sqrt{3}\,\pi \times 12.5$$

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

$$= 68\ \%$$

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 as shown in the figure.
- 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.
- Thus the two dimentional co-ordination number is 4.
- If the centres of these 4 immediate neighbouring spheres are joined, a square is formed. Hence this packing is called square close packed layer.

16. What is meant by the term "coordination number"? What is the coordination number of atoms in a bcc structure? [AUG-21, QY-24]

- The number of nearest neighbours that surrounding a particle in a crystal is called the coordination number of that particle.
- Coordination number of atoms in a bcc structure 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.

Unit cell (a) = 288pm. The density of the element (ρ) = 7.2gcm^{-3}. For the Bec structure (n) = 2

$$\rho = \frac{nM}{a^3 N_A} = 7.2\text{gcm}^{-3} = \frac{2M}{(288\times10^{-10}cm)^3\times(6.023\times10^{23}mol^{-1})}$$

$$7.2\text{gcm}^{-3} = \frac{2M}{(2.38\times10^{-23}cm^3)\times(6.023\times10^{23}mol^{-1})} = \frac{2M}{14.33cm^3mol^{-1}}$$

7.2g = 0.140M mol

$$M = \frac{7.2g}{0.140\ mol} = 51.42\text{g mol}^{-1}$$

By mole concept, 51.42 g of the element contains 6.023 x 10^{23} atom

208 g of the element will contain = $6.023\times10^{23}\times(208/51.42)$ atoms
= 24.17×10^{23} atoms (or) 2.417×10^{24} atoms

18. Aluminium crystallizes in a cubic close packed structure. Its metallic radius is 125pm. Calculate the edge length of unit cell. [FMT-22]

Given, Radius (r) = 125 pm, Edge length of unit cell (a) = ?
Since aluminium crystallizes in Face centered cubic $a = 2\sqrt{2} \times r$
$= 2 \times 1.414 \times 125 = 353.5$
a = 353.5 pm

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

We know that two Na^+ ions are replaced by each of the Sr^{2+} ions while $SrCl_2$, is doped with NaCl. But in this case, only one lattice point is occupied by each of the Sr^{2+} ions and produce one cation vacancy.
Here 10^{-2} mole of $SrCl_2$, is doped with 100 moles of NaCl. Thus, 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 = $10^{-2}/100$ moles of $SrCl_2$
= 10^{-4} moles of $SrCl_2$
Total cationic vacancies, = 10^{-4} x Avogadro's number
= 10^{-4} x 6.023×10^{23}
= 6.023×10^{19} vacancies
So, that the concentration of cation vacancies created by $SrCl_2$ is 6.023×10^{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})

For fcc structure n = 4; ρ =2.48 g cm^{-3}; for KF, M=39+19= 58g mol^{-1}; $N_A = 6.023 \times 10^{23}$; **a = ?**

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

$$a^3 = \frac{4 \times 58}{2.48 \times 6.023 \times 10^{23}} = 0.1553 \times 10^{-21}\ cm^3$$

$a = 0.5375 \times 10^{-7}$ cm = 5.375×10^{-8} cm = 537.5 pm

Distance between K+ and F- = $\frac{a}{\sqrt{2}} = \frac{537.5}{1.414}$ = 380.12 pm

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

Density = 10 g cm^{-3}; Unit cell edge length, a = 100pm = 100×10^{-10} cm; Avogadro number, $N_A = 6.023 \times 10^{23}$; No. of atoms per unit cell, n = 4 (for fcc)

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

$M = 10 \times (100 \times 10^{-10})^3 \times (6.023 \times 10^{23}) / 4$
M = 1.506 g mol^{-1}
No. of atoms in 1g = ?

$$\text{No. of mole} = \frac{Weight}{molar\ mass} = \frac{1}{1.506} = 0.664$$

∴No. of atoms = No. of mole x N_A
$0.664 \times 6.023 \times 10^{23} = 4 \times 10^{23}$ atoms

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?

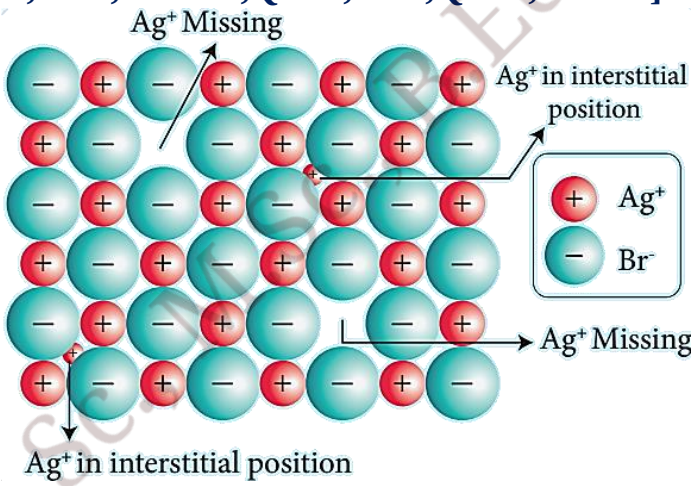
Atoms X and Y form bcc crystalline structure. Atom X is present at the corners of the cube Atom Y is present at the centre of the cube. No of atoms of X in the unit cell = Nc/8 = 8/8 = 1
No of atoms of Y in the unit cell = Nb / 1 = 1 / 1 = 1
Ratio of atoms X : Y = 1 : 1 Hence formula of the compound = XY.

23. Na metal crystallizes in bcc structure with the edge length of the unit cell 4.3×10^{-8} cm. Calculate the radius of sodium atom. [QY-19]

Edge length of the unit cell (a) = 4.3×10^{-8}cm; Radius of sodium atom **(r) = ?**
For bcc structure, $r = 3\sqrt{4}a = 3\sqrt{4}\ (4.3 \times 10^{-8}\text{cm}) = 1.86 \times 10^{-8}$ cm = 1.86Å

24. Write a note on Frenkel defect. [MAR-20, HY,FRT,JUL-22,QY23,SRT,QY24,FRT25]

- 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. Unlike Schottky defect, this defect does not affect the density of the crystal.
- For example AgBr, in this case, small Ag ion leaves its normal site and occupies an interstitial position as shown in the figure.



Evaluate Yourself

25. 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?

Mass = 100g; Density = 8.9 g cm^{-3}; Edge length = 352.4pm = 352.4×10^{-10}cm; $N_A = 6.023 \times 10^{23}$

$\rho = \frac{nM}{a^3 N_A}$ $\quad 8.9\text{cm}^{-3} = \frac{4 \times M}{(6.023 \times 10^{23} \times (352.4 \times 10^{-10})^3}$

M = 58.6g/mole Moles of element = $\frac{Mass\ of\ element}{Molar\ mass\ of\ element} = \frac{100g}{58.6g/mol}$ = 1.7 moles.

As, 1 mol contains 6.023×10^{23} number of atoms. So, 1.7 mole contains, = 1.7 x 6.023 x 10^{23}
= 10.24 x 10^{23} no. of atoms

Since each Fcc cube contains 4 atoms, therefore total number of atoms in 100 g of element is 10.24 x 10^{23} atoms

26. Determine the density of CsCl which crystallizes in a bcc type structure with an edge length 412.1 pm.

Molar mass of CsCl = 168.5 g /mol; No. of atoms in per unit cell for bcc (CsCl) n = 1;
Edge length (a) = 412.1 pm; Density **(ρ) = ?**

$$\rho = \frac{nM}{a^3 N_A} = \frac{1 \times 168.5\text{g mol}^{-1}}{(412.1 \times 10^{-10}\text{cm})^3 \times (6.023 \times 10^{23}\text{mol}^{-1})} = \frac{168.5\text{g cm}^{-3}}{6.998 \times 10^{-23} \times 6.023 \times 10^{23}}$$

$$= \frac{168.5}{42.148}\text{g cm}^{-3}$$

$$\rho = 3.997\ \text{g cm}^{-3}$$

27. A face centered cubic solid of an element (atomic mass 60) has a cube edge of 4 Å. Calculate its density.

For FCC n = 4; Edge length (a) = 4Å = 4 x 10^{-8}cm; Mass (M) = 60 g mol^{-1}; Density **ρ = ?**

$$\rho = \frac{nM}{a^3 N_A} = \frac{4 \times 60 \text{g mol}^{-1}}{(4\times10^{-8}\text{cm})^3 \times (6.023\times10^{23}\text{mol}^{-1})} = \frac{240 \text{ g mol}^{-1}}{6.4\times10^{-23}\text{cm}^3 \times 6.023\times10^{23}\text{mol}^{-1}} = \frac{240}{38.54}\text{g cm}^{-3}$$

$\rho = 6.227$ g cm^{-3}

GOVERNMENT EXAM QUESTION PAPER

1. State Bragg's law. (OR) Explain Bragg's Equation. [QY-23, FUT-24]

The fundamental equation that gives a simple relation between the wavelength of the X-rays, the interplanar distance in the crystal and the angle of reflection is known as Bragg's equation.

$$n\lambda = 2d \sin\Theta$$

where **n** is the order of reflection; **λ** is the wavelength of X-rays; **d** is the interplanar distance in the crystal; **Θ** is the angle of reflection

2. Define packing efficiency. [JUL-22]

The percentage of total volume occupied by these constituent spheres gives the packing efficiency of an arrangement. Let us calculate the packing efficiency in simple cubic arrangement

$$\left\{\begin{matrix}\text{Packing fraction}\\ \text{(or) efficiency}\end{matrix}\right\} = \frac{\left\{\begin{matrix}\text{Total volume occupied by}\\ \text{spheres in a unit cell}\end{matrix}\right\}}{\text{Volume of the unit cell}} \times 100$$

3. If the no. of close packed sphere is 6, calculate the number of Octahedral voids and Tetrahedral voids generated. [MAR-20]

If the number of close packed sphere is 6. So, Octahedral voids is **6** & Tetrahedral voids is **12**

4. Distinguish between Isotropy and Anisotropy in solids. [SEP-20, FRT-22, FRT-24]

S.No.	Isotropy	Anisotropy
1	Isotropy means uniformity in all directions	Anisotropy is the property which depends on the direction of measurement.
2	In solid state isotropy means having identical values of physical properties such as refractive index, electrical conductance etc., in all directions	Crystalline solids are anisotropic and they show different values of physical properties when measured along different directions

5. Define covalent solids. [MAY-22]

In covalent solids, the constituents (atoms) are bound together in a three dimensional network entirely by covalent bonds. Examples: Diamond, silicon carbide etc.

6. What is metal deficiency defect? Give example. [FRT-22, HY-23]

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.

Example: O^{2-}, Fe^{2+}, Fe^{3+}

7. ZnO is colourless at room temperature, but it turns yellow colour on heating. Why? [FRT-22]

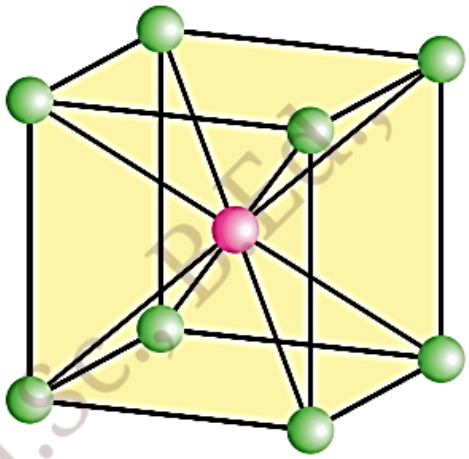
ZnO is colourless at room temperature. When it is heated, it becomes yellow in colour. On heating, it loses oxygen and thereby forming free Zn^{2+} ions. The excess Zn^{2+} ions move to interstitial sites and the electrons also occupy the interstitial positions.

8. Classify molecular crystals with an example for each type. [QY-19]

- Non-polar molecular crystals **Eg:** Naphthalene, Anthracene
- Polar molecular crystals solid **Eg:** Solid CO_2, Solid NH_3
- Hydrogen bonded molecular crystals **Eg:** H_2O, glucose, urea.

9. Barium has a body centred cubic unit cell with a length of 508pm along an angle. What is the density of barium in gcm^{-3}? (M = 137.3 $gmol^{-1}$) [HY-19, FUT,QY-23, FUT24]

$$\rho = \frac{n\,M}{a^3 N_A}$$



In this case,

n=2 ; M=137.3 $gmol^{-1}$; a = 508pm= $5.08X10^{-8}$cm

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

$$\rho = \frac{2 \times 137.3}{(5.08)^3 \times 10^{-24} \times 6.023 \times 10^{23}} \text{ g cm}^{-3}$$

$$\rho = 3.5 \text{ g cm}^{-3}$$

10. Classify the following into covalent, molecular, ionic and metallic solids. [AUG-21]
(i) Diamond, (ii) Brass, (iii) NaCl, (iv) Naphthalene, (v) Glucose, (vi) SiO_2

(i) Diamond - Covalent Network Solid
(ii) Brass - Metallic Solid
(iii) NaCl - Ionic Solid
(iv) Naphthalene - Molecular Solid
(v) Glucose - Covalent (Molecular) Solid
(vi) SiO_2 - Covalent Network Solid

11. Imperfection in solids play an important role in various processes. Justify. [FRT-22]

Imperfection in solids play an important role in various processes. For example, a process called doping leads to a crystal imperfection and it increases the electrical conductivity of a semiconductor material such as silicon. The ability of ferromagnetic material such as iron, nickel etc., to be magnetized and demagnetized depends on the presence of imperfections.

12. The composition of a sample of Wurtzite is $Fe_{0.93}O_{1.00}$ [QY-19]

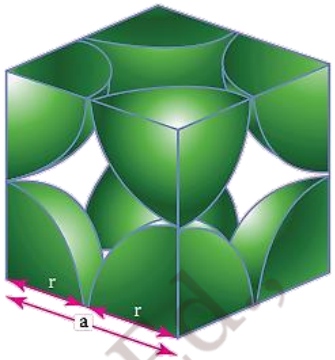
The number of Fe^{2+} ions in the crystal be *x*, The number of Fe^{3+} ions in the crystal be *y*
Total number of Fe^{2+} and Fe^{3+} ions is $x + y$
Given that $x + y$ = 0.93
Total charges = 0
$x(2+) + (0.93 - x)(3+) - 2 = 2x + 2.97 - 3x - 2 = 0$
$x = 0.79$
Percentage of Fe^{3+} $= \left(\frac{(0.93-0.79)}{(0.93)}\right) \times 100$
= 15.05%

13. Classify the following allotropic form of sulphur as crystalline and amorphous:
(a) α sulphur (b) β sulphur (c) γ sulphur (d) Colloidal suphur [HY-19]

(a) α sulphur - Crystalline form (b) β sulphur - Crystalline form
(c) γ sulphur - Amorphous form (d) Colloidal suphur - Amorphous form

14. Calculate the percentage of packing efficiency in simple cubic crystal. [FRT,FMT-22, APR-24]

$$\left\{\begin{matrix}\text{Packing fraction}\\ \text{(or) efficiency}\end{matrix}\right\} = \frac{\left\{\begin{matrix}\text{Total volume occupied by}\\ \text{spheres in a unit cell}\end{matrix}\right\}}{\text{Volume of the unit cell}} \times 100$$



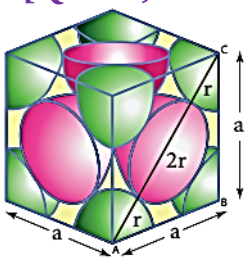
Let us consider a cube with an edge length 'a' as shown in figure.
Volume of the cube with edge length a is = a × a × a = a^3
Let 'r' is the radius of the sphere. From the figure, a=2r ⇒ r = a/2
∴ Volume of the sphere with radius 'r'

$$= \frac{4}{3}\pi r^3 \qquad = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{4}{3}\pi\left(\frac{a^3}{8}\right) \qquad = \frac{\pi a^3}{6}$$

In a simple cubic arrangement, number of spheres belongs to a unit cell is equal to one
∴ Total volume occupied by the spheres in sc unit cell = 1 x $\left(\frac{\pi a^3}{6}\right)$

Packing fraction = $\frac{\left(\frac{\pi a^3}{6}\right)}{(a^3)} \times 100 = \frac{100\pi}{6} =$ **52.38%**

15. Calculate the percentage efficiency of packing in case of face centred cubic crystal. [QY-23, SRT-25]



From the figure
AC = 4r
$4r = a\sqrt{2}$
$r = \frac{a\sqrt{2}}{4}$

In ΔABC
$AC^2 = AB^2 + BC^2$
$AC = \sqrt{AB^2 + BC^2}$
$AC = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2}\,a$

Volume of the sphere with radius r is $= \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3 = \frac{4}{3}\pi\left(\frac{2\sqrt{2}a^3}{64}\right)$

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

Total number of spheres belongs to a single fcc unit cell is 4

∴ the volume of all spheres in a fcc unit cell $= 4 \times \left(\frac{\sqrt{2}\,\pi a^3}{24}\right) = \left(\frac{\sqrt{2}\,\pi a^3}{6}\right)$

$$\text{packing efficiency} = \frac{\left(\frac{\sqrt{2}\,\pi\, a^3}{6}\right)}{\left(a^3\right)} \times 100$$

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

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

$$= 74\%$$

16. What are the properties of Metallic Solids? [FMT-22]

Metallic solid are hard, and have high melting point. Metallic solids possess excellent electrical and thermal conductivity. They possess bright lustre.

17. Calculate the number of atoms per unit cell in SC, BCC and FCC lattice. [FUT-23]

Number of atoms in a sc unit cell = $\frac{N_c}{8} = \frac{8}{8} = 1.$

Number of atoms in a bcc unit cell = $\frac{N_c}{8} + \frac{N_b}{1} = \frac{8}{8} + \frac{1}{1} = 1 + 1 = 2.$

Number of atoms in a fcc unit cell = $\frac{N_c}{8} + \frac{N_f}{2} = \frac{8}{8} + \frac{6}{2} = 1 + 3 = 4.$

18.Define Impurity Defects. [HY-24]

A general method of introducing defects in ionic solids is by adding impurity ions. If the impurity ions are in different valance state from that of host, vacancies are created in the crystal lattice of the host.

For example, addition of $CdCl_2$ to AgCl yields solid solutions where the divalent cation Cd^{2+} occupies the position of Ag^+. This will disturb the electrical neutrality of the crystal. In order to maintain the same, proportional number of Ag^+ ions leaves the lattice. This produces a cation vacancy in the lattice, such kind of crystal defects are called impurity defects.

UNIT – 7 – CHEMICAL KINETICS

II. Answer the following questions:

1. Define average rate and instantaneous rate.

Average rate of chemical reaction:

The average rate is defined as the ratio of change in the final concentration of reactants and the initial concentration of reactants over the entire time period of reaction.

Average rate = $\frac{(Final\ concentration\ of\ reactants - Initial\ concentration\ of\ reactants)}{Change\ in\ Time}$

The rate of the reaction at a particular instant during the reaction is called the instantaneous rate.

Average rate of chemical reaction:

It may be defined as the rate of a reaction of a particular instant. Instantaneous reaction rate $\frac{d[l_2]}{dt}$ where, $d(l_2)$ = small change in concentration. $d+$ = small change in time.

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 equation.

xA + yB → products

Rate = $k[A]^m[B]^n$ k = Rate constant

Rate constant: For a reaction involving the reactants A and B, Reaction rate = $k[A]^m[B]^n$. The constant k is called rate constant of the reaction. If [A] = 1M and [B] = 1M; Reaction rate = k. Thus, the rate constant (k) of a reaction is equal to the rate of reaction when the concentration of each reactant is equal to 1 mol L-1. The change in the concentration of reactant or product per unit time under the condition of unit concentration of all the reactant.

3. Derive integrated rate law for a zero order reaction A → product. [PTA6, QY-19, MAR-20, AUG-21, JUL-22]

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.

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

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

$$-d[A] = kdt$$

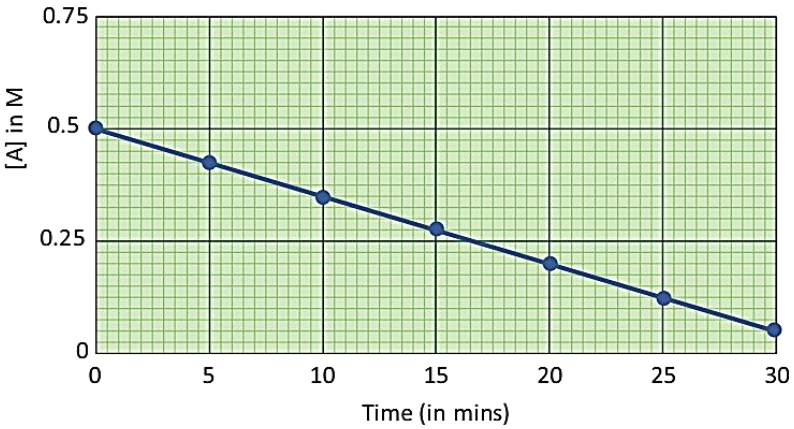
Integrate the above eq. between the limits of $[A^0]$ at zero time and [A] at some later time 't',

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

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

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

$$k = \frac{[A_0]-[A]}{t}$$



Equation (2) is in the form of a straight line

$y = mx + c$

ie., $[A] = -kt + [A_0]$

$y = c + mx$

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. [PTA-5, QY-22, HY-23, FUT-24]

- The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value.
- For a 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

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

$$\text{at } t = t_{1/2} \; ; \; [A] = [A_0]/2$$

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

$$k = \frac{2.303}{t_{1/2}}\log 2$$

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

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

5. What is an elementary reaction? Give the differences between order and molecularity of a reaction. [PTA-1, QY-19, QY,HY, JUL-22, QY-23, FRT,FUT-24]

Each and every single step in a reaction mechanism is called an elementary reaction.

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 a overall reaction.	It is assigned for each elementary step of mechanism.

6. Explain the rate determining step with an example. [PTA-4, HY-23]

Let us consider reaction, the decomposition of hydrogen peroxide catalysed by I^-.

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

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 $H_2O_{2(aq)} + I^-_{(aq)} \rightarrow H_2O_{(l)} + OI^-_{(aq)}$ (1)

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

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 1ST order reaction. (or) Derive integrated rate law for a 1st order reaction A → product. [PTA-2, MAR-20, HY,JUL-22, FUT, SRT23, QY-24]

A reaction whose rate depends on the reactant concentration raised to the first power is called a first order reaction. Let us consider the following first order reaction, $A \longrightarrow$ product

Rate law can be expressed as $\text{Rate} = k\,[A]^1$

Where, k is the first order rate constant.

$$\frac{-d[A]}{dt} = k\,[A]^1$$

$$\Rightarrow \frac{-d[A]}{[A]} = k\,dt$$

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.

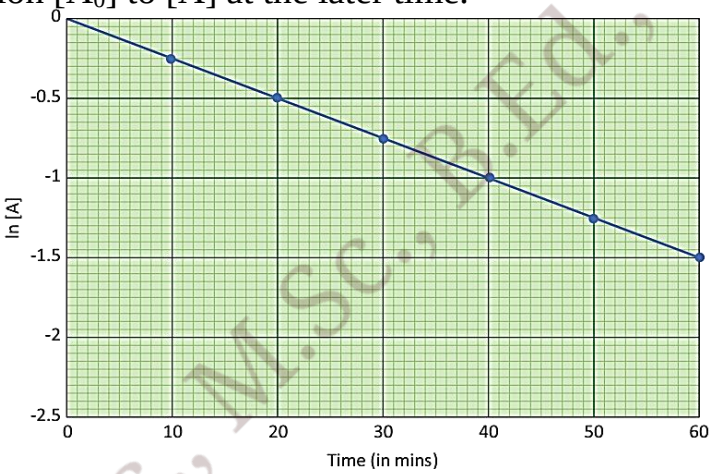
$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]} = k\int_0^t dt$$

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

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

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

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



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

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

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

Equation (2) can be written in the form y = mx + c as below

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

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

$$\Rightarrow y = c + mx$$

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 slope. 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 = $k[x]^{3/2}\,[y]^0$

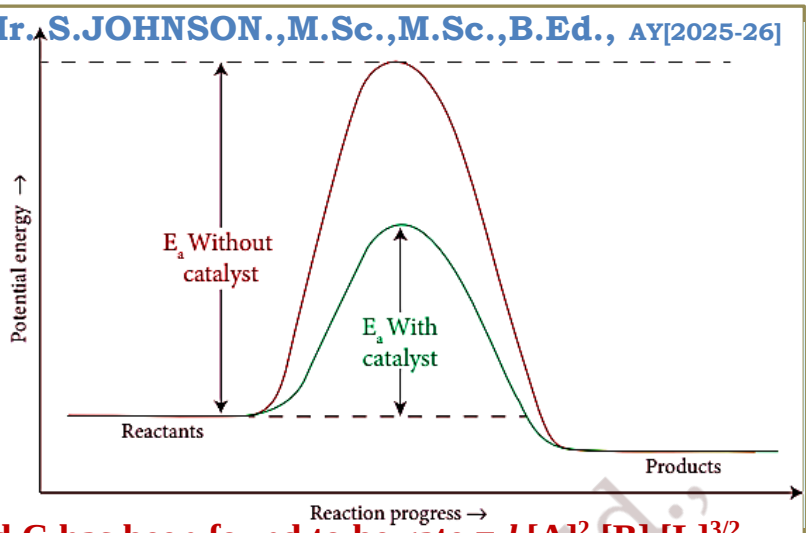
(b) The reaction $2NO + Br_2 \rightarrow 2NOBr$ is second order in NO and first order in Br_2.

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

9. Explain the effect of catalyst on reaction rate with an example. [SEP-20, QY24]

- A catalyst is substance which alters the rate of a reaction without itself undergoing any permanent chemical change.
- They may participate in the reaction, but again regenerated at the end of the reaction.

- 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.



$$2\,KClO_3(s) \xrightarrow{MnO_2} 2\,KCl(s) + 3\,O_2(g)$$

MnO_2 acts as a catalyst.

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 (i) Concentration of [L] is quadrupled (ii) Concentration of both [A] and [B] are doubled (iii) Concentration of [A] is halved (iv) Concentration of [A] is reduced to (1/3) and concentration of [L] is quadrupled.

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

(i) When [L] = [4L]

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

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

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

(ii) 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) When [A] = [A/2]

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

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

Comparing (1) and (4); rate is reduced to $\frac{1}{4}$ times.

(iv) 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 x 10^{-3} mol L^{-1} s^{-1} at 0.05 mol L^{-1} monomer concentration. Calculate the rate constant. [PTA-2]

For a second order reaction $k = \frac{R}{[A]^2}$

Where k = rate constant of reaction; R = rate of reaction;

[A] = concentration of reactant or products using equation

$$k = \frac{7.5 \times 10^{-3}}{(0.05)^2} = \frac{0.0075}{0.0025} = 3\ mol^{-1}\ L\ s^{-1}$$

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

Rate = k $[x]^{\left(\frac{3}{2}\right)}[y]^{\left(\frac{1}{2}\right)}$ Overall order = $\left(\frac{3}{2}+\frac{1}{2}\right)$ = 2

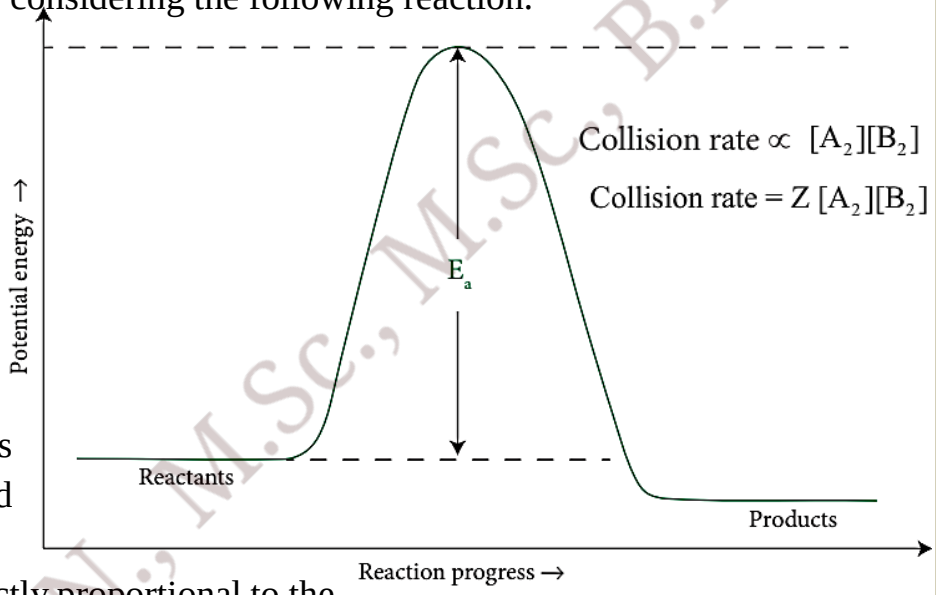
i.e., second order reaction. Since the rate expression does not contain the concentration of *z*, the reaction is zero order with respect to *z*.

13. Explain briefly the collision theory of bimolecular reactions. [QY-22, SRT-23, FRT-24,25]

- Collision 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.
- Let us understand this theory by considering the following reaction.

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

- If we consider that, the reaction between A_2 and B_2 molecules proceeds through collisions between them, then the rate would be proportional to the number of collisions per second.
- Rate ∝ number of molecules colliding per litre per second (collision rate)



- The number of collisions is directly proportional to the concentration of both A_2 and B_2.
- Where, Z is a constant. 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.
- Thus, if every collision resulted in reaction, the reaction would be complete in 10^{-9} second. In actual practice this does not happen.
- 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.
- The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.
- Fraction of effective collisions (*f*) is given by the following expression

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

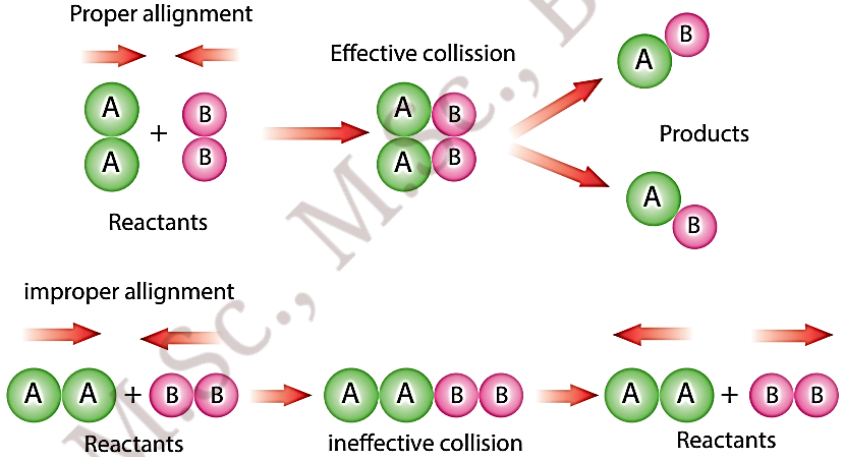
- To understand the magnitude of collision factor (f), Let us calculate the collision factor (f) for a reaction having activation energy of 100 kJ mol^{-1} at 300K.

$$f = e^{-\left(\frac{100\times10^{3}\,J\,mol^{-1}}{8.314\,J\,K^{-1}\,mol^{-1}\,\times\,300K}\right)}$$

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

- Thus, out of 10^{18} collisions only four collisions are sufficiently energetic to convert reactants to products.
- This fraction of collisions is further reduced due to orientation 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.
- The figure illustrates the importance of proper alignment of molecules which leads to reaction.

Orientation of reactants – schematic representation



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

$\Rightarrow$ Rate = p x f x collision rate

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

As per the rate law,

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

- Where k is rate constant on comparing equation (1) and (2), the rate constant k is

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

14. Write Arrhenius equation and explains the terms involved. [QY-19, QY-22, MAY-22, FUT-23, SRT,MAR-24]

The exact dependence of the rate of a chemical reaction on temperature is given by Arrhenius equation. $K = Ae^{-E_a/RT}$

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}.

$k = \frac{2.303}{t} log \frac{[A_0]}{[A]} = \frac{2.303}{1\,min} log \frac{[0.08]}{[0.04]}$ = 2.303 *log* 2 = 2.303 x 0.3010 = 0.6932 min^{-1}

$k = \left(\frac{0.6932}{60}\right) s^{-1}$ = **1.153 x 10^{-2} s^{-1}**

16. Give two (or) three examples for zero order reaction. [HY-19, QY-23, SRT-25]

- Photochemical reaction between H_2 and I_2

$H_2(g)+Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$

- Decomposition of N_2O on hot platinum surface

$N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2}O_2(g)$

- Iodination of acetone in acid medium is zero order with respect to iodine.

$CH_3COCH_3 + I_2 \xrightarrow{H^+} ICH_2COCH_3 + HI$

17.Explain pseudo first order reaction with an example. [QY-19, QY-23, MAR-25]

Kinetic study of a higher order reaction is difficult to follow, for example, in a study of a second order reaction involving two different reactants; the simultaneous measurement of change in the concentration of both the reactants is very difficult. To overcome such difficulties, 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. Let us consider the acid hydrolysis of an ester,

$$CH_3COOCH_3\ (aq) + H_2O\ (l) \xrightarrow{H^+} CH_3COOH\ (aq) + CH_3OH\ (aq)$$

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

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. Now, we can define $k\,[H_2O] = k'$; Therefore the above rate equation becomes

$$\text{Rate} = k'\,[CH_3COOCH_3]$$

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 $[A]^{1/2}$ $[B]^2$

(i) Since, Rusting of iron is a very slow reaction, it is difficult its rate.

Hence, it is difficult to write the rate law and difficult to predict the order of rusting of iron.

(ii) Radioactive disintegration of $_{92}U^{238}$ is a first order reaction.

All radio active reaction are first order reactions.

(iii) Order with respect to A = $\frac{1}{2}$ Order with respect to B = 2

Order of overall reaction = $\frac{1}{2} + 2 = \frac{3}{2}$

19.A gas phase reaction has energy of activation 200 kJ mol^{-1}. If the frequency factor of the reaction is 1.6 x 10^{13} s^{-1}. Calculate the rate constant at 600K. ($e^{-40.09}$ = 3.8 x 10^{-18})

$k = Ae^{-\left(\frac{Ea}{RT}\right)}$

k = 1.6 x 10^{13} s^{-1} $e^{-\left(\frac{200\times10^3\ J\ mol^{-1}}{8.314\ JK^{-1}\ mol^{-1}\times600K}\right)}$ = 1.6 x 10^{13} s^{-1} $e^{-(40.1)}$

k = 1.6 x 10^{13} s^{-1} x 3.8 x 10^{-18} **= 6.21 x 10^{-5} s^{-1}**

20.For the reaction 2x + y → L. Find the rate law from the following data.

[x] (M)	[y] (M)	Rate (M s^{-1})
0.2	0.02	0.15
0.4	0.02	0.30
0.4	0.08	1.20

Rate = $k[x]^n[y]^m$

$0.15 = k[0.2]^n[0.02]^m$ (1)

$0.30 = k[0.4]^n[0.02]^m$ (2)

$1.20 = k[0.4]^n[0.08]^m$ (3)

By dividing equation $\frac{(3)}{(2)}$

$$\frac{1.2}{0.3} = \frac{k[0.4]^n[0.08]^m}{k[0.4]^n[0.02]^m}$$

$$4 = \left(\frac{[0.08]}{[0.02]}\right)^m = (4)^m$$

$\therefore m = 1$

By dividing equation $\frac{(2)}{(1)}$

$$\frac{0.30}{0.15} = \frac{k[0.4]^n[0.02]^m}{k[0.2]^n[0.02]^m}$$

$$2 = \left(\frac{[0.4]}{[0.2]}\right)^n = (2)^n$$

$\therefore n = 1$

Rate $= k[x]'[y]'$

$0.15 = k[0.2]'[0.02]'$ $\quad \frac{0.15}{[0.2]'[0.02]'} = k$ $\quad$ **k = 37.5 mol $L^{-1}s^{-1}$**

21.How do concentrations of the reactant influence rate of reaction?

- The rate of a reaction increases with the increase in the concentration of the reactants.
- The effect of concentration is explained on the basis of collision theory of reaction rates.
- Higher the concentration, greater is the possibility for collision and hence the rate.
- According to this theory, the rate of a reaction depends upon the number of collisions between the reacting molecules.

22.How do nature of the reactant influence rate of reaction?

- The chemical reaction involves breaking of certain existing bonds of the reactant and forming new bonds which lead to the product.
- The net energy involved in this process is dependent on the nature of the reactant and hence the rates are different for different reactants.

Let us compare the following two reactions that you carried out in volumetric analysis.

- Redox reaction between ferrous ammonium sulphate (FAS) and $KMnO_4$
- Redox reaction between oxalic acid and $KMnO_4$
- The oxidation of oxalate ion by $KMnO_4$ is relatively slow compared to the reaction between $KMnO_4$ and Fe^{2+}. In fact heating is required for the reaction between $KMnO_4$ and Oxalate ion and is carried out at around 60°C.
- The physical state of the reactant also plays an important role to influence the rate of reactions. Gas phase reactions are faster as compared to the reactions involving solid or liquid reactants. For example, reaction of sodium metal with iodine vapours is faster than the reaction between solid sodium and solid iodine.

23.The rate constant for a first order reaction is 1.54 x 10^{-3} s^{-1}. Calculate its half life time. [PTA-6, SEP-20, MAR-25]

$t_{1/2} = 0.693 / k$ $\quad = 0.693 / (1.54 \times 10^{-3}\ sec^{-1})$ $\quad = 450$ 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, $k = \frac{0.6932}{t_{\frac{1}{2}}}$ $\quad k = \frac{0.6932}{8.0\ minutes} = 0.087\ min^{-1}$

For a first order reaction, $t = \frac{2.303}{0.087\ min^{-1}} \log\left(\frac{100}{1}\right)$ **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?

(i) Order of a reaction = 1; $t_{\frac{1}{2}}$ = 60 seconds; k = ?

We know that, $k = \frac{0.6932}{t_{\frac{1}{2}}}$ = **0.01155 s^{-1}**

(ii) $[A_0]$ = 100%; t = 180 s; k = 0.01155 s^{-1}; [A] = ?

For the first order reaction

$k = \frac{2.303}{t} log \frac{[A_0]}{[A]}$ $0.01155 = \frac{2.303}{180} log \frac{[A_0]}{[A]}$

$\frac{0.01155 \times 180}{2.303} = log \frac{100}{[A]}$ 0.9027 = log 100 – log [A]

log [A] = 2 – 0.9027 [A] = antilog of (1.0973) **= 12.5%**

After 180 second 12.5% of A will be left over.

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? [FRT-25]

Let A = 100M, $[A_0] - [A]$ = 20M,

For the zero order reaction

$K = \left(\frac{[A_0]-[A]}{t}\right) = \left(\frac{20M}{20\ min}\right)$ = 1M min^{-1}

Rate constant for a reaction = **1M min^{-1}**

To calculate the time for 80% of completion

k = 1M min-1, $[A_0]$ = 100M, $[A_0] - [A]$ = 80M, t = ?

Therefore,

$t = \left(\frac{[A_0]-[A]}{t}\right) = \left(\frac{80M}{1\ M\ min^{-1}}\right)$ = **80 min.**

27. The activation energy of a reaction 22.5 k Cal mol^{-1} and the value of rate constant at 40°C is 1.8 x 10^{-5} s^{-1}. Calculate the frequency factor, A.

Here, we are given that

Ea = 22.5kcal mol^{-1} = 22500 cal mol^{-1}, T = 40°C = 40 + 273 = 313K, k = 1.8 x 10^{-5} sec^{-1}

Substituting the values in the equation.

$\log A = \log k + \left(\frac{E_a}{2.303RT}\right)$ $= \log (1.8 \times 10^{-5}) + \left(\frac{22500}{2.303 \times 1.987 \times 313}\right)$

log A = log (1.8)(-5) + (15.7089) = 10.9642

A = antilog (10.9642) = **9.208 x 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 10g 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 follow the first order kinetics. What is the value of the rate constant?

For a first order reaction $k = \frac{2.303}{t} log \frac{[A_0]}{[A]}$ $= \frac{2.303}{t} log \frac{V_\infty}{V_\infty - V_t}$

In the present case, V_∞ = 58.3 ml.

The value of *k* at different time can be calculated as follows.

t (min)	V_t	$V_\infty - V_t$	$\frac{2.303}{t} log \frac{[A_0]}{[A]}$
6	19.3	58.3 – 19.3 = 39.0	$k = \frac{2.303}{6} log \left(\frac{58.3}{39}\right) = 0.0670\ min^{-1}$
12	32.6	58.3 – 32.6 = 25.7	$k = \frac{2.303}{12} log \left(\frac{58.3}{25.7}\right) = 0.0683\ min^{-1}$
18	41.3	58.3 – 41.3 = 17.0	$k = \frac{2.303}{18} log \left(\frac{58.3}{17}\right) = 0.0685\ min^{-1}$
24	46.5	58.3 – 46.5 = 11.8	$k = \frac{2.303}{24} log \left(\frac{58.3}{11.8}\right) = 0.0666\ min^{-1}$

Since *k* values are nearly constant, the reaction follows first order kinetics. The mean value of k = 0.0676 min^{-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 KMnO4 solution required for titrating the same volume of the reaction mixture.

$k = \frac{2.303}{t} log \frac{[A_0]}{[A]}$ $\quad\quad$ $k = \frac{2.303}{24} log \left(\frac{V_0}{V_t}\right)$

In the present case, V_0 = 46.1 ml.

The value of k at each instant can be calculated as follows:

t (min)	Vt	$k = \frac{2.303}{24} log \left(\frac{V_0}{V_t}\right)$
10	29.8	$k = \frac{2.303}{10} log \left(\frac{46.1}{29.8}\right) = 0.0436\ min^{-1}$
20	19.3	$k = \frac{2.303}{20} log \left(\frac{46.1}{19.3}\right) = 0.0435\ min^{-1}$

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? [GMQ-19]

For the first order reaction $k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$

Assume, $[A_0]$ = 100%, t = 50 minutes

Therefore, [A] = 100 – 40 = 60

$k = \frac{2.303}{50} log \left(\frac{100}{60}\right) = 0.010216\ min^{-1}$

Hence the value of the rate constant is **0.010216 min^{-1}**

t=?, when the reaction is 80% completed, [A] = 100 – 80 = 20%

from above, *k* = 0.010216 min^{-1}

$t = \frac{2.303}{0.010216} log \left(\frac{100}{20}\right) = 157.58\ min$

The time at which the reaction will be 80% complete is **157.58 min.**

Evaluate Yourself

1. Write the rate expression for the following reactions, assuming them as elementary reactions. (i) $3A + 5B_2 \rightarrow 4CD$ (ii) $X_2 + Y_2 \rightarrow 2XY$

(i) Rate = $k\,[A]^3[B_2]^5$ (ii) Rate = $k\,[X_2][Y_2]$

2. Consider the decomposition of $N_2O_{5(g)}$ to form $NO_{2(g)}$ and $O_{2(g)}$. At a particular instant, N_2O_5 disappears at a rate of 2.5 x 10^{-2} mol dm^{-3} s^{-1}. At what rates are NO_2 and O_2 formed? What is the rate of the reaction?

$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$ from the stoichiometry of the reaction.

$\frac{d[N_2O_5]}{dt}$ = 2.5 x 10^{-2} mol dm^{-3} s^{-1}

$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = 2\left(-\frac{d[N_2O_5]}{dt}\right)$ = 2 x 2.5 x 10^{-2} = **5 x 10^{-2} mol dm^{-3} s^{-1}**

$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{d[O_2]}{dt} = \frac{1}{2}\left(-\frac{d[N_2O_5]}{dt}\right) = \frac{1}{2}$ x 2.5 x 10^{-2} = **1.25 x 10^{-2} mol dm^{-3} s^{-1}**

3. For a reaction, X + Y → Product quadrupling [x], increases the rate by a factor of 8. Quadrupling both [x] and [y] increases the rate by a factor of 16. Find the order of the reaction with respect to x and y. what is the overall order of the reaction?

X + Y → Product

Rate law is Rate = k $[X]^m[Y]^n$ = 1 (1)

Quadrupling [X] ie [4X], Rate = 8

k $[4X]^m[Y]^n$ = 8

k$4^m[X]^m[Y]^n$ = 8 (2)

Quadrupling [X] and [Y] ie [4X] and [4Y], Rate = 16

k $[4X]^m[4Y]^n$ = 16

k$4^m[X]^m4^n[Y]^n$ = 16 (3)

Dividing (2) by (1)

$\frac{k4^m[X]^m[Y]^n}{k[X]^m[Y]^n} = \frac{8}{1}$ $\therefore 4^m = 8$

$(2^2)^m = 2^3$ $2m = 3$ $m = \frac{3}{2} = 1.5$

$\therefore$ Order of the reaction w.r.t X is 1.5

Dividing (3) by (2)

$\frac{k4^m[X]^m4^n[Y]^n}{k4^m[X]^m[Y]^n} = \frac{16}{8}$ $\therefore 4^n = 2$

$(2^2)^n = 2^1$ $2n = 1$ $n = \frac{1}{2} = 0.5$

$\therefore$ Order of the reaction w.r.t Y is 0.5

Overall order of the reaction = m + n = 1.5 + 0.5 = **2**

4. Find the individual and overall order of the following reaction using the given data.

$2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$

Experiment Number	Initial concentration		Initial rate
	NO	Cl_2	NOCl mol L^{-1} s^{-1}
1	0.1	0.1	7.8 x 10^{-5}
2	0.2	0.1	3.12 x 10^{-4}
3	0.2	0.3	9.36 x 10^{-4}

For experiment 1, the rate law is, Rate 1 = k $[NO]^m$ $[CI_2]^n$

7.8 x 10^{-5} = k $[0.1]^m$ $[0.1]^n$……..(1)

For experiment 2, the rate law is, Rate 2 = k $[NO]^m$ $[CI_2]^n$

3.12 x 10^{-4} = k $[O.2]^m$ $[0.1]^n$……...(2)

For experiment 3, the rate law is, Rate 3 = k $[NO]^m$ $[CI_2]^n$

9.36 x 10^{-4} = k $[O.2]^m$ $[0.3]^n$……..……(3)

Dividing (2) by (1)

$\frac{3.12\times10^{-4}}{7.8\times10^{-5}} = \frac{k[0.2]^m[0.1]^n}{k[0.1]^m[0.1]^n}$ $\quad 4 = \left(\frac{0.2}{0.1}\right)^m$ $\quad 4 = 2^m$

$\therefore 2^2 = 2^m$ $\quad \therefore \mathbf{m = 2}$

Order w.r.t NO is 2. Dividing (3) by (2)

$\frac{9.36\times10^{-4}}{3.12\times10^{-4}} = \frac{k[0.2]^m[0.3]^n}{k[0.2]^m[0.1]^n}$ $\quad 3 = \left(\frac{0.3}{0.1}\right)^n$ $\quad 3 = 3^n$

$\therefore 3^1 = 3^n$ $\quad \therefore \mathbf{n = 1}$

Order w.r.t Cl_2 is 1. Overall order of the reaction = m + n = 2 + 1 = **3**

5. In a first order reaction A → products, 60% of the given sample of A decomposes in 40 min. what is the half life of the reaction?

$k = \frac{\mathbf{2.303}}{\boldsymbol{t}} \log \frac{[\boldsymbol{A_0}]}{[\boldsymbol{A}]} = \frac{\mathbf{2.303}}{\mathbf{40}} \log \frac{[100]}{[\mathbf{40}]} = \frac{\mathbf{2.303}}{\mathbf{40}} \log 2.5 = \frac{\mathbf{2.303}}{\mathbf{40}} \times 0.3979 = \mathbf{0.0229\ min^{-1}}$

$t_{\frac{1}{2}} = \frac{0.6932}{k} = \frac{0.6932}{0.0229} = \mathbf{30.27\ min}$

6. The rate constant for a first-order reaction is 2.3 x 10^{-4} s^{-1}. If the initial concentration of the reactant is 0.01 M. what concentration will remain after 1 hour?

Rate constant of a first order reaction k = 2.3 x 10^{-4} s^{-1}

Initial concentration of the reactant $[A_0]$ = 0.01 M

Concentration will remain after 1 hour [A] =7

$k = \frac{\mathbf{2.303}}{\boldsymbol{t}} \log \frac{[\boldsymbol{A_0}]}{[\boldsymbol{A}]}$ $\quad 2.3 \times 10^{-4} = \frac{\mathbf{2.303}}{\mathbf{1\ hour}} \log \frac{[0.01]}{[\boldsymbol{A}]}$

$\frac{2.3\times10^{-4}\times1}{2.303} = \log[0.01] - \log[A]$

$9.986 \times 10^{-5} = -2 - \log[A]$

$11.986 \times 10^{-5} = -\log[A]$

$[A] = \text{antilog}(-11.986 \times 10^{-5}) = \mathbf{0.997\ M}$

7. Hydrolysis of an ester in an aqueous solution was studied by titrating the liberated carboxylic acid against sodium hydroxide solution. The concentrations of the ester at different time intervals are given below.

Time (min)	0	30	60	90
Ester concentration mol L^{-1}	0.85	0.80	0.754	0.71

Show that, the reaction follows first order kinetics.

$k = \frac{\mathbf{2.303}}{\boldsymbol{t}} \log \frac{[\boldsymbol{A_0}]}{[\boldsymbol{A}]}$

$k_1 = \frac{\mathbf{2.303}}{\mathbf{30}} \log \frac{0.85}{0.80} = \frac{\mathbf{2.303}}{\mathbf{30}} \log 1.0625 = \frac{\mathbf{2.303}}{\mathbf{30}} \times 0.0263 = 2.01 \times 10^{-3}\ min^{-1}$

$k_2 = \frac{\mathbf{2.303}}{\mathbf{60}} \log \frac{0.85}{0.754} = \frac{\mathbf{2.303}}{\mathbf{60}} \log 1.127 = \frac{\mathbf{2.303}}{\mathbf{60}} \times 0.0519 = 1.992 \times 10^{-3}\ min^{-1}$

$k_3 = \frac{\mathbf{2.303}}{\mathbf{90}} \log \frac{0.85}{0.71} = \frac{\mathbf{2.303}}{\mathbf{90}} \log 1.197 = \frac{\mathbf{2.303}}{\mathbf{90}} \times 0.0781 = 2 \times 10^{-3}\ min^{-1}$

Since all the *k* values are constants, the reaction follows first order kinetics.

8. For a first-order reaction the rate constant at 500K is 8 x 10^{-4} s^{-1}. Calculate the frequency factor, if the energy of activation for the reaction is 190 kJ mol^{-1}.

k = 8 x 10^{-4} s^{-1}; T = 500K; Ea = 190 kJ mol^{-1}; A = ?

According to Arrhenius equation, $k = Ae^{\frac{-Ea}{RT}}$ $\quad \log k = \log A - \frac{Ea}{2.303\ RT}$

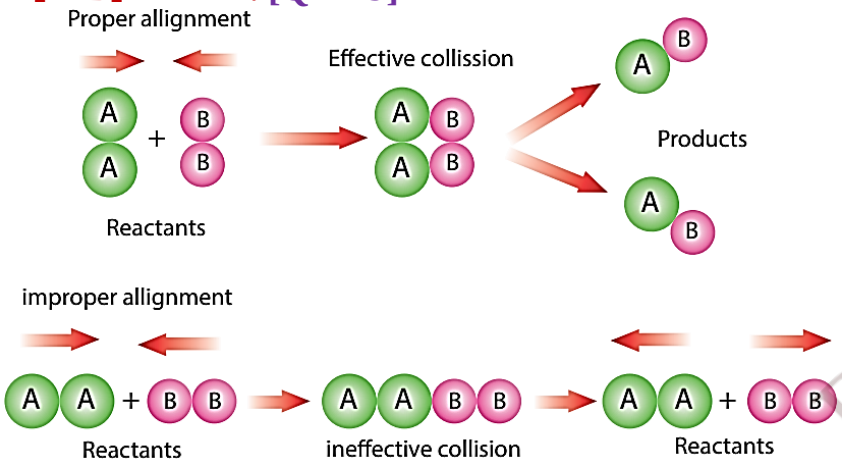
$\log A = \log k + \frac{Ea}{2.303\ RT} = \log(8 \times 10^{-4}\ s^{-1}) + \left(\frac{190\times10^3\ J\ mol^{-1}}{2.303\times8.314\ JK^{-1}\ mol^{-1}\times500\ K}\right)$

$\log A = -3.096 + 19.8463 = 16.7493$

$A = \text{Antilog}(16.7493) = \mathbf{5.6 \times 10^{16}\ s^{-1}}$ (approximately)

GOVERNMENT EXAM QUESTION PAPER

1. Give the schematic representation of proper and improper alignment of reactant for a general reaction $A_2 + B_2 \rightarrow 2AB$. [QY-19]



2. Give examples for the first order reaction. [MAY-22, SRT,HY-24]

(i) Decomposition of dinitrogen pentoxide $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

(ii) Decomposition of sulphurylchloride; $SO_2Cl_2(l) \longrightarrow SO_2(g) + Cl_2(g)$

(iii) Decomposition of the H_2O_2 in aqueous solution; $H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$

(iv) Isomerisation of cyclopropane to propene.

3. The rate of reaction $x + 2y \rightarrow$ product is 4×10^{-3} mol L^{-1} s^{-1}, if [x] = [y] = 0.2 M and rate constant at 400K is $2 \times 10^{-2} s^{-1}$, what is the overall order of the reaction? [SEP-20]

Rate = $k[x]^n[y]^m$ $\quad 4 \times 10^{-3}$ mol L^{-1} $s^{-1} = 2 \times 10^{-2} s^{-1} (0.2 \text{ mol } L^{-1})^n (0.2 \text{ mol } L^{-1})^m$

$\frac{4 \times 10^{-3} \, mol \, L^{-1} \, s^{-1}}{2 \times 10^{-2} \, s^{-1}} = (0.2)^n (0.2)^m$ $\quad (0.2 \text{ mol } L^{-1}) = (0.2)^{n+m}$

Compare the powers on both sides, we get n + m = 1. ∴ The overall order of the reaction is **1.**

4. Show that for a first order reaction the time required for 99.9% completion is about 10 times its half life period. [QY-19, QY-23,24, SRT25]

Let

$[A_0] = 100$;

when $t = t_{99.9\%}$; $[A] = (100 - 99.9) = 0.1$

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

$$t_{99.9\%} = \frac{2.303}{k} \log\left(\frac{100}{0.1}\right)$$

$$t_{99.9\%} = \frac{2.303}{k} \log 1000$$

$$t_{99.9\%} = \frac{2.303}{k} (3)$$

$$t_{99.9\%} = \frac{6.909}{k}$$

$$t_{99.9\%} \simeq 10 \times \frac{0.69}{k}$$

$$t_{99.9\%} \simeq 10 \, t_{1/2}$$

5. Write the differences between rate & rate constant of a reaction. [PTA3,AUG21,HY24]

S. NO.	RATE OF A REACTION	RATE CONSTANT OF A REACTION
1	It is measured as decrease in the concentration of the reactants or increase in the concentration of products.	It is equal to the rate of reaction, when the concentration of each of the reactants is unity

2	It depends on the initial concentration of reactants.	It does not depend on the initial concentration of reactants.
3	It generally decreases with the progress of reaction	It does not depend on the progress of reaction
4	Its unit is mol $L^{-1}cm^{-1}$.	It changes according to order of reaction.

6. What is an order of a reaction? [MAR-24]

Order of a reaction is the sum of the powers of concentration terms involved in the experimentally determined rate law. It can be zero (or) fractional (or) integer values. It is assigned for a overall reaction.

7. Mention the factors that affected the rate of chemical reaction. [QY-23]

The rate of a reaction is affected by the following factors,

- Nature and state of the reactant
- Concentration of the reactant
- Surface area of the reactant
- Presence of a catalyst

8. Define the following terms. a) Rate b) Rate law [FUT24, FRT-25]

a) Rate: A rate is a change in a particular variable per unit time. Similarly in a chemical reaction, the change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction.

Let us consider a simple general reaction $A \rightarrow B$

$$\text{Rate} = \frac{-[Change\ in\ the\ concentration\ of\ the\ reactent]}{Change\ in\ time}$$

b) 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 equation.

$xA + yB \rightarrow$ products

$\text{Rate} = k[A]^m[B]^n$ k = Rate constant