STANDAR XII

CHEMISTRYQUESTION BANK
2019-20
(BASED ON NEW SYLLABUS)

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UNIT – 1 METALLURGY

I. Text Book Questions and Answers

1. What is the difference between minerals and ores?

SNo.	Minerals	Ores
1	Naturally occurring substances obtained by mining which contain the metals in free state or in the form of compounds like oxides, sulphides, etc. are called minerals.	Minerals that contain high percentage of metal from which it can be extracted conveniently and economically are called ores.
2	All the minerals are not ores	All the ores are minerals
3	Mineral of Al is Bauxite ($Al_2O_3\ nH_2O$) and China clay ($Al_2O_3\ SiO_2\ .2H_2O$)	Ore of Al is Bauxite ($Al_2O_3\ nH_2O$)

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

Steps involved in extraction of pure metals from their ores are

i) Concentration of the ore

ii) Extraction of the crude metal.

iii) Refining of the crude metal.

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

Lime stone (CaO_3) is used as a basic flux in the extraction of iron from its oxide Fe_2O_3. Limestone decomposes to form CaO

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

Impurity silica (SiO_2)react with CaOform fusible slagcalcium silicate.

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

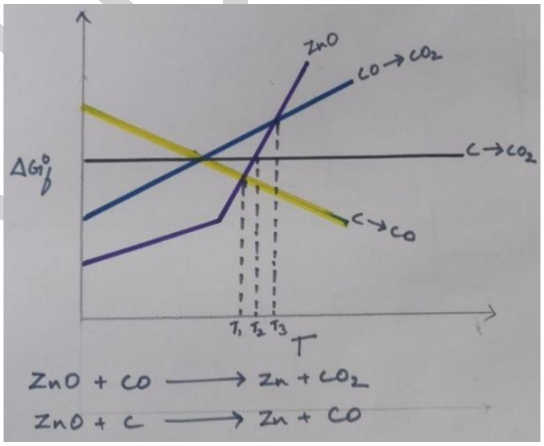
Flux Gaugue Slag

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

Sulphide ores can be concentrated by froth flotation method.

(eg) Galena (PbS), Zinc blende (ZnS)

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



Out of coke and CO, coke is better reducing agent than CO for the reduction of ZnO.

$$ZnO_{(s)} + C \rightarrow Zn_{(s)} + CO_{(g)}\uparrow$$

- In Ellingham diagram formation ZnO line lies above the formation C→CO at low temperature (T_1), ZnO line also lies above the CO → CO_2 but at high temperature.

- Hence carbon can be used as a better reducing agent than CO for the reduction of ZnO. Below the temperature T_1 both Coke and COcannot reduce ZnO

6. Describe a method for refining nickel.

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

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

On heating nickel tetra carbonyl around 460K, decomposes to give pure nickel.

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

7. Explain zone refining process with an example

The principle is fractional crystallisation.

- When an impure metal is melted and allowed to solidify, the impurities will prefer to remain in the molten region. 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 crystallises 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 semiconductor are refined by this process.

8. Using the Ellingham diagram given below.

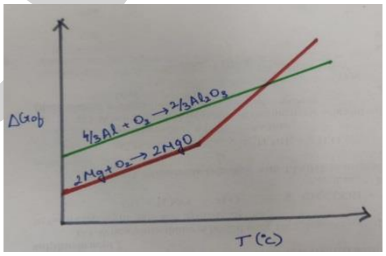
(A) Predict the conditions under which

i) Aluminium might be expected to reduce magnesia.

ii) Magnesium could alumina.

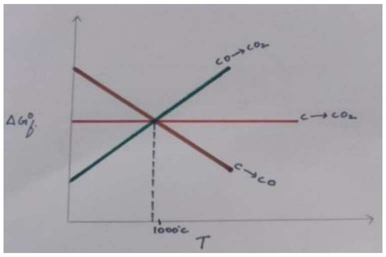
B) Carbon monoxide is more effective reducing agent than carbon below 983K but, above this temperature, the reverse is true - Explain.

C) It is possible to reduce Fe_2O_3 by coke at a temperature around 1200K



A) i) Ellingham diagram for the formation of Al_2O_3 and MgO intersects around 1600K. Above this temperature aluminium line 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)The two lines for $CO \rightarrow CO_2$ and $C \rightarrow CO$ cross at about 983K. Below this temperature the reaction to form CO_2 is energetically more favourable hence CO is more effective reducing agent than carbon. But above 983K the formation of CO is preferred, hence carbon is more effective reducing agent than CO above this temperature.

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

9. Give uses of zinc.

1. Metallic zinc is used in galvanisation to protect iron and steel structures from rusting and corrosion.
2. Zinc is used to produce die - castings in the automobile, electrical and hardware industries.
3. Zinc oxide is used in the manufacture of paints, rubber, cosmetics, pharmaceuticals, plastics, inks, batteries, textiles and electrical equipment.
4. Zinc sulphide is used in making luminous paints, fluorescent lights and x - ray screens.
5. Brass an alloy of zinc is used in water valves and communication equipment as it is highly resistant to corrosion

10. Explain the electrometallurgy of aluminium.

Hall – Herold Process
Cathode: Iron tanked lined with carbon
Anode: Carbon blocks
Electrolyte: 20% solution of alumina obtained from bauxite + Molten Cryolite + 10% calcium chloride (lowers the melting point of the mixture)
Temperature: Above 1270K
Ionisation of Alumina $Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}$
Reaction at cathode: $2Al^{3+}(melt) + 6e^- \rightarrow 2Al_{(l)}$
Reaction at anode: $6O^{2-}(melt) \rightarrow 3O_2 + 12e^-$
Since carbon acts as anode the following reaction also takes place on it.
$C_{(s)} + O^{2-}(melt) \rightarrow CO + 2e^-$
$C_{(s)} + 2O^{2-}(melt) \rightarrow CO_2 + 4e^-$
During electrolysis anodes are slowly consumed due to the above two reactions. Pure aluminium is formed at the cathode and settles at the bottom.
Net electrolysis reaction is
$4Al^{3+}(melt) + 6O^{2-}(melt) + 3C_{(s)} \rightarrow 4Al_{(l)} + 3CO_{2(g)}$

11. Explain the following terms with suitable examples. i) Gangue ii) Slag

i) Gangue:
The non metallic impurities, rocky materials and siliceous matter present in the ores are called gangue. (eg): SiO_2 is the gangue present in the iron ore Fe_2O_3 .

ii) Slag: Slag is a fusible chemical substance formed by the reaction of gangue with a flux.

$$\underset{\text{Flux}}{CaO_{(s)}} + \underset{\text{gangue}}{SiO_{2(s)}} \rightarrow \underset{\text{slag}}{CaSiO_{3(s)}}$$

12. Give the basic requirement for vapour phase refining.

The metal is treated with a suitable reagent to form a volatile compound.

Then the volatile compound is decomposed to give the pure metal at high temperature.

13. Describe the role of the following in the process mentioned.
i) Silica in the extraction of copper.
ii) Cryolite in the extraction of aluminium.
iii) Iodine in the refining of Zirconium.
iv) Sodium cyanide in froth floatation.

i) In the extraction of copper, silica acts as an acidic flux to remove FeO as slag $FeSiO_3$.

$$\underset{}{FeO_{(s)}} + \underset{\text{Flux}}{SiO_{2(s)}} \rightarrow \underset{\text{Slag}}{FeSiO_{3(s)}}$$

ii) As Al_2O_3 is a poor conductor, cryolite improves the electrical conductivity.
In addition, cryolite serves as an added impurity and lowers the melting point of the electrolyte.

iii) First Iodine forms a Volatile tetraiodide with impure metal, which decomposes to give pure metal. Impure zirconium metal is heated in an evacuated vessel with iodine to form the volatile zirconium tetraiodide (ZrI_4). The impurities are left behind, as they do not react with iodine.

$$Zr_{(s)} + 2I_{2(s)} \rightarrow ZrI_{4(Vapour)}$$

On passing volatile zirconium tetraiodide vapour over a tungsten filament, it is decomposed to give pure zirconium.

$$ZrI_{4(Vapour)} \rightarrow Zr_{(s)} + 2I_{2(s)}$$

iv) Sodium cyanide acts as a depressing agent in froth floatation process. When a sulphide ore of a metal contains other metal sulphides, the depressing agent sodium cyanide selectively prevent other metal sulphides coming to the froth. eg: NaCN depresses the floatation property ZnS present in Galena (PbS) by forming a layer of Zinc complex $Na_2\,[Zn(CN)_4]$on the surface of Zinc sulphide.

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

Crude metal is refined by electrolysis carried out in an electrolytic cell.
Cathode: Thin strips of pure metal.
Anode: Impure metal to be refined.
Electrolyte: Aqueous solution of the salt of the metal with dilute acid.
As current is passed, the metal of interest dissolves from the anode and pass into the electrolytic solution.
At the same time same amount of metal ions from the electrolytic solution will be deposited at the cathode.
Less electro positive impurities in the anode settle down as anode mud.
eg : Electro refining of silver:
Cathode: Pure silver
Anode: Impure silver rods.
Electrolyte: Acidified aqueous solution of silver nitrate.
When current passed, the following reactions will take place.
Reaction at anode: $Ag_{(s)} \rightarrow Ag^+_{(aq)} + e^-$
Reaction at cathode: $Ag^+_{(aq)} + e^- \rightarrow Ag(s)$
At anode silver atoms lose electrons and enter the solution. From the solution, silver ions (Ag^+)migrate towards the cathode. At cathode silver ions get discharged by gaining electrons and deposited on the cathode.

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

- A suitable reducing agent is selected based on the thermodynamic considerations.
- For a spontaneous reaction ΔG should be negative.

- Thermodynamically, the reduction of metal oxide with a given reducing agent can occur if ΔG for the coupled reaction is negative.
- Hence the reducing agent is selected in such a way that it provides a large negative ΔG value for the coupled reaction.
- Ellingham diagram is used to predict thremodynamic feasibility of reduction of oxides of one metal by another metal.
- Any metal can reduce the oxides of other metals that are located above it in the diagram.
- Ellingham diagram for the formation of FeO and CO intersects around 1000K. Below this temperature the carbon line lies above the iron line.
- Hence FeO is more stable than CO and the reduction is not thermodynamically feasible.
- However above 1000K carbon line lies below the iron line. Hence at this condition FeO is less stable than CO and the reduction is thermodynamically feasible. So coke can be used as a reducing agent above this temperature.
- Following free energy calculation also confirm that the reduction is thermodynamically favoured.

From the Ellingham diagram at 1500K

$2Fe_{(s)}+O_{2(g)}\rightarrow 2FeO_{(g)} \quad \Delta G_1 = -350\ kJmol^{-1}$ 1

$2C_{(s)} + O_{2(g)}\rightarrow 2CO_{(g)} \quad \Delta G_2 = -480\ kJmol^{-1}$ 2

Reverse the reaction 1

$2FeO_{(s)}\rightarrow 2Fe_{(s)} + O_{2(g)}\Delta G_1 = 350\ kJmol^{-1}$ 3

Couple the reactions 2 and 3

$2FeO_{(s)}+2C_{(s)}\rightarrow 2Fe_{(s)} + 2CO_{(g)}\Delta G_3 = -130\ kJmol^{-1}$ 4

- The standard free energy change for the reduction of one mole of FeO is

  $\frac{\Delta G_3}{2} = -65\ Jmol^{-1}$

16. **Give the limitations of Ellingham diagram.**

Ellingham diagram is constructed based only on thermodynamic considerations.

1. It gives information about the thermodynamic feasibility of a reaction.
2. It does not tell anything about the rate of the reaction.
3. More over it does not give any idea about the possibility of other reactions that might be taking place.
4. The interpretation of ΔG is based on the assumption that the reactants are in equilibrium with the product which is not always true.

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

- 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 method the metal salts are taken in fused form or in solution form.
- The metal ion present can be reduced by treating the solution with suitable reducing agent or by electrolysis.
- Gibbs free energy change for the electrolysis is

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

  n = number of electrons involved in the reduction

  F = Faraday = 96500 coulombs

  E^o = electrode potential of the redox couple.
- If E^o is positive, ΔG^o is negative and the reduction is spontaneous.
- Hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive.

- A more reactive metal displaces a less reactive metal from its salt solution.
  eg: $Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$
- Zinc is more reactive than copper and displaces copper from its salt solution.

II. 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.

In the metallurgy of silver metal is leached with a dilute solution of NaCN in the presence of air (O_2)

$4Ag + 8CN^- + 2H_2O + O_2 \rightarrow 4[Ag(CN)_2] + 4OH^-$

In this reaction, $Ag \rightarrow Ag^+$ oxidation number of Ag increases from 0 to +1, hence oxidation

$O_2 \rightarrow OH^-$ (oxidation number of oxygen decreases from 0 to -2, hence reduction)

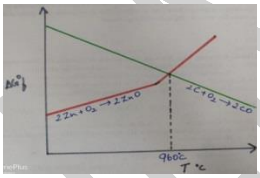
Hence Leaching of silver is a redox reaction.

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

Magnesite (Magnesium carbonate) is heated in the absence of oxygen decomposes to form Magnesium oxide (Magnesia)

$MgCO_3 \rightarrow MgO + CO_2\uparrow$

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 1233K Below this temperature, 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 1233K carbon line lies below the zinc line, hence carbon can be used as a reducing agent above 1233K.

$2Zn + O_2 \rightarrow 2ZnO$ 1

$2C + O_2 \rightarrow 2CO$ 2

Reversing 1 and adding with equation 2

$2ZnO \rightarrow 2Zn + O_2$

$2C + O_2 \rightarrow 2CO$

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

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.

Sodium metal is prepared by Down's process. This involves the electrolysis of fused NaCland $CaCl_2$ at 873K During electrolysis sodium is discharged at the cathode and Cl_2 is obtained at the anode.

$NaCl_{(l)} \rightarrow Na^+_{(melt)} + Cl^-_{(melt)}$

Cathode: $Na^+_{(melt} + e^- \rightarrow Na_{(s)}$

Anode: $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$

If an aqueous solution of NaCl is electrolysed, H_2 is evolved at cathode and Cl_2 is evolved at anode. NaOH is obtained in the solution..

$NaCl_{(aq)} \xrightarrow{\text{Electrolysis}} Na^+_{(aq)} + Cl^-_{(aq)}$

Cathode: $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

$$\text{Anode: } Cl^{-}_{(aq)} \rightarrow \frac{1}{2} Cl_{2(g)} + 2e^{-}$$

Na^{+} and OH^{-} ions to form NaOH .

Hence solution is basic in nature.

IV. ADDITIONAL QUESTIONS AND ANSWERS

1. What is concentration of ores?

The removal of non-metallic impurities, rocky materials and siliceous matter (called as gangue) from the ores is known as concentration of ores.

2. What is leaching?

In this method crushed ore is allowed to dissolve in a suitable solvent to form a soluble metal salt or complex leaving the gangue undissolved is called leaching.

3. What is ammonia leaching?

Crushed ore containing nickel, copper and cobalt is treated with aqueous ammonia under suitable pressure.

Ammonia selectively leaches these metals by forming their soluble complexes namely $[Ni(NH_3)_6]^{2+}$, $[Cu(NH_3)_4]^{2+}$ and $[Co(NH_3)_5H_2O]^{3+}$ from the ore.

The gangue left behind are iron (III) oxides / hydroxides and alumino silicate.

4. What is acid leaching?

Sulphide ores ZnS, PbS can be leached with hot aqueous sulphuric acid.

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

$$2ZnS_{(s)} + 2H_2SO_{4(aq)} + O_{2(g)} \rightarrow 2ZnSO_{4(aq)} + 2S_{(s)} + 2H_2O$$

5. What are the steps involved in the extraction of crude metal?

1.Conversion of the ore into metal oxide either by roasting or calcination.

2.Reduction of the metal oxide into metal.

6. In the extraction of metal, ore is first converted into metal oxide before reduction into metal. Why?

- In the concentrated ore the metal exists in positive oxidation state and hence it is to be reduced to elemental state.
- From the principles of thermodynamics, the reduction of oxide is easier compared to the reduction of other compounds of metal.
- Hence before reduction the ore is first converted into metal oxide.

7. Write about the extraction of metal by the process of reduction by hydrogen.

This method can be applied to the oxides of the metals (Fe, Pb, Cu) which are less electropositive than hydrogen.

$$Ag_2O_{(s)} + H_{2(g)} \rightarrow Ag_{(s)} + H_2O_{(l)}\uparrow$$

Nickel oxide is reduced to nickel by a mixture of hydrogen and carbon monoxide(water gas)

$$2NiO_{(s)} + CO_{(g)} + H_{2(g)} \rightarrow 2Ni_{(s)} + CO_{2(g)} + H_2O_{(l)}\uparrow$$

8. What is auto reduction of metallic ores?

Simple roasting of some of the metallic ores give the crude metal.

Use of reducing agent is not necessary because of low thermal stability

(eg) Cinnabar is roasted to give mercury.

$$HgS_{(s)} + O_{2(g)} \rightarrow Hg_{(l)} + SO_{2(g)}\uparrow$$

9. Write the applications of copper.

1. Copper is the first metal used by humans and extended use of its alloy bronze resulted in a new era, 'Bronze age'.

2.Used for making coins and ornaments along with gold and other metals.

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

10. Write the applications of gold.

1.Gold is one of the expensive and precious metals.

2.Used for coinage and has been used as standard for monetary systems in some countries.
3.Extensively used in jewellery in its alloy form with copper.
4. Used in electroplating to cover other metals with a thin layer of gold, which are used in watches, artificial limb joints, cheap jewellery, dental fillings and electrical connectors.
5.Gold nanoparticles are used for increasing the efficiency of solar cells.
6.Used as a catalyst.

11. Write about alumino thermite process.

- In this method a metal oxide such as Cr_2O_3 is reduced to metal by aluminium.
- Metal oxide (Cr_2O_3) is mixed with aluminium powder in a fire clay crucible.The reduction process is initiated by ignition mixture of Magnesium power and barium peroxide.

$$BaO_2 + Mg \rightarrow BaO + MgO$$

- It is an exothermic process where heat is liberated.
- Temperature = 2400°C Heat liberated = $852 kJmol^{-1}$.This heat initiate the reduction of Cr_2O_3 by Al.

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

12. What is refining process of a metal?

Metals extracted from its ore contains impurities such as unreacted oxide ore, other metals, non metals etc,. Removal of such impurities from crude metal is known as refining process of a metal.

13. Write about distillation process of refining a metal?

This method is used for low boiling volatile metals like zinc and mercury. In this method impure metal is heated to evaporate and the vapours are condensed to get pure metal.

14. Write about liquation process of refining a metal?

- This method is used to remove the impurities with high melting points from metals having relatively low melting points.(eg) Tin, lead, mercury, bismuth.
- The impure metal is placed on sloping hearth of a reverberatory furnace and it is heated just above the melting point of the metal in the absence of air, the molten metal flows down and impurities are left behind .The molten metal is collected and solidified.

15. Give example for the following

1. Frothing agent 2. Collector 3. Depressing agent

Frothing agent **:**Pine oil , eucalyptus oil
Collector **:**Sodium ethyl xanthate
Depressing agent **:**Sodium cyanide , sodium carbonate

16. What is cementation ?

Gold can be recovered by reacting the deoxygenated leached solution with Zinc. In this process Gold is reduced to its elemental state (zero oxidation state) and the process is called cementation

$$Zn_{(S)} + 2[Au(CN)_2]^{-}_{(aq)} \rightarrow [Zn(CN)_4]^{2-}_{(aq)} + 2Au_{(S)}$$

17. Why Fe, Pb , Cu are reduced by hydrogen ?

The oxides of metal Fe ,Pb , Cu having less electropositive character than hydrogen , these metal oxide can be reduced by hydrogen.

$$Ag_2O_{(S)} + H_{2(g)} \rightarrow Ag_{(S)} + H_2O_{(l)}\uparrow$$

$$Fe_2O_{3(S)} + 4H_{2(g)} \rightarrow 4Fe_{(S)} + 4H_2O_{(l)}\uparrow$$

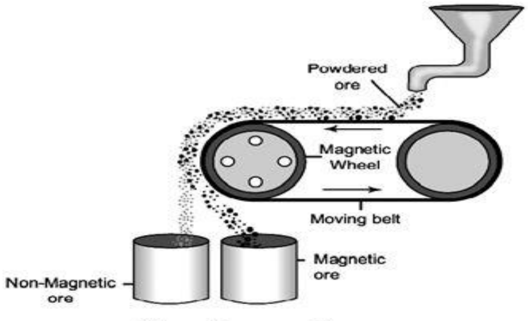
18. Write about gravity separation or hydraulic wash?

- Ore with high specific gravity is separated from gaugue with low specific gravity by simply washing with running water.
- Finely powdered ore is treated with rapidly flowing current of water.
- Lighter gaugue particles are washed away by the running water.

- This method is used for concentrating native ore such as gold and oxide ores such as haematite(Fe_2O_3), tin stone(SnO_2).

19. Write about magnetic separation.

- This method is applicable to ferromagnetic ores.
- It is based on the difference in the magnetic properties of the ore and the impurities.
- Non-magnetic tin stone can be separated from the magnetic impurities wolframite.
- Similarly magnetic ores chromite, pyrolusite can be removed from non magnetic siliceous impurities.
- The crushed ore is poured to an electromagnetic separator with a belt moving over two rollers of which one is magnetic.
- Magnetic part of the ore is attached towards the magnet and falls as a heap close to the magnetic region.
- Non- magnetic part falls away from it.



Magnetic separation

20. Write about calcination.

- Calcination is the process in which the concentrated ore is strongly heated in the absence of air.
- During this process water of crystallisation present in the hydrated oxide escapes as moisture.
- Any organic matter present also get expelled leaving the ore porous.
- This method can also be carried out with a limited supply of air.
- During calcination of carbonate ore is decomposed to metal oxide and carbon dioxide is liberated.

$$PbCO_3 \xrightarrow{\Delta} PbO + CO_2\uparrow \qquad CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$$

$$Al_2O_3.2H_2O \xrightarrow{\Delta} Al_2O_{3(s)} + 2H_2O_{(g)}\uparrow$$

21. Write about Van – Arkel method for refining zirconium/titanium?

- This method is based on the thermal decomposition of gaseous metal compounds to metals.(eg) Titanium and Zirconium.
- Impure titanium is heated in an evacuated vessel with iodine at 550K to form volatiletitanium tetra iodide.
- The impurities do not react with iodine.

$$Ti(s) + 2I_2(s) \xrightarrow{550\text{ K}} TiI_4(vapour)$$

- Volatile titanium tetraiodide is passed over a tungsten filament at 1800K.
- Titanium tetraiodide is decomposed to pure titanium which is deposited over the filament.Iodine is reused.

$$TiI_{4(vapour)} \xrightarrow{1800\text{ K}} Ti_{(s)} + 2I_{2(s)}$$

22. Write the applications of aluminium.

1. Used for making heat exchangers/sinks.

2. Used for making our day to day cooking vessels.
3. Used for making aluminium foils for packing, food items.
4. Alloys of aluminium with copper, manganese, magnesium, silicon are light weight and strong hence used in design of aeroplanes and other forms of transport.
5. Due to its high resistance to corrosion, it is used in the design of chemical reactors, medical equipment's, refrigeration units and gas pipelines.
5. It is a good electrical conductor and cheap, hence used in electrical over head cables with steel core for strength.

23. Write the applications of iron.

1.Iron is one the most useful metals and its alloys are used everywhere including bridges, electricity pylons, bicycle chains, cutting tools and rifle barrels.
2.Cast iron is used to make pipes, valves and pump stoves etc.
3.Magnets can be made from iron , its alloys and compounds.
4.Important alloy of iron is stainless steel which is very resistant to corrosion.
5.It is used in architecture, bearings, cutlery, surgical instruments and jewellery.
6.Nickel steel is used for making cables, automobiles, and aeroplane parts.
7.Chrome steels are used for manufacturing cutting tools and crushing machines.

24. Explain froth floatation method.

- This is used to concentrate sulphide ores such as galena (PbS) Zinc blende (ZnS) etc.
- Metallic ore particles preferentially wetted by oil can be separated from gangue.
- Crushed ore is mixed with water and a frothing agent like pine oil or eucalyptus oil.
- A small amount of sodium ethyl xanthate is added as a collector.
- A froth is formed by blowing air through the mixture.
- The collector molecules attach to the ore particles 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.
- Gangue particles preferentially wetted by water settle at the bottom.
- When sulphide ore contains other metal sulphides as impurities, depressing agents such as sodium cyanide, sodium carbonate etc. are used to selectively prevent other from coming to the froth
- For example , When impurities such as ZnS is present in Galena (PbS) , Sodium cyanide NaCN is added to depresses the flotation property of ZnS) by forming a layer of zinc complex $Na_2[Zn(CN)_4]$ on the surface of ZnS.

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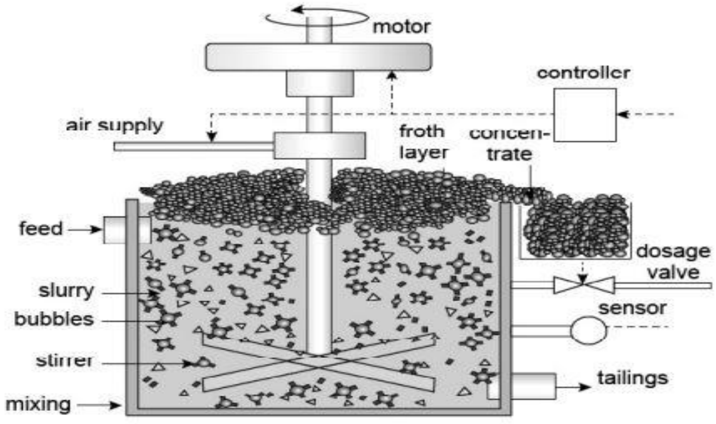

UNIT 2
p – Block element I
Text Book Exercise Questions and Answers:
I Answer the following question:

1. **Write a short note on anamolous properties of the first element of p-block.**
   (i) Small size of the first member
   (ii) High ionization enthalpy and high electronegativity
   (iii) Absences of d-orbital in their valence shell

2. **Describe briefly allotropism in p-block elements with specific reference to carbon.**
   Some elements exist in more than one crystalline or molecular forms in the same physical state. This phenomenon is called allotropism and the different forms of an element are called allotropes.
   Eg: carbon exist as diamond, graphite, graphene, fullerenes and carbon nanotubes

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3. **Boron does not react directly with hydrogen. Suggest one method to prepare diboranefrom BF_3.**

$$\underset{\text{Boron trifluoride}}{2BF_3} + 6NaH \xrightarrow{450K} \underset{\text{Diborane}}{B_2H_6} + 6NaF$$

4. **Give the uses of borax.**
   (i) Borax is used for the identification of coloured metal ions
   (ii) It is used as a flux in metallurgy.
   (iii) It act as a preservative.

5. **What is catenation? Describe briefly the catenation property of carbon.**
   Catenation is an ability of an element to form chain of atoms.
   The following conditions are necessary for catenation.
   (i) The valency of element is greater than or equal to two
   (ii) Element should have an ability to bond with itself
   (iii)The self-bond must be as strong as its bond with other elements
   Carbon possesses all the above properties and forms a wide range of compounds with itself and with other elements such as H, O, N, S and halogens.

6. **Write a note on Fisher tropsch synthesis.**
   The reaction of carbon monoxide with hydrogen at pressure of less than 50 atm using metal catalysts at 500 – 700K yields saturated and unsaturated hydrocarbons

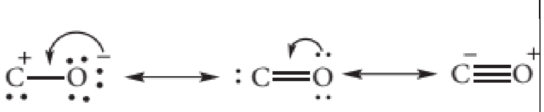
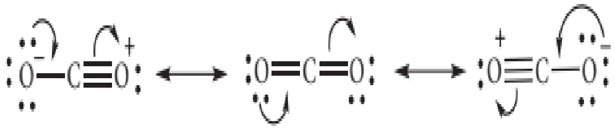
$$nCO + (2n+1)H_2 \rightarrow C_nH_{(2n+2)} + nH_2O$$

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

   Carbon monoxide forms complex compounds with transition metals. **Eg** : Nickel tetracarbonyl.

7. **Give the structure of CO and CO_2.**

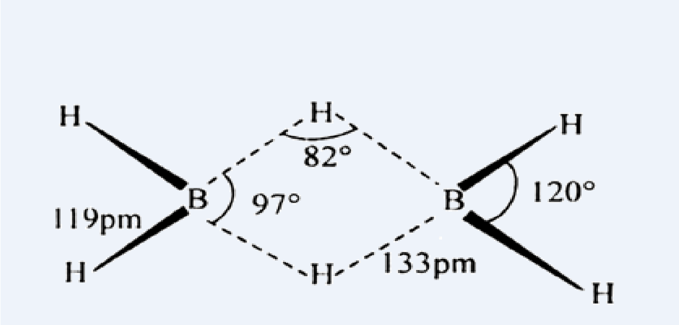
Structure of CO	**Structure of CO_2**
• It has a linear structure.	• It has a linear structure.

• The C—O bond distance is 1.128A°.	• It has equal bond distance for both C—O bonds.
	

8. **Give the uses of silicones.**(i) Silicones are used for low temperature lubrication.
   (ii) Silicones are used for making water proofing clothes.
   (iii)Silicones are used as insulating material in electric motor.

9. **$AlCl_3$ behaves like a lewis acid. Substantiate this statement.**
   $AlCl_3$ is electron deficient. Al forms three bonds with chloride and hence outer shell has six electron. It needs two more electrons to complete its octet. So readily accept a pair of electrons. Hence $AlCl_3$ is a Lewis acid and forms addition compounds with ammonia and phosphate.

10. **Describe the structure of diborane.**



- In diborane twoBH_2 units are linked by two bridged hydrogens. Therefore, it has eight B-H bonds. However, diborane has only 12 valence electrons and are not sufficient to form normal covalent bonds.
- The four terminal B-H bonds **(two centre – two electron bond or 2c-2e bond)** are normal covalent bonds.
- The remaining four electrons have to be used for the bridged bonds. i.e. two three centred B-H-B bonds utilize two electrons each. **Hence, these bonds are three centre –two electron bonds (3c-2e)**
- The bridging hydrogen atoms are in a plane. In diborane, the boron is sp^3 hybridised.

11. **Write a short note on hydroboration.**
    Diborane adds on alkenes and alkynes in ether solvent at room temperature. This reaction is called hydroboration.

$$\underset{\text{Diborane}}{B_2H_6} + 6RCH = CHR \rightarrow \underset{\text{trialkyl borane}}{2B(RCH - CH_2R)_3}$$

12. **Give one example for each of the following:**
    (i) Icosagens --- Boron family (group 13) --- Eg : aluminium
    (ii) Tetragen --- Carbon family (group 14) --- Eg : Silicon
    (iii)Pnictogen ---Nitrogen family(group 15) --- Eg : Phosphorous
    (iv)Chalcogen --- Oxygen family (group 16) --- Eg : Sulphur

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

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

14. Complete the following reactions:

a. $B(OH)_3 + NH_3 \longrightarrow$
b. $Na_2B_4O_7 + H_2SO_4 \longrightarrow$
c. $B_2H_6 + 2NaOH + 2H_2O \longrightarrow$
d. $B_2H_6 + CH_3OH \longrightarrow$
e. $4BF_3 + 3H_2O \longrightarrow$
f. $HCOOH + H_2SO_4 \longrightarrow$
g. $SiCl_4 + NH_3 \longrightarrow$
h. $SiCl_4 + C_2H_5OH \longrightarrow$
i. $2B + 6NaOH \longrightarrow$
j. $H_2B_4O_7 \xrightarrow{\text{Red hot}}$

Ans:

a. $B(OH)_3 + NH_3 \longrightarrow BN + 3H_2O$
b. $Na_2B_4O_7 + H_2SO_4 + H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4$
c. $B_2H_6 + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 6H_2$
d. $B_2H_6 + CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$
e. $4BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3H^+ + 3[BF_4]^-$
f. $HCOOH + H_2SO_4 \longrightarrow CO + H_2O + H_2SO_4$
g. $SiCl_4 + NH_3 \longrightarrow Cl_3Si\text{-}NH\text{-}SiCl_3$ (chlorosilazanes)
h. $SiCl_4 + C_2H_5OH \longrightarrow Si(OC_2H_5O)_4 + 4HCl$
i. $2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$
j. $H_2B_4O_7 \xrightarrow{\text{Red hot}} 2B_2O_3 + H_2O$

15. How will you identify borate radical?

When boric acid or borate salt is heated with ethyl alcohol in presences of conc.H_2SO_4 a n ester, trialkylborate is formed. The vapour of this ester burns with a green edged flame and this reaction is used to identify the presence of borate.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{\text{nc.H2SO4}} B(OC_2H_5)_3 + 3H_2O$$

16. Write a note on zeolites.

- Zeolites are three dimensional crystalline solids containing aluminium, silicon and oxygen.
- The general formula $NaO.(Al_2O_3).x(SiO_2).yH_2O$.
  - The Si and Al atoms are tetrahedrally coordinated with each other through shared oxygen atoms.

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

$$\underset{\text{Boric acid}}{H_3BO_3 + NH_3} \xrightarrow{800K} \underset{\text{Boron nitride}}{BN + 3H_2O}$$

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

$$\underset{(A)}{2LiH} + \underset{(B)}{B_2H_6} \xrightarrow{\text{Ether}} \underset{(C)}{2LiBH_4}$$

A – Lithium Hydride (B) – Diborane (C) – Lithium Borohydride

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

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

Potash alum (A) (B) Burnt alum

20. COis a reducing agent.Justify with an example.

Carbon monoxide is a strong reducing agent. It reduce the oxides of the less active metals to theirrespective metals and itself gets oxidised to carbon dioxide in the process.

Eg: $3CO + Fe_2O_3 \xrightarrow{Heat} 2Fe + 3CO_2$

II.Additional Question with Answers:

1. Why boron does not form B^{3+} ions?

Because of its small size and sum of first three ionization enthalpies is high, boron does not lose all its valence electrons to form B^{3+} ions.

2. Why the ionization enthalpy from aluminium to thallium is only a marginal difference?

This is due to the presence of inner d and f-electrons which has poor shielding effect compared to s and p-electrons.

3. What isInert pair effect?

Inert pair effect: In heavier post transition metals, the outer s-electrons (ns) have a tendency to remain inert andshow reluctance to take part in the bonding is known as inert pair effect

4. What happen when boron burns with nitrogen and oxygen (or) air?

(i) $2B + N_2 \longrightarrow 2BN$

(ii) $4B + 3O_2 \xrightarrow{900K} 2B_2O_3$

5. Write any two methods for the preparation of metal borides

(i) $Cr + nB \xrightarrow{1500K} CrB_n$

(ii) $BCl_3 + W \xrightarrow{1500K} WB + Cl_2 + HCl$

6. Write any three uses of boron.

a. Amorphous boron is used as a rocket fuel igniter.
b. Boron is essential for the cell walls of plants.
c. Isotope of boron$^{10}B_5$ is used as a moderator in nuclear reactors.

7.How borax is prepared from colemanite ore?

$$2Ca_2B_6O_{11} + 2Na_2CO_3 + H_2O \xrightarrow{heat} 3Na_2B_4O_7 + 3CaCO_3 + Ca(OH)_2$$

Colemanite borax

8. Why Borax solution is basic in nature?

Borax solution in hot-water is alkaline as it dissociates into boric acid and sodium hydroxide

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

9.How borax reacts with acid ?

Borax reacts with acids to form sparingly soluble boric acid

$Na_2B_4O_7 + 2HCl + 7H_2O \rightarrow 4H_3BO_3 + 2NaCl$

$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3 + Na_2SO_4$

10. What happen when borax is heated ?

When borax is heated it forms a transparent borax beads.

$Na_2B_4O_7.10H_2O \xrightarrow{\textbf{heat}} Na_2B_4O_7 \xrightarrow{\textbf{heat}} 2NaBO_2 + B_2O_3$

Borax Sodium tetraborate sodium metaborate

11. What happen when borax is treated with ammonium chloride?

When borax is treated with ammonium chloride it forms boron nitride

$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2NaCl + 2BN + B_2O_3 + 4H_2O$

12. How Boric acid is prepared from borax and colemanite?(OR)
What happens when a borax solution is acidified? Write a balanced equation for the reaction.

$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$

$Ca_2B_6O_{11} + H_2SO_4 + SO_2 \rightarrow Ca(HSO_3)_2 + H_3BO_3$

Colemanite Boric acid

13. What happen when boric acid is heated?

$4H_3BO_3 \xrightarrow{\textbf{373K}} 4HBO_2 \xrightarrow{\textbf{413K}} H_2B_4O_7 \xrightarrow{\textbf{Redhot}} 2B_2O_3$

Boric acid metaboric acid tetraboric acid

14. Why Boric acid is a weak monobasic acid ?

Boric acid act as a weak acid by accepting a hydroxide ion of water and releasing a proton into the solution

$H_3BO_3 + H_2O \longrightarrow H_3O^+ + [B(OH)_4]^-$

15. How sodium metaborate and sodium tetraborate are prepared from boric acid

$NaOH + H_3BO_3 \rightarrow NaBO_2 + 2H_2O$

sodium metaborate

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

Sodium tetraborate

16. Explain the structure of boric acid

Boric acid has a two dimensional layered structure. It consists of $[BO_3]^{3-}$ unit and these are linked to each other by hydrogen bonds

17. Write the uses of boric acid

- 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.

18. What happen when diborane react with water and alkali?

$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

Diborane boric acid

$B_2H_6 + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 6H_2$

Diborane sodium metaborate

19. What happen when diborane react with metal hydride?

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

Diborane Lithium aluminiumhydride

$B_2H_6 + 2NaH \xrightarrow{\text{Diglyme}} 2NaBH4$

Diborane Sodium borohydride

20. How to prepare trimethyl borate?

$B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$

Diborane methylalcohol trimethyl Borate

21. What happen when diborane react with ammonia?

(**OR)**

How to prepare borazine or borazole or inorganic benzene?

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

Diborane diboranediammonate

$3B_2H_6 + 2NH_3 \xrightarrow{\text{High tmp}} 2B_3N_3H_6$

Diborane Borazole

22. Why BF_3 forms a coordinate covalent bonds with ammonia and water?

Boron trifluoride is an electron deficient compound and accept electron pairs from ammonia and water to form coordinate covalent bond

$BF_3 + NH_3 \longrightarrow F_3B \leftarrow NH_3$

$BF_3 + H_2O \longrightarrow F_3B \leftarrow OH_2$

23. Explain McAfee process

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

$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{\text{heat}} 2AlCl_3 + 3CO_2$

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

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

24. Why anhydrous aluminium chloride produces fumes in moist air ?

Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HClgas. Moist HCl appears white in colour.

$AlCl_3 + H_2O \longrightarrow Al(OH)_3 + HCl$

25. What is silicate?

The mineral which contains silicon and oxygen in tetrahedral $[SiO_4]^{4-}$ units linked together indifferent patterns are called silicates.

26. Explain the types of silicates

(i) Ortho silicates (or) Neso silicates:

- Discrete $[SiO_4]^{4-}$ tetrahedral units.
- **Eg :** Phenacite (Be_2SiO_4)

(ii)Pyro silicate (or) Soro silicates:

- Silicates which contain $[Si_2O_7]^{6-}$ ions,
- They are formed by joining two $[SiO_4]^{4-}$ tetrahedral units by sharing one oxygen atom at one corner.
- **Eg** : Thortveitite – $Sc_2Si_2O_7$.

(iii)Cyclic silicate (or) Ring silicates:

- Silicates which contain $(SiO_3)_n^{2n-}$ ions.
- Which are formed by linking three or more tetrahedral $SiO4^{4-}$units.
- Each silicate unit shares two of its oxygen atoms with other units
- **Eg** : Beryl $[Be_3Al_2(SiO_3)_6]$

(iv)Inosilicates:

- Silicates which contain ‘n’ number of silicate units liked by sharing two or more oxygen atoms are called inosilicates.
- They are further classified as chain silicates and double chain silicates.

(v)Chain silicates (or) Pyroxenes:

- These silicates contain $[SiO_3)]^{2n-}$ ions formed by linking ‘n’ number of tetrahedral $[SiO_4]^{4-}$ units linearly.
- Each silicate unit shares two of its oxygen atoms with other units.
- Eg : Spodumene – $LiAl(SiO_3)_2$.

(vi) Double chain silicates(or) amphiboles:

- These silicates contain $[Si_4O_{11}]^{6n-}$ ions.
- In these silicates there are two different types of tetrahedral :
  (i) Those sharing 3 vertices
  (ii) those sharing only 2 vertices.
- **Eg :** Asbestos.

(vii) Sheet (or) phyllo silicates:

- Silicates which contain $(Si_2O_5)_n^{2n-}$ ions.
- Each $[SiO_4]^{4-}$ tetrahedron unit share three oxygen atoms with others and thus by forming two dimensional sheets.
- **Eg :** Talc, Mica etc...

(viii)Three dimensional silicates (or) tecto silicates:

- Silicates in which all the oxygen atoms of $[SiO_4]^{4-}$ tetrahedral are shared with other tetrahedralto form three-dimensional network are called three dimensional silicate.
- They have general formula $(SiO_2)_n$.
- **Eg** : Quartz.

UNIT - 3.

p - Block Elements II

I Text Book Question & Answer

1. **What is inert pair effect?**

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

2. **Chalcogens belongs to p - block give reason?**

1 Their outer electronic configuration isns^2np^4.

2 In these elements, the last electron enter np orbital.

3 Hence they belong to p-block elements.

4 Since the outer most electron of Chalcogens enter into ‘p’ orbital it belongs to ‘p’ block. Its group number is16.

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

1. Since fluorine is the most electronegative element, it exhibits only a negative oxidation state of -1.
2. Due to the absence of d-orbital, fluorine does not show positive oxidation state.

4. **Give the oxidation state of halogen in the following**

a) OF_2, b) O_2F_2, c) Cl_2O_3, d) I_2O_4

Fluorine shows only -1 oxidation state. Hence

a) Oxidation state of‘F’ inOF_2 is-1

b) Oxidation state of ‘F’ in O_2F_2 is -1

c) Cl_2O_3

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

$2x - 6 = 0$

$2x = 6$

$X=3$

Oxidation state of Cl is +3

d) I_2O_4

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

$2x - 8 = 0$

$2x = 8$

$X=4$

Oxidation state of Iodine is +4

5. **What are interhalogen compounds? Give example?**

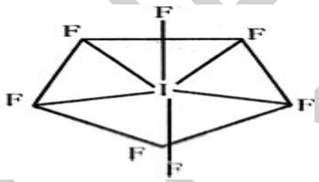
Each halogen combines with other halogen to form a series of compounds called interhalogen compounds
Eg : ClF, BrCl, IF_7

6. **Why fluorine is more reactive than other halogens?**
Fluorine is the most reactive element among halogen. This is due to the low value of F-F bond dissociation energy.

7. **Give the uses of helium.**
1. It is much less denser than air and hence used for filling air balloons.
2.Helium has lowest boiling paint and hence used in cryogenics.
3.Helium is used to provide inert atmosphere in electric arc welding metals.
4.Helium and oxygen mixture is used by the divers in place of air oxygen mixture. This prevents the painful dangerous condition called bends.

8. **What is the hybridisation of iodine in IF_7? Give its structure?**
Hybridisation of IF_7 is sp^3d^3

Structure of IF_7



Structure - Pentagonal Bipyramidal

9. **Give the balanced equation for the reaction between chlorine with cold NaOH and hot NaOH.**
1. Chlorine reacts with cold NaOH to give sodium chloride and sodium hypochlorite.

$Cl_2 + 2\ NaOH \rightarrow NaOCl + NaCl + H_2O$
Sodium hypochlorite

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

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

10. **How will you prepare chlorine in the laboratory?**
In the laboratory, chlorine is prepared by the oxidation of hydrochloric acid by $KMnO_4$.

$2KMnO_4 + 16HCl \rightarrow 2\ KCl + 2\ MnCl_2 + 8H_2O + 5Cl_2\uparrow$

11. **Give the uses of sulphuric acid ?**
i. Sulphuric acid is used in the manufacture of fertilizers, ammonium sulphate and super phosphates and other chemicals such as hydrochloric acid, nitric acid etc.
ii. It is used as a drying agent and also used in the preparation of pigments, explosives etc.

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

It is highly soluble in water and has strong affinity towards water and hence it can be used as a dehydrating agent.

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

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

$(COOH)_2 + H_2SO_4 \rightarrow CO + CO_2 + H_2SO_4.H_2O$

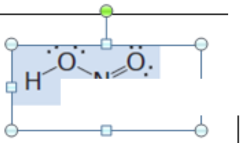
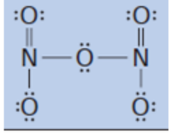
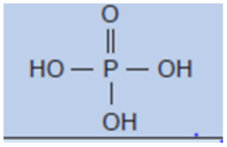
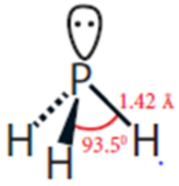
$HCOOH + H_2SO_4 \rightarrow CO + H_2SO_4.H_2O$

13. Write the reason for the anamolous behaviour of nitrogen?

1. Small size
2. High ionisation enthalpy and high electronegativity.
3. Absence of d-orbitals in their valence shell.
4. Nitrogen is a diatomic gas unlike the other members of the group.

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

a) Nitric Acid b) Dinitrogen Pentoxide c) Phosphoric acid d) Phosphine

COMPOUND	MOLECULAR FORMULA	STRUCTURL FORMULA
a)Nitric Acid	HNO_3	
b)Dinitrogen Pentoxide	N_2O_5	
c)Phosphoric Acid	H_3PO_4	 $HO-\underset{\underset{OH}{\mid}}{\overset{\overset{O}{\|}}{P}}-OH$
d)Phosphine	PH_3	

15. Give the uses of Argon?

Argon prevents the oxidation of hot filament and prolongs the life in filament bulbs

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

Valence shell electronic configuration of group 15 elements ns^2np^3

Nitrogen	$[He]2s2p^3$
Phosphorous	$[Ne]\ 3s^2 3p^3$
Arsenic	$[Ar]3d^{10}4s^2 4p^3$
Antimony	$[Kr]\ 4d^{10}5s^2 5p^3$
Bismuth	$[Xe]\ 5d^{10}6s^2 6p^3$

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

(i) **Basic nature** : Phosphine is weakly basic and forms phosphonium salts with halogen acids.

$PH_3 + HI \xrightarrow{\Delta} PH_4I.$

ii) **Reducing property** : 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?

Nitric acid reacts with basic oxides to form salt and water.

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

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

19. What happens when PCl_5 is heated?

On heating phosphorous penta chloride, it decomposes into phosphorous trichloride and chlorine.

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

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

Hydrofluoric acid is a weak acid due to the presence of intermolecular hydrogen bonding in it and it cannot be completely ionized and hydrogen ion concentration will not be increased. But other hydrohalic acids are completely ionized and therefore they are strong acids.

21. Deduce the Oxidation number of Oxygen in Hypofluorous acid -HOF?

HOF

$+1 + x - 1 = 0$

$x = 0$

Hence oxidation number of oxygen in HOF is zero.

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

a) BrF_5 - sp^3d^2

b) BrF_3 - sp^3d

23. Complete the following reactions

1. $NaCl + MnO_2 + H_2SO_4 \rightarrow$

2. $NaNO_2 + HCl \rightarrow$

3. $IO_3^- + I^- + H^+ \rightarrow$

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

5. $P_4 + NaOH + H_2O \rightarrow$
6. $AgNO_3 + PH_3 \rightarrow$

7. $Mg + HNO_3 \rightarrow$
8. $KClO_3 \xrightarrow{\Delta}$

9. $Cu + H_2SO_4 \xrightarrow{\text{Hot Conc}}$

10. $Sb + Cl_2 \rightarrow$
11. $HBr + H_2SO_4 \rightarrow$

12. $XeF_6 + H_2O \rightarrow$

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

14. $XeOF_4 + SiO_2 \rightarrow$

15. $Xe + F_2 \xrightarrow[400^0C]{Ni/200atm}$

Ans:

1. $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow Cl_2 + MnCl_2 + 4NaHSO_4 + 2H_2O$

2. $NaNO_2 + HCl \rightarrow NaCl + HNO_2$

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

4. $I_2 + 2S_2O_3^{2-} \rightarrow 2I- + S_4O_6^{2-}$

5. $P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3\uparrow$

6. $3AgNO_3 + PH_3 \rightarrow Ag_3P + 3HNO_3$

7. $4Mg + 10HNO_3 \rightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$

   $4Mg + 10HNO_{3\ (dilute)} \rightarrow 4Mg(NO_3)_2 + N_2O + 5H_2O$

8. $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2\uparrow$

9. $Cu + 2H_2SO_{4(Hot\ Conc.)} \rightarrow CuSO_4 + SO_2 + 2H_2O$

10. $2Sb + 3Cl_2 \rightarrow 2SbCl_3$

11. $2HBr + H_2SO_4 \rightarrow 2H_2O + Br_2 + SO_2$

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

13. $5XeO_6^{4-} + 2\,Mn^{2+} + 14\,H^+ \rightarrow 2MnO^- + 5XeO_3 + 7H_2O$

14. $2\,XeOF_4 + SiO_2 \rightarrow 2XeO_2F_2 + SiF_4$

15. $Xe + F_2 \xrightarrow[400^\circ C]{Ni/200\ atm} XeF_2$

II. EVALUATEYOURSELF

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

$$\underset{(dilute)}{4Zn + 10HNO_3} \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$\underset{(very\ dilute)}{4Zn + 10HNO_3} \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$\underset{(Conc.)}{Zn + 4HNO_3} \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

II. ADDITIONALQUESTIONS

1) **How is pure nitrogen gas prepared?**

Thermal decomposition of sodium azide about 573K gives pure nitrogen gas.

$2NaN_3 \rightarrow 2Na + 2N_2.$

2) **Give reason for the chemically inert character of nitrogen.**

Nitrogen is chemically inert due to

i) High bonding energy of the molecules (225 cal mol^{-1} (or)945$kJmol^{-1}$).

ii) Triply bonded N≡N.

3) **Mention the only metal that reacts with nitrogen at room temperature and give its reaction.**

Only metal that reacts with nitrogen at room temperature is lithium.

$6Li + N_2 \rightarrow 2Li_3N.$

4) **How does nitrogen reacts with the following elements at hightemperature? (i) Calcium (ii) Boron**

1. $3Ca + N_2 \rightarrow Ca_3N_2$
2. $2B + N_2 \rightarrow 2BN$

5) **Give the uses of nitrogen.**

i) Nitrogen is used for the manufacture of ammonia, nitric acid and calcium cyanamide.

ii) Liquid nitrogen is used for producing low temperature required in cryosurgery and so in biological preservation.

6) **Write the reaction of hydrolysis of urea.**

Hydrolysis of Urea gives ammonia.

$NH_2CONH_2+H_2O\rightarrow 2NH_3+CO_2$

7) **How is ammonia prepared in the laboratory?**

Ammonia is prepared in the laboratory by heating ammonium salts with a base.

$2NH_4^{+} + OH^{--} \rightarrow 2NH_3 + H_2O$

$2NH_4Cl + CaO \rightarrow CaCl_2 + 2NH_3 + H_2O$

8) **How is ammonia prepared from magnesium nitride?**

$Mg_3N_2 + 6\,H_2O \rightarrow 3Mg(OH)_2+2NH_3$

By heating magnesium nitride with water ammonia is formed.

9) **What happens when ammonia is heated above500°C?**

When ammonia is heated above 500°C, it decomposes into Nitrogen and hydrogen.

$$2NH_3 \xrightarrow{>500^{o}C} N_2+3H_2$$

10) **Illustrate the reducing property of ammonia with an example**

When Ammonia is passed over heated lead oxide, it is reduced into lead

$3PbO + 2NH_3 \rightarrow 3Pb +N_2+3H_2O$

11) **The Affinity of ammonia for proton is greater than that of water .Justify it.**

When treated with acids ammonia forms ammonium salts. This reaction shows that the affinity of ammonia for proton is greater than that of water.

12) **What happens when nitric acid is exposed to sunlight (or) heating? (or)**
Colourless pure concentrated nitric acid turns yellow on standing. why?

Nitric acid decomposes on exposure to sunlight (or) on being heated.

$4HNO_3\rightarrow 4NO_2 + 2H_2O + O_2$`

13) **Mention the uses of nitricacid**

i) Nitric acid is used as a oxidizing agent in the preparation of aquaregia
ii) Salts of nitric acid are used in photography ($AgNO_3$) and gun powder for firearms($NaNO_3$)

14) **Mention the three common allotropic forms of phosphorous.**

The three common allotropic forms of phosphorous are white, red and black phosphorous.

15) **How do you convert**

i) White phosphorous → Red Phosphorous
ii) Red phosphorous → White phosphorous

i) The White phosphorous can be changed into red phosphorous by heating it to 420°C in the absence of air and light
ii) The red phosphorous can be converted back into white phosphorous by boiling it in an inert atmosphere and condensing the vapour underwater.

16) Mention the uses of phosphorous.

1. The red phosphorous is used in the matchboxes.
2. It is also used for the production of certain alloys such as phosphorbronze.

17) What happens when phosphorous acid is heated?

By heating phosphorous acid phosphine is prepared in pure form. $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3 \uparrow$

18) What is the reaction of phosphonium iodide with caustic soda solution?

A pure sample of phosphine is prepared by heating phosphonium iodide with caustic soda solution

$PH_4I + NaOH \xrightarrow{\Delta} PH_3 + NaI + H_2O$

19) Write the reaction of phosphine with Lewisacid

$BCl_3 + PH_3 \rightarrow [Cl_3\,B \leftarrow\ :PH_3]$

Phosphine reacts with lewis acid like boron trichloride and gives co-ordination compound.

20) What is known as Holme's signal?

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 holme's signal.

21) Prove that phosphorous trichloride is a chlorinating agent.

$C_2H_5OH + PCl_3 \rightarrow C_2H_5Cl + H_3PO_3$

$C_2H_5COOH + PCl_3 \rightarrow C_2H_5COCl + H_3PO_3$

Above reactions prove that phosphorous trichloride is a good chlorinating agent.

22) Mention the allotropic forms of oxygen.

Oxygen exists in two allotropic forms namely dioxygen (O_2) and ozone or trioxygen (O_3).

23) What are known as pyrophoricmetals?

Some of less reactive metals react when powdered finely and made to react exothermically with oxygen at room temperature, but a lump of metal is unaffected under same condition. These finely divided metals are known as pyrophoric and when set the powder on fire, heat is liberated during a reaction.

24) What happens when SO_2 is dissolved in water?

Sulphur dioxide dissolves in water to give sulphurous acid

$SO_2 + H_2O \rightleftharpoons H_2SO_3$

$H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{2-}$

25) Give the allotropic forms of Sulphur .

Sulphur exists in crystalline as well as amorphous allotropic forms. The crystalline form includes rhombic sulphur (α sulphur) and monoclinic sulphur (β sulphur). Amorphous allotropic form includes plastic sulphur (γ sulphur), milk of sulphur and colloidal sulphur.

26) Why H_2SO_4 is used as a dehydratingagent?

It is highly soluble in water and has strong affinity towards water and hence it can be used as a dehydrating agent.

27) Illustrate the dehydrating property of con.H_2SO_4 with (i) sucrose (ii) formic acid (iii) oxalic acid?

$C_{12}H_{22}O_{11} + H_2SO_4 \rightarrow 12C + H_2SO_4.11H_2O$
$HCOOH + H_2SO_4 \rightarrow CO + H_2SO_4.H_2O$
$(COOH)_2 + H_2SO_4 \rightarrow CO + CO_2 + H_2SO_4.H_2O$

28) What happens when H_2SO_4 is heated to high temperature?

Sulphuric acid is stable, however, it decomposes at high temperature to sulphur trioxide.

$H_2SO_4 \rightarrow H_2O + SO_3$

29) What is the reaction of H_2SO_4 withNH$_3$?

$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$

30) Prove the oxidizing property of H_2SO_4 with twoexamples.

Sulphuric acid is an oxidizing agent as it produces nascent oxygen. Sulphuric acid oxidises elements such as C, S and P. It also oxidizes bromide and Iodide to Bromine and Iodine respectively

$H_2SO_4 \rightarrow H_2O + SO_2 + (O)$ $C + 2H_2SO_4 \rightarrow 2SO_2 + 2H_2O + CO_2$
$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$

31) What is the role of H_2SO_4 in the conversion of H_2S to S? Give the reaction.

It acts as an oxidizing agent in the conversion of H_2S to S.

$H_2S + H_2SO_4 \rightarrow SO_2 + 2H_2O + S$

32) What happens when benzene reacts with con.H_2SO_4?

It reacts with organic compounds such as benzene to give sulphonic acids.

$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$

33) How is ammonia prepared by Haber's process?

Nitrogen reacts with hydrogen under high pressure and optimum temperature in presence of iron catalyst to give ammonia.

$N_2 + 3H_2 \rightleftharpoons 2NH_3, \Delta H_f = -46.2\ kJmol^{-1}$

34) Explain the following reactions.

i) Reaction of excess of ammonia with chlorine
ii) Reaction of ammonia with excess of chlorine

i) Chlorine with excess of ammonia

$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$
$6HCl + 6NH_3 \rightarrow 6NH_4Cl$
OVER ALL REACTIONS
$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$

ii. Ammonia with excess of chlorine

$NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$

$3NH_3 + 3HCl \rightarrow 3NH_4Cl$
OVER ALL REACTIONS
$4NH_3 + 3Cl_2 \rightarrow NCl_3 + 3NH_4Cl$

35) How does ammonia react with metallic salts?

i) Fe^{3+} ii)Cu^{2+}

Ammonia reacts with metallic salts to give metal hydroxides (in case of Fe) (or) forming complexes (in case of Cu).

$$Fe^{3+} + 3NH_4^+ \rightarrow Fe(OH)_3 + 3NH_4^+$$

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

Tetraamminecopper(II)ion

36) Prove that nitric acid is an oxidizing agent.

$$C + 4HNO_3 \rightarrow 2H_2O + 4\,NO_2 + CO_2$$

$$S + 2HNO_3 \rightarrow H_2SO_4 + 2\,NO$$

37) Write a note on nitration of benzene.

In organic compounds replacement of a - H atom with NO_2 is referred to as nitration.

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

Nitration takes place due to the formation of nitronium ion.

$$HNO_3 + H_2SO_4 \rightarrow NO_2^{\ +} + H_3O^+ + HSO_4^-$$

38) Write the reaction of conc.HNO_3 with copper.

$$Cu + 4HNO_3 \rightarrow Cu\,(NO_3)_2 + 2\,NO_2 + 2H_2O$$

39) What is called phosphorescence?

The freshly prepared white phosphorous is colourless but becomes pale yellow due to the formation of a layer of red phosphorous on standing. It is poisonous and has a characteristic garlic smell. It glows in the dark due to oxidation which is called phosphorescence.

40) Give an account on structure of phosphorous.

Phosphorous has a layer structure. The four atoms in phosphorous have polymeric structure with chains of P_4 linked tetrahedrally. P≡P is less stable than P-P single bonds. Hence phosphorous atoms are linked through single bonds rather than triple bonds.

41) How is phosphine obtained from yellow phosphorous?

Yellow phosphorous reacts with alkali on boiling in an inert atmosphere and it liberates phosphine.

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

42) How do you prepare orthophosphoric acid from phosphorous?

When phosphorous is treated with conc.nitric acid in presence of iodine catalyst ortho phosphoric acid is formed.

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

43) Mention the hydride of phosphorous and give its hybridization and structure. The hydride of phosphorous is phosphine (PH_3).The hybridization of phosphorous in phosphine is sp^3.Three orbitals are occupied by bond pair with fourth corner occupied by lone pair of electrons. Hence bond angle is reduced to 94°. It has pyramidal shape.

44) How do you prepare phosphine from metallic phosphides?

Metallic phosphides on hydrolysis with water (or) dilute mineral acids give phosphine.

$$Ca_3P_2 + 6H_2O \rightarrow 2PH_3\uparrow + 3Ca(OH)_2$$

$$AlP + 3HCl \rightarrow PH_3\uparrow + AlCl_3$$

45) How is phosphine converted into meta phosphoricacid?

When phosphine is heated with air or oxygen it burns to give meta phosphoric acid

$4PH_3 + 8O_2 \xrightarrow{\Delta}\rightarrow P_4O_{10}+6H_2O$

$P_4O_{10} + 6H_2O \rightarrow 4HPO_3 + 4H_2O$

46) Show that phosphine is weakly basic in nature.

Phosphine forms phosphonium salts with halogen acids. It shows that phosphine is weakly basic in nature.

$PH_3 + HI \rightarrow PH_4I$

$PH_4I + H_2O \xrightarrow{\Delta} PH_3 + H_3O^+ + I^-$

47) Mention the phosphorous compound which has the smell of rotten fish and what is the action of heat on it in the absence of air?

Phosphine has rotten fish smell. Phosphine decomposes into its elements , when heated in absence of air at 317K.

$4PH_3 \xrightarrow{317K} P_4 + 6H_2$

48) Illustrate the reducing property of phosphine.

Phosphine precipitates some metal from their salt solutions. It illustrates the reducing property of phosphine.

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

49) Mention the uses ofphosphine.

i) Phosphine is used for producing smokescreen.

ii) It is used in the Holme's signal (i.e) signal to the approaching ships.

50) What is the action of PCl_3on

i) Ethyl alcohol ii) Acetic acid

i) $C_2H_5OH + PCl_3 \rightarrow C_2H_5Cl + H_3PO_3$

ii) $C_2H_5COOH + PCl_3 \rightarrow C_2H_5COCl + H_3PO_3$

51) How is O_2 prepared in the laboratory fromH_2O_2

The decomposition of H_2O_2 in the presence of catalyst (MnO_2) or by the oxidation with potassium permanganate produces oxygen.

$2H_2O_2 \rightarrow 2H_2O + O_2$

$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 8H_2O + 2Mn^{2+}$

52) How is ozone prepared in the laboratory?

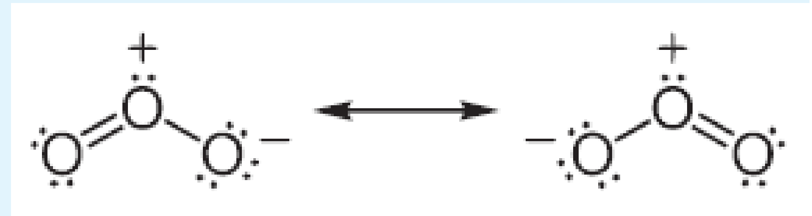
In the laboratory ozone is prepared by passing electrical discharge through oxygen at a potential of 20,000V about 10% of oxygen is converted into ozone. It gives a mixture known as ozonised oxygen. Pure ozone is obtained as a pale blue gas by the fractional distillation of liquefied ozonised oxygen.

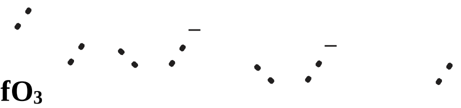
$O_2 \rightarrow 2(O)$

$O_2 + (O) \rightarrow O_3$

53) Write briefly on the structure ofozone?

The ozone molecule have a bent shape and symmetrical with delocalized bonding between the oxygen atoms.





54) Mention the uses ofO_3

i) Oxygen is one of the essential components for the survival of living organisms.
ii) It is used in welding (oxy acetylene welding)
iii) Liquid oxygen is used as fuel in rockets etc.

55) Write the reaction which is used in the estimation ofO_3.

Ozone is a powerful oxidizing agent and it reacts with many substances under conditions where oxygen will not react. For example, it oxidizes potassium iodide to iodine. This reaction is Quantitative and can be used for estimation of ozone.

$$O_3 + 2KI + H_2O \rightarrow 2KOH + O_2 + I_2$$

56) Illustrate the oxidizing property ofSO_2.

SO_2 oxidizes hydrogen sulphide to sulphur and Magnesium to Magnesium oxide. $2H_2S + SO_2 \rightarrow 3S + 2H_2O$

$$2Mg + SO_2 \rightarrow 2MgO + S$$

57) How is sulphur dioxide prepared in the laboratory?

Sulphur dioxide is prepared in the laboratory by treating a metal or metal sulphite with sulphuric acid.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

$$SO_3^- + 2H^+ \rightarrow H_2O + SO_2$$

58) Illustrate the reducing property of SO_2 with an example.

As it can be readily oxidized, it acts as a reducing agent. It reduces chlorine into hydrochloride acid.

$$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$$

59) What happens when SO_2 is passed through acidified $K_2Cr_2O_7$?

It reduces acidified $K_2Cr_2O_7$ to Cr^{3+}.

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

60) How is SO_3 prepared by contact process and mention the Inorganic acid obtained from it?

Sulphur dioxide is oxidised to sulphur trioxide upon heating with oxygen at high temperature in the presence of V_2O_5 catalyst

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

This reaction is used for the manufacture of sulphuric acid by contact process.

61) Give an account on bleaching action ofSO_2.

In the presence of water, SO_2 bleaches coloured wool, silk, sponges & straw into colourless product due to its reducing property.

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2[H]$$

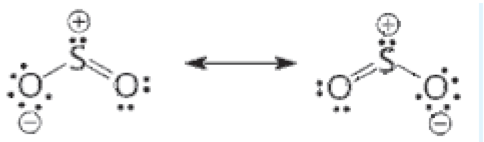
$$\underset{\text{(coloured)}}{X} + 2[H] \rightarrow \underset{\text{(colourless)}}{XH_2}$$

However,when the bleached product (colourless) is allowed to stand in air, it is reoxidised by atmospheric oxygen to its original colour. Hence bleaching action of SO_2 is temporary.

62) **Mention the uses of SO_2.**

1. Sulphurdioxide is used in bleaching hair, silk, wool etc.,
2. It can be used for disinfecting crops and plants in agriculture.

63) **Mention the hybridization of S in SO_2 and give its structure.**



In sulphur dioxide, sulphur atom undergoes, sp^2 hybridization. A double bond arises between S and O is due to pπ- dπoverlapping.

64) **Prove that sulphuric acid is a strong dibasicacid.**

It forms two types of salts namely sulphates and bisulphates with sodium hydroxide and hence it is a dibasic acid.

$H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O$

Sodium bisulphate

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Sodium Sulphate

65) **Give two test for sulphuric acid /sulphates?**

Dilute solution of sulphuric acid / aqueous solution of sulphate gives white precipitates (barium sulphate) with barium chloride solution. It can also be detected using lead acetate solution. Here a white precipitate of lead sulphate is obtained.

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

$(CH_3COO)_2Pb + H_2SO_4 \rightarrow PbSO_4 + 2CH_3COOH$

Group 17 (Halogen group) Elements

66) **Name the halogen liberated from bleaching powder on reaction with mineral acids. Give reaction**

Chlorine is liberated from bleaching powder on reaction with mineral acids

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

67) **What is the action of hydrochloric acid on potassiumdichromate**

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

68) **What happens when chlorine is burnt with turpeatine**

When Chlorine is burnt with turpentine it forms carbon and hydrochloric acid

$C_{10}H_{16} + SCl_2 \rightarrow 10C + 16HCl$

69) **When chlorine water is exposed to sunlight it loses its colour and smell. Give reason**

Chlorine is converted into hydrochloric acid when chlorine water is exposed to sunlight. Hence it loses it's colour and smell

$2Cl_2 + H_2O \rightarrow O_2 + 4HCl$

70) **Show that chlorine is a strong bleaching agent**

Chlorine is a strong bleaching agent because of the nascent oxygen

$H_2O + Cl_2 \rightarrow HCl + HOCl$ - Hypochlorous acid

$HOCl \rightarrow HCl + (O)$

Colouring matter + Nascent oxygen → Colourless oxidation product

71) Show that chlorine is a strong oxidizing agent

Chlorine is a strong oxidizing agent because of the nascent oxygen. It oxidizes ferrous sulphate to ferric sulphate

$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$

72) How is bleaching powder prepared?

Bleaching Powder is prepared by passing chlorine gas through dry slaked time (Calcium hydroxide)

$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$

73) Write two displacement redox reactions of chlorine

Chlorine displaces bromine from bromides and iodine from iodide salts

$Cl_2 + 2KBr \rightarrow 2KCl + Br_2$

$Cl_2 + 2KI \rightarrow 2KCl + I_2$

74) Give the uses of chlorine

Chlorine is used in

i) Purification of drinking water
ii) Bleaching of cotton textiles paper and rayon
iii) Extraction of gold and platinum

75) What is aqua regia (Royal water) mention it's use

When three parts of concentrated hydrochloric acid and one part of concentrated Nitric acid are mixed aquar egia is obtained. It is used for gold, platinum etc.,

76) What is the action of gold on aquaregia

$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$

77) Give the reaction of platinum on aquaregia

$Pt + 8H^+ + 4NO_3^- + 6Cl^- \rightarrow [Pt\,Cl_6]^{2-} + 4\,NO_2 + 4\,H_2O$

78) Give the uses of hydrochloric acid

i) Hydrochloric acid is used for the manufacture of chlorine, ammonium chloride, glucose from corn starch etc.,
ii) It is used in the extraction of glue from bone and also for purification of bone black

79) Thermal stability of hydrogen halide decreases from hydrogen fluoride to iodide Give reason

Bond dissociation enthalpy decreases from hydrogen fluoride to hydrogen iodide and hence thermal stability decreases. For eg, hydrogen iodide decomposes at 400°C while hydrogen fluoride and hydrogen chloride are stable at this temperature.

80) Hydrofluoric acid is a weak acid whereas other hydrohalic acids are strong acids Give reason

Hydrofluoric acid is a weak acid due to the presence of intermolecular hydrogen bonding in it and it cannot be completely ionized and hydrogen ion concentration will not be increased. But other hydrohalic acids are completely ionized and hydrogen therefore they are strong acids.

81) **Hydrofluoric acid is a weak acid at low concentration, but becomes stronger as the concentration increases why?**

0.1M HF is only 10% ionized and hence it is a weak acid but 5M and 15M solution of HF is stronger acid due to the equilibrium

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

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

At high concentration, the equilibrium involves the removal of fluoride ions. It affects the dissociation of hydrogen fluoride and increases the hydrogen ion concentration and hence HF becomes stronger acid.

82) **Hydrofluoric acid cannot be stored in silica and glass bottles why?**

Moist hydrofluoric acid rapidly reacts with silica and glass and thus it cannot be stored init

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

$$Na_2SiO_3 + 6HF \rightarrow Na_2\,SiF_6 + 3H_2O$$

83) **Show that hydrogen iodide is a good reducing agent, and how is it tested?**

Hydrogen iodide is readily oxidized to iodine hence it is a good reducing agent

$2HI \rightarrow 2H^+ + I_2 + 2C^-$

Liberated iodine gives blue-black colouration with starch (Test for Iodine).

84) **Give the conditions for formation of interhalogen compounds**

i) The central atom must be less electronegative and larger insize
ii) It can be formed only between two halogens and not with more than two halogens.

85) **Fluorine cannot act as central atom in inter halogen compoundsWhy?**

Fluorine cannot act as central atom in inter halogen compounds because it is highly electronegative and smallest among halogens.

Group 18 (Inert Gases) Elements

86) **How are xenon fluorides prepared?**

Xenon fluorides are prepared by direct reaction of xenon and fluorine under different conditions.

$$Xe + F_2 \xrightarrow[400^0\,C]{Ni} XeF_2$$

$$Xe + F_2 \xrightarrow[400^0\,C]{Ni/\ acetone} XeF_4$$

$$Xe + 3F_2 \xrightarrow[400^0\,C]{Ni/\ 200atm} XeF_6$$

87) What happens when X_eF_6 is hydrolysed?

On hydrolysis of X_6F_6 with water vapour it gives
X_eO_3 $X_eF_6 + 3H_2O \rightarrow X_eO_3 + 6HF$

88) How is sodium per xenate obtained fromX_eF_6?
When XeF_6 reacts with 2.5m NaOH, sodium perxenate is obtained
$2XeF_6 + 16\ NaOH \rightarrow \underset{\text{(Sodium per xenate)}}{Na_4XeO_6} + Xe + O_2 + 12\ NaF + 8H_2O$

89) Show that sodium per xenate is has strong oxidizing property?

Sodium per xenate oxidises manganese(II) ion into permanganate ion even in the absence of catalyst
$5XeO_6^{4-} + 2Mn^{2+}\ 14H^+ \rightarrow 2MnO_4^- + 5XeO_3 + 7\ H_2O$

90) Xenon is used in high speed electronic flash bulbs used by photographers Why?

Xenon emits an intense light in discharge tubes instantly. Due to this it is used in high speed electronic flash bulbs used by photographers.

ADDITIONAL 5 MARK QUESTIONS

1) Explain commercial method of preparation of nitric acid by ostwald's process.

2) Write the primary, secondary and tertiary reactions of metals with nitric acid.

3) Give the various steps involved in the reaction of dilute nitric acid with
i. copper ii. magnesium

4) Mention the oxides of nitrogen and give their preparation.

5) Give the structures of oxides of nitrogen.

6) Give the structures of oxoacids of nitrogen.

7) Mention the oxoacids of nitrogen and give their method of preparation.

8) Give one method of preparation for each oxyacids of phosphorous.

9) Write briefly on allotropic form of Sulphur.

10) Explain any three methods of preparation of sulphur dioxide with equations.

11) Phosphorous compound 'A' which is poisonous and has the smell of rotten fish reacts with chlorine and gives 'B' 'B' reacts with water to give an oxyacid of phosphorous 'C' which is tribasic in nature Identify the compounds A, B and C and explain the reactions.

12) How is chlorine manufactured by the electrolysis of brine solution?

13) Explain deacon's process of manufacture of Chlorine

14) Mention the hybridization, geometry and number of bond pair and lone pairs of electrons present in different types of inter halogen compounds.

UNIT – 4

TRANSITION AND INNER TRANSITION ELEMENTS

I. Text book question and Answer:

1. What are transition metals? Give four examples

Transition metal as an element whose atom has an incomplete d sub shell or which can give rise to cations with an incomplete d sub shell. Example : Iron, Cobalt, Nickel, Copper.

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

- At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state become stable.
- Hence the first and last elements show less number of oxidation states and the middle elements with more number of oxidation states.

4d series elements	Oxidation states
Y	+3
Ru	From +2 to +8
Cd	+2

3. What are inner transition elements?

- 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.
- In the inner transition elements there are two series of elements.

1) Lanthanoids (Previously called lanthanides)
2) Actinoids (Previously called actinides)

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

- The actual position of Lanthanoids in the periodic table is at group number 3 and period number6.
- In sixth period after lanthanum, the electrons are preferentially filled in inner 4f sub shell and these fourteen elements following lanthanum show similar chemical properties. Similarly, the fourteen elements following actinium resemble in their physical and chemical properties.

- Therefore these elements are grouped together and placed at the bottom of the periodic table.
- This position can be justified as follows.

1. Lanthanoids have general electronic configuration $[Xe]4f^{1-14}\,5d^{0-1}6s^{2}$
2. The common oxidation state of Lanthanoids is+3
3. All these elements have similar physical and chemical properties. Hence a separate position is provided to the inner transition elements.

5. What are actinides? Give three examples.

The fourteen elements following actinium, i.e. from Thorium (Th) to Lawrentium (Lr) are called actinoids.

Examples : Thorium (Th), Uranium (U) and Plutonium (Pu)

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

Electronic configuration of Gd is $[Xe]4f^{7}5d^{1}6s^{2}$

Electronic configuration of Gd^{3+} is $[Xe]\ 4f^{7}5d^{0}6s^{0}$

In Gd^{3+}, no electrons are there in outer 5d orbitals.

d-d transition is not possible. So Gd^{3+} is colourless.

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

Cu^{2+}	Zn^{2+}
1) Electronic configuration of Cu^{2+} is $[Ar]3d^{9}$	Electronic configuration of $Zn^{2+}$is $[Ar]3d^{10}$
2) It has one unpaired electron.	It has no unpaired electron.
3) Due to d-d transition Cu is coloured.	d-d transition is not possible.Hence Zn^{2+} is colourless.

8. Describe the preparation of potassiumdichromate

Ore : Chromite Ore

Concentration : Gravity Separation

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

Chromite Ore — SodiumChromate

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

Sodium Chromate (Yellow) — Sodium di Chromate (OrangeRed)

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + NaCl$

Sodium di Chromate (OrangeRed) → Potassim di Chromate (OrangeRed)

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

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

Consequences of lanthanoid contraction:

1) As we move from Ce^{3+} to Lu^{3+}, the basic character of Ln^{3+} ions decreases. 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) Because of this very small change in radii of lanthanoids, their chemical properties are quite similar.
3) The elements of the second and third transition series resemble each other more closely than the elements of the first and second transition series.

10. Complete the following:

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

$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

b) $C_6H_5CH_3 \xrightarrow[\text{KMnO}_4]{\text{acidified}}$?

$C_6H_5CH_3 \xrightarrow[\text{KMnO}_4]{\text{acidified}} C_6H_5COOH$

c) $MnO^-_4 + Fe^{2+} \longrightarrow$?

$2MnO^-_4 + 10Fe^{2+} + 16H^+ \longrightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O$

d) $KMnO_4 \xrightarrow[\text{Red hot}]{\triangle}$?

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

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

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

f) $Na_2Cr_2O_7 + KCl \longrightarrow$?

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

11. What are interstitial compounds?

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. Example : TiC, $ZrH_{1.92}$,Mn_4N

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

13.

Ti^{3+}	Mn^{2+}
1) Electronic Configuaration of Ti^{3+} is [Ar] $3d^1 4s^0$	1) Electronic Configuration of Mn^{2+} is [Ar] $3d^5 4s^0$
2) No. of unpaired electron = 1	2) No. of unpaired electron = 5
3) Spin only magnetic moment $\mu_s = \sqrt{n(n+2)}$ $= \sqrt{1(1+2)} = \sqrt{3}$ = **1.732 μB**	3) Spin only magnetic moment $\mu_s = \sqrt{n(n+2)}$ $= \sqrt{5(5+2)} = \sqrt{35}$ = **5.92μB**

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

Electronic Configuration of Ce^{4+} = [Xe] $4f^0 5d^0 6s^0$

Electronic configuration of Co^{2+} = $[Ar]3d^7 4s^0$

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

$E^0_{M^{2+}/M}$ for 3d series upto Mn is highly negative. Therefore +2 states become more stable in the first half of the first row transition elements.

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

Fe^{3+}	Fe^{2+}
Electronic configuration =[Ar] $3d^5 4s^0$	nic configuration =[Ar] $3d^6 4s^0$
It consists of 5 unpaired electrons	It consists of 4 unpaired electrons.
lf filled d sub shell and more stable.	Partially filled d sub shell and less stable

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

16. Explain the variation $E^{O}_{M^{3+}/M^{2+}}$ in 3dseries

- The standard electrode potential for the M^{3+}/M^{2+} half cell gives the relative stability between M^{3+} and M^{2+}.
- The negative values for titanium, vanadium and chromium indicate that the higher oxidation state is preferred. If we want to reduce such a stable Cr^{3+} ion, strong reducing agent which has high negative value for reduction potential like metallic zinc (E=-0.76V) is required.
- The high reduction potential of Mn^{3+} / Mn^{2+} indicates Mn^{2+} is more stable than Mn^{3+}. For Fe^{3+} / Fe^{2+} the reduction potential is 0.77V, and this low value indicates that both Fe^{3+} and Fe^{2+} can exist under normal conditions.

17. Compare lanthanides and actinides.

	Lanthanoids	Actinoids
1	Differentiating electrons enters in 4f orbital.	Differentiating electrons enters in 5f orbital.
2	Binding energy of 4f orbitals are higher.	Binding energy of 5f orbitals are lower.
3	They show less tendency to form complexes	They show greater tendency to form complexes.
4	Most of the lanthanoids are colourless.	Most of the actinoids are coloured. For Eg. U^{3+} (Red), U^{4+}(Green),UO_2^{2+} (Yellow)
5	They do not form oxo cations	They do not form oxo cations such $U0_2^{2+}$,NpO_2^{2+}
6	Besides +3 oxidation states lanthanoids show +2 and +4oxidationstates in few cases.	Besides +3 oxidation states actinoids show higher oxidationstates such as +4, +5, +6 and +7.

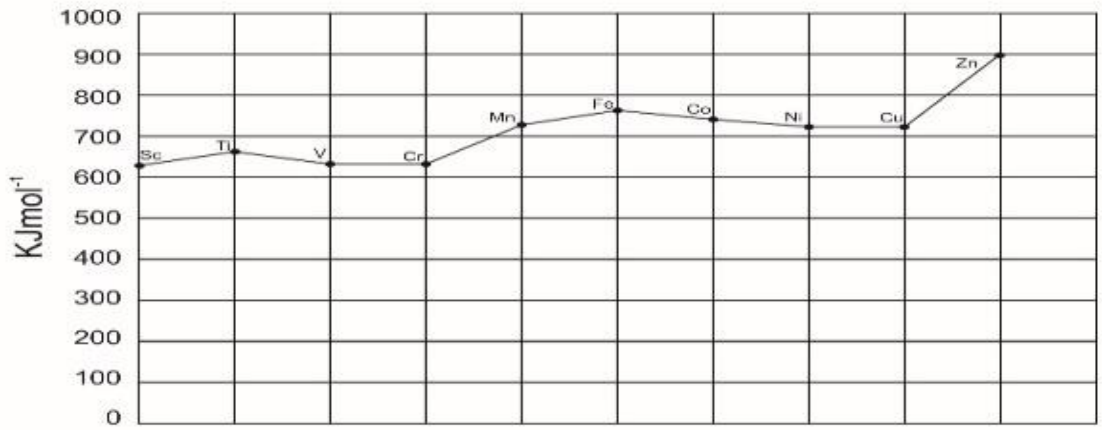
18. Explain why Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing.

Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half filled t_{2g} level. On the other hand, the change from Mn^{2+} to Mn^{3+} results in the half – filled (d^5) configuration which has extra stability.

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

Ionization energy of transition elements 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 change corresponding to the filling of d electrons.

IONIZATION ENTHALPIES OF FIRST SERIES



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

This is due to poor shielding effect by 5f electrons in actinoids as compared to that by 4f electrons in lanthanoids.

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

La $(OH)_3$	**$Lu(OH)_3$**
1)Size of La^{3+} is large	1) Size of Lu^{3+} is small
2)Ionic characters of La-OH bond is high	2) Ionic characters of Lu-OH bond is low
3)Covalent character of La-OH bond is low.	3) Covalent character of Lu-OH bond is high.
4)$La(OH)_3$ is more basic.	4) $Lu(OH)_3$ is less basic.

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

Europium (II)	**Cerium (II)**
Electronic configuration of Europium $[Xe]4f^7 5d^0 6s^0$	Electronic configuration of Cerium (II) is $[Xe]4f^1 5d^1 6s^0$
In Eu^{2+}, 4f sub shell is half filled	In Ce^{2+}, 4f and 5d sub shells are partially filled.
Eu^{2+} is more stable	Ce^{2+} is less stable

23. Why do Zirconium and Hafnium exhibit similar properties?

Zirconium and Hafnium exhibit similar properties due to lanthanoid contraction.

Series	Element	Atomic radius
4d series	Zr	145 pm
5d Series	Hf	144 pm

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

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

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

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

Since Cr^{2+} has larger negative value of E^0, Cr^{2+} is a stronger reducing agent than Fe^{2+}.

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

$E^0_{M^{2+}/M}$ for any metal depends upon the sum of the enthalpy changes taking place in the following steps.

$M_{(s)} + \Delta H_{(atom)} \longrightarrow M(g)$ $\quad$ ($\Delta H_{(atom)}$ = Enthalpy of atomization)

$M_{(g)} + \Delta H_{(IE)} \longrightarrow M^{2+}_{(g)} + 2e^-$ $\quad$ ($\Delta H_{(IE)}$ = Ionization Enthalpy)

$M^{2+}_{(g)} + H_2O \rightarrow M^{2+}_{(aq)} + \Delta H_{(HYD)}$ $\quad$ ($\Delta H_{(HYD)}$ = Hydration Enthalpy

Copper possesses a high enthalpy of atomization and low enthalpy of hydration. Hence $E^0_{Cu^{2+}/Cu}$ is positive.

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

Ions	Electronic configuration						Reason
Ti^{2+}	$3d^2$	↑	↑				These ions are coloured. Due to the presence, of unpaired 'd' electrons where d-d transition is possible.
V^{3+}	$3d^2$	↑	↑				
Fe^{3+}	$3d^5$	↑	↑	↑	↑	↑	
Ni^{2+}	$3d^8$	↑↓	↑↓	↑↓	↑	↑	
Co^{3+}	$3d^6$	↑↓	↑	↑	↑	↑	
Ti^{4+}	$3d^0$						Colourless due to the absence of d electrons.
Sc^{3+}	$3d^0$						
Cu^{+}	$3d^{10}$	↑↓	↑↓	↑↓	↑↓	↑↓	Colourless due to completely filled d orbital where there is no d-d transition.

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

The first transition metal scandium exhibits only +3 oxidation state, but all other transition elements exhibit variable oxidation states by losing electrons from (n-1)d orbital and ns orbitals as the energy difference between them is very small.

The first and last elements show less number of oxidation states and the middle elements with more number of oxidation states.

3d Series Elements	Oxidation States
Sc Mn Cu	+3 From +2 to +7 +1 and +2

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

Copper exhibits +1 oxidation state in the 3d series.

Reason : Electronic configuration of Cu = [Ar] $3d^{10}4s^1$

It can easily lose $4s^1$ electron to give stable $3d^{10}$ configuration. Hence, it exhibits +1 oxidation state.

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

Chromium	Zinc
1) Chromium (Z=24)	1) Zinc (Z=30)
2)Electronic Configuration of Chromium is [Ar] $3d^5\,4s^1$	2) Electronic configuration of Zinc is [Ar] $3d^{10}4s^2$
3) It can easily lose $4s^1$ electron to give stable half filled ($3d^5$) configuration. Hence first ionization enthalpy of chromium is less	3) It is difficult to remove one electron from $4s^2$ (completely filled). Hence first ionization enthalpy of zinc is comparatively more.

30. Transition metals show high melting points.Why?

The high melting points of transition metals are attributed to the involvement of greater number of electrons in the inter atomic metallic bonding from (n-1)d electrons in addition to ns electrons.

II Evaluate yourself

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

Electronic Configuration.

Fe^{3+} : [Ar] $3d^5$ Fe^{2+} : [Ar] $3d^6$

Mn^{2+} :[Ar] $3d^5$ Mn^{3+} : [Ar] $3d^4$

Fe^{3+} ion has half filled d orbital which is more sable than partially filled d orbital of Fe^{2+}

Mn^{2+} ion has half filled d orbital which is more stable than partially filled d orbital of Mn^{3+}

2. **Compare the stability of Ni^{4+} and Pt^{4+} from their ionization enthalpy values**

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

For Ni $IE_1+IE_2+IE_3+IE_4$=11,182 kJ

For Pt $IE_1+IE_2+IE_3+IE_4$= 9605 kJ

Pt^{4+} is thermodynamically more stable than Ni^{4+} .Smaller the Ionisation enthalpy greater will be the thermodynamic stability of its compounds

III.ADDITIONAL QUESTIONS

1.How d block elements are classified?

i.	3d series (4th period)	-	Scandium to Zinc
ii.	4d series (5th period)	-	Yttrium to Cadmium
iii.	5d serried (6th period)	-	Lanthanum,Haffinium to Mercury
iv.	6d series (7th period)	-	Actinium, Rutherfordium to Copernicium.

2.Which transition series contains radioactive elements?

6dseries(7th period) Ac,Rf to Cn.

In this period all the elements are radioactive and have very low half –life period.

3.Write the electronic configuration of Cr and Cu

Cr : Z=24

Cr : [Ar] $3d^5 4s^1$

Cu : Z=29

Cu :[Ar] $3d^{10} 4s^1$

4.**a In transition metals, which group elements are not hard?**

b. Which metal has highest electrical conductivity at room temperature.

a. Group 11 elements are not hard

b. Silver

5 Give reason for the slight increase in atomic radius of Zn

The **d** orbitals of Zn contain 10 electrons in which the repulsive interaction between the electrons is more than the effective nuclear charge and hence the orbitals slightly expand and atomic radius slightly increases.

6. Ionisation enthalpy to form Ni^{2+} =2490kJ

Ionization enthalpy to form Pt^{2+} =2655kJ

Which is thermodynamically stable Ni^{2+} (or) Pt^{2+}? Why?

The energy required to form **Ni^{2+}** is less than that of **Pt^{2+}** so **Ni^{2+}**compounds are thermodynamically more stable than **Pt^{2+}**compounds.

7. Calculate the number of unpaired electrons for the following ions?

a. Cu^+ b. Ni^{2+}

a) For

↑↓	↑↓	↑↓	↑↓	↑↓

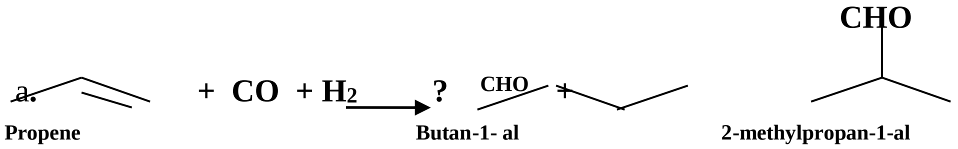
Cu^+ : Ar] $3d^{10}$

Number of unpaired electrons are zero (n=0)

b) For ↑↓ ↑↓ ↑↓ ↑ ↑ Ni^{2+} : [Ar] $3d^8$

Number of unpaired electrons are two (n = 2)

8. Name the catalyst used for the following reaction?



b. $CH_3CHO + CO \longrightarrow$? CH_3-COOH

Acetaldehyde Acetic acid

c. In the manufacture of Sulphuric acid from SO_3

a.$Co_2(CO)_8$

b.Rh / Ir Complex

c.Vanadium pentoxide (V_2O_5)

9. Why transition metals form number of alloys ?

Atomic sizes of transition metals are similar and one metal atom can be easily replaced by another metal atom from its crystal lattice to form an alloy.

10. Why transition elements form complexes?

i. Transition metal ions are small and highly charged
ii. They have vacant low energy orbitals to accept an electron pair donated by other group

11. Under what oxidation state do transition metals form ionic oxide and covalent oxides?

Metals in lower oxidation state form ionic oxides.
Metals in higher oxidation state form covalent oxides
Example Mn_2O_7 is covalent. Oxidation state is +7.

12. Zn, Cd and Hg do not have partially filled d-orbitals why they are treated as transition elements?

They are treated as transition elements because their properties are an extension of the properties of the respective transition elements.

13. When potassium dichromate acts as oxidizing agent in the presence of H+ ion, what is the change in oxidation state of Chromium? Give equation ?

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

Oxidation state of chromium changes from +6 to +3

14.What is the action of heat on $K_2Cr_2O_7$?

On heating it decomposes and forms Cr_2O_3 and molecular oxygen

$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2\ Cr_2O_3 + 3O_2$

Red orange yellow

15.How neutral $KMnO_4$ oxidizes thio sulphate ion? Give equation?

It oxidizes thio sulphate into sulphate

$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 6SO_4^{2-} + 8MnO_2 + 2\ OH^-$

16.a. Which element in 3d series does not form ionic metal oxide ?

b. What is the acid formed when Mn_2O_7 dissolved in water?

a. Scandium

b .Mostly higher oxide are acidic. Mn_2O_7 dissolved in water to give permanganic acid ($HMnO_4$)

17. Why d orbitals containing symmetrical distribution of electron is more stable?

When the d – Orbitals are considered together , they will constitute a sphere. So the half filled and fully filled configuration leads to complete symmetrical distribution of electron density. An unsymmetrical distribution of electron density will result in building up of a potential difference. To decrease this and to achieve a tension free State with lower energy, a symmetrical distribution is preferred.

18. In first transition series from Sc to V atomic radius decreases, thereafter up to Cu atomic radius nearly the same. Why ?

The added 3d electrons only partially shield the increased nuclear charge and hence the effective nuclear change increases slightly. At the same time the extra electrons added to the 3d sub shell strongly repel the 4s electron These two forces are operated in opposite direction As they tend to balance each other it leads to constancy in atomic radius

19.Which is more acidic in nature MnO(Mn^{2+}) or Mn_2O_7 (Mn^{7+}) why?

Mn_2O_7 is more acidic in nature. Acidic strength increases with increase in oxidation state of the element. In higher oxidation state there is no scope for further loss of electron, rather it can accept electrons. So it is more acidic in nature.

20.Classify the following oxides as acidic, basic and amphoteric oxides?

i.CrO ii. Cr_2O_3 iii.CrO_3

i.CrO –Basic oxide
ii.Cr_2O_3 – Amphoteric oxide
iii. CrO_3 – Acidic oxide

21. Calculate spin magnetic moment of Co^{2+}?

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

Number of unpaired electrons n=3

Magnetic moment $\mu = \sqrt{n(n+2)}$

$= \sqrt{3(3+2)}$

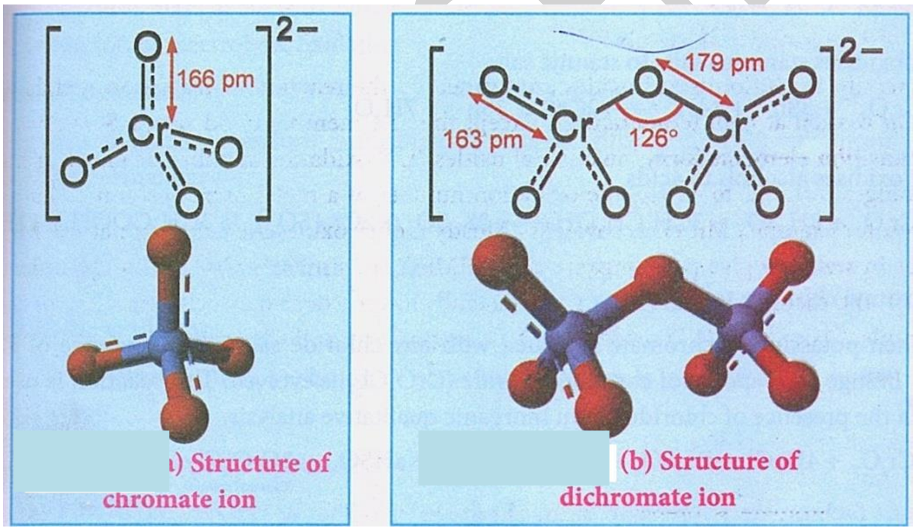
$= \sqrt{15} = 3.87\ \mu_B$

22.Why transition metal and its compound act as good catalyst?

Transition metal has energetically available d orbitals.

d-orbitals can accept electrons from reactant molecule and form bond with reactant molecule using its d electron.

23. Draw the structure of chromate ion and dichromate ion ?



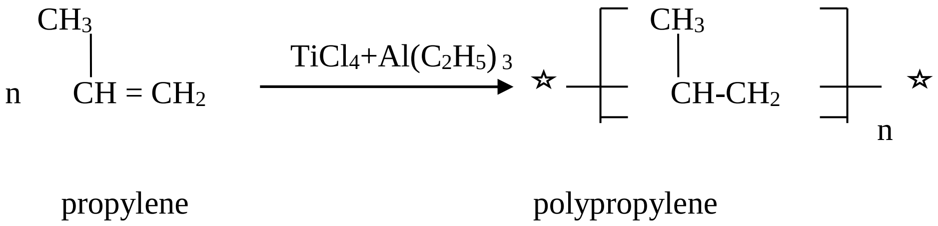
[redacted]) Structure of chromate ion

[redacted] (b) Structure of dichromate ion

24.What is zeigler – Natta Catalyst?Give a reaction in which it catalysis?

zeigler – Natta Catalyst ($TiCl_4 + Al(C_2H_5)_3$

Mixture of $TiCl_4$ and trialkyl aluminium.



$$n\ \overset{CH_3}{\overset{|}{CH}}=CH_2 \xrightarrow{TiCl_4+Al(C_2H_5)_3} ☆\!-\!\left[\overset{CH_3}{\overset{|}{CH}}-CH_2\right]_n\!-\!☆$$

propylene polypropylene

25.a) What is the oxidation state of chromium in chromate and dichromate ion?
b) Which is predominant in alkaline and acidic solution?

a) In both chromate and dichromate ion, oxidation state of chromium is +6

b) In aqueous solution chromate and dichromate ions are inter convertible.

In alkaline solution chromate ion is predominant.

In acidic solution dichoromate ion is predominant.

26.**Give the reaction of cold and hot conc H_2SO_4 with $KMnO_4$?**

<u>Cold conc H_2SO_4</u>

$$\underset{}{2KMnO_4 + 2\underset{\text{(Cold)}}{H_2SO_4}} \longrightarrow Mn_2O_7 + 2\ KHSO_4 + H_2O$$

$$Mn_2O_7 \longrightarrow 2MnO_2 + 3O_2$$

<u>Hot conc H_2SO_4</u>

$$4KMnO_4 + 6\ \underset{\text{(Hot)}}{H_2SO_4} \longrightarrow 4MnSO_4 + 2K_2SO_4 + 6\ H_2O + 5O_2$$

27. Exhibit the oxidizing property of MnO_4^- ion in acid medium, neutral medium and alkaline medium ?

In acid medium, permanganate ion is converted into Mn^{2+} ion

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

In neutral medium, it is reduced to MnO_2

$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$

In alkaline medium, , permanganate ion is converted into manganate

$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$

This manganate is further reduced to MnO_2 by some reducing agent

$MnO_4^{2-} + H_2O \rightarrow MnO_2 + 2OH^- + [O]$

Over all reaction

$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$

It is similar as that for neutral medium

28. HCl and HNO_3 are not used for generating acidic medium for $KMnO_4$Why ? Suggest suitable acid medium for $KMnO_4$?

HCl cannot be used. Since It reacts with $KMnO_4$

$2MnO_4^- + 10Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$

HNO_3 also cannot be used since it is a good oxidizing agent and react with reducing agents in the reaction.

H_2SO_4 is the most suitable acid since it does not react with potassium permanganate

29. Calculate the equivalent weight of $KMnO_4$?

Equivalent weight of $KMnO_4$ in acid medium $= \dfrac{\text{Molecular weight of } KMnO_4}{\text{No of moles of electrons transferred}}$

$=158/5$

$= 31.6$

Equivalent weight of $KMnO_4$ in Basic medium $= \dfrac{\text{Molecular weight of } KMnO_4}{\text{No of moles of electrons transferred}}$

$=158/1$

$=158$

Equivalent weight of $KMnO_4$ in neutral medium$=\dfrac{\text{Molecular weight of } KMnO_4}{\text{No of moles of electrons transferred}}$

$=158/3$

$=52.67$

30. Write the uses of $KMnO_4$?

i. It is used as a strong oxidizing agent.
ii. It is used for the treatment of various skin infections and fungal infections of the foot.
iii. It used in water treatment industries to remove iron and hydrogen sulphide from well water.
iv. It is used as a Bayer's reagent for detecting unsaturation in an organic compound.

v. It is used in quantitative analysis for the estimation of ferrous salts, oxalates, hydrogen peroxide and iodides.

31. Complete the following reaction and give the balanced equation?

i $MnO_4^- + \begin{matrix} COO^- \\ | \\ COO^- \end{matrix} + H^+ \longrightarrow ?$

ii $MnO_4^- + H_2S \longrightarrow ?$

i. $2MnO^-_4 + 5 \begin{matrix} COO^- \\ | \\ COO^- \end{matrix} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

ii. $2MnO_4^- + 3H_2S \longrightarrow 2MnO_2 + 3S + 2\,OH^- + 2H_2O$

32. What is the hybridization in Mn^{7+} ion of $KMnO_4$ and what is the structure of permanganate ion?

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

33. Compound A is an orange red crystalline solid which on heating with NaCl and conc H_2SO_4 evolves red orange vapours B. On passing the vapors of B into a solution of NaOH and then adding the solution of acetic acid and lead acetate, yellow precipitate C is obtained. Identify A,B, andC. Give chemical equations for these reactions

What is the name of this test?

(i) $\underset{(A)}{K_2Cr_2O_7} + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + \underset{(B)}{2CrO_2Cl_2} + 3H_2O$

Chromylchloride

(ii) $CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$

$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4 + 2CH_3COONa$

A - $K_2Cr_2O_7$
B - CrO_2Cl_2
C - $PbCrO_4$

This is chromyl chloride Test.

34.What are the properties of Interstitial compound?

They are hard and show electrical and thermal conductivity

i. They have high melting points higher than those of pure metals
ii. Transition metal hydrides are used as powerful reducing agents
iii. Metallic carbides are chemically inert.

35. Complete the following reactions and give the balanced equations?

$Cr_2O_7^{2-} + S^{2-} + H^+ \longrightarrow ?$

$MnO_4 + I^- + H^+ \longrightarrow ?$

$Cr_2O_7^{2-} + 3S^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O$

$2Mn\bar{O}_4 + 1\bar{0}\,I + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

36. What is Hume- Rothery rule to form a substitute alloy?

i. The difference between the atomic radius of solvent and solute is less than 15%
ii. Both the solvent and solute must have the same crystal structure and valence.
iii. The eletronegativity difference between solvent and solute must be close to zero.

37.What are the uses of potassium dichromate?

i. It is used as a strong oxidizing agent.
ii. It is used in dyeing and printing.
iii.It used in leather tanneries for chrome tanning.
iv.It is used in quantitative analysis for the estimation of iron compounds and iodides.

UNIT- 5

COORDINATION CHEMISTRY

TEXTBOOK QUESTIONS AND ANSWERS

Answer the following questions:

1. Write the IUPAC names for the following complexes.

i) $Na_2[Ni(EDTA)]$ - Sodium 2,2’,2’’,2’’’-(ethane-1,2-diyldinitrilo)tetraacetatoNickelate(II)

ii) $[Ag(CN)_2]^-$ -dicyanidoargentate(I) ion

iii) $[Co(en)_3]_2(SO_4)_3$ -tris(ethane1,2-diamine)cobalt(III)sulphate

iv) $[Co(ONO)(NH_3)_5]^{2+}$ -pentaamminenitrito-κ-O-cobalt(III)ion

v) $Pt(NH_3)_2Cl(NO_2)]$ -diamminechloridonitrito- κ-N-platinum(II)

2. Write the formula for the following coordination compounds.

a) potassiumhexacyanidoferrate(II) – $K_4[Fe(CN)_6]$

b) pentacarbonyliron(0) - $[Fe(CO)_5]$

c) pentaamminenitrito- κ -N-cobalt(III)ion – $[Co(NH_3)_5(NO_2)]^{2+}$

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

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

3. Arrange the following in order of increasing molar conductivity

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

On ionisaton

i) $Mg[Cr(NH_3)(Cl)_5] \rightarrow Mg^{2+} + [Cr(NH_3)(Cl)_5]^{2-}$

ii) $[Cr(NH_3)_5Cl]_3[CoF_6]_2 \rightarrow 3[Cr(NH_3)_5Cl]^{2+} + 2[CoF_6]^{3-}$

iii) $[Cr(NH_3)_3Cl_3] \rightarrow$ does not ionize

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

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

4. Ni^{2+} is identified using alcoholic solution of dimethyl glyoxime. Write the structural formula for the rosy red precipitate of a complex formed in the reaction.

Complex : $[Ni(DMG)_2]$ Rosy red

5. $[CuCl_4]^{2-}$exists while $[CuI_4]^{2-}$does not exist why?

Both the species contains Cu^{2+} ions

In $[CuCl_4]^{2-}$ the chloride ion does not reduce Cu^{2+} to Cu^+	In $[CuI_4]^{2-}$complex iodide ion reduces Cu^{2+} to Cu^+ therefore the complex is unstable.

6. Calculate the ratio of $\frac{[Ag+]}{[Ag(NH3)]2+}$ in 0.2 M solution of NH_3. If the stability constant for the complex $[Ag(NH_3)_2]^+$ is 1.7 X 10^7.

$$Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^{2+}$$

$$\beta = \frac{[Ag(NH3)2]2+}{[Ag+][NH3]2}$$

$$\frac{[Ag(NH3)2]}{[Ag+]} = \beta\ [NH_3]^2$$

$$= 1.7x10^7 \text{ x } (0.2)^2$$

$$\frac{[Ag(NH3)2]}{[Ag+]} = 1/1.7x10^7x(0.2)^2 = \ 14.7 \text{ x } 10^{-7}$$

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

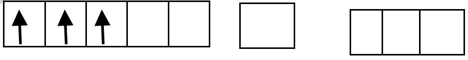
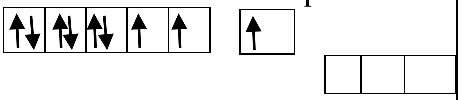
<u>Coordination compound used in medicine:</u>

Ca- EDTA chelate	radioactive poisoning	removing lead and radioactive metal ions from body.
Cis- Platin	antitumour drug	cancer treatment

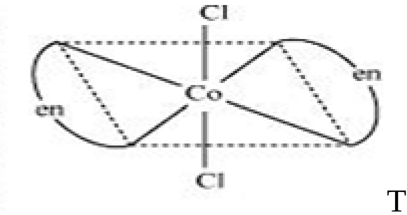
<u>Biologically important coordination compounds:</u>

COORDINATION COMPLEX	**CENTRALMETALION**	**USES**
RBC COMPOSED OF HEME GROUP	Fe^{2+}	Carrying oxygen from lungs to tissue, CO_2 from tissue to lungs
CHLOROPHYLL	Mg^{2+}	Photosynthesis

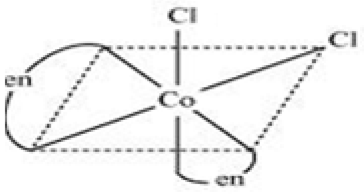
8. Based on VB theory explain why $[Cr(NH_3)_6]^{3+}$ is paramagnetic, while $[Ni(CN)_4]^{2-}$ is diamagnetic.

Complex	**$[Cr(NH_3)_6]^{3+}$**	**$[Ni(CN)_4]^{2-}$**
Central metal atom/ ion and its electronic configuration	Cr(III) $3d^3\ 4s^0$	Ni(II) $3d^8 4s^0$
Outer orbitals of metal atom/ion	$3d^3$ $4s^1 4p$ 	$3d^8$ $4s^2$ $4p$ 
Nature of ligand	NH_3 is a weak ligand pairing of 3d electrons in the metal does not take place	CN^- is a strongfield ligand causes the pairing of 3d electrons in the metal
Magnetic property	The number of unpaired electron n=3 Therefore the magnetic moment is $\mu_s = \sqrt{n(n+2)}$ $\mu_s = \sqrt{3(3+2)}$ =3.87 BM	The number of unpaired electron n=0 Therefore the magnetic moment is μ_s= 0 BM

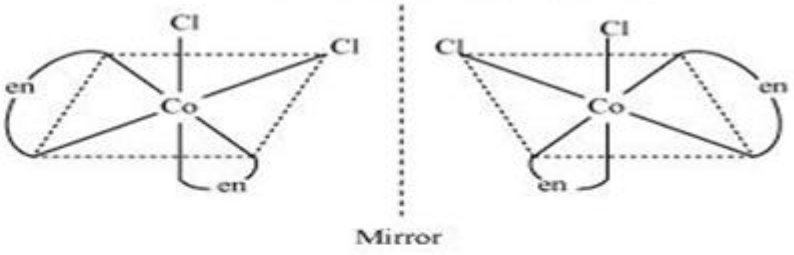
9. Draw all possible geometrical isomers of the complex $[Co(en)_2Cl_2]^+$ and identify the optically active isomer.



Trans isomer $[Co(en)_2Cl_2]^+$ does not show optical isomerism because of plane of symmetry



Cis isomer shows optical isomerism because it lacks symmetry



Cis $[CoCl_2(en)_2]^+$ isomer-optically active
(Non-superimposable mirror images)

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

CONTENT	$[Ti(H_2O)_6]^{3+}$	$[Sc(H_2O)_6]^{3+}$
Central metal ion	Ti^{3+}	Sc^{3+}
Electronic Configuration	$3d^1$ [↑][ ][ ][ ][ ]	$3d^0$ [ ][ ][ ][ ][ ]
Number of unpaired electron	1	0
	Ti^{3+} has one unpaired electron for d-d transition, hence it is coloured	No unpaired electron, so d-d transition is not possible hence it is not coloured

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

$[PdI_2(ONO)_2(H_2O)_2]$ Diaquadiiododinitrito-κ -O Palladium (IV)

$[PdI_2(NO_2)(H_2O)_2]$ Diaquadiiododinitrito-κ -N palladium (IV)

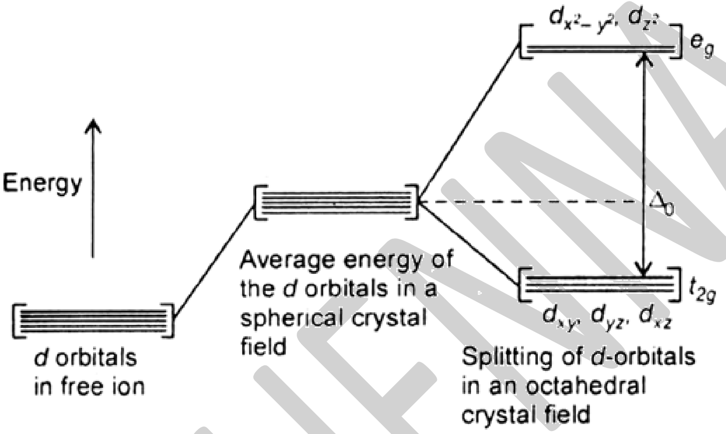
They will exhibit linkage isomerism

12. Give one test to differentiate $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5 SO_4]Cl$.

$[Co(NH_3)_5Cl]SO_4 \rightarrow [Co(NH_3)_5Cl]^{2+} + SO_4^{2-}$	**$[Co(NH_3)_5SO_4]Cl \rightarrow [Co(NH_3)_5SO_4]^{+} + Cl^{-}$**
• This complex produces sulphate ion in aqueous solution. • On addition of $BaCl_2$, white precipitate of $BaSO_4$ is produced. • No reaction with $AgNO_3$	• This complex produces chloride ion in aqueous solution. • On addition of $AgNO_3$, curdy white precipitate of AgCl is produced. • No reaction with $BaCl_2$

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

The energy of the orbitals dx^2-$y^2$and dz^2(represented as e_g orbitals) will increase by $\frac{3}{5}\Delta_o$ while that of the other three orbitalsd_{xy}, d_{yz}andd_{zx}(represented as t_{2g} orbitals) decrease by $\frac{2}{5}\Delta_o$. Here, Δ_o represents the crystal field splitting energy in the octahedral field.



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

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.($-NO_2$/$-ONO^-$)

Example :

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

15**. Write briefly about the applications of coordination compounds in volumetric analysis.**

Complexometric Titrations:

An example of this is the use of EDTA in the volumetric determination of a wide variety of metal ions in solution, e.g. Zn^{2+}, Pb^{2+},Ca^{2+},Co^{2+},Ni^{2+},Cu^{2+}, etc. By careful adjustment of the pH and using suitable indicators, mixtures of metals can be analysed, e.g. Bi^{3+} in the presence of Pb^{2+}. Alternatively, EDTA may be used as a masking agent to remove a metal ion which would interfere with the analysis of a second metal ion present.

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

a) NH_3b) en c) ox^{2-} d) triaminotriethylaminee) pyridine

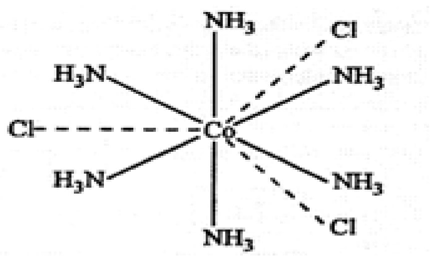
Ligand	**Number of donoratom**	**Type of ligand**
NH_3	1 (N-donor)	monodentate
en	2 (2N-donor)	Bidentate
ox^{2-} (oxalato)	2 (2 –O- donor)	Bidentate
Triaminotriethylamine	3 (3N-donor) Central nitrogen atom cannotbecooridnated	Tridentate
Pyridine	1 (N-donor)	monodentate

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

S.NO	Doublesalt	Coordinationcompound
1.	Double salts lose their identity in aqueous solution by completely dissociating in to ions in the solvent	They don't lose their identity in aqueous solution as they do not ionize completely (the complex ion further doesnot get ionized)
2.	They give test for all the constituent ions	They do not show test for all their constituent ions for example in $K_4[Fe(CN)_6]$, it does not show the test for Fe^{2+} and CN^-
	Example : $K_2SO_4.Al_2(SO_4)_3.24H_2O$	Example : $K_4[Fe(CN)_6]$

18. Write the postulates of Werner's theory.

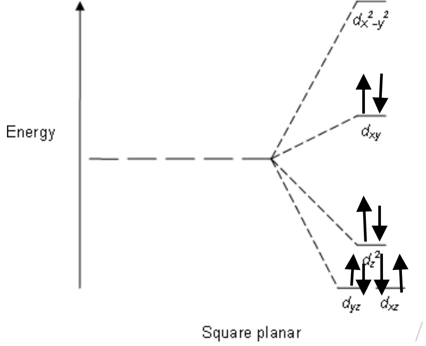
1. Most of the elements exhibit, two types of valence.
- Primary valence
- Secondary valence
2. Primary valence is referred as the oxidation state of the metal atom and the Secondary valence as the coordination number.
3. The primary valence of a metal ion is positive in most of the cases and zero in certain cases. They are always satisfied by negative ions.
4. The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these.
5. 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.
    - The outer sphere is called ionisation sphere.
6. The primary valences - non-directional
   the secondary valences - directional.
7. The geometry of the complex is determined by the spacial arrangement of the groups which satisfy the secondary valence.
   Six - octahedral geometry.
   Four -either tetrahedral or square planar geometry.



19. **$[Ni(CN)_4]^{2-}$ is diamagnetic, while $[Ni(Cl)_4]^{2-}$ is paramagnetic using crystal field theory?**

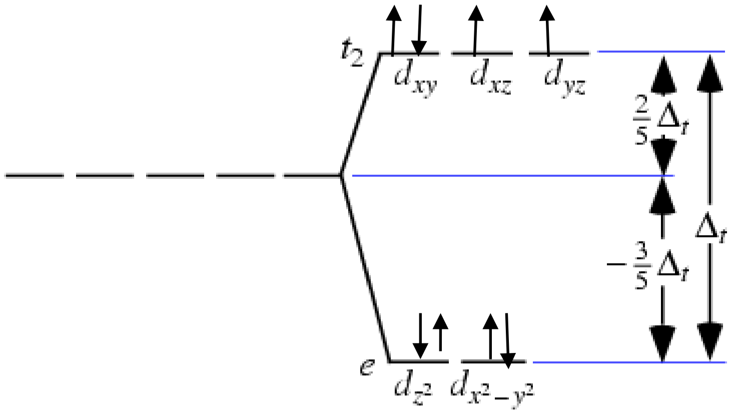
Square planar geometry of **$[Ni(CN)_4]^{2-}$**experience undergo Jahn Teller Distortion

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



Jahn Teller distrotion
The d orbitals fill with 8 electrons, then, with a *low spin* configuration. The even number of d orbitals will get filled (dyz,dxz,dz^2,dxy) with an even number of 3d electrons.
This gives rise to a **diamagnetic** configuration, as expected.

$[NiCl_4]^{2-}$:
Splitting in the tetrahedral field



The d orbitals here fill with 8 electrons, but instead, *high spin*. So, the dz^2 and $dx^2\text{−}y^2$fill with one electron each, then the dxy, dxz, and dyz with one electron each, and then pairing occurs only after that, filling the dz^2, $dx^2\text{−}y^2$, and dxy completely. This leaves two unpaired electrons in the t2 orbitals, and thus this complex is **paramagnetic** with two unpaired electrons, as expected.

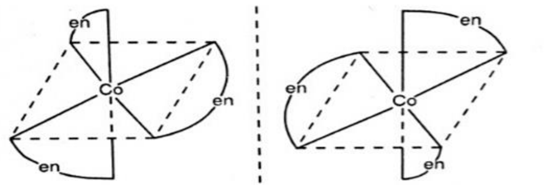
20. Why tetrahedral complexes do not exhibit geometrical isomerism.

- All the four ligands are **adjacent or equidistant** to one another in tetrahedral complex.
- As the relative positions of donor atoms of ligands attached to the central atom are same with respect to each other.

21. Explain optical isomerism in coordination compounds with an example.
Optical Isomerism

- Coordination compounds which possess chirality exhibit optical isomerism.
- 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.

  Example:



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

The exchange water molecules in the crystal lattice with a ligand in the coordination entity will give different isomers. These type of isomers are called hydrate isomers.

Example :

$CrCl_3.6H_2O$ has three hydrate isomers as shown below.

$[Cr(H_2O)_6]Cl_3$	violet colour	gives three chloride ions in solution
$[Cr(H_2O)_5Cl]Cl_2.2H_2O$	pale green colour	two chloride ions in solution
$[Cr(H_2O)_5Cl_2]Cl.H_2O$	dark green colour	one chloride ion in solution.

23. What is crystal field splitting energy?

The splitting of five d-orbitals of the metal ion in the presence of ligand field into two sets having different energies is called crystal field splitting or energy level splitting. The difference in the energy of the two sets is called crystal field splitting energy.

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

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

CFSE (ΔE_o) = $\{E_{LF}\} - \{E_{iso}\}$

$= \{[nt_{2g}(-0.4)+n_{eg}(0.6)]\ \Delta o + n_pP\} - \{n'_p\ P\}$

nt_{2g} is the number of electrons in t_{2g} orbitals

negis number of electrons in eg orbitals

npis number of electron pairs in the ligand field

n'pis the number of electron pairs in the isotropic field (barycentre).

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

CONTENT	$[Ni(H_2O)_6]^{2+}$	$[Ni(CN)_4]^{2-}$
Central metal ion	Ni^{2+}	Ni^{2+}
Electronic Configuration	$3d^8$ ↑↓ ↑↓ ↑↓ ↑ ↑ $4s^0$ ☐	Since CN^- is a strong ligand pairing of electron takes place $3d^8$ ↑↓ ↑↓ ↑↓ ↑↓ ☐ $4s^0$ ☐
Number of unpaired electron	2 The 2 unpaired electron which don't pair up in the presence of weak H_2O ligand. So d-d transition is possible.	0 d-d transition not possible

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

In metal carbonyls, the bond between metal atom and the carbonyl ligand consists of two components.

- An electron pair donation from the carbon atom of carbonyl ligand into a vacant d-orbital of central metal atom.

σ

- This electron pair donation forms M←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 ←CObond in metal carbonyls.

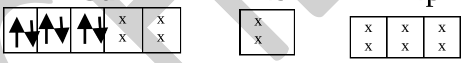
27. What is the coordination entity formed when excess of liquid ammonia is added to an aqueous solution copper sulphate?

When excess of liquid ammonia is added to an aqueous solution of copper sulphate it gives tetraammine copper (II) sulphate.

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

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

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

	$[Co(C_2O_4)_3]^{3-}$
Central metal /atom	Co(III)
Electronic configuration	Co: $3d^7$ $4s^2$ 4p 
	$C_2O_4^{2-}$ is a strong field ligand.
$[Co(C_2O_4)_3]^{3-}$	$3d^6$ $4s^0$ 4p 
Geometry	Inner orbital (low spin) complex
Hybridization	Octahedral
Number of unpaired electron	d^2sp^3
	n = 0 ; DIAMAGNETIC

29. What are the limitations of VB theory?

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

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

	$K_4[Mn(CN)_6]$
Oxidation state	4(+1) + x + 6(-1) = 0; x = +2
Coordination number	6
Nature of ligand	CN^-Monodentate ligand
Magnetic property	Paramagnetic(one unpaired electron)
Electronic configuration in octahedral crystal field	CN^- is strong field ligand. $t^5_{2g}e^0_g$

EVALUVATE YOURSELF

1. When a cooridantion 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.

One mole of silver chloride is formed therefore there is one ionizable chloride ion Cl^- (counter ion)
There are no free solvent molecules therefore all the water molecules are coordinated
Hence, the coordination compound is $[Cr(H_2O)_4Cl_2]Cl$
Secondary valency is 6

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

(i) Central metal atom/ion	Pt^{2+}
(ii) Ligands and their types	NO_2 is negative ligand, H_2O and NH_3 neutral monodentate ligand
(iii) Coordiantion entity	$[Pt (NO_2)(H_2O)(NH_3)_2]^{+1}$
(iv) Oxidation number of central metal atom	2+
(v) Coordination number	4

3. Write the IUPAC name for the following compounds.

(i) $K_2[Fe(CN)_3(Cl)_2(NH_3)]$ - Potassium amminedichloridotricyanidoFerrate(III)

(ii) $[Cr(CN)_2(H_2O)_4][Co(ox)_2(en)]$ Tetraaquadicyanidochromium(III)(ethane1,2-diamine)di(oxalato) cobaltate(III)

(iii) $[Cu(NH_3)_2Cl_2]$ diamminedichloridocopper(II)

(iv) $[Cr(NH_3)_3(NC)_2(H_2O)]^+$ triammineaquadicyandio-κ -N-chromium(III) ion

(v) $[Fe(CN)_6]^{4-}$ Hexacyanidoferrate(II) ion

4. Give the structure for the following compounds.

(i) diamminesilver(I) dicyanidoargentate(I) - $[Ag(NH_3)_2][Ag(CN)_2]$

(ii) pentamminenirtrito-κ -Ncobalt(III) ion – $[Co(NH_3)_5NO_2]^{+2}$

(iii) hexafluoridocobaltate(III) ion - $[CoF_6]^{3-}$

(iv) dichloridobis(ethylenediamine)Cobalt(III) sulphate - $[Co(en)_2Cl_2]_2SO_4$

(v) Tetracarbonylnickle(0) - $[Ni(CO)_4]$

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?

Silver nitrate reacts with chloride ions to give silver chloride white precipitate, therefore in one isomer the Cl^- is the counter ion. Whereas silver nitrate reacts with Iodide ion to form yellow precipitate therefore the counter ion is I^-. Therefore the isomers are called ionization isomer

ISOMERS	
$[Co(NH_3)_4I_2]$ Cl – white precipitate	$[Co(NH_3)_4Cl\ I]I$ - Yellow precipitate

6. Three compounds A,B and C have the molecular 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 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: $[Cr(H_2O)_5Cl]Cl_2.\ H_2O$

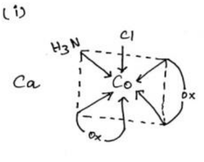
Compound C: $[Cr(H_2O)_3Cl_3].\ 3H_2O$

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

Given Compound	**Isomer**	**Type**
$[Co(en)_3][Cr(CN)_6]$	$[Cr(en)_3][Co(CN)_6]$	Coordiantion Isomerism
$[Co(NH_3)_5(NO_2)]^{2+}$– N attached	$[Co(NH_3)_5(ONO)]^{2+}$ - O attached	Linkage Isomerims
$[Pt(NH_3)_3(NO_2)]Cl$	$[Pt(NH_3)_3Cl]NO_2$	Ionization Isomerism

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

(i)



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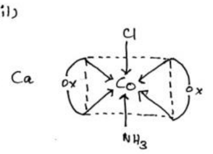

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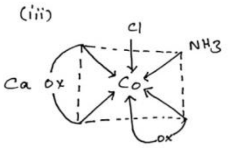

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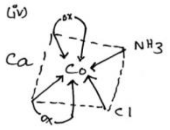

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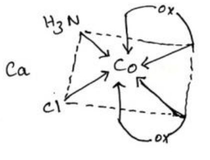
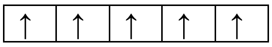


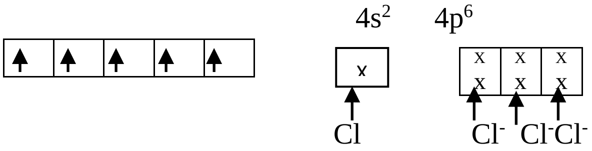
9. The spin only magnetic moment of tetrachloridomanganate(II) ion is 5.9 BM. On the basis of VBT predict the type of hybridization and geometry of the compound

Given complex $[MnCl_4]^{2-}$
When magnetic moment is 5.9BM it means it has 5 unpaired electron i.e., n=5
$3d^5$



Chlorido is a weak ligand therefore no pairing takes place .

$[MnCl_4]^{2-}$



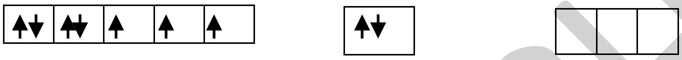
Hybridization sp^3
Shape : Tetrahedral

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

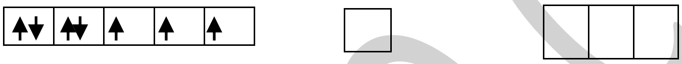
Co : $3d^7$ $4s^2$ 4p

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

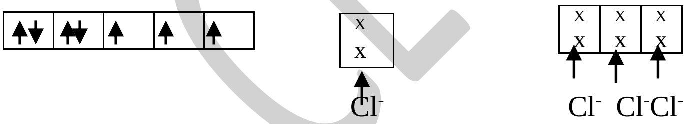
Co : $3d^7$ $4s^2$ 4p



Co^{2+}:$3d^7$ $4s^0$ 4p



Cl^- is a weak ligand therefore pairing does not takeplace
$[CoCl_4]^{2-}$



Number of unpaired electron, n=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. Where as 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^-
$[Co(en)_2Cl_2]Br$	$[Co(en)_2ClBr]Cl$

12. The mean pairing energy and octahedral field splitting energy $[Mn(CN)_6]^{4-}$ are 28,800 cm^{-1} and 38500 cm^{-1} respectively. Whether this complex is stable in low spin or high spin?

Given mean pairing energy 28000 cm^{-1} and Octahedral splitting energy is 38500 cm^{-1}
For $[Mn(CN)_4]^{4-}$ the electronic configuration Mn^{3+} is $3d^4$

↑	↑	↑	↑	

Case I: High Spin complex $t_{2g}^3\ e_g^1$ CFSE: $\{[n_{t2g}(-0.4) + n_{eg}(0.6)]\ \Delta_o + n_p P\} – \{n_p' P\}$ $=\{3(-0.4) + 1(0.6)]\ \Delta_o + 0xP\} – 0$ $= \{-1.2 +0.6\}\Delta_o$ $= -0.6\ \Delta_o$ $= -0.6 \times 38500$ $= -23100\ cm^{-1}$	Case II: low Spin complex $t_{2g}^4\ e_g^0$ CFSE: $\{[n_{t2g}(-0.4) + n_{eg}(0.6)]\ \Delta_o + n_p P\} – \{n_p' P\}$ $=\{4(-0.4) + 0(0.6)]\ \Delta_o + 1xP\} – 0$ $= \{-1.6\}\Delta_o + P$ $= -1.6(38500) + 28800$ $= - 61600 + 28800$ $= - 32800\ cm^{-1}$
Large negative CFSE indicate in case II that the complex is stable in low spin	

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

$[Cu(H_2O)_6]^{2+}$ ion is a stretched octahedron. The electronic configuration of copper(II) ion is [Ar} $3d^9$. When the complex ion formed by Cu^{2+} has an octahedral structure, the d orbitals will split in to two different orbitals t_{2g} and e_g. The electronic configuration is $(t_{2g})^6\ (e_g)^3$, the 3 electrons in $e_g$level can be arranged in two different ways $t_{2g}^6\ e_g^3\ (d_{z2})^2\ (d_{x2-y2})^1$ or $t_{2g}^6\ e_g^3\ (d_{z2})^1\ (d_{x2-y2})^2$. To break the degeneracy there is a distortion of the octahedral splitting
The presence of one unpaired electron in the e_g level makes $[Cu(H_2O)_6]^{2+}$ as paramagnetic

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

Given mean pairing energy 21000 cm^{-1} and Octahedral splitting energy is 13000 cm^{-1}
Forthe $[CoF_6]^3$ electronic configuration Co^{3+} is $3d^6$

↑↑	↑	↑	↑	↑

Case I: High Spin complex $t_{2g}^4\ e_g^2$ CFSE: $\{[n_{t2g}(-0.4) + n_{eg}(0.6)]\ \Delta_o + n_p P\} – \{n_p' P\}$ $=\{4(-0.4) + 2(0.6)]\ \Delta_o + 1xP\} – 1P$ $= \{-1.6 +1.2\}\Delta_o$ $= -0.4\ \Delta_o$ $= -0.4 \times 13000$ $= -5200\ cm^{-1}$	Case II: low Spin complex $t_{2g}^6\ e_g^0$ CFSE: $\{[n_{t2g}(-0.4) + n_{eg}(0.6)]\ \Delta_o + n_p P\} – \{n_p' P\}$ $=\{6(-0.4) + 0(0.6)]\ \Delta_o + 3xP\} – 1P$ $= \{-2.4\}\Delta_o +2\ P$ $= -2.4(13000) + 2x21000$ $= 10,800\ cm^{-1}$
High positive CFSE indicate in case II that low spin complex is not favorable one	

<u>**EXTRA QUESTIONS**</u>

1. Write the coordination number and oxidation state of platinum in the complex $[Pt(en)_2Cl_2]$

Coordination number and oxidation state of Pt in the complex $[Pt(en)_2Cl_2]$ are 6 and +2 because en is a bidentate and neutral ligand

2. What type of isomerism is exhibited by the complex $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_6][Cr(CN)_6]$?

Ionization isomerism and coordination isomerism respectively.

3.Write the postulates of Valence bond theory.

1. 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.

2. Each ligand should have at least one filled orbital containing a lone pair of electrons.
3. 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.
4. 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.
5. 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.
6. The hybridised orbitals are directional and their orientation in space gives a definite geometry to the complex ion.

Coordination number	Hybridisation	Geometry	Geometry
2	Sp	Linear	$[CuCl2]^-$, $[Ag(CN)_2]$

UNIT 6

SOLID STATE

I TEXT BOOK QUESTION AND ANSWERS

1. **Define unit cell.**
   A basic repeating structural unit of a crystalline solid is called a unit cell.
2. **Give any three characteristics of ionic crystals**.

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

3. Differentiate crystalline solids and amorphous solids.

S.NO	CRYSTALLINE SOLIDS	AMORPHOUS SOLIDS
1	Long range orderly arrangement of constituents	Short range random arrangement of constituents
2	Definite shape	Irregular shape
3	Anisotropic in nature	Isotropic in nature
4	They are true solids	They are pseudo solids (or) super cooled liquids
5	Definite Heat of fusion	Heat of fusion is not definite
6	They have sharp melting points	They do not have sharp melting points

4 Classify the following solids

a. P_4 b. Brass c. diamond d. NaCl e. Iodine

a	P_4	Covalent solid
b	Brass	Metallic solid
c	diamond	Covalent solid
d	NaCl	Ionic solid
e	Iodine	Molecular solid

5. Explain briefly seven types of unit cell.

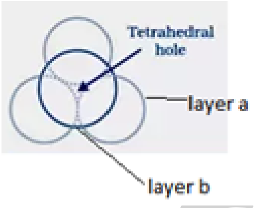
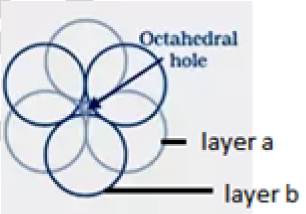
There are seven primitive crystal systems. They differ in the arrangement of their crystallographic axes and angles.

S.NO	NAME OF THE UNIT CELL	EDGE LENGTH	ANGLES
1	Cubic	$a=b=c$	$\alpha=\beta=\gamma=90^o$
2	Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq90^o$
3	Hexagonal	$a=b\neq c$	$\alpha=\beta= 90^o, \gamma=120^o$
4	Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90^o$
5	Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90^o$
6	Monoclinic	$a\neq b\neq c$	$\alpha= \gamma=90^o, \beta\neq90^o$
7	Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq90^o$

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

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

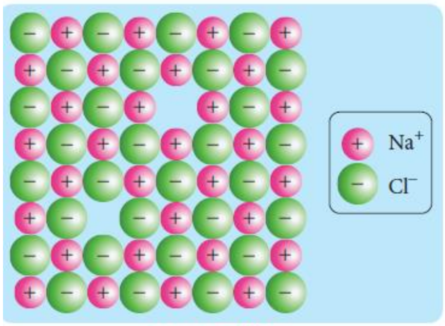
7. Distinguish tetrahedral and octahedral voids.

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

8. What are point defects?

Point defects are the deviations from ideal arrangement that occurs at some points or atoms in a crystalline substance.

9. Explain Schottky defect.

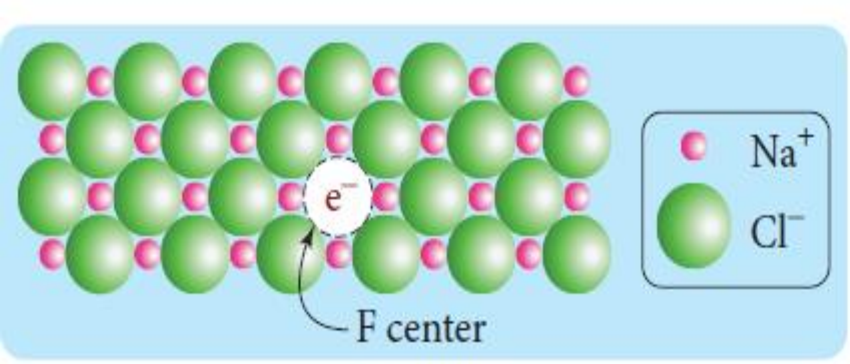


Schottky Defect

- Schottky defect arises due to the missing of equal number of cations and anions from the crystal lattice .Hence stoichiometry of the crystal is not changed.
- Ionic solids in which the cation and anion are of almost of similar size show schottky defect. Example: **NaCl**.
- Presence of large number of schottky defects in a crystal lowers its density.

10. Write short note on metal excess and metal deficiency defect with an example.(or) Write a short note on non-stoichiometric defects.

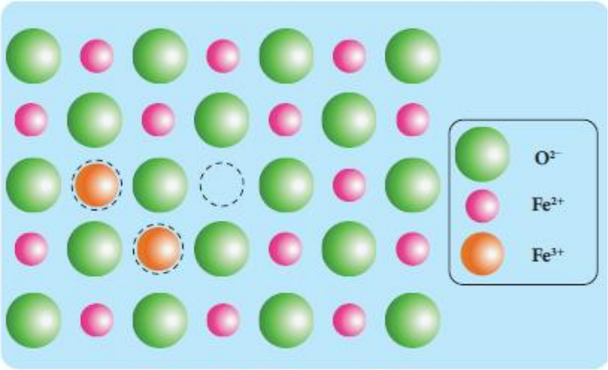
Metal excess defect:



Metal Excess Defect

- Metal excess defect arises due to the presence of more number of metal ions than the anions. Ex: **NaCl, KCl**
- The electrical neutrality of the crystal is 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 .
- The anionic vacancies, which are occupied by unpaired electrons are called **F centers.**

Metal deficiency defect:



Metal Deficiency Defect

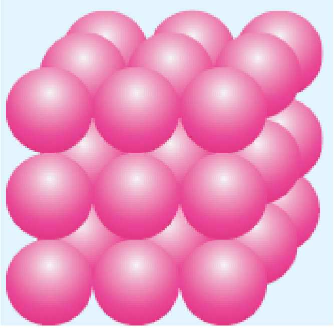
- Metal deficiency defect arises due to the presence of less number of cations than the anions.
- This defect is observed in a crystal in which the cations have variable oxidation state. For example, in **FeO** crystal, some of the Fe^{2+} ions are missing from the crystal lattice. To maintain the electrical neutrality, twice the number of other Fe^{2+}oxidized to Fe^{3+} ions.
- In such cases, overall number of Fe^{2+} and Fe^{3+} ions is less than the O^{2-} ions.

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

Number of atoms in fcc unit cell $= \frac{\mathrm{Nc}}{8} + \frac{\mathrm{Nf}}{2} = \frac{8}{8} + \frac{6}{2} = 1 + 3 = 4$

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

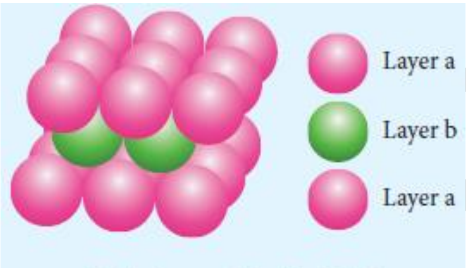
i. AAAA three dimensional packing:



Simple Cubic (SC)

- It occurs in simple cubic arrangement.
- This type of three dimensional packing arrangements 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.
- In simple cubic packing , each sphere is in contact with 6 neighbouring spheres- Four in its own layer, one above and one below and hence the coordination number is 6.

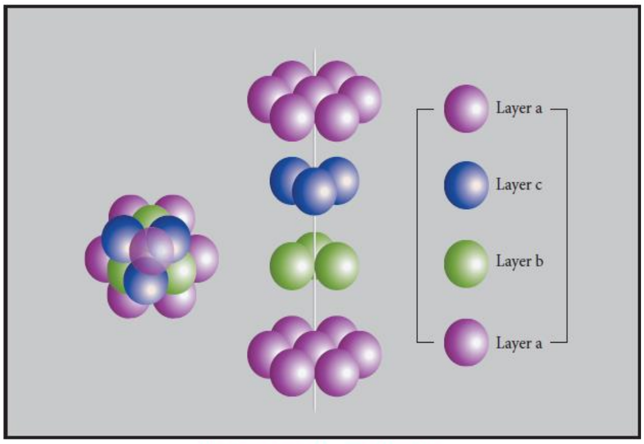
ii ABABA three dimensional packing:



Body Certered Cubic (BCC)

- It occurs in body centeredcubic arrangement.
- In this arrangement, the spheres in the **first layer(a)** are slightly separated and the **second layer (b)** is formed by arranging the spheres in the depressions between the spheres in **first layer (a)** .
- The third layer is a repeat of the first.
- This pattern ABABAB is repeated throughout the crystal.
- In this arrangement, each sphere is in contact with 8 neighbouring spheres- Four in the above layer and four in the below layer and hence the coordination number is 8.

iii ABCABC three dimensional packing:



abc arrangement – ccp structure

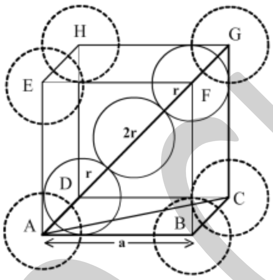
- The **first layer (a)** is formed by arranging the spheres as in the case of two dimensional ABAB arrangements.
- The **second layer (b)** is formed by placing the spheres in the depressions of the first layer.
- A **tetrahedral void(x) and octahedral voids(y)** are formed in the first layer.
- The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

13. Why ionic crystals are hard and brittle?

- Ionic crystal are hard due to strong electrostatic force of attraction between cations and anions.
- They are brittle because ionic bonds are non directional.

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

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



$In\ \Delta ABC$

$AC2 = AB^2 + BC^2$

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

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

In ΔACG

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

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

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

But $\sqrt{3}$ a = 4 r : $\quad r = \frac{\sqrt{3}}{4} a$

Volume of the sphere with radius 'r' = $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi \left[\frac{\sqrt{3}}{4}\ a\right]^3 = \frac{\sqrt{3}}{16}\pi a^3$

Number of spheres in bcc unit cell = 2

Total volume of all spheres in bcc unit cell= $2 \times \frac{\sqrt{3}}{16}\pi\ a^3 = \frac{\sqrt{3}}{8}\pi\ a^3$

Volume of the cube with edge length a = a x a x a = a^3

Packing fraction = $\frac{\text{Total volume occupied by all spheres in a unit cell}}{\text{Volume of unit cell}} \times 100$

$$=\frac{\frac{\sqrt{3}}{8}\pi a^3}{a^3} \text{ x } 100 = \frac{\sqrt{3}\pi}{8} \text{ x } 100 = \sqrt{3}\pi \text{ x } 12.5 = 1.732 \text{ x } 3.14 \text{ x } 12.5 = 68\%$$

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

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

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

Number of Ni^{2+} ion = x
Number ofNi^{3+} ion = y
x + y = 0.96
x = 0.96 –y
The charge on Ni^{2+} ion and charge on Ni^{3+} ion are balanced by the charge on O^{2-} ion.
Therefore,
2x + 3y = 2
2(0.96 – y) + 3y = 2
1.92 – 2y + 3y = 2
1.92+ y = 2
y = 2 – 1.92 = 0.08
x = 0.96– 0.08= 0.88
Percentage of Ni^{2+} in$Ni_{0.96}$ $O_{1.00}$ = 0.88 x 100 / 0.96 =**91.67 %**
Percentage of Ni^{3+} in$Ni_{0.96}$ $O_{1.00}$ = 0.08 x 100 / 0.96 =**8.33 %**

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

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

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

Given:

Edge of bcc (a)= 288pm = 2,88 x 10^{-8} cm (since density is given as gcm^{-3}, the edge length should be converted to cm). For bcc, Z = 2
Density = 7.2 gcm^{-3}
Mass of element = 208g

$$M = \frac{a^3\rho \text{ x } N_A}{n} = \frac{(2.88 \text{ x } 10^{-8})^3 \text{x } 7.2 \text{ x } 6.023 \text{ x } 10^{23}}{2}$$

$$= \frac{1035.9 \text{ x } 10^{-24} \text{ x } 10^{23}}{2} = 51.795 gmol^{-1}$$

Number of atoms of an element $= \frac{\text{mass}}{\text{atomic mass}}$x 6.023 x 10^{23}

Number of atoms present in 208g $= \frac{208}{51.795}$ x 6.023 x 1023 = **2.418 x 10^{24} atoms**

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

Given: r = 125pm.

For ccp $r = \frac{a\sqrt{2}}{4} = \frac{a\sqrt{2}}{2x\sqrt{2x\sqrt{2}}} = \frac{a}{2\sqrt{2}}$

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

$= 2 \times 1.414 \times 125\ \text{pm} = \mathbf{353.5\ pm}$

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

100 moles of NaCl is dopped with 10^{-2} moles of $SrCl_2$

Therefore 1 mole of NaCl is dopped with $10^{-2} / 100 = 10^{-4}$ moles of $SrCl_2$

Each Sr^{2+} ion will create 1 cation vacancy in NaCl.

Numberof cationic vacancy produced by 10^{-4} mol Sr^{2+} ion $= 6.023 \times 10^{23} \times 10^{-4}$

$= 6.023 \times 10^{19}$

Number of cation vacancies produced by $SrCl_2$ = $\mathbf{6.023 \times 10^{19}}$ **per mol**

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

Molar mass of KF = 39.1 + 19 = 58.1g/mol

$$a^3 = \frac{n \times M}{N_A \times \rho} = \frac{4 \times 58.1}{6.023 \times 10^{23} \times 2.48} = 15.56 \times 10^{-23} = 1.56 \times 10^{-24}$$

$$a = \sqrt[3]{1.56} \times 10^{-8} = 1.1597 \times 10^{-8}\ \text{cm}$$

$$\text{Inter ionic distance (d)} = \frac{a}{\sqrt{2}} = \frac{1.1597 \times 10^{-8}}{1.414} = 0.8202 \times 10^{-8} = 8.202 \times 10^{-9}\text{cm}$$

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

Given:

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

Number of atoms in fcc unit cell = 4

$$M = \frac{a^3 \rho \times N_A}{n} = \frac{(100 \times 10^{-10})^3 \times 10 \times 6.023 \times 10^{23}}{4}$$

$$= \frac{(1 \times 10^{-8})^3 \times 10 \times 6.023 \times 10^{23}}{4} = \frac{6.023}{4} = 1.505\ \text{gmol}^{-1}$$

$$\text{Number of atoms of an element} = \frac{\text{mass}}{\text{atomic mass}} \times 6.023 \times 10^{23}$$

Number of atoms in 1 g of crystal == $\frac{1}{1{,}505} \times 6.023 \times 10^{23}$= $\mathbf{4 \times 10^{23}}$**atoms**

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

Number of corner atoms (X) = $\frac{N_c}{8} = \frac{8}{8} = 1$

Number of body centre atoms(Y) $= \frac{N_b}{1} = \frac{1}{1} = 1$

Formula of the compound = **XY**

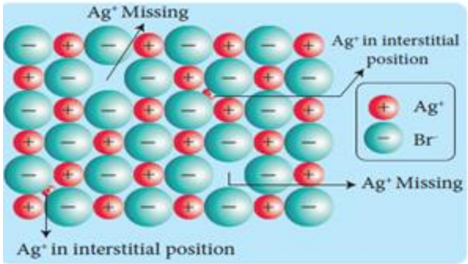
24. Sodium metal crystallizes in bcc structure with the edge length of the unit cell $4.3 \times 10^{-8}cm$. Calculate the radius of sodium atom.

Given: a = $4.3 \times 10^{-8}cm$.

For bcc

$$r = \frac{\sqrt{3}}{4} a = \frac{1.732 \times 4.3 \times 10^{-8}}{4} = \mathbf{1.86 \times 10^{-8}\ cm}$$

25. Explain Frenkel defect



Frenkel Defect

- Frenkel defect arises due to the dislocation of ions from its crystal lattice.
- The ion which is missing from the lattice point occupies an interstitial position.
- This defect occurs when cation and anion differ in size.
- Unlike Schottky defect, this defect does not affect the density of the crystal.Ex: AgBr

II EVALUATE YOURSELF:

1. **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?**

Given: Density =8.9 *gcm*$^{-3}$: a = 352.4 pm = 3.524×10^{-8}cm , Mass = 100g , Z = 4

$$M = \frac{a^3\rho \text{ x } N_A}{n} = \frac{(3.524\text{x } 10^{-8})^3\text{x } 8.9 \text{ x } 6.023 \text{ x } 10^{23}}{4}$$

$$= \frac{2345.9\text{x } 10^{-1}}{4} = 586.5\text{x}10^{-1} = 58.65 \text{ gmol}^{-1}$$

Number of atoms of an element=$\frac{\text{mass}}{\text{atomic mass}}$x 6.023 x 10^{23}

Number of atoms in 100g of an element = $\frac{100}{58.65}$x 6.023 x10^{23}= **10.27x 10^{23}atoms**

2. **Determine the density of CsCl which crystallizes in a bcc type structure with an edge length 412.1 pm.**

Given: M=133 + 35.5 =168.5 gmol^{-1}, a= 412.1 pm= 4.121×10^{-8} cm , Z=1

$$\rho = \frac{\text{M x n}}{a^3 \text{ x } N_A} = \frac{168.5 \text{ x } 1}{(4.121\text{x } 10^{-8})^3\text{x } 6.023 \text{ x } 10^{23}} = \frac{168.5}{42.15} = 3.99$$

Density of CsCl crystal = **4gcm^{-3}**

3. **A face centered cubic solid of an element (atomic mass 60) has a cube edge of 4A^0. Calculate its density.**

Given: M=60 gmol^{-1}, a = 4 A^0= 4 x 10^{-8} cm , Z=4

$$\rho = \frac{\text{M x n}}{a^3 \text{ x } N_A} = \frac{60 \text{ x } 4}{(4 \text{ x } 10^{-8})^3\text{x } 6.023 \text{ x } 10^{23}} = \frac{240}{38.54} = \mathbf{6.227gcm^{-3}}$$

Density of an element = **6.227gcm^{-3}**

III TEXTBOOK EXAMPLES:

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

Given: M=137.3 gmol^{-1}, a= 508pm = 5.08x 10^{-8}cm , Z=2

$$\rho = \frac{\text{M x n}}{a^3 \text{ x } N_A} = \frac{137.3\text{x } 2}{(5.08 \text{ x } 10^{-8})^3\text{x } 6.023 \text{ x } 10^{23}} = \frac{274.6}{78.96} = 3.478\text{gcm}^{-3} = \mathbf{3.5gcm^{-3}}$$

IV ADDITIONAL QUESTIONS:

1. **How solids are classified?**

Solids are classified into two types

(i) Crystalline solids (ii) Amorphous solids..Ex: glass, rubber

Crystalline solids are further classified depending upon nature of their constitutents.
(a) Ioniccrystals. Ex: NaCl, KCl
(b) Covalent crystals Ex: Diamond, SiO_2
(c) Molecular crystals. Ex: Naphthalene, Anthracene, Glucose

(d) Metallic crystals. Ex: Na,Mg,Au,Ag
(e) Atomic solids. Ex: Frozen elements of group 18

2. Explain isotropy and anisotropy ?

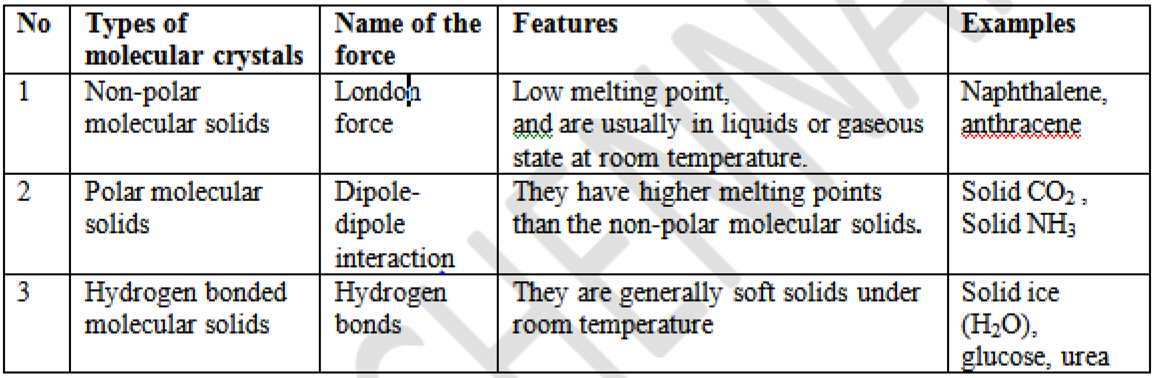
- Isotropy means having identical values of physical properties (refractive index, electrical conductance) in all directions. Ex-amorphous solids.
- Anisotropy means having different values of physical properties when measured along different directions. Ex- crystalline solids

3. Give a note on covalent solids ?

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

.4. What are molecular crystals? How are they classified?

- In molecular solids, the constituents are neutral molecules.
- They are held together by weak Vanderwaals forces.
- Generally, molecular solids are soft and they do not conduct electricity
- Molecular solids are further classified into three types.



No	Types of molecular crystals	Name of the force	Features	Examples
1	Non-polar molecular solids	London force	Low melting point, and are usually in liquids or gaseous state at room temperature.	Naphthalene, anthracene
2	Polar molecular solids	Dipole-dipole interaction	They have higher melting points than the non-polar molecular solids.	Solid CO_2 , Solid NH_3
3	Hydrogen bonded molecular solids	Hydrogen bonds	They are generally soft solids under room temperature	Solid ice (H_2O), glucose, urea

5. Explain metallic solids.

- In metallic solids, the lattice points are occupied by positive metal ions and a cloud of electrons pervades the space.
- They are hard, and have high melting point.
- Metallic solids possess excellent electrical and thermal conductivity. They possess bright lustre.
- Examples: Metals and metal alloys belong to this type of solids, for example Cu, Fe, Zn, Ag ,Au, Cu- Zn etc.

6. Name the parameters that characterize a unit cell

A unit cell is characterised by the three edge lengths or lattice constants a ,b and c and the angle between the edges α, β and γ.

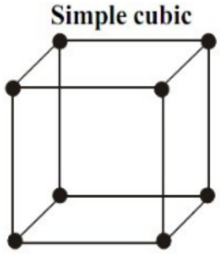
7. What are primitive and non-primitive unit cell?

A unit cell that contains only one lattice point is called a primitive unit cell,

A unit cell that contains additional lattice points, either on a face or within the unit cellis called anon-primitive unit cells.

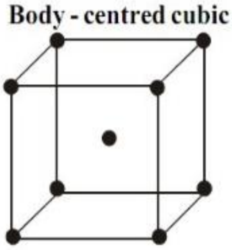
8. Sketch i.sc ii.bcc iii.fcc&calculate its numberof atoms per unit cell

i .sc



Number of atoms in scunit cell = $\frac{\mathrm{Nc}}{8} = \frac{8}{8} = 1$

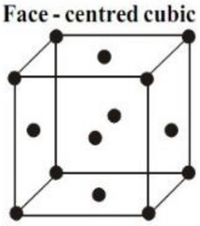
ii. bcc



Number of atoms in bcc unit cell = $\frac{\mathrm{Nc}}{8} + \frac{\mathrm{N}_b}{1} = \frac{8}{8} + \frac{1}{1}$

$= 1 + 1 = 2$

iii.fcc



Number of atoms in fcc unit cell = $\frac{\mathrm{Nc}}{8} + \frac{\mathrm{Nf}}{2} = \frac{8}{8} + \frac{6}{2}$

$= 1 + 3 = 4$

9. How inter planar distance are calculated in unit cell?

The inter planar distance (d) between two successive planes of atoms can be calculated using the following equation form the X-Ray diffraction data

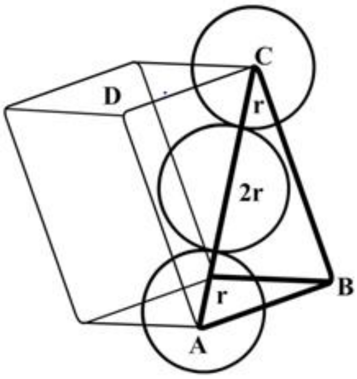
$2d\sin\theta = n\lambda$

The above equation is known as Bragg's equation, where

λ-wavelength of X-ray used for diffraction. θ-angle of diffraction n – order of refraction
By knowing the values of λ, θ and n we can calculate the value of d.

$d = n\lambda/2d\sin\theta$

10 .Explain the relationship between atomic radius and edge length of fcc unit cell and calculate its packing efficiency



In ΔABC

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

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

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

From the figure

AC = 4r

$4r = a\sqrt{2}$

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

Volume of the sphere with radius 'r' = $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left[\frac{\sqrt{2}}{4}\,a\right]^3$

$= \frac{4}{3}\pi\frac{2\sqrt{2}}{64}a^3 = \frac{\sqrt{2}}{24}\pi\,a^3$

Total number of spheres in fcc unit cell = 4

Total volume of all spheres in fcc unit cell = $4 \times \frac{\sqrt{2}}{24}\pi\,a^3 = \frac{\sqrt{2}}{6}\pi a^3$

Volume of the cube with edge length a = axax a = a^3

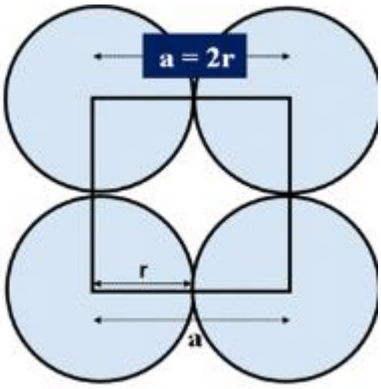
Packing fraction = $\frac{\text{Total volume occupied by all spheres in a unit cell}}{\text{Volume of unit cell}} \times 100$

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

$= \frac{\sqrt{2}\pi}{6} \times 100 = \frac{1.414 \times 3.14 \times 100}{6} = \mathbf{74\ \%}$

11. Calculate the packing efficiency of polonium.

Polonium crystallizes in simple cubic pattern. So let us consider simple cubic system. Let us consider a cube with an edge length 'a' as shown in fig.



Volume of the cube with edge length a is = a x a x 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’ = $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left[\frac{a}{2}\right]^3 = \frac{4}{3}\pi\frac{a^3}{8} = \frac{\pi a^3}{6}$

Total number of spheres in sc unit cell =1

Total volume of all spheres insc unit cell $= \frac{\pi a^3}{6} \times 1 = \frac{\pi a^3}{6}$

$$\text{Packing fraction} = \frac{\text{Total volume occupied by all spheres in a unit cell}}{\text{Volume of unit cell}} \times 100$$

$$= \frac{\frac{\pi a^3}{6}}{a^3} \times 100 = \frac{100\pi}{6} = \frac{100 \times 3.14}{6} = \mathbf{52.33\%}$$

12. Radius ratio of an ionic solid is found to be 0.415. Where the cations are occupied?

Cations occupies the octahedral voids.
{Hint: radius ratio <0.4 – tetrahedral voids
radius ratio >0.4 – octahedral voids}

13. Write the possible octahedral voids and tetrahedral voids exist per atom in a crystal.

Number of tetrahedral voids = 2
Number of octahedral voids = 1

14. How electrical neutrality is maintained in stoichiometric ionic crystals?

In stoichiometric ionic crystals, a vacancy of one ion must always be associated with either by the absence of another oppositely charged ion (or) the presence of same charged ion in the interstitial position so as to maintain the electrical neutrality.

15. Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as impurity in it. (Impurity defect)

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

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

16. What happens when ZnO is heated?

- ZnO is colourless at room temperature.
- When it is heated, it becomes yellow in colour.
- On heating, it loses oxygen and thereby forming free Zn^{2+} ions.
- The excess Zn^{2+} ions move to interstitial sites and the electrons also occupy the interstitial positions.

17. Why Frenkel defect is not found in alkali halides?

Larger size of alkali metal ions dose not allow them to fit in interstitial sites.

18. Schottky defect lowers the density of the ionic solid. Why?

The total number of ions in a crystal with this defect is less than the theoretical value of ions. Thus the density of the solid crystal is less than expected.

19. How F centers are formed when NaCl crystals are heated in the presence of sodium vapour, excess of Na^+ ions are observed. Justify your answer.

- 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^+
- 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 **$Na_{1+x}Cl$**

20. Give the relationship between atomic radius (r), inter atomic distance (d) and packing efficiency of the unit cell of a cubic crystal.

UNIT CELL	NO; OF ATOMS	COORDINATION NUMBER	INTER ATOMIC DISTANCE (d)	ATOMIC RADIUS (r)	PACKING EFFICIENCY
SIMPLE CUBIC	1	6	d = a	$r = \frac{a}{2}$	52.33%
BODY CENTERED CUBIC	2	8	$d = \frac{\sqrt{3}}{2}a$ = 0.866 a	$r = \frac{\sqrt{3}}{4}a$ = 0.433 a	68%
FACE CENTERED CUBIC	4	12	$d = \frac{a}{\sqrt{2}}$ = 0.7076 a	$r = \frac{a}{2\sqrt{2}}$ = 0.3536 a	74%

UNIT-7

CHEMICAL KINETICS

I. ANSWER THE FOLLOWING QUESTIONS

1. Define average rate and instantaneous rate.

Average rate	Instantaneous rate
It is the rate between the intervals of time	It is the rate at a particular time. Average rate becomes instantaneous rate when $\Delta t \rightarrow 0$

2. Define rate law and rate constant.

Rate Law

$aA + bB \longrightarrow \text{products}$

rate $\propto [A]^x [B]^y$

rate = $k [A]^x [B]^y$

Rate is given in terms of molar concentration of reactants raised to the power which may or may not equal to stoichiometric coefficient.

Rate constant

Rate constant is same as rate of reaction when concentration of all the reactants is unity.

3. Derive integrated rate law for a zero order reaction $A \longrightarrow$ product.

Rate is independent of the concentration of reactant is called zero order reaction.

Consider a general zero order reaction. $\mathbf{A} \longrightarrow$ **Product**

At t = 0 concentration of reactant = $[A_0]$

At time t, concentration of reactant left = $[A]$

rate = $k[A]^0$

$$-\frac{d[A]}{dt} = k$$

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

Integrate between limits of $[A_0]$ at t = 0 and $[A]$ at time 't'.

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

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

$[A_0] - [A] = k$

$$\boxed{k = \frac{[A]_0 - [A]}{t}}$$

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

Time required for the reactant concentration to reach one half its of initial value is called half life of a reaction.

First order reaction half-life

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

when $t = t_{1/2}$ then $[A] = \frac{[A_0]}{2}$

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

$$t_{1/2} = \frac{2.303}{k}\log 2$$

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

$$\boxed{t_{1/2} = \frac{0.693}{k}}$$

No concentration terms involved, so half life is independent on initial concentration of reactant.

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

Each and every single step in a reaction mechanism is called an elementary reaction.

No	Order of a reaction	Molecularity of a reaction
1.	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.
2.	It can be zero (or) fraction (or) Integer	It is always whole number, cannot be zero or fraction.
3.	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.

Consider a reaction $\boxed{2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2}$

This reaction takes place in two steps

<u>Step – 1</u> $H_2O_{2(aq)} + I^-_{(aq)} \xrightarrow[RDS]{slow} H_2O(l) + OI^-_{(aq)}$

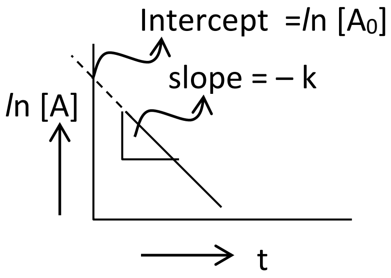
<u>Step – 2</u> $H_2O_{2(aq)} + OI^-_{(aq)} \longrightarrow H_2O(l) + I^-_{(aq)} + O_{2(g)}$

Overall reaction $2H_2O_{2(aq)} \longrightarrow 2H_2O(l) + O_{2(g)}$

Step – 1 is a slow step and rate determining step. In this step H_2O_2 and I^- are involved, hence it is bimolecular reaction.

7. Describe the graphical representation of first order reaction.

$$k = \frac{1}{t} ln \frac{[A_0]}{[A]}$$



$kt = ln\,[A_0] - ln[A]$

$ln\,[A] = -kt + ln\,[A_0]$

$y = -mx + C$

Plot of ln [A] Vs t gives straight line with negative slope.

Slope equal to –k and intercept equals to ln[A].

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 $[X]^{3/2}$ $[Y]^0$

rate = k $[X]^{3/2}$

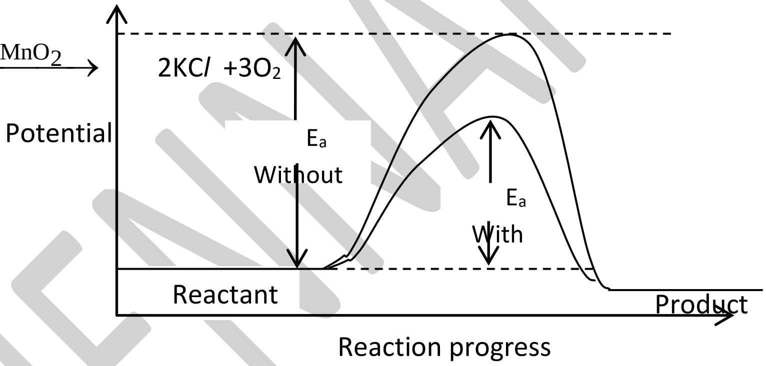
(b) rate = k $[NO]^2$ $[Br_2]^1$

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

1. A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.
2. It may participate in a reaction but regenerated at the end of reaction.
3. A catalyst increases rate of reaction by lowering the activation energy.

Example : $2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$

MnO_2 acts as catalyst.



10. The rate law for a reaction of A, B and L 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.

(i)	rate = k $[A]^2$ [B] $[L]^{3/2} \longrightarrow$ (1) x rate = k $[A]^2$ [B] $[4L]^{3/2} \longrightarrow$ (2) $\frac{(2)}{(1)} \Rightarrow \frac{x\ \cancel{rate}}{\cancel{rate}} = \frac{\cancel{k}\,\cancel{[A]}^2\,\cancel{[B]}[4\cancel{L}]^{3/2}}{\cancel{k}\,\cancel{[A]}^2\,\cancel{[B]}\,\cancel{[L]}^{3/2}}$ x = $4^{3/2}$ $x = (4)^{3\times\frac{1}{2}}$	**(ii)**	(ii) x rate = k $[2A]^2$ [2B] $[L]^{3/2} \longrightarrow$ (3) $\frac{(3)}{(1)} \Rightarrow \frac{x\ \cancel{rate}}{\cancel{rate}} = \frac{\cancel{k}[2\cancel{A}]^2[2\cancel{B}]\cancel{[L]}^{3/2}}{\cancel{k}\,\cancel{[A]}^2\,\cancel{[B]}\,\cancel{[L]}^{3/2}}$ x = $(2)^2$ (2) x = 8 Rate increase by 8 times

	x = 8 $x = (64)^{\frac{1}{2}}$ Rate increase by 8 times		
(iii)	x rate = $k\left[\frac{A}{2}\right]^2 [B][L]^{3/2} \longrightarrow (4)$ $\frac{(4)}{(1)} \Rightarrow \frac{x\ \cancel{rate}}{\cancel{rate}} = \frac{\cancel{k}\left[\frac{\cancel{A}}{2}\right]^2 [\cancel{B}][\cancel{L}]^{3/2}}{\cancel{k}[\cancel{A}]^2[\cancel{B}][\cancel{L}]^{3/2}}$ $x = \left(\frac{1}{2}\right)^2$ $x = \frac{1}{4}$ Rate decrease by $\frac{1}{4}$ times	**(iv)**	x rate = $k\left[\frac{A}{3}\right]^2 [B][4L]^{3/2} \longrightarrow (5)$ $\frac{(5)}{(1)} \Rightarrow \frac{x\ \cancel{rate}}{\cancel{rate}} = \frac{\cancel{k}\left[\frac{\cancel{A}}{3}\right]^2 [\cancel{B}][\cancel{4L}]^{3/2}}{\cancel{k}[\cancel{A}]^2[\cancel{B}][\cancel{L}]^{3/2}}$ $x = \left(\frac{1}{3}\right)^2 (4)^{3/2}$ x = $\left(\frac{1}{9}\right)(8)$ Rate decrease by $\frac{8}{9}$ times

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

rate = k [monomer]^2

$$7.5\times10^{-3} = k\times(0.05)^2$$

$$k = \frac{7.5\times10^{-3}}{(0.05)^2} = \frac{7.5\times10^{-3}}{(5\times10^{-2})^2} = \frac{7.5\times10^{-3}}{25\times10^{-4}} = \frac{7.5\times10^{1}}{25} = \frac{75}{25} = 3\ \text{molL}^{-1}\text{s}^{-1}$$

12. For a reaction X + Y + Z $\longrightarrow$ 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 reactionwith respect to z.

X + Y + Z $\longrightarrow$ product

rate = k [X]$^{3/2}$ [Y]$^{1/2}$

order w.r.to Z = 0

overall order = $\frac{3}{2}+\frac{1}{2} = 2$

13.Explain briefly the collision theory of bimolecular reactions. (or) Derive $k = pz\, e^{\frac{-Ea}{RT}}$

Consider a bimolecular reaction between A_2 and B_2 proceeds through collision betweenthem which is proportional to number of collision per second

Rate αCollision rate

Collision rate $\alpha[A_2]\,[B_2]$

Collision rate $= Z\,[A_2]\,[B_2]$ Z is the collision Frequency

Collision rate in gas phase reaction is calculated from kinetic theory of gas and its value is 10^9collision per seconds at 298K and 1 atm pressure.

All these collisions are not effective and in order for reaction to takes place, the colliding molecules must possess activation energy.

Fraction of effective collision (f) is given by $f = e^{-\frac{E_a}{RT}}$

In addition to activation energy, orientation factor(p) also necessary for reaction to take place.

rate = p × f × collision rate

$$\text{rate} = p \times e^{-\frac{E_a}{RT}} \times Z\,[A_2]\,[B_2] \longrightarrow (1)$$

As per rate lawrate = k $[A_2]\,[B_2] \longrightarrow (2)$

comparing (1) and (2)

$$\boxed{k = pze^{-\frac{E_a}{RT}}}$$

14. Write Arrhenius equation and explains the terms involved.

Arrhenius equation $k = Ae^{-\frac{E_a}{RT}}$

k is rate constant

A is Frequency factor

E_a is Activation energy($Jmol^{-1}$)

T is Temperature in Kelvin

R is gas constant (8.314 $JK^{-1}\,mol^{-1}$)

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

Calculate the rate constant in s^{-1}.

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

$$k = \frac{2.303}{60}\log\frac{0.08}{0.04} = \frac{2.303}{60}\log 2 = \frac{2.303}{60}\times 0.3010 = \frac{0.6932}{60} = 0.011553\ s^{-1}$$

$$\boxed{k\ =\ 1.153\times10^{-2}s^{-1}}$$

17. Explain pseudo first order reaction with an example.

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

Example : Acid hydrolysis of ester

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

18. Identify the order for the following reactions

(i) Rusting of Iron

(ii) Radioactive disintegration of $_{92}U^{238}$

(iii) $2A + 3B \longrightarrow$ products ; rate = $[A]^{1/2}[B]^2$

(i) First order

(ii) First order

(iii) $\frac{1}{2}+2=\frac{1+4}{2}=\frac{5}{2}$

19. A gas phase reaction has energy of activation 200 kJ mol^{-1}. If the frequency factor of the reaction is $1.6 \times 10^{13}\ s^{-1}$. Calculate the rate constant at 600 K. ($e^{-40.09} = 3.8 \times 10^{-18}$)

E_a = 200 kJ mol^{-1}

A = $1.6 \times 10^{13}\ s^{-1}$

T = 600 K andR = 8.314 J K^{-1} mol^{-1}

k = ?

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$= \log 1.6\times10^{13} - \frac{2000\cancel{0}\cancel{0}}{2.303\times8.314\times6\cancel{0}\cancel{0}}$$

$$= \log 1.6\times10^{13} - \frac{2000}{2.303\times8.314\times6}$$

$$= \log 1.6\times10^{13} - \frac{2000}{114.88}$$

$$= \log 1.6\times10^{13} - 17.409$$

= log 1.6 + 13 – 17.409

= 0.2041 + 13 – 17.409

= 13.2041 – 17.409

log k = – 4.2049

= – 4 – 0.2049 + 1 – 1

= – 5 + 0.7951

= $= \bar{5}.7951$

$$k = \text{Anti}\log\ \bar{5}.7951$$

$$\boxed{k = 6.238\times10^{-5}s^{-1}}$$

20. **For the reaction $2x + y \longrightarrow L$. Find the rate law from the following data.**

[x] (min)	[y] (min)	rate (M s^{-1})
0.2	**0.02**	**0.15**
0.4	**0.02**	**0.30**
04	**0.08**	**1.20**

rate = k $[X]^a$ $[Y]^b$

$0.15 = k (0.2)^a (0.02)^b \longrightarrow$ (1)

$0.30 = k (0.4)^a (0.02)^b \longrightarrow$ (2)

$1.20 = k\,(0.4)^a\,(0.08)^b \longrightarrow (3)$

$$\frac{(2)}{(1)} \Rightarrow \frac{\cancel{0}.30}{\cancel{0}.15} = \frac{k\cancel{(0.4)^a}\,(0.02)^b}{k\cancel{(0.2)^a}\,(0.02)^b}$$

$$2 = 2^a$$

order w.r.to X = 1

$$\frac{(3)}{(2)} \Rightarrow \frac{\cancel{1.20}}{\cancel{0.30}} = \frac{k(0.4)^a\,(0.08)^b}{k(0.4)^a\,(0.02)^b}$$

$4 = 4^b$

$b = 1$

order w.r.to y = 1

rate law is rate = $k\,[X]^1\,[Y]^1$

21. How do concentrations of the reactant influence the rate of reaction?

Rate of reaction increases with increases of concentration of reactant.

rateα[Reactant]

As reactant concentration is more, which leads to more collision of reactant molecules which increases the rate of reaction.

22. How do nature of the reactant influence rate of reaction. (or)

Titration between potassium per mangate and oxalic acid is carried out at 60°C where as titration between potassium per manganate and ferrous ammonium sulphate at room temperature. Give reason.

Chemical reaction involves bond breaking and bond formation. The net energy involved in this process depends on nature of reactants and hence rate differs for different reactants.

For example, titration between $KMnO_4$ vs FAS takes place at room temperature whereas titration between $KMnO_4$ vs Oxalic acid is heated to 60°C. This is because oxidation of oxalate ion by $KMnO_4$ is slow compared to reaction between $KMnO_4$ and Fe^{2+}.

23. The rate constant for a first order reaction is $1.54 \times 10^{-3}\ s^{-1}$. Calculate its half life time.

$k = 1.54 \times 10^{-3}\ s^{-1}$

$t_{1/2} = ?$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.54\times10^{-3}} = \frac{0.693\times10^{3}}{1.54} = \frac{693}{1.54}$$

$$\boxed{t_{1/2} = 450 \text{ sec}}$$

24. The half life of the homogeneous gaseous reaction $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ which obeys first orderkinetics 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?

$t_{1/2} = 8$ min t = ?

$[A_0]$ = 100

[A] = 1% of initial value

$$[A] = \frac{1}{100}\times100 = 1$$

$$k = \frac{0.693}{t_{1/2}}$$

$$\boxed{k = \frac{0.693}{8}\ \text{min}^{-1}}$$

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

$$\frac{0.693}{8} = \frac{2.303}{t}\log\frac{100}{1}$$

$$\frac{0.693}{8} = \frac{2.303}{t}\times2$$

$$\frac{0.693}{8} = \frac{4.606}{t}$$

$$t = \frac{4.606\times8}{0.693} = \frac{36.848}{0.693}$$

$$\boxed{t = 53.17 \text{ min}}$$

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) $t_{1/2} = 60\,\text{sec}$ k = ?

(ii)t = 180 sec [A] = ?

$[A_0] = 100$

(i) $t_{1/2} = \frac{0.693}{k}$

$$k = \frac{0.693}{t_{t_{1/2}}} = \frac{0.693}{60} = 0.01155\ \text{sec}^{-1}$$

(ii) $k = \frac{0.693}{t_{t_{1/2}}} \log \frac{[A_0]}{[A]}$

$$0.01155 = \frac{2.303}{180} \log \frac{[A_0]}{[A]}$$

$$\log \frac{100}{[A]} = \frac{0.01155 \times 180}{2.303}$$

$$\log \frac{100}{[A]} = \frac{2.079}{2.303}$$

$$\log \frac{100}{[A]} = 0.9027$$

$$\frac{100}{[A]} = \text{Anti}\log 0.9027$$

$$\frac{100}{[A]} = 7.993$$

$$[A] = \frac{100}{7.993}$$

[A] = 12.5%

26. A zero order reaction is 20% complete in 20 minutes. Calculate the value of the rate constant.

In what time will the reaction be 80% complete?

(i) $[A_0] = 100$ [A] = 80

t = 20 min k = ?

(ii) t = ? [A] = 20

(i) $k = \frac{[A_0]-[A]}{t} = \frac{100-80}{20} = \frac{20}{20}$

$$\boxed{k = 1 \text{ mol L}^{-1}\text{min}^{-1}}$$

(ii) $k = \frac{[A_0]-[A]}{t}$

$$1 = \frac{100-20}{t}$$

$$\boxed{t = 80 \text{ min}}$$

27. The activation energy of a reaction is 225 k cal mol^{-1} and the value of rate constant at 40°C is1.8 × 10^{-5} s^{-1}. Calculate the frequency factor A.

$E_a = 225 \text{ k cal.mol}^{-1}$ = 225000 cal .mol^{-1}

k = 1.8×10^{-5} s^{-1}

R = 1.987 cal K^{-1} mol^{-1}

T = 40°C = 40 + 273 = 313 K

A = ?

log k = log A – $\frac{E_a}{2.303RT}$

log 1.8×10^{-5} = log A – $\frac{22500}{2.303 \times 1.987 \times 313}$

log 1.8×10^{-5} = log A – $\frac{22500}{1432}$

log 1.8×10^{-5}= log A – 15.7089

log 1.8×10^{-5}= log A – 15.7089

log 1.8 – 5 = log A – 15.7089

0.2553 – 5 = log A – 15.7089

log A = 15.7089 + 0.2553 – 5

log A = 10.9642

A = Antilog 10.9642

$$\boxed{\mathrm{A = 9.208 \times 10^{10}\, collisons\ s^{-1}}}$$

28. **Benzene diazonium chloride in aqueous solution decomposes according to the equation**

$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$. Starting with an initial concentration of 10 g L^{-1},

the volume of N_2 gas obtained at 50°C at different intervals of time was found to be as under:

t (min) :	**6**	**12**	**18**	**24**	**30**	**∞**
Vol. of N_2 (ml):	**19.3**	**32.6**	**41.3**	**46.5**	**50.4**	**58.3**

Show that the above reaction follows the first order kinetics. What is the value of the rate constant?

$$\mathrm{k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}}$$

(i) $\mathrm{k = \frac{2.303}{6}\log\frac{58.3}{58.3-19.3} = \frac{2.303}{6}\log\frac{58.3}{39} = \frac{2.303}{6}\log 1.495 = \frac{2.303}{6}\times 0.1746 = 0.067\,min^{-1}}$

(ii) $\mathrm{k = \frac{2.303}{12}\log\frac{58.3}{58.3-32.6} = \frac{2.303}{12}\log\frac{58.3}{25.7} = \frac{2.303}{12}\log 2.268 = \frac{2.303}{12}\times 0.3556 = 0.0682\,min^{-1}}$

(iii) $\mathrm{k = \frac{2.303}{18}\log\frac{58.3}{58.3-41.3} = \frac{2.303}{18}\log\frac{58.3}{17} = \frac{2.303}{18}\log 3.429 = \frac{2.303}{18}\times 0.5351 = 0.0685\,min^{-1}}$

(iv) $\mathrm{k = \frac{2.303}{24}\log\frac{58.3}{58.3-46.5} = \frac{2.303}{24}\log\frac{58.3}{11.8} = \frac{2.303}{24}\log 4.9407 = \frac{2.303}{24}\times 0.6938 = 0.666\,min^{-1}}$

Average k = 0.0676 min^{-1} and as follows first order kinetics.

29. **From the following data, show that the decomposition of hydrogen peroxide is a reaction of the first order :**

t (min)	**0**	**10**	**20**
V (ml)	**46.1**	**29.8**	**19.3**

Where t is the time in minutes and V is the volume of standard $KMnO_4$ solution required for titrating the same volume of the reaction mixture.

$$k = \frac{2.303}{t}\log\frac{V_0}{V_t}$$

(i) $k = \frac{2.303}{10}\log\frac{46.1}{29.8} = \frac{2.303}{10}\log 1.5469 = \frac{2.303}{10}\times 0.1895 = 0.0436\,\text{min}^{-1}$

(ii) $k = \frac{2.303}{20}\log\frac{46.1}{19.3} = \frac{2.303}{20}\log 2.3886 = \frac{2.303}{20}\times 0.3781 = 0.0435\,\text{min}^{-1}$

Average k = 0.04355min^{-1} and as follows first order kinetics.

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?

(i) t = 50 min $[A_0]$ = 100 [A] = 60 k = ?

(ii) [A] = 20 t = ?

(i) $k = \frac{2.303}{t}\log\frac{[A_0]}{[A]} = \frac{2.303}{50}\log\frac{100}{60} = \frac{2.303}{50}\log 1.667 = \frac{2.303}{50}\times 0.2219 =$

$\boxed{0.01022\,\text{min}^{-1}}$

(ii) $k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$

$0.01022 = \frac{2.303}{t}\log\frac{100}{20}$ $0.01022 = \frac{2.303}{t}\log 5$

$0.01022 = \frac{2.303}{t}\times 0.6990$

$t = \frac{2.303}{k}\times 0.6990 = \frac{1.61}{0.01022}$ $\boxed{t\ =\ 157.51\text{ min}}$

II. EXAMPLES

Example-1 (Page 211)

Consider the oxidation of nitric oxide to form NO_2

$2NO(g) + O_2(g) \longrightarrow 2NO_2\,(g)$

(a) Express the rate of the reaction in terms of changes in the concentration of NO, O_2 and NO_2.

(b) At a particular instant, when $[O_2]$ is decreasing at 0.2 mol $L^{-1}\,s^{-1}$ at what rate is $[NO_2]$ increasing at that instant?

(a) $$-\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

(b) $$-\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

$$0.2 = \frac{1}{2}\frac{d[NO_2]}{dt}$$

$$\frac{d[NO_2]}{dt} = 0.2 \times 2 = 0.4\ mol \cdot L^{-1}s^{-1}$$

Example-2 (Page 211)

What is the order with respect to each of the reactant and overall order of the following reaction?

(a) $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow$ **$3Br_2(l)$ + $3H_2O(l)$**

The experimental rate law is Rate = k $[Br^-]$ $[BrO_3]$ $[H^+]^2$

(b) $CH_3CHO(g) \xrightarrow{\Delta} CH_4(g) + CO(g)$ **the experimental rate law is** $Rate = k[CH_3CHO]^{3/2}$

(a)Order w.t.to Br^- is 1

Order w.t.to BrO_3^- is 1

Order w.t.to H^+ is 2

Overall order is 1 + 1 + 2 = 4

(b)order = 3/2

Example-3 (Page 211)

The rate of the reaction x + 2y → product is 4 × 10 –3 mol L –1 s –1, if [x] = [y] = 0.2 M and rate constant at 400 K is 2 × 10 –2 s –1, What is the overall order of the reaction.

rate = k $[X]^9$ $[Y]^6$

$4 \times 10^{-3} = 2 \times 10^{-2} \times (0.2)^a (0.2)^b$

$$\frac{4\times10^{-3}}{2\times10^{-2}} = (0.2)^{a+b}$$

$$2\times10^{-1} = (0.2)^{a+b}$$

$$0.22 = (0.2)^{a+b}$$

Comparing the powers a + b = 1

Overall order = a + b = 1

Example-4 (Page 216)

A first order reaction takes 8 hours for 90% completion. Calculate the time required for 80% completion. (log 5 = 0.6989 ; log 10 = 1)

t = 8 hr

$[A_0] = 100$

[A] = 10

t = ?for [A] = 20 (80% completion)

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]} = \frac{2.303}{8}\log\frac{100}{10} = \frac{2.303}{8}\log 10$$

$$\boxed{k = \frac{2.303}{8}\ hr^{-1}}$$

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

$$\frac{2.303}{8} = \frac{2.303}{t}\log\frac{100}{20}$$

$$\frac{2.303}{8} = \frac{2.303}{t}\log 5$$

$$\frac{2.303}{8} = \frac{2.303}{t}\times 0.6989$$

$$\frac{2.303}{8} = \frac{1.6096}{t}$$

$$t = \frac{1.6096}{2.303} = \frac{12.876}{2.303}$$

$$\boxed{t = 5.59\ hr}$$

Example-5 (Page 216)

The half life of a first order reaction x → products is 6.932×10^4 s at 500 K. What percentage

of x would be decomposed on heating at 500 K for 100 min. ($e^{0.06} = 1.06$)

$t_{1/2} = 6.932 \times 10^4$ s

t = 100 min = 100 × 60 = 6000 s

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{6.932 \times 10^4} = \frac{\cancel{0.693} \times 10^{-1}}{\cancel{6.932} \times 10^4} = \frac{\cancel{0.693} \times 10^{-1}}{\cancel{6.932} \times 10^4} \boxed{= 10^{-5} s^{-1}}$$

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

$$10^{-5} = \frac{2.303}{6000} \log \frac{[A_0]}{[A]}$$

$$\log \frac{[A_0]}{[A]} = \frac{6000 \times 10^{-5}}{2.303} = \frac{6 \times 10^3 \times 10^{-5}}{2.303} = \frac{6 \times 10^{-2}}{2.303} = 2.605 \times 10^{-2}$$

$$\log \frac{[A_0]}{[A]} = 0.02605$$

$$\frac{[A_0]}{[A]} = \text{Anti}\log(0.02605)$$

$$\frac{[A_0]}{[A]} = 1.0618$$

$$\frac{100}{[A]} = 1.0618$$

$$[A] = \frac{100}{1.0618}$$

[A] = 94179

Left out concentration of reactant x = 94.179 mol .L^{-1}.   Reacted amount = 5.82%

Example-6 (Page 217)

Show that in case of first order reaction, the time required for 99.9% completion is nearly ten times the time required for half completion of the reaction.

$t_{99.9\%}$

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

$t_{99.9\%} = \frac{2.303}{k} \log\frac{100}{0.1}$

$t_{99.9\%} = \frac{2.303}{k} \log 1000$

$t_{99.9\%} = \frac{2.303}{k} \times 3$

$\boxed{t_{99.9\%} = \frac{6.909}{k}} \longrightarrow$ (1)

$\boxed{t_{50\%} = \frac{0.693}{k}} \longrightarrow$ (2)

From $\frac{(1)}{(2)}$, $\frac{t_{99.9\%}}{t_{50\%}} = \frac{6.909}{k} \times \frac{k}{0.693}$

$\frac{t_{99.9\%}}{t_{50\%}} = 10$

$\boxed{t_{99.9\%} = 10\ t_{50\%}}$

Hence proved.

Example-7 (Page 221)

The rate constant of a reaction of a reaction at 400 and 200 K are 0.04 and 0.02 s $^{-1}$ respectively. Calculate the value of activation energy.

$T_1 = 200$ K $\qquad k_1 = 0.02\ s^{-1}$

$T_2 = 400$ K $\qquad k_1 = 0.04\ s^{-1}$

$R = 8.314\ JK^{-1}mol^{-1}$

$E_a = ?$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\frac{0.04}{0.02} = \frac{E_a}{2.303 \times 8.314}\left(\frac{400 - 200}{400 \times 200}\right)$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \frac{2\cancel{0}\cancel{0}}{800\cancel{0}\cancel{0}}$$

$$0.3010 = \frac{E_a}{2.303 \times 8.314} \times \frac{2}{800}$$

$$0.3010 = \frac{E_a}{2.303 \times 8.314} \times \frac{1}{400}$$

$$E_a = 2.303 \times 8.314 \times 400 \times 0.3010$$

$$\boxed{E_a = 2.305 \text{ J mol}^{-1}}$$

<u>Example-8 (Page 221)</u>

Rate constant k of a reaction varies with temperature T according to the following Arrhenius equation

$$\mathbf{\log k = \log A \frac{E_a}{2.303R}\left(\frac{1}{T}\right)}$$

Where $\mathbf{E_a}$ is the activation energy. When a graph is plotted for log k Vs $\mathbf{\frac{1}{T}}$ astraight line with a slope of –4000 K is obtained. Calculate the activation energy

Slope = –4000 K

E_a= ?

$$\text{slope} = -\frac{E_a}{2.303R}$$

$$\cancel{-}4000\text{K} = \cancel{-}\frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1}\text{mol}^{-1}}$$

$$E_a = 2.303 \times 8.314 \text{ J}\cancel{\text{K}^{-1}}\text{mol}^{-1} \times 4000\cancel{\text{K}}$$

$$\boxed{E_a = 76589 \text{ J mol}^{-1}}$$

<u>Solved Problem in page 209</u>

For the reaction $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ the following data were obtained.

Expt.	**[NO] × 10 $^{-2}$ (mol L $^{-1}$)**	**[O$_2$] × 10 $^{-2}$ (mol L $^{-1}$)**	**Initial rate × 10 $^{-2}$ (mol L $^{-1}$ s $^{-1}$)**
1.	**1.3**	**1.1**	**19.26**

2.	**1.3**	**2.2**	**38.40**
3.	**2.6**	**1.1**	**76.80**

Determine order with respect to NO, O_2 and overall order.

$$\text{rate} = k[NO]^x[O_2]^y$$

$$19.26\times10^{-2} = k(1.3\times10^{-2})^x(1.1\times10^{-2})^y \longrightarrow (1)$$

$$38.40\times10^{-2} = k(1.3\times10^{-2})^x(2.2\times10^{-2})^y \longrightarrow (2)$$

$$76.80\times10^{-2} = k(2.6\times10^{-2})^x(1.1\times10^{-2})^y \longrightarrow (3)$$

$$\frac{(2)}{(1)} \Rightarrow \frac{38.40\times\cancel{10^{-2}}}{19.26\times\cancel{10^{-2}}} = \frac{\cancel{k}\ \cancel{(1.3\times10^{-2})^x}\ (2.2\times\cancel{10^{-2}})^y}{\cancel{k}\ \cancel{(1.3\times10^{-2})^x}\ (1.1\times\cancel{10^{-2}})^y}$$

$2 = 2^x$

$x = 1$

order w.r.to NO = 1

$$\frac{(3)}{(1)} \Rightarrow \frac{76.80\times\cancel{10^{-2}}}{19.26\times\cancel{10^{-2}}} = \frac{\cancel{k}(2.6\times10^{-2})^x\ \cancel{(1.1\times10^{-2})^y}}{\cancel{k}(1.3\times10^{-2})^x(2.1\times\cancel{10^{-2}})^y}$$

$4 = 2^x$

$x = 2$

order w.r.to $O_2 = 2$

rate = $k\ [NO]_1\ [O_2]^2$

Overall order = 1 + 2 = 3

<u>III EVALUATE YOURSELF</u>

Evaluate Yourself-1 (Page 211)

(1) Write the rate expression for the following reactions, assuming them as elementary reactions.

(i) $3A + 5B_2 \longrightarrow 4CD$ **(ii)** $X_2 + Y_2 \longrightarrow 2XY$

(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 2.5×10^{-2} mol dm $^{-3}$ s $^{-1}$. At what rate are NO_2 and O_2 formed? What is the rate of the reaction?

(1) (i) rate = k $[A]^3 [B_2]^5$

(ii)rate = k $[X_2]^1 [Y_2]^1$

(2) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt}$$

$$\frac{1}{2} \times 2.5 \times 10^{-2} = \frac{1}{4}\frac{d[NO_2]}{dt}$$

$$\frac{d[NO_2]}{dt} = \frac{4}{2} \times 2.5 \times 10^{-2} = 2 \times 2.5 \times 10^{-2} = 5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{d[O_2]}{dt}$$

$$\frac{1}{2} \times 2.5 \times 10^{-2} = \frac{d[O_2]}{dt}$$

$$\frac{d[O_2]}{dt} = 1.25 \times 10^{-2} \text{mol L}^{-1}\text{s}^{-1}$$

Evaluate Yourself-2 (Page 212)

(1) For a reaction, X + Y $\longrightarrow$ product ; quadrupling [x], increases the rate by a factor of 8. Quadrupling both [x] and [y], increases the rate by a factor 16. Find the order of the reaction with respect to x and y. What is the overall order of the reaction?

(2) Find the individual and overall order of the following reaction using the given date

$$\mathbf{2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)}}.$$

Expt.	**[NO]**	**[Cl₂]**	**Initial rate**
1.	**0.1**	**0.1**	**7.8×10^{-5}**
2.	**0.2**	**0.1**	

3.	**0.2**	**0.3**	**3.12×10^{-4}** **9.36×10^{-4}**

(1)rate = k $[X]^a\,[Y]^b \longrightarrow$ (1)

8 rate = k $[4X]^a\,[Y]^b \longrightarrow$ (2)

16 rate = k $[4X]^a\,[Y]^b \longrightarrow$ (3)

$$\frac{(2)}{(1)} \Rightarrow \frac{8\,\cancel{\text{rate}}}{\cancel{\text{rate}}} = \frac{\cancel{k}[4\cancel{X}]^a[\cancel{Y}]^b}{\cancel{k}[\cancel{X}]^a[\cancel{Y}]^b}$$

$$8 = 4^a$$

$2^3 = 2^{2a}$

3 = 2a

a = 3/2

order w.r.to X = 3/2

$$\frac{(3)}{(2)} \Rightarrow \frac{16\,\cancel{\text{rate}}}{\cancel{8\text{rate}}} = \frac{\cancel{k}[\cancel{4X}]^a[4\cancel{Y}]^b}{\cancel{k}[\cancel{4X}]^a[\cancel{Y}]^b}$$

$$2 = 4^b$$

b = 1/2

order w.r.to Y = 1/2

(2) $\text{rate} = k[NO]^x[Cl_2]^y$

$$7.8\times10^{-5} = k(0.1)^x(0.1)^y \longrightarrow (1)$$

$$3.12\times10^{-4} = k(0.2)^x(0.1)^y \longrightarrow (2)$$

$$9.36\times10^{-4} = k(0.2)^x(0.3)^y \longrightarrow (3)$$

$$\frac{(2)}{(1)} \Rightarrow \frac{3.12\times10^{-4}}{7.8\times10^{-5}} = \frac{\cancel{k}(0.2)^x\cancel{(0.1)^y}}{\cancel{k}(0.1)^x\cancel{(0.1)^y}}$$

$4 = 2^x$

$x = 2$

order w.r.to NO = 2

$$\frac{(3)}{(2)} \Rightarrow \frac{9.36\times10^{-4}}{3.12\times10^{-4}} = \frac{\cancel{k}\ \cancel{(0.2)^x}\ (0.1)^y}{\cancel{k}\ \cancel{(0.2)^x}\ (0.3)^y}$$

$$3 = \left(\frac{1}{3}\right)^y$$

$$3 = (3^{-1})^y$$

$$3 = 3$$

Equating the powers

$$1 = -y$$

$$y = -1$$

order w.r.to O_2 = 1

rate = k $[NO]_2$ $[O_2]^{-1}$

overall order = 2 – 1 = 1

Evaluate Yourself-3 (Page 217)

(1) 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?

(2) The rate constant for a first order reaction is 2.3 × 10 –4 s –1. If the initial concentration of the reactant is 0.01 M. What concentration will remain after 1 hour?

(3) 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.

(1) t = 40 min

[A_0] = 100

[A] = 40

$t_{1/2}$ = ?

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]} = \frac{2.303}{40}\log\frac{100}{40} = \frac{2.303}{40}\log 2.5 = \frac{2.303}{40}\times 0.3979 = \frac{0.9163}{40}$$

$$\boxed{k = 0.0229\ \text{min}^{-1}}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0229}$$

$t_{1/2}$ = 3.026 min

$$\boxed{t_{1/2} = 3\,\text{min}}$$

(2) k = 2.3×10^{-4} s^{-1}

[A_0] = 0.01 M

t = 1 hour = 3600 s

[A] = ?

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

$$2.3\times10^{-4} = \frac{2.303}{3600}\log\frac{0.01}{[A]}$$

$\log\frac{0.01}{[A]} = \frac{\cancel{2.3}\times10^{-4}\times3600}{\cancel{2.303}}$ = 3600×10^{-4} = $36 \times 10^{2}\times10^{-4}$ = 36×10^{-2}

$$\log\frac{0.01}{[A]} = 0.36$$

$$\frac{0.01}{[A]} = \text{Anti}\log\ \ 0.36$$

$$\frac{0.01}{[A]} = 2.29$$

$[A] = \frac{0.01}{2.29}$ = 0.0044 M = 4.4×10^{-3} M

(3) $k = \frac{2.303}{t}\log\frac{V_0}{V_t} = \frac{2.303}{30}\log\frac{0.85}{0.80} = \frac{2.303}{30}\log 1.0625 = \frac{2.303}{30}\times 0.0263 = \frac{0.0606}{30}$ = 0.002019 min^{-1}

$$\boxed{k = 2.019\times 10^{-3}\,\text{min}^{-1}}$$

$$k = \frac{2.303}{60}\log\frac{0.85}{0.754} = \frac{2.303}{60}\log 1.061 = \frac{2.303}{60}\times 0.0257 = \frac{0.05918}{30}$$

$$= 0.001972$$

$$\boxed{k = 1.972\times 10^{-3}\,\text{min}^{-1}}$$

$$k = \frac{2.303}{90}\log\frac{0.85}{0.71} = \frac{2.303}{90}\log 1.1972 = \frac{2.303}{90}\times 0.782 = \frac{0.18009}{90} = 0.002001\,\text{min}^{-1}$$

$$\boxed{k = 2.001\times 10^{-3}\,\text{min}^{-1}}$$

As all k values are nearly same, ester hydrolyzing follows first order kinetics.

Evaluate Yourself-4(Page 221)

For a first order reaction the rate constant at 500 K is $8\times 10^{-4}\ s^{-1}$. Calculate the frequency factor, if the energy of activation for the reaction is 190 kJ mol^{-1}.

T = 500 K

$k = 8\times 10^{-4}\ s^{-1}$

A = ?

$E_a = 190\ kJ\ mol^{-1} = 190000\ J\ mol^{-1}$

$R = 8.314\ JK^{-1}\ mol^{-1}$

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

$$\log 8\times 10^{-4} = \log A - \frac{1900\cancel{0}\,\cancel{0}}{2.303\times 8.314\times 5\cancel{0}\,\cancel{0}}$$

$$\log 8\times 10^{-4} = \log A - \frac{1900}{95.735}$$

$\log 8\times 10^{-4} = \log A - 19.846$

$\log 8 + \log 10^{-4} = \log A - 19.846$

$\log 8 - 4 = \log A - 19.846$

0.9031 – 4 = log A – 19.846

log A = 0.9031 – 4 + 19.846

= 20.7491 – 4

log A = 16.7491

A = Antilog 16.7491

$$\boxed{A = 5.6117 \times 10^{16} \text{collision s}^{-1}}$$

IV ADDITIONAL QUESTIONS WITH ANSWERS

1. **Define rate of a reaction.**

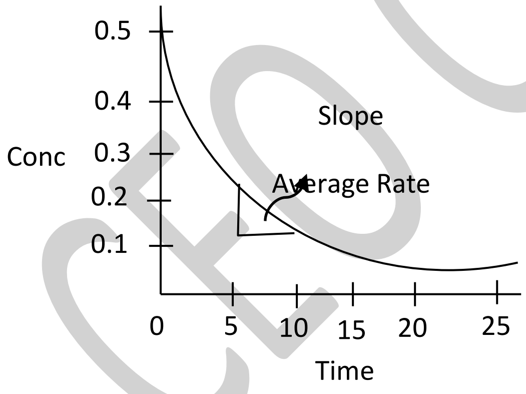
Rate is defined as change in concentration of reactant or product with respect to time.

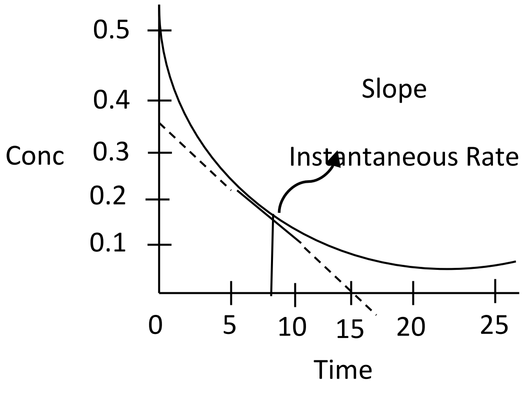
2. **Give the unit of rate of reaction for (i) aqueous reaction (ii) Gaseous reaction**

(i) mol L^{-1} s^{-1} (ii) atm s^{-1}

3. **How to determine rate of a reaction.**

Draw a plot of concentration vs time graph. The slope of the curve between the interval of time gives the average rate.
Instantaneous rate is the rate at a particular time which is calculated by drawing a tangent at that point on the concentration vs time graph. The slope of the tangent gives the instantaneous rate.





4. **Differentiate rate and rate constant.**

No	Rate of a reaction	Rate constant of a reaction
1.	It represents the speed at which the reactants are converted intoproducts at any instant.	It is a proportionality constant
2.	It is measured as decrease in the concentration of the reactants or increase in the concentration of	It is equal to the rate of reaction, when the concentration of

	products.	each of the reactants in unity.
3.	It depends on the initial on the concentrations of reactants.	It does not depend on the initial concentration of reactants.

5. **Define molecularity.**

It is the total number of reactant speciesthat are involved in an elementary step.

6. **Define order of a reaction.**

$$aA + bB \longrightarrow \text{products}$$

rate = k $[A]^x [B]^y$

overall order = x + y

It is the sum of the powers of concentration terms involved in the experimentally determined rate law.

7. **Derive an expression of half life of a zero order reaction.**

$$k = \frac{[A_0]-[A]}{t}$$

t = $t_{1/2}$ then $[A] = \frac{[A_0]}{2}$

$$k = \frac{[A_0]-\frac{[A_0]}{2}}{t_{1/2}}$$

$$t_{1/2} = \frac{2[A_0]-[A_0]}{2k} \qquad \boxed{t_{1/2} = \frac{[A_0]}{2k}}$$

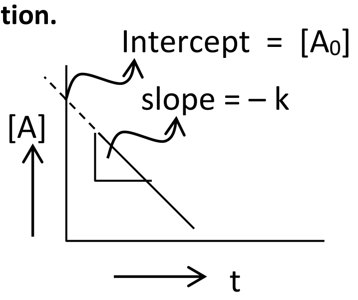
8. **Give general expression for half life of nth order reaction.**

Half life of nth order reaction is $t_{1/2} = \frac{2^{n-1}-1}{(n-1)k[A_0]^{n-1}}$

9. **Draw a plot of concentration vs time for zero order reaction.**

$$k = \frac{[A_0]-[A]}{t}$$

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



$y = -mx + C$

Plot of [A] Vs t gives straight line with negative slope.

Slope equal to –k and intercept equals to [A].

10. Give examples of first order reaction.

(i) $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

(ii) $SO_2Cl_2(l) \longrightarrow SO_2(g) + Cl_2(g)$

(iii) $H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$

(iv) All radioactive decay

(v) Isomerisation of cyclopropane to propene

11. Give two examples of zero order reaction.

(i) $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$

(ii) $N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2}O_2(g)$

12. Give units of rate constant of

(a) first order reaction (b) zero order reaction

(a) sec^{-1} (b) mol $L^{-1}s^{-1}$

13. What is collision frequency?

Number of collisions per second per unit volume is called collision frequency.

14. Why molecularity can never be more than 3?

Probability of simultaneous collision of more than three reactants is rare.

So molecularity can never be more than three.

15. Define activation energy?

In order to react, the colliding molecules must possess a minimum energy called activation energy.

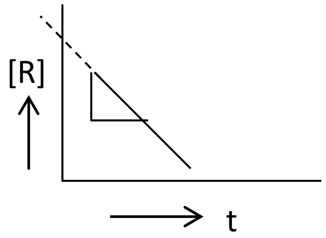
16. What is the usefulness of Arrhenius equation.

With the help of Arrhenius equation, we can calculate activation energy of the reaction provided rate constants at two different temperatures are given.

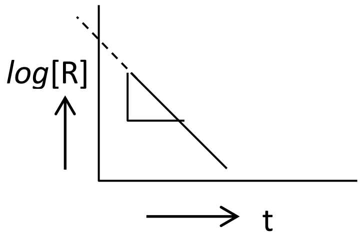
17. Mention the factors affecting rate of reaction.

1. Nature and state of reactant
2. Concentration of reactant.
3. Surface area of reactant.
4. Temperature of reaction.
5. Presence of catalyst.

18. **What does the slope represent in the following graphs.**



Slope = -k



Slope = -k/2.303

19. **Which of the following reaction is fast. Give reason.**

(i) $2Na_{(s)} + I_{2(s)} \longrightarrow 2NaI_{(s)}$

(ii) $2Na_{(s)} + I_{2(g)} \longrightarrow 2NaI_{(s)}$

Second reaction is fast because the state of reactant is gas. Gaseous reaction is faster than solid state reactants.

20. **Which of the two reacts faster? Why?**

(i) Powdered $CaCO_3$ with dil. HC*l*

(ii) Lump of $CaCO_3$ as marble with dil. HC*l*

First reaction is faster because powdered form of reactant has more surface area.

21. **Derive integrated rate law for a first order reaction A $\longrightarrow$ product.**

Rate is directly proportional to the concentration of one reactant is called first order reaction.

Consider a general first order reaction**A** $\longrightarrow$ **Product**

At t = 0 concentration of reactant = $[A_0]$

At time t, concentration of reactant left = [A]

rate = $k[A]^1$

$$-\frac{d[A]}{dt} = k[A]$$

$$-\frac{d[A]}{[A]} = k\ dt$$

Integrate between limits of $[A_0]$ at t = 0 and [A] at time 't'.

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

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

$-l$n [A] – ($-l$n $[A_0]$) = k (t – 0)

$-l$n [A] + ln $[A_0]$ = kt

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

$$k = \frac{1}{t}l\,n\frac{[A_0]}{[A]}$$

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

***

Page 219 Computing $e^{-40} = 4 \times 10^{-18}$

$$f = e^{-40}$$

$$f = e^{\frac{1}{40}}$$

Let x = e^{40}

Take log(ln) on both sides

ln x = ln e^{40}

ln x = 40 ln e $\quad ((\because l\,n\,e = 1)$

ln x = 40

2.303 log x = 40

$$\log x = \frac{40}{2.303}$$

log x = 17.3686

x = Antilog 17.3686

x = 2.34×10^{17}

$$f = \frac{1}{2.34\times10^{17}} = 0.4 \times 10^{-17} \boxed{= 4\times10^{-18}}$$