

# **XII – CHEMISTRY**

## **VOLUME 1**

**Name :**

**Class : Sec:**

**School :**

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# BLUE STARS HIGHER SECONDARY SCHOOL

## XII – CHEMISTRY

### UNIT – 1 METALLURGY

#### I. ANSWER THE FOLLOWING QUESTIONS:

##### 1. What is the difference between minerals and ores?

Minerals	ores
i) Minerals contain a low percentage of metal.	i) Ores contain a large percentage of metal
ii) Metal cannot be extracted from minerals	ii) Ores can be used for extraction of metals on a large scale readily and economically.
iii) Clay- $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ is the mineral of aluminium	iii) Bauxite- $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ is the ore of aluminium.

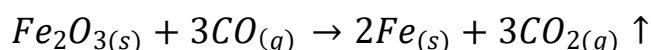
##### 2. What are the various steps involved in extraction of pure metals from their ores?

Steps involved in extraction of pure metals from their ores are

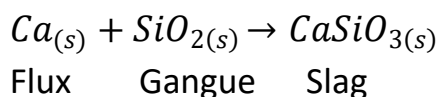
- Concentration of the ore
- Extraction of the crude metal.
- Refining of the crude metal.

##### 3. What is the role of Limestone in the extraction of Iron from its oxide $\text{Fe}_2\text{O}_3$ ?

- Lime stone ( $\text{CaO}$ ) is used as a flux in the extraction of iron from its oxide  $\text{Fe}_2\text{O}_3$ .
- A flux is a chemical substance that forms an easily fusible slag with gangue.
- Oxide of iron can be reduced by carbon monoxide as follows



- In this extraction a basic flux quick lime (or) lime ( $\text{CaO}$ ) reacts with acidic gangue silica to form the slag calcium silicate.

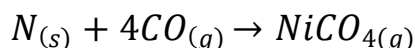


##### 4. Which type of ores can be concentrated by froth floatation method? Give two examples for such ores.

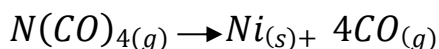
- Sulphide ores can be concentrated by froth floatation method.
- (eg) Galena ( $\text{PbS}$ ), Zinc blende ( $\text{ZnS}$ )

##### 5. 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.



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



##### 6. Explain zone refining process with an example using the Ellingham diagram given

**below.**

**Zone refining :**

- 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. ie; impurities are more soluble in the melt than in the solid state metal.
- In this process the impure metal is taken in the form of a rod. One end of the rod is heated using a mobile induction heater, melting the metal on that portion of the rod.
- When the heater is slowly moved to the other end pure metal 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.

**7. Using the Ellingham diagram,**

**(i) Predict the conditions under which**

**a. Aluminium might be expected to reduce magnesia.**

**b. Magnesium could reduce alumina.**

**(ii) It is possible to reduce  $\text{Fe}_2\text{O}_3$  by coke at a temperature around 1200K**

(i) a) Ellingham diagram for the formation of  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  intersects around 1600K. Above this temperature aluminium line lies below the magnesium line. Hence we can use aluminium to reduce magnesia above 1600K.

b) In Ellingham diagram below 1600K magnesium line lies below aluminium line. Hence below 1600K magnesium can reduce alumina.

(ii) In Ellingham diagram above 1000K carbon line lies below the iron line. Hence it is possible to reduce  $\text{Fe}_2\text{O}_3$  by coke at a temperature around 1200K.

**8. Give uses of zinc.**

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

**9. Explain the electrometallurgy of aluminium.**



not react with iodine.

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

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

### 13. Explain the principle of electrolytic refining with an example.

- 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.  
On passing current the following reactions will take place.  
Reaction On passing current the following reactions will take place.  
Reaction at anode:  $A_{(s)} \rightarrow Ag^+_{(aq)} + e^-$   
Reaction at cathode :  $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$
- At anode silver atoms lose electrons and enter the solution. From the solution silver ions migrate towards the cathode. At cathode silver ions get discharged by gaining electrons and deposited on the cathode.

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

- A suitable reducing agent is selected based on the thermodynamics considerations.
- For a spontaneous reaction, the change in free energy ( $\Delta G$ ) should be negative.
- Therefore, thermodynamically, the reduction of metal oxide with a given reducing agent can occur if the free energy change for the coupled reaction is negative.
- Hence, the reducing agent is selected in such a way that it provides a large negative ( $\Delta G$ ) value for the coupled reaction.

### 15. Give the limitations of Ellingham diagram.

Ellingham diagram is constructed based only on thermodynamic considerations.

- It gives information about the thermodynamic feasibility of a reaction.
- It does not tell anything about the rate of the reaction.
- More over it does not give any idea about the possibility of other reactions that might be taking place.
- The inter preparation of  $\Delta G$  is based on the assumption that the reactants are in

equilibrium with the product which is not always true.

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

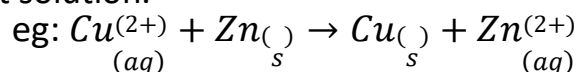
- Reduction of oxides of active metals such as sodium, potassium etc. by carbon is thermodynamically not feasible.
- Such metals are extracted from their ores by using electrochemical methods.
- In this method the metal salts are taken in fused form or in solution form.
- The metal ion present can be reduced by treating the solution with suitable reducing agent or by electrolysis.
- Gibbs free energy change for the electrolysis is

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

n = number of electrons involved in the reduction F = Faraday = 96500 coulombs

$E^\circ$  = electrode potential of the redox couple.

- If  $E^\circ$  is positive,  $\Delta G^\circ$  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.



- Zinc is more reactive than copper and displaces copper from its salt solution.

## UNIT – 2 (P-BLOCK ELEMENTS - I)

### ANSWER THE FOLLOWING QUESTIONS:

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

The following factors are responsible for the anomalous properties of the first elements of p-block.

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

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

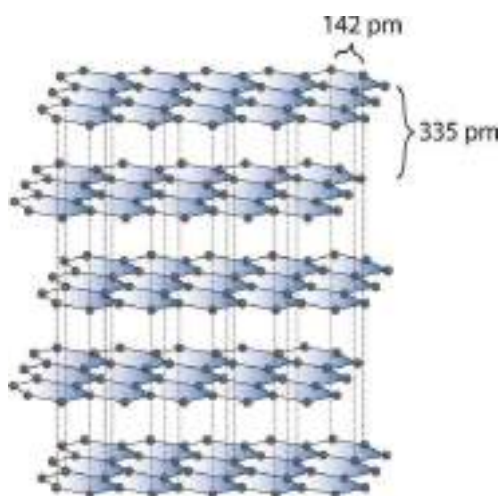
- Some elements exist in more than one crystalline or molecular forms in the same physical state.
- This phenomenon is called allotropism.
- The different forms of an element are called allotropes.

(Example: Carbon exists as diamond, graphite, graphene, fullerenes, carbon nanotubes)

(i) **Graphite:**

- It is the most stable allotropic form of carbon at normal temperature and pressure .
- It is soft and conducts electricity.
- It is composed of flat two dimensional sheets of carbon.
- Each sheet is a hexagonal net of  $sp^2$  hybridised carbon atoms with a c-c bond length of  $1.41 \text{ \AA}$ .

**Structure of graphite**

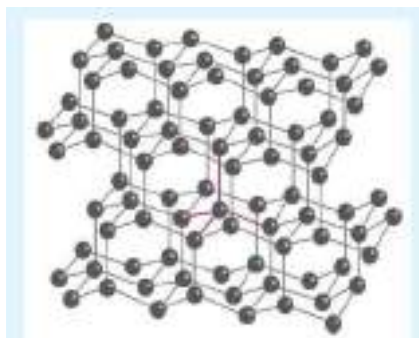


(ii) **Diamond:**

- It is very hard.
- The carbon atoms in diamond are  $sp^3$  hybridised, with a c-c bond length of  $1.54 \text{ \AA}$ .
- In the diamond, carbon atoms are arranged in tetrahedral manner.



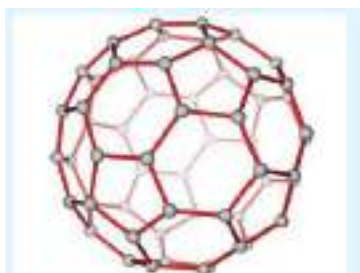
## Structure of Diamond



### (iii) Fullerenes:

- It is newly synthesized allotropes of carbon
- The C<sub>60</sub> molecules have a soccer ball like structure and is called buckminster fullerene.
- It has a fused ring structure consists of 20 six membered rings and 12 five membered rings.
- Each carbon atom is sp<sup>2</sup> hybridised.
- The C-C bond distance is 1.44 Å and C=C distance is 1.38 Å.

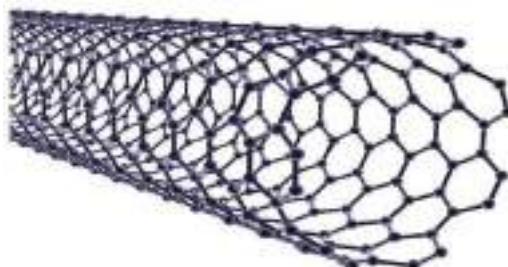
### Structure of fullerene



### (iv) Carbon nanotubes:

- It is recently discovered allotropes, have graphite like tubes with fullerene ends.
- These nanotubes are stronger than steel and conduct electricity.

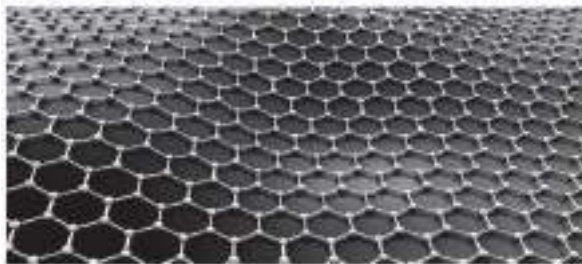
Structure of carbon nanotubes



### (v) Graphene:

- It has a single planar sheet of sp<sup>2</sup> hybridised carbon atoms that are densely packed in a honey comb crystal lattice.

## Structure of graphene



### 3. Give the uses of Borax.

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

### 4. What is catenation? Describe briefly the catenation property of carbon.

Catenation is an ability of an element to form chain of atoms.

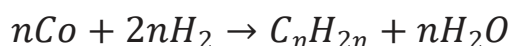
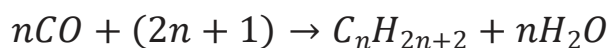
The conditions for catenation are

- i) The valency of the element is greater than or equal to two.
- ii) The element should have an ability to bond with itself.
- iii) The self bond must be as strong as its bond with other elements.
- iv) Kinetic inertness of catenated compound towards other molecules.

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

### 5. Write a note on Fisher tropesch synthesis:

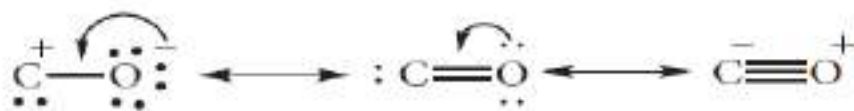
This is a reaction in which carbon monoxide reacts with hydrogen at a pressure less than 50 atm and temperature 500 - 700 K in presence of metal catalysts to give saturated and unsaturated hydrocarbons.



### 6. Give the structure of CO and CO<sub>2</sub>.

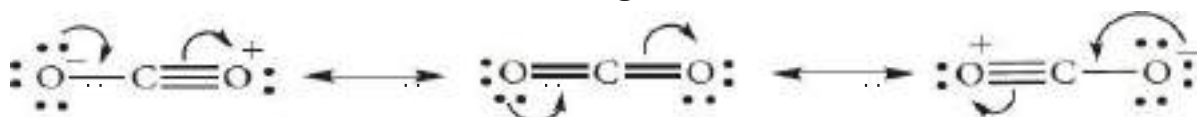
#### Structure of CO:

- Structure is linear.
- Three electron pairs are shared between carbon and oxygen.
- C-O bond distance is 1.128 Å.
- The structure can be considered as the resonance hybrid of the following two canonical forms.



### Structure of CO<sub>2</sub>:

- Structure is linear.
- Equal bond distance for both C–O bonds.
- There are two C–O sigma bonds.
- In addition there is 3C - 4e bond covering all the three atoms.

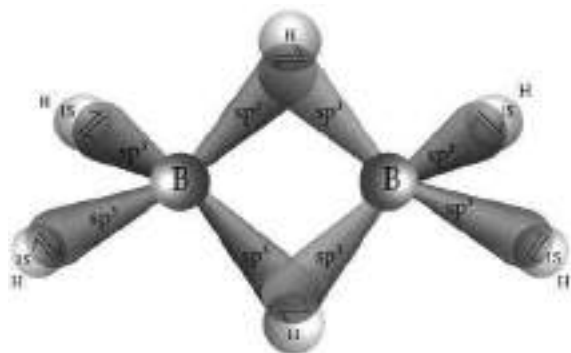


### 7. Give the uses of silicones.

- i) Used for low temperature lubrication.
- ii) Used in vacuum pumps.
- iii) Used in high temperature oil baths.
- iv) Used for making water proof cloths.
- v) Used as insulating material in electrical motor and other appliances.
- vi) Mixed with paints and enamels to make them resistant towards high temperature, sunlight, dampness and chemicals.

### 8. Describe the structure of diborane.

#### Structure of diborane



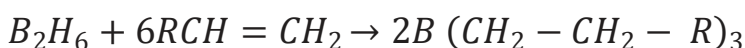
- In diborane two BH<sub>2</sub> units are linked by two bridged hydrogens. Therefore it has eight B–H bonds.
- Diborane has only 12 valence electrons and are not sufficient to form normal covalent bonds.
- The four terminal B–H bonds are normal covalent bonds. (2C – 2e bond) (Totally 8e<sup>-s</sup>)
- The remaining four electrons have to be used for the bridged bonds. i.e two 3 centred B–H–B bonds utilise two electrons each.
- Hence these bonds are 3C - 2e bonds.
- The bridging hydrogen atoms are in a plane.
- In diborane, boron is sp<sup>3</sup> hybridised.

- Three  $sp^3$  hybridised orbitals contain single electron and the fourth orbital is empty.
- Two half filled  $sp^3$  hybridised orbitals of each boron overlap with two hydrogens to form four terminal  $2C - 2e$  bonds.
- One empty and one half filled  $sp^3$  hybridised orbital on each boron is left.
- Empty  $sp^3$  hybridised orbital of one boron, overlaps with half filled  $sp^3$  hybridised orbital of the other boron and  $1s$  orbital of hydrogen to form two bridged  $3C - 2e$  B-H-B bonds.

### 9. Write a short note on hydroboration.

Diborane adds on to alkenes and alkynes in ether solvent at room temperature.

- This reaction is known as hydroboration.
- This is used in synthetic organic chemistry especially for anti Markovnikov addition.



Organoborane

### 10. Give one example for each of the following:

- i) icosagens      ii) tetragen      iii) prictogen      iv) chalcogen

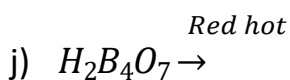
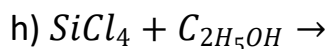
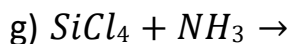
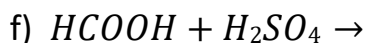
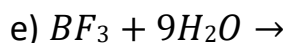
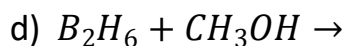
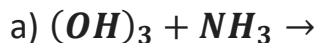
	Group Name	Example
i	Icosagens	Boron
ii	Tetragens	Carbon
iii	Prictogen	Nitrogen
iv	Chalcogens	Oxygen

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

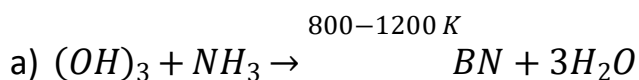
- The tendency of an element to form a cation by losing electrons is known as electro positive or metallic character.
- This character depends on the ionisation energy.
- Generally on moving down a group ionisation energy decreases and hence the metallic character increases.
- In p-block, the elements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

Group	Non metals	Metalloids	Metals
13	–	B	Al, Ga, In, Tl
14	C	Si, Ge	Sn, Pb
15	N, P	As, Sb	Bi
16	O, S, Se	Te, Po	–
17	F, Cl, Br, I	–	–
18	He, Ne, Ar, Kr, Xe	–	–

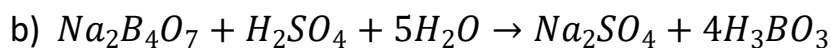
12. Complete the following reactions:



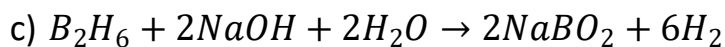
**Ans:**



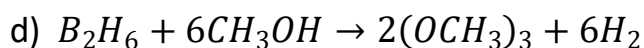
Boron nitride



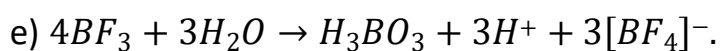
Ortho boric acid



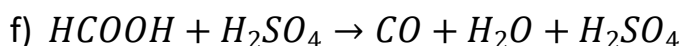
Sodium meta borate



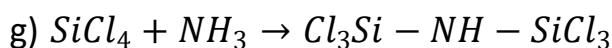
Tri Methyl borate



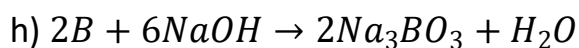
Boric acid



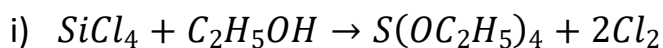
carbonmonoxide



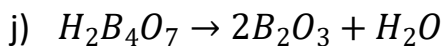
Chlorosilazanes



### Sodium borate



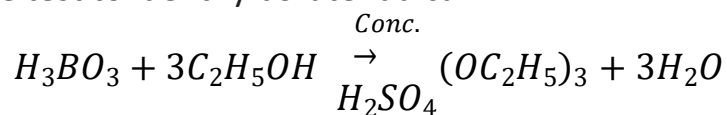
Tetraethoxy silane



Boric anhydride

### 13. How will you identify borate radical?

- When boric acid or borate salt is heated with ethyl alcohol in presence of conc. sulphuric acid, an ester tri alkyl borate is formed.
- The vapour of this ester burns with a green edged flame.
- This is ethyl borate test to identify borate radical.



(Ethyl borate (Green edged flame))

### 14. Write a note on zeolites.

- Zeolites are three dimensional crystalline solids containing aluminium, silicon and oxygen in their regular three dimensional frame work.
- They are hydrated sodium alumino silicates.
- General formula is  $\text{NaO} \cdot (\text{Al}_2\text{O}_3)_x \cdot (\text{SiO}_2)_y \cdot (\text{H}_2\text{O})_z$  where  $x = 2$  to  $10$ ;  $y = 2$  to  $6$
- Zeolites have porous structure in which the monovalent sodium ions and water molecules are loosely held.
- Si and Al atoms are tetrahedrally coordinated with each other through shared oxygen atoms.
- Zeolites are similar to Clay minerals but they differ in their crystalline structure.
- Zeolites have a three dimensional crystalline structure looks like a honey comb consisting of a network of interconnected tunnels and cages.
- Water molecules move freely in and out of these pores but the zeolite frame work remains rigid.
- Another special aspect of this structure is that the pore / channel sizes are nearly uniform, allowing the crystal to act as a molecular sieve.
- Zeolites are used in the removal of permanent hardness of water.



## UNIT – 3 (P – BLOCK ELEMENTS – II)

### ANSWER THE FOLLOWING QUESTIONS:

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

- As we move down the group in p–block elements the  $ns^2$  electrons become inert and do not involve in chemical combination.
- Only np electrons take part in chemical combination.
- This is known as inert pair effect.  
(eg) In 13 Group  $Tl^{3+}$  is less stable and  $Tl^+$  is more stable due to inert pair effect.

#### 2. Chalcogens belongs to p–block. Give reason.

- Chalcogens belong to p–block elements.
- Because their outer electronic configuration is  $ns^2 np^4$ .
- In these elements( O,S,Se,Te and Po) the last electron enters np orbital.
- Hence they belong to p–block elements.
- Chalcogens are ore forming elements.
- Most of the ores are oxides and sulphides.

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

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

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

- a)  $OF_2$                       b)  $O_2F_2$                       c)  $Cl_2O_3$                       d)  $I_2O_4$

Since Fluorine exhibits only – 1 oxidation state the oxidation number of fluorine in

a)  $OF_2$  is –1

b)  $O_2F_2$  is –1

c)  $Cl_2O_3$

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

$$2x - 6 = 0$$

$$2x = +6$$

$$\boxed{x = +3}$$

d)  $I_2O_4$

$$2(x) + 4(-2) = 0; 2x = +8 ;$$

#### 5. What are inter halogen compounds? Give examples

- Each halogen combines with other halogens to form a series of compounds called inter halogen compounds.

(ex)  $ClF$ ,  $BrF_3$ ,  $IF_5$ ,  $IF_7$



## 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.

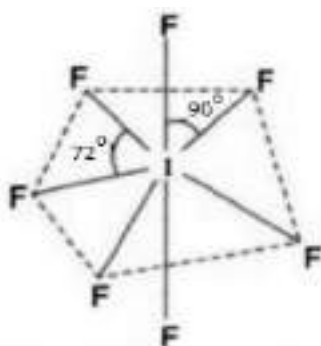
## 7. Give the uses of helium.

- Helium and oxygen mixture is used by divers in place of air oxygen mixture. This prevents the painful dangerous condition called bends.
- Helium is used to provide inert atmosphere in electric arc welding of metals.
- Helium has lowest boiling point hence used in cryogenics (Low temperature science)
- Helium is much less denser than air and hence used for filling air balloons.

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

Inter halogen	Hybridisation	Structure
$IF_7$	$Sp^3d^3$	Pentagonal bipyramidal

### Structure of $IF_7$



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

- Chlorine reacts with cold NaOH to give sodium hypochlorite



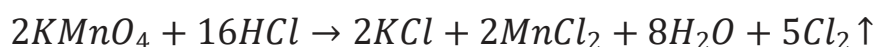
Sodium hypochlorite

- Chlorine reacts with hot NaOH to give sodium chlorate

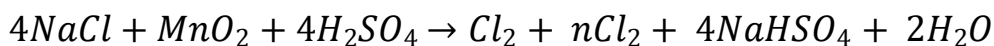


## 10. How will you prepare chlorine in the laboratory?

In the laboratory chlorine is prepared by the oxidation of hydrochloric acid by potassium permanganate.



Action of sulphuric acid on chlorides in the presence of manganese dioxide.



**11. Give the uses of sulphuric acid.**

Sulphuric acid is used

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

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

- Sulphuric acid is highly soluble in water.
- It has strong affinity towards water.
- Hence it can be used as a dehydrating agent.
- When dissolved in water, it forms mono ( $H_2SO_4 \cdot H_2O$ ) and dihydrates ( $H_2SO_4 \cdot 2H_2O$ ) and the reaction is exothermic.
- (ex)  $C_{12}H_{22}O_{11} + H_2SO_4 \rightarrow 12C + H_2SO_4 \cdot 11H_2O$
- $HCOOH + H_2SO_4 \rightarrow CO + H_2SO_4 \cdot H_2O$
- $(COOH)_2 + H_2SO_4 \rightarrow CO + CO_2 + H_2SO_4 \cdot H_2O$

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

Reason for the anomalous behaviour of nitrogen

- Small size
- High electronegativity
- Non – availability of d – orbitals in valency shell
- Chemically inert due to high bonding energy

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

Compound	Molecular Formula	Structural Formula
a) Nitric acid	$\text{HNO}_3$	
b) <u>Dinitrogenpentoxide</u>	$\text{N}_2\text{O}_5$	
c) Phosphoric acid	$\text{H}_3\text{PO}_4$	
d) <u>Phosphine</u>	$\text{PH}_3$	

15. Give the uses of argon.

- Argon prevents the oxidation of hot filament and prolongs the life in filament bulbs.
- Argon is used in radio valves and tubes.

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

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

Nitrogen -  $[\text{He}] 2s^2 2p^3$

Phosphorous -  $[\text{Ne}] 3s^2 3p^3$

Arsenic -  $[\text{Ar}] 3d^{10} 4s^2 4p^3$

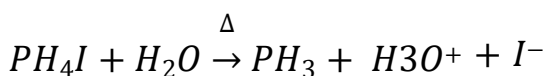
Antimony -  $[\text{Kr}] 4d^{10} 5s^2 5p^3$

Bismuth -  $[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^3$

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

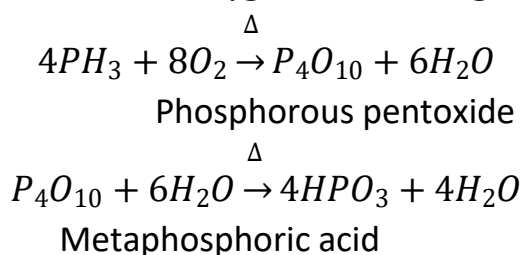
➤ **Basic Nature :**

Phosphine is weakly basic and forms phosphonium salts.



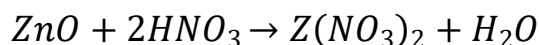
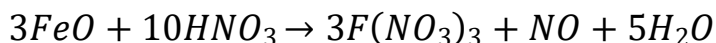
**Combustion :**

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



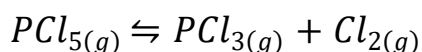
**18. Give a reaction between nitric acid and a basic oxide.**

Nitric acid reacts with a basic oxide to form salt and water.



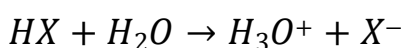
**19. What happens when  $PCl_5$  is heated?**

On heating Phosphorous penta chloride decomposes into phosphorus trichloride and chlorine.



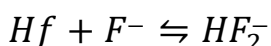
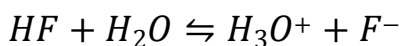
**20. Suggest a reason why HF is a weak acid, whereas binary acids of the all other halogens are strong acids.**

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



(X – F, Cl, Br, or I)

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

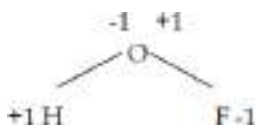


**21. Deduce the oxidation number of oxygen in hypofluorous acid – HOF.**

In case of O-F bond, Fluorine is most electronegative than, so its oxidation number is -1, oxygen oxidation number is +1.

In case of O-H bond, O is electronegative than H. so its oxidation number is -1.

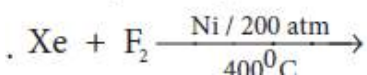
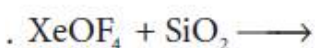
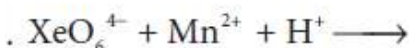
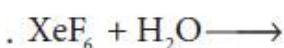
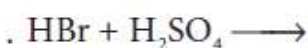
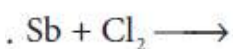
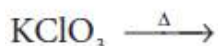
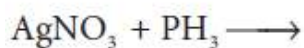
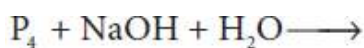
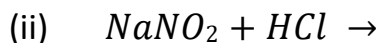
Hydrogen oxidation number is +1.



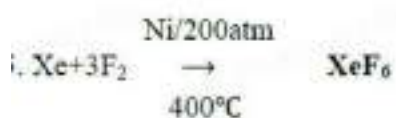
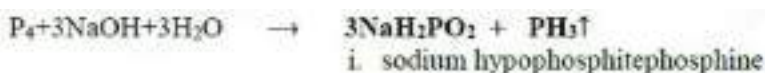
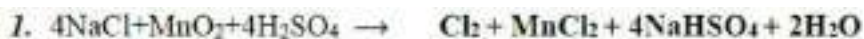
**22. What type of hybridisation occur in a)  $BrF_5$  b)  $BrF_3$**

	Inter Halogen Compound	Hybridisation	Shape
a)	$BrF_5$	$sp^3d^2$	Square pyramidal
b)	$BrF_3$	$sp^3d$	T-Shape

### 23. Complete the following reactions.



### ANSWERS:





## UNIT – 4 TRANSITION AND INNER TRANSITION

### ANSWER THE FOLLOWING:

#### 1. What are transition metals?. Give four examples

- ❖ IUPAC defines 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.
- ❖ Their properties are transitional between highly reactive metals of s block and elements of p block which are mostly non metals.

**Example :** Fe , Cu , Ni , CO

#### 2. Explain the oxidation state of 4d series elements

- 1) The oxidation states of 4d metals vary from **+3 for Y and La** to **+8 for Ru and Os**.
- 2) The highest oxidation state of 4d elements are found in their compounds with the higher electronegative elements like O, F and Cl. for example:  $\text{RuO}_4$ ,  $\text{OsO}_4$  and  $\text{WCl}_6$ .
- 3) First element of 4d series Yttrium has only one oxidation state +3.
- 4) Last element of 4d series has only one oxidation state +2.
- 5) Middle element Ru has seven different oxidation states from +2 to +8.
- 6) +2 & +3 are their common oxidation states.

#### 3. What are inner transition elements?

- ❖ The elements in which the extra electron enters (n-2)f orbitals are called f – block elements.
- ❖ They are called as **inner transition elements** they form a **transition series within the transition elements**.

#### 4. Justify the position of lanthanoids and actinoids in periodic table

- 1) The actual position of Lanthanoids in the periodic table is at group number 3 and period
- 2) number 6.
- 3) However, in the sixth period after lanthanum, the electrons are preferentially filled in inner 4f sub shell and these fourteen elements following lanthanum show similar chemical properties.
- 4) Therefore these elements are grouped together and placed at the bottom of the periodic table.
- 5) If we place these elements after Lanthanum in the periodic table below 4d series, the properties of the elements belongs to a group would be different and it would affect the proper structure of the periodic table.
- 6) Hence a separate position is provided to the inner transition elements.

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

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

The **common oxidation state** of lanthanoids and actinoids are **+3**

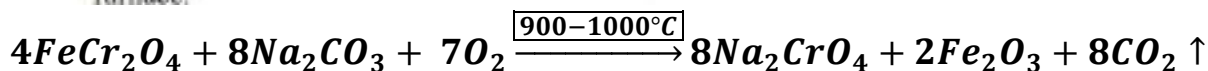
#### 5. What are actinides ?. Give three examples

- ❖ The fourteen elements following actinium ,i.e., from Thorium (Th) to Lawrentium (Lr) are called actinoids.
- ❖ Similar to lanthanoids, they are placed at the bottom of the periodic table.
- ❖ **Actinoids** have general electronic configuration  $[\text{Rn}]5f^{2-14}6d^{0-2}7s^2$

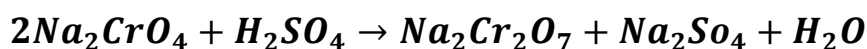
**Ex :** Actnium , Thorium , Uranium

## 6 Describe the preparation of potassium dichromate

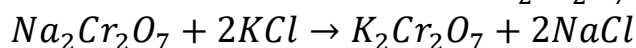
- ❖ It is prepared from chromate ore.
- ❖ The ore is concentrated by gravity separation.
- ❖ It is then mixed with excess sodium carbonate and lime and roasted in a reverberatory furnace.



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



- The above solution is concentrated to remove less soluble sodium sulphate. The resulting solution is filtered and further concentrated.
- It is cooled to get the crystals of  $\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$
- The saturated solution of sodium dichromate in water is mixed with KCl and then, concentrated to get crystals of NaCl.
- It is filtered while hot and the filtrate is cooled to obtain  $\text{K}_2\text{Cr}_2\text{O}_7$  crystals.



Potassium dichromate  
(Orange red)

## 7 What is lanthanide contraction and what are the effects of lanthanide contraction?

### Lanthanide 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.

### Effects of lanthanide contraction

#### 1. Basicity differences

As we go from  $\text{Ce}^{3+}$  to  $\text{Lu}^{3+}$ , the basic character of  $\text{Ln}^{3+}$  ions decrease. Due to the decrease in the size of  $\text{Ln}^{3+}$  ions, the ionic character of  $\text{Ln-OH}$  bond decreases (covalent character increases) which results in the decrease in the basicity.

#### 2. Similarities among lanthanoids:

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

10. Complete the reaction

- $3\text{MnO}_4^{2-} + 4\text{H}^+ \longrightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
- $\text{C}_6\text{H}_5\text{CH}_3 + 2\text{KMnO}_4 \xrightarrow[\text{KOH}]{\text{acidified}} \text{C}_6\text{H}_5\text{COOH} + 2\text{MnO}_2 + 2\text{KOH}$
- $\text{MnO}_4^- + 5\text{Fe}^{2+} \xrightarrow{\text{H}^+} 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- $2\text{KMnO}_4 \xrightarrow[\text{Red. box}]{\Delta} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
- $\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$

### 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. They are usually non-stoichiometric compounds

Example :  $\text{TiC}$ ,  $\text{ZrH}_{1.02}$



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

$Ti^{3+}$  -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$  No of unpaired electron = 1

$$\mu = \sqrt{n(n+2)} = \sqrt{1(3)} = \sqrt{3} = 1.732 \text{ B.M}$$

$Mn^{2+}$  -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$  No of unpaired electron = 5

$$\mu = \sqrt{n(n+2)} = \sqrt{5(7)} = \sqrt{35} = 5.92 \text{ B.M}$$

similarly

Ion	Configuration	n	$\mu = \sqrt{n(n+2)} \mu_B$	$\mu_{\text{(observed)}}$
$Sc^{3+}, Ti^{4+}, V^{5+}$	$d^0$	0	$\mu = \sqrt{0(0+2)} = 0 \mu_B$	diamagnetic
$Ti^{3+}, V^{4+}$	$d^1$	1	$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \mu_B$	1.75
$Ti^{2+}, V^{3+}$	$d^2$	2	$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \mu_B$	2.76
$Cr^{3+}, Mn^{4+}, V^{2+}$	$d^3$	3	$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \mu_B$	3.86
$Cr^{2+}, Mn^{3+}$	$d^4$	4	$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89 \mu_B$	4.80
$Mn^{2+}, Fe^{3+}$	$d^5$	5	$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.91 \mu_B$	5.96
$Co^{3+}, Fe^{2+}$	$d^6$	4	$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89 \mu_B$	5.3-5.5
$Co^{2+}$	$d^7$	3	$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \mu_B$	4.4-5.2
$Ni^{2+}$	$d^8$	2	$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \mu_B$	2.9-3.4
$Cu^{2+}$	$d^9$	1	$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.732 \mu_B$	1.8-2.2
$Cu^+, Zn^{2+}$	$d^{10}$	0	$\mu = \sqrt{0(0+2)} = 0 \mu_B$	diamagnetic

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

$Ce^{4+}$  -  $[Xe]4f^0$  or  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^0$

$Co^{2+}$  -  $[Ar]3d^7$  or  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$

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

❖ It is observed that except Sc all other metals possess +2 oxidation state

❖ In the first half of the first row transition elements from Sc to Mn atomic number increases from 21 – 25 so that number of electrons in 3d – orbital also increases from 1 to 5.

$Sc^{+2}$  -  $d^1$

$Ti^{+2}$  -  $d^2$

$V^{+2}$  -  $d^3$

$Cr^{+2}$  -  $d^4$

$Mn^{+2}$  -  $d^5$

❖ +2 oxidation state is attained by the loss of two electrons by these metals

❖ Number of d electrons in +2 oxidation state increases from  $Ti^{+2}$  to  $Mn^{+2}$  the stability of +2 state increases

❖ As a result d – orbital is becoming more and more half – filled which is more stable

13. Which is more stable?  $Fe^{3+}$  or  $Fe^{2+}$  - explain.

$Fe^{3+}$  has  $3d^5$  configuration in its outermost shell

$Fe^{2+}$  has  $3d^6$  config. in its outermost shell

$Fe^{3+}$  ion is more stable due to its half filled configuration



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

- ❖ In 3d series as we move from Ti to Zn, the standard reduction potential ( $E_{M^{2+}/M}^0$ ) value is approaching towards less negative value and copper has a positive reduction potential. i.e., elemental copper is more stable than  $Cu^{2+}$ .
- ❖ There are two deviations., In the general trend, value for manganese and zinc are more negative than the regular trend.
- ❖ It is due to extra stability which arises due to the half filled  $d^5$  configuration in  $Mn^{2+}$  and completely filled  $d^{10}$  configuration in  $Zn^{2+}$ .

15. Compare lanthanides and actinides

Lanthanoids	Actinoids
Differentiating electron enters in <b>4f orbital</b>	Differentiating electron enters in <b>5f orbital</b>
<b>Binding energy</b> of 4f orbitals are higher	<b>Binding energy</b> of 5f orbitals are lower
They show <b>less tendency to form complexes</b>	They show <b>greater tendency to form complexes</b>
Besides +3 oxidation states lanthanoids show +2 and +4 oxidation states in few cases.	Besides +3 oxidation states actinoids show higher oxidation states such as +4, +5, +6 and +7
They do <b>not form oxo cations</b>	They do form <b>oxo cations such as <math>UO_2^{2+}</math></b>
Most of the lanthanoids are <b>colourless</b>	Most of the actinoids are <b>coloured</b> . For example. $U^{3+}$ (red),

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

- ❖  $Cr^{2+}$  is strongly reducing in nature .It has  $d^4$  configuration. While acting as reducing agent , it get oxidized to  $Cr^{3+}$  which has  $d^3$  configuration.
- ❖ This  $d^3$  configuration can be written as  $3t_{2g}$  configuration which is most stable configuration.
- ❖ For  $Mn^{3+}$  which has  $d^4$  configuration acts as an oxidizing agent and get reduced to  $Mn^{2+}$  which has  $d^5$  configuration
- ❖ It has half filled configuration , so it is more stable.

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

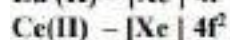
- 1) Ionization energy of transition element is **intermediate between those of s and p block elements.**
- 2) As we move **from left to right** in a transition metal series, the **ionization enthalpy increases** as expected.
- 3) This is due to **increase in nuclear charge** corresponding to the filling of d electrons.
- 4) The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular.
- 5) The added electron **enters (n-1)d orbital** and the inner electrons act as a shield and decrease the effect of nuclear charge on valence ns electrons. Therefore, it leads to variation in the ionization energy values.
- 6) In 3d series ionisation enthalpy of **first four members (Sc , Ti , V , Cr ) show little differences** in values
- 7) Because , effective nuclear charge is more than that of repulsive force of d electron on electrons on its outer most shell .Last four (Fe , Co , Ni , Cu ) are also fairly close
- 8) **Zn shows high values** due to extra stability of **completely filled d orbitals.**

18. Actinoid contraction is greater from element to element than the lanthanoid contraction, why?
- ❖ These 5f orbital have **poor shielding effect** than 4f orbital which leads to decrease in atomic or ionic radii.
  - ❖ Therefore in **actinoids effective nuclear charge experienced by outermost electrons is more** than experienced by lanthanoids.
  - ❖ So actinoid shows greater contraction.

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

- ❖  $\text{La}(\text{OH})_3$  is more basic than  $\text{Lu}(\text{OH})_3$ .
- ❖ As we move from  $\text{Ce}^{3+}$  to  $\text{Lu}^{3+}$ , the basic character of  $\text{Ln}^{3+}$  decrease.
- ❖ Due to decrease in size of  $\text{Ln}^{3+}$  on account of lanthanoid contraction, the ionic character of Ln - OH bond decreases ( Covalent character increases ) which result in the decrease in the basicity.

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



Eu (II) has half filled subshell which provide more stability due to exchange of energy.

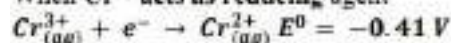
21. Why do zirconium and Hafnium exhibit similar properties?

- ❖ In the complete f - series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed, because of this very small change in radii of lanthanoids, their chemical properties are quite similar.
- ❖ Due to lanthanoid contraction, second and third rows of d - block transition elements are quite close in properties

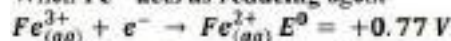
23

- Which is stronger reducing agent  $\text{Cr}^{2+}$  or  $\text{Fe}^{2+}$  ?

When  $\text{Cr}^{2+}$  acts as reducing agent



When  $\text{Fe}^{2+}$  acts as reducing agent



24. ❖ If the standard electrode potential ( $E^0$ ), of a metal is large and negative, the metal is a powerful reducing agent, because it loses electrons easily.
- ❖ Thus  $\text{Cr}^{2+}$  is easily oxidized to  $\text{Cr}^{3+}$  but  $\text{Fe}^{2+}$  cannot be easily oxidized to  $\text{Fe}^{3+}$
  - ❖ Hence  $\text{Cr}^{2+}$  is powerful reducing agent

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

- ❖ Copper has **high atomisation energy** (Energy observed), but **low hydration enthalpy** (energy released).
- ❖ Hence the  $E^0$  value for copper is positive (+0.34 v) i.e elemental copper is more stable than  $\text{Cu}^{2+}$

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

- 1) 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 orbital as the energy difference between them is very small.
- 2) At the beginning of the series, +3 oxidation state is stable but towards the end **+2 oxidation state becomes stable**.
- 3) The number of oxidation states increases with the number of electrons available, and it decreases as the number of paired electrons increases.
- 4) Hence, **the first and last elements show less number of oxidation states and the middle elements with more number of oxidation states**.
- 5) For example, the first element Sc has **only one oxidation state +3**; the middle element Mn has **six different oxidation states from +2 to +7**. The last element Cu shows +1 and +2 oxidation states only.

25. Which metal in the 3d series exhibits +1 oxidation state most frequently and why?
- 1) Cu is only metal in the 3d series exhibits +1 oxidation state
  - 2) Cu has electronic configuration  $[\text{Ar}] 3d^{10}4s^1$  and after losing one electron it acquires a stable  $3d^{10}$  configuration which is more stable.
26. Why first ionization enthalpy of chromium is lower than that of zinc?
- $\text{Zn} : 3d^{10} 4s^2$      $\text{Cr} : 3d^5 4s^1$
- In Cr first electron has to be removed from  $4s^1$  (half filled) orbital with less amount of energy.
- In Zn first electron has to be removed from  $4s^2$  (completely filled) orbital, so it requires high energy to remove electron from it.
- So first ionization enthalpy of chromium is lower than that of zinc.
27. Transition metals show high melting points why?
- The melting point of the transition metals are high due to greater number of unpaired d electrons for metallic bonding.

7



## UNIT – 5 CO-ORDINATION CHEMISTRY

Answer the following:

1. Write the IUPAC names for the following complexes.

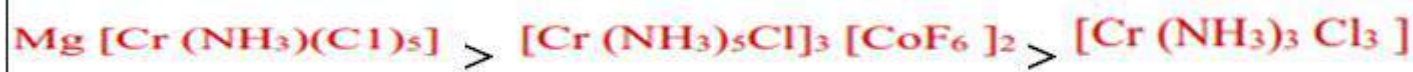
- i)  $\text{Na}_2 [\text{Ni} (\text{EDTA})]$  - Sodium 2,2',2'',2''' -(ethane-,2diyl)dinitrilotetraacetato)nickelate(II)
- ii)  $[\text{Ag} (\text{CN})_2]^-$  Dicyanidoargentate(I)ion
- iii)  $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$  --Tris(ethane1,2diamine)cobalt(III) Sulphate
- iv)  $[\text{Co} (\text{ONO})(\text{NH}_3)_5]^{2+}$  Pentaamminenitrito-*k*-O-cobalt(III)ion
- v)  $[\text{Pt} (\text{NH}_3)_2 \text{Cl}(\text{NO}_2)]$  -- Diamminechloridionitro *k*-Nplatinum(II)

2. Write the formula for the following coordination compounds.

- a) potassiumhexacyanidoferrate(II) -- $\text{K}_4 [\text{Fe}(\text{CN})_6]$
- b) pentacarbonyliron(0) -  $[\text{Fe}(\text{CO})_5]$
- c) pentaamminenitrito -*K* -*N* -cobalt(III)ion - $[\text{Co} (\text{ONO})(\text{NH}_3)_6]^{2+}$
- d) hexaamminecobalt(III)sulphate - $[\text{Co}(\text{NH}_3)_6] (\text{SO}_4)_3$
- e) sodiumtetrafluorido dihydroxidochromate(III)  $\text{Na}_3 [\text{CrF}_4(\text{OH})_2]$

3. Arrange the following in order to increasing molar conductivity.

- i)  $\text{Mg} [\text{Cr} (\text{NH}_3)(\text{Cl})_5]$                       ii)  $[\text{Cr} (\text{NH}_3)_5\text{Cl}]_3 [\text{CoF}_6]_2$                       iii)  $[\text{Cr} (\text{NH}_3)_3 \text{Cl}_3]$



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

- Cis-platin is used as an antitumour drug in cancer treatment.
- Biologically important compounds.
  - i) Haemoglobin – Oxygen carrier in blood.
  - ii) Chlorophyll – useful in photo synthesis in plants.

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

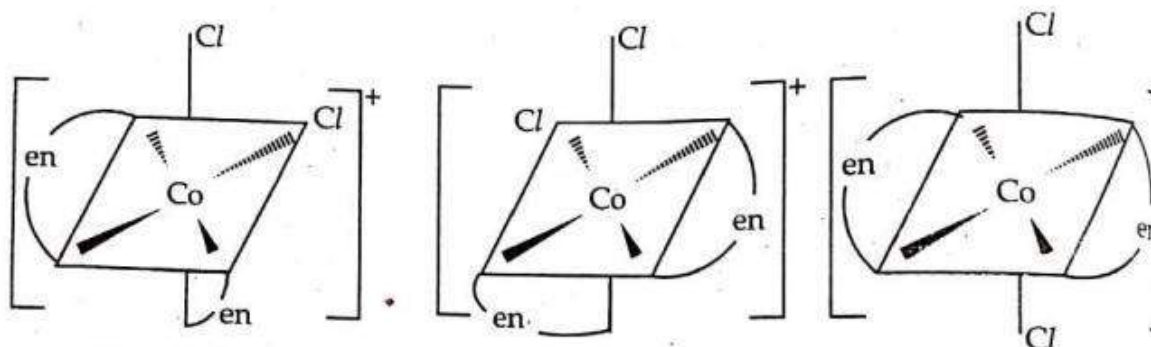
a)  $[Cr(NH_3)_6]^{3+}$

Complex	$[Cr(NH_3)_6]^{3+}$
Central metal ion and its outer electronic configuration	$Cr^{3+}: 3d^3 4s^0$
Outer orbitals of metal ion	
Nature of ligand	Weak field ligand does not pair up the 3d electrons in the metal
Outer orbitals of metal ion/in presence of ligands	
Hybridisation	Coordination number – 6 Hybridisation $d^2sp^3$
Hybridised orbitals of the metal atom in the complex	
Geometry	Octahedral In this complex inner d orbitals are involved in hybridisation and hence the complex is called inner orbital complex.
Magnetic property	(n) No. of unpaired electrons = 3 Hence paramagnetic.

b)  $[N(CN)_4]^{2-}$

Complex	$[Ni(CN)_4]^{4-}$
Central metal atom/ion and its outer electronic configuration	$Ni^{2+}: 3d^8, 4s^0$
Outer orbitals of metal atom/ion	
Nature of ligand	$CN^-$ Strong field ligand causes the pairing of 3d electrons in the metal
Outer orbitals of metal atom/ion in presence of ligands	
Hybridisation	Coordination number - 4 Hybridisation - $dsp^2$
Hybridised orbitals of the metal atom in the complex	
Geometry	Square planar
Magnetic property	No. of unpaired electrons = 0; Hence diamagnetic
Magnetic moment (Using spin only formula)	$\mu_s = \sqrt{n(n+2)} = 0$

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



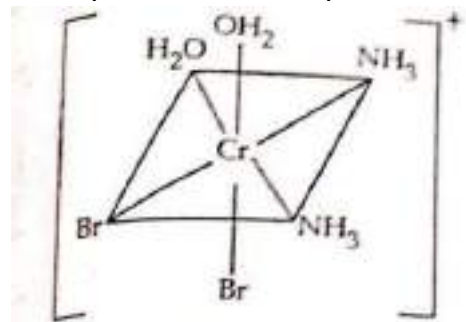
Two Cis  $[C(en)_2Cl_2]^+$  isomer – optically active    One trans  $[Co(en)_2Cl_2]^+$  isomer – optically inactive

7.  $[T(H_2O)_6]^{3+}$  is coloured, while  $[Sc(H_2O)_6]^{3+}$  is colourless – explain.

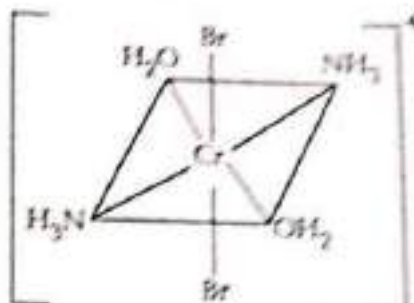
- In  $[T(H_2O)_6]^{3+}$ , the outer electronic configuration of metal ion  $Ti^{3+}$  is  $3d^1$ .
- This single electron present in lower energy  $t_{2g}$  orbitals in the octahedral aqua ligand field absorbs light and excited to higher energy  $e_g$  level.
- This is known as d-d transition.
- For this excitation absorption maximum is at  $2000\text{ cm}^{-1}$  corresponding to the CFSE is  $239.7\text{ KJmol}^{-1}$ .
- The transmitted colour associated with this absorption is purple and hence the complex appears purple in colour.
- But in  $[Sc(H_2O)_6]^{3+}$ , the outer electronic configuration of metal ion  $Sc^{3+}$  is  $3d^0$ .
- Since there is no electron in d orbital, d-d transition is not possible.
- Hence  $[Sc(H_2O)_6]^{3+}$  is colourless.

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

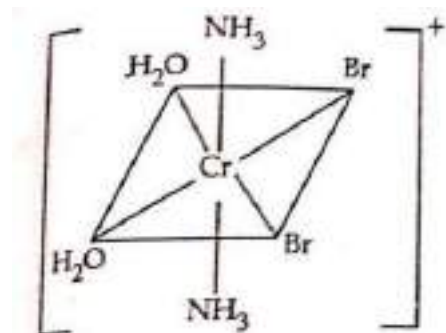
Example for the complex of the type  $[Ma_2b_2c_2]$  is  $[Cr(NH_3)_2(H_2O)_2Br_2]^+$



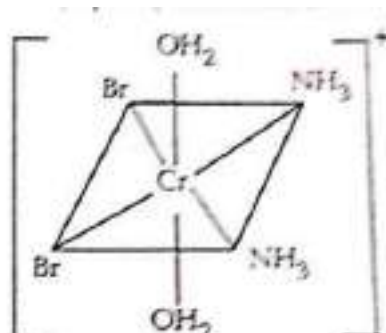
Cis – dibromodiaqua diammine chromium (III) ion (Geometrical isomer)



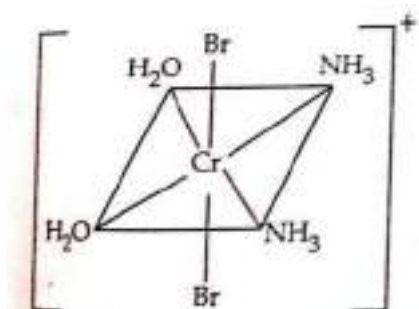
trans – dibromodiaquadiammine chromium (III) ion (Geometrical isomer)



Cis-dibromo diaqua – trans diammine bromium (III) ion (Geometrical isomer)

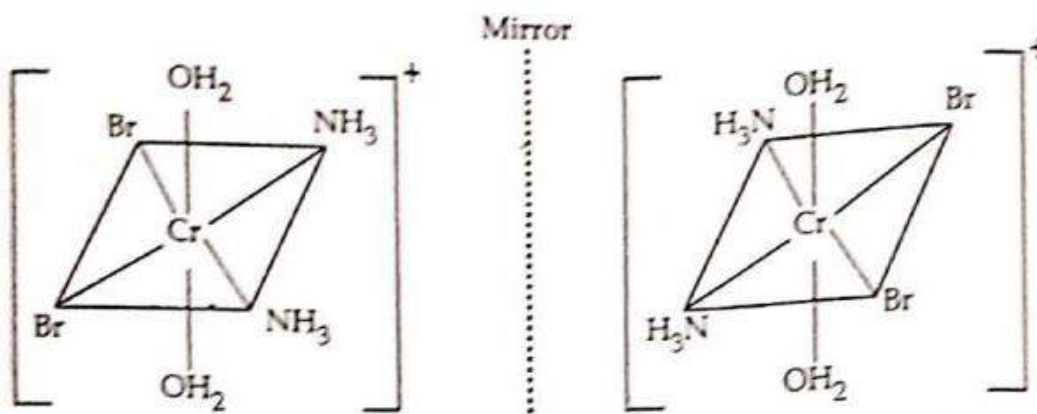


Cis – dibromodiammine trans-diaqua chromium (III) ion (Geometrical isomer)



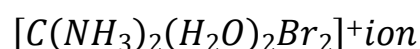
Optical Isomer - 1 (d, l - form)

Cis - diammine diaqua - trans dibromo chromium (III) ion (Geometrical isomer)



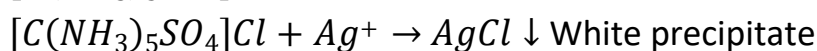
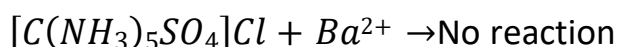
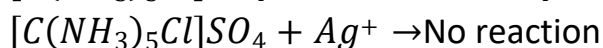
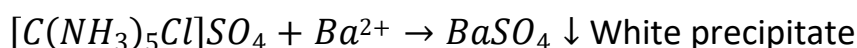
d-Cis isomer of  $[Cr(NH_3)_2(H_2O)_2Br_2]^+$  ion

d-Cis isomer of



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

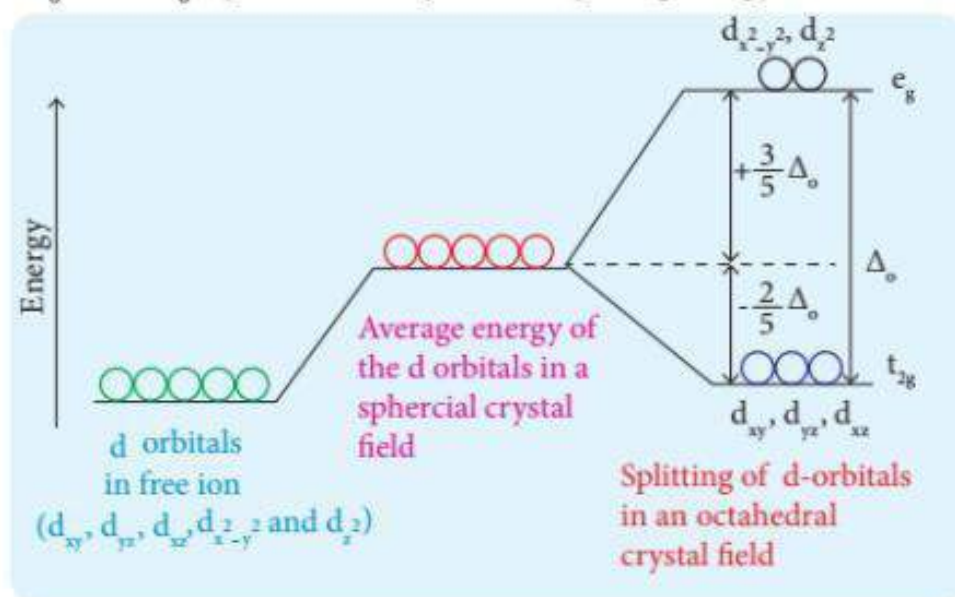
When ionization isomers are dissolved in water, they ionize to give different ions. These ions then react differently with different reagents to give different products.



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

**Crystal field splitting in octahedral complexes:**

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

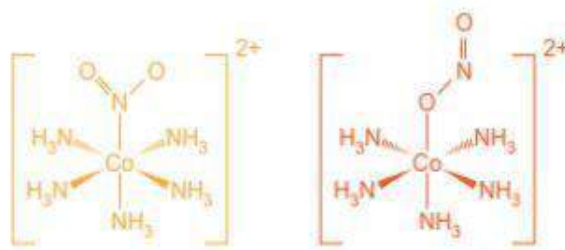
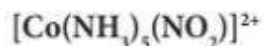




## 11. What is linkage isomerism? Explain with an example.

### Linkage isomers:

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



## 12. Classify the following ligand based on the number of donor atoms. a) $\text{NH}_3$ b) en c) $\text{OX}^{2-}$ d) triaminotriethylamine e) pyridine

a)  $\text{NH}_3$  ---- Mono dentate

b) en ---- Bi dentate

c)  $\text{ox}^{2-}$  ---- Bidentate

d) triaminotriethylamine --- Polydentate

e) pyridine ---- Mono dentate

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

S.No	Double Salts	Coordination compounds
1.	Lose their identity	Do not lose their identity
2.	Dissociate into their constituent simple ions in solutions	Never dissociate to give simple ions.
3.	(eg) Mohr's salt $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	$\text{K}_3[\text{Fe}(\text{SCN})_6]$
4.	Answer the tests for simple ions $\text{Fe}^{2+}$ , $\text{NH}_4^+$ , $\text{SO}_4^{2-}$ ions.	Does not answer for simple ions $\text{Fe}^{3+}$ , $\text{SCN}^-$ ions

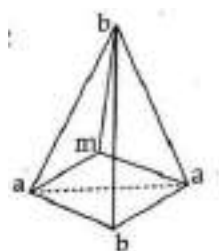
## 14. Write the postulates of Werner's theory.

In a complex every metal atom possesses two types of valency. (i) Primary Valency  
(ii) Secondary valency

S.No	Primary valency	Secondary valency
1.	Refers to the Oxidation State of metal ion	Refers to Coordination number of metal ion
2.	Always satisfied by negative ions	Satisfied by negative ions, neutral molecules or positive ions.
3.	These ions generally written outside the bracket are called counter ions	These ions written inside the bracket are called ligands
4.	The outer sphere in which these ions present are called ionisation sphere	The inner sphere in which these ions present are called coordination sphere
5.	The groups present in this sphere are loosely bound to the central metal ion and can be separated into ions	The groups present in this sphere are firmly attached to the central metal atom and cannot be separated into ions
6.	This Valency is ionisable	This valency is non-ionisable
7.	This valency is non directional	This valency is directional and determines the geometry of the complex.

### 15. Why tetrahedral complexes do not exhibit geometrical isomerism.

Cis-trans isomerism is not possible in tetrahedral complexes because all the four ligands are adjacent to one another  $Ma_2b_2$



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

- Coordination compounds which possess chirality exhibit optical isomerism similar to organic compounds.
- The pair of two optically active isomers which are mirror images of each other are called enantiomers.
- Their solutions rotate the plane of the plane polarised light.
- If the rotation is in the clockwise direction the isomer is called dextro rotatory 'd' form.

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

- The exchange of free solvent molecules such as water, ammonia, alcohol etc, in the crystal lattice with a ligand in the coordination entity will give Solvate isomers.
- If the solvent molecule is water, then these isomers are called hydrate isomers.
- Example:  $CrCl_3 \cdot 6H_2O$  has three hydrate isomers.

Complex	Colour	Number of Chloride ions in solutions
$[Cr(H_2O)_6]Cl_3$	Violet	3
$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$	Pale green	2
$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$	Dark green	1

### 18. What is crystal field splitting energy?

The splitting of five degenerate d orbitals of the metal ion into two sets of orbitals having different energies is called crystal field splitting. The separation in energy is called the crystal field splitting energy  $\Delta$ .

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

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

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

Where

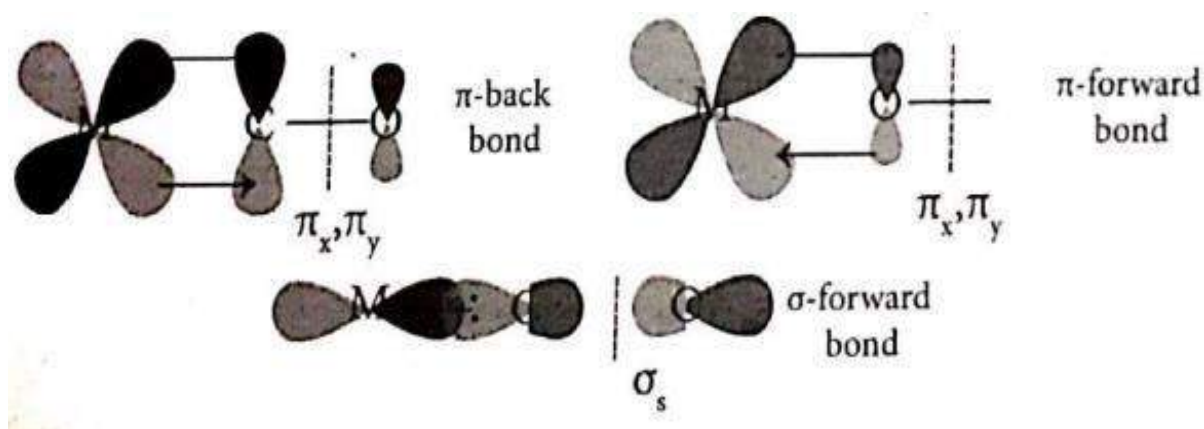
$n_{t_{2g}}$  = No. of electrons in  $t_{2g}$  orbitals

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

- In  $[Ni(H_2O)_6]^{2+}$ , the  $Ni^{2+}$  ion has two unpaired electrons which do not pair up in presence of weak ligand  $H_2O$ .
- Hence d-d-transition is possible.
- Red colour is absorbed and complementary colour green is emitted. So it is green in colour.
- In  $[Ni(CN)_4]^{2-}$ , the  $Ni^{2+}$  ion has no unpaired electrons because the strong ligand  $CN^-$  pairs up the electrons.
- Hence no d-d transition is possible.
- So  $[Ni(CN)_4]^{2-}$  is colourless.

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

- In metal carbonyls, the bond between metal atom and the carbonyl ligand consists of two components.
- The first component is an electron pair donation from the carbon atom of carbonyl ligand into a vacant d-orbital of central metal atom.
- This electron pair donation forms  $M \leftarrow CO$  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  $\pi^*$  orbital on the carbonyl ligand and transfers the added electron density back to the ligand.
- This second component is called  $\pi$  –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  $M \leftarrow CO$  bond in metal carbonyls.
- This is shown diagrammatically as follows.



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

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



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

<b>Complex</b>	$[Co(C_2O_4)_3]^{3-}$																														
Central metal atom / ion & its outer electronic configuration	$Co^{3+}; 3d^6, 4s^0$																														
Outer orbitals of metal atom/ion	<table style="display: inline-table; border-collapse: collapse;"> <tr> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> </tr> <tr> <td colspan="5" style="text-align: center; border: none;"><math>3d^6</math></td> </tr> </table> <table style="display: inline-table; border-collapse: collapse; margin-left: 10px;"> <tr> <td style="border: 1px solid black; padding: 2px;"> </td> </tr> <tr> <td style="text-align: center; border: none;"><math>4s</math></td> </tr> </table> <table style="display: inline-table; border-collapse: collapse; margin-left: 10px;"> <tr> <td style="border: 1px solid black; padding: 2px;"> </td> <td style="border: 1px solid black; padding: 2px;"> </td> <td style="border: 1px solid black; padding: 2px;"> </td> </tr> <tr> <td colspan="3" style="text-align: center; border: none;"><math>4p</math></td> </tr> </table>	↑↓	↑	↑	↑	↑	$3d^6$						$4s$				$4p$														
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Hybridisation	Coordination number 6; Hybridisation $sp^3d^2$																														
Hybridised orbitals of the metal atom in the complex	<table style="display: inline-table; border-collapse: collapse;"> <tr> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> </tr> <tr> <td colspan="5" style="text-align: center; border: none;"><math>3d^6</math></td> </tr> </table> <table style="display: inline-table; border-collapse: collapse; margin-left: 10px;"> <tr> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑↓</td> </tr> <tr> <td colspan="6" style="text-align: center; border: none;"><math>sp^3d^2</math> Hybridised orbitals</td> </tr> </table> <table style="display: inline-table; border-collapse: collapse; margin-left: 10px;"> <tr> <td style="border: 1px solid black; padding: 2px;"> </td> <td style="border: 1px solid black; padding: 2px;"> </td> <td style="border: 1px solid black; padding: 2px;"> </td> </tr> <tr> <td colspan="3" style="text-align: center; border: none;"><math>4d^0</math></td> </tr> </table>	↑↓	↑	↑	↑	↑	$3d^6$					↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	$sp^3d^2$ Hybridised orbitals									$4d^0$				
↑↓	↑	↑	↑	↑																											
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$sp^3d^2$ Hybridised orbitals																															
$4d^0$																															
Geometry	Octahedral. Outer d-orbitals are involved, hence it is outer orbital complex																														
Magnetic property	No. of unpaired electrons $n=4$ ; Paramagnetic																														
Magnetic moment (spin only)	$\mu_s = \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.899 B.M$																														

**24. What are the limitations of VB theory?**

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

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

- Oxidation state of central metal ion is  $+2(II)$
- Coordination number is 6.
- Nature of ligand  $CN^-$  is strong field ligand.
- The number of unpaired electron is one, hence paramagnetic.

## UNIT – 6 SOLID STATE

Answer the following:

### 1. Define unit cell.

- ✓ A basic repeating structural unit of a crystalline solid in a three dimensional pattern is called 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  $\alpha$ ,  $\beta$  and  $\gamma$

### 2. Give any three characteristics of ionic crystals

- 1) Ionic solids have high melting points.
- 2) These solids do not conduct electricity, because the ions are fixed in their lattice positions.
- 3) They do conduct electricity in molten state (or) when dissolved in water because, the ions are free to move in the molten state or solution.
- 4) They are hard as only strong external force can change the relative positions of ions.

### 3. Differentiate crystalline solids and amorphous solids

Crystalline Solids	Amorphous solids
Long range orderly arrangement of constituents.	Short range, random arrangement of constituents.
Definite shape	Irregular shape
Anisotropic in nature	Isotropic in nature
They are true solids	They are considered as pseudo solids (or) super cooled liquids
Definite Heat of fusion	Heat of fusion is not definite
They have sharp melting points.	Gradually soften over a range of temperature and so can be moulded
<b>Examples:</b> NaCl, diamond,	<b>Examples:</b> Plastics, glass

### 4. Classify the following solids

(a)  $P_4$  (b) Brass (c) Diamond (d) NaCl (e) Iodine

(a)  $P_4$  - Molecular solid

(b) Brass - Metallic solid

(c) Diamond - Covalent solid

(d) NaCl - Ionic solid

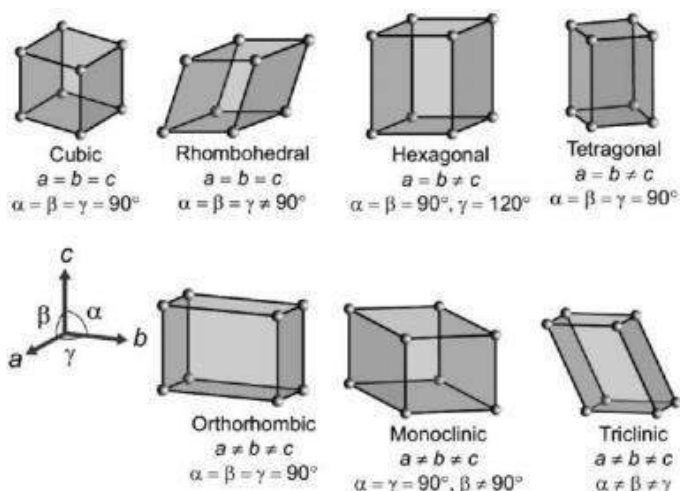
(e) Iodine - Molecular solid

### 5. Explain seven types of unit cell.

There are seven primitive crystal systems

- 1) Cubic - NaCl
- 2) Tetragonal -  $TiO_2$
- 3) Orthorhombic -  $BaSO_4$
- 4) Hexagonal - ZnO
- 5) Monoclinic -  $PbCrO_4$
- 6) Triclinic -  $H_3BO_3$
- 7) Rhombohedral - HgS

They differ in the arrangement of their crystallographic axes and angles





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

Hexagonal Close packing	Cubic Close packing
'ABA' arrangement	'ABC' arrangement
The spheres of the third layer is exactly aligned as first layer	The spheres of the third layer is not aligned with those of either the first or second layer.
The hexagonal close packing is based on hexagonal unit cells with sides of equal length	The cubic close packing is based on the face centered cubic unit cell.
Tetrahedral voids of the second layer are covered by the sphere of the third layer	Octahedral voids of the second layer are covered by the sphere of the third layer
The unit cell of hexagonal close packing has 6 spheres.	The unit cell of cubic close packing has 4 spheres
This type is found in metals like <b>Mg, Zn.</b>	This type is found in metals like <b>Cu, Ag.</b>

### 7. Distinguish tetrahedral and octahedral voids.

Tetrahedral Void	Octahedral Void
When a sphere of second layer (b) is above the void (x) of the first layer (a), tetrahedral void is formed.	When the voids (y) in the first layer (a) are partially covered by the spheres of layer (b), octahedral void (a)

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
This constitutes four spheres, three on the lower (a) and one in the upper layer (b).	This constitutes six spheres the lower layer (a) and three in the upper layer (b)
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.
The coordination number is <b>4.</b>	The coordination number is <b>6.</b>

## 8. What are point defects?

- ✓ If the deviation in the perfect crystal occurs due to missing atoms, displaced atoms or extra atoms the imperfection is called as point defect.
- ✓ It occurs due to imperfect packing during the original crystallisation or they may arise from thermal vibrations of atoms at elevated temperature.

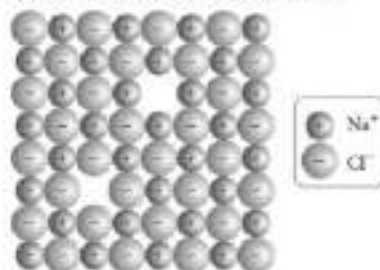
**Types :** Stoichiometric, Non stoichiometric, Impurity defect

## 9. Explain Schottky defect

- ✓ Schottky defect arises due to the missing of equal number of cations and anions from the crystal lattice.
- ✓ This effect **does not change the stoichiometry** of the crystal.
- ✓ Ionic solids in which the **cation and anion are of almost of similar size** show schottky defect.

**Example:** NaCl.

- ✓ Presence of large number of schottky defects in a crystal, **lowers its density**.
- ✓ Example: vanadium monoxide (VO). Theoretical density is  $6.5 \text{ g cm}^{-3}$ , but the actual Experimental density is  $5.6 \text{ g cm}^{-3}$ .
- ✓ Approximately **14% Schottky defect** in VO crystal.

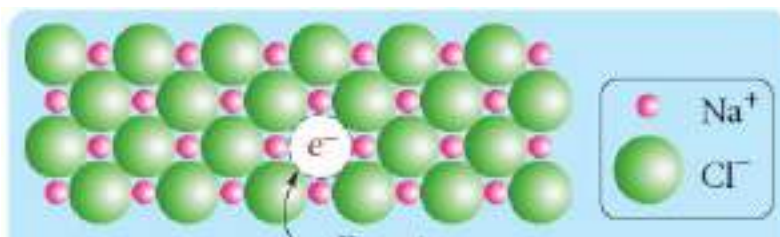


## 10. Write short note on metal excess and metal deficiency defect with an example

### Metal excess defect

- ✓ It arises due to the **presence of more number of metal ions** as compared to anions.
- ✓ Alkali metal halides **NaCl, KCl** show this type of defect.
- ✓ The electrical neutrality of the crystal can be maintained by the presence of anionic vacancies equal to the excess metal ions (or) by the presence of extra cation and electron present in interstitial position.

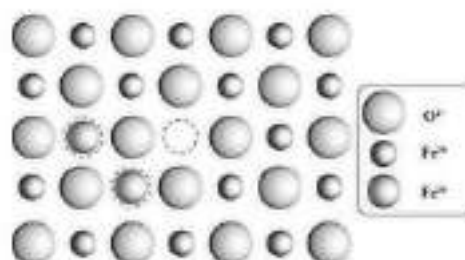
**Example :** ZnO is colourless at room temperature. When it is heated, it becomes yellow in colour. On heating, it loses oxygen and thereby forming free  $\text{Zn}^{2+}$  ions. The excess  $\text{Zn}^{2+}$  ions move to interstitial sites and the electrons also occupy the interstitial positions.



### Metal deficiency defect

- ✓ It arises due to the presence of less number of cations than the anions.
- ✓ This defect is observed in a crystal in which, the cations have variable oxidation states.

**Example :** In FeO crystal, some of the  $\text{Fe}^{2+}$  ions are missing from the crystal lattice. To maintain the electrical neutrality, twice the number of other  $\text{Fe}^{2+}$  ions in the crystal is oxidized to  $\text{Fe}^{3+}$  ions. In such cases, overall number of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions is less than the  $\text{O}^{2-}$  ions.





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

In a face centered cubic unit cell, identical atoms lie at each corner as well as in the centre of each face.

$$N_c = 8 \text{ (Number of atoms in corners)} \quad N_f = 6 \text{ (Number of atoms in face)}$$

$$\begin{aligned} \text{Number of unit cell in fcc} &= \frac{N_c}{8} + \frac{N_f}{2} \\ &= \frac{8}{8} + \frac{6}{2} \\ &= 1 + 3 = 4 \end{aligned}$$

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

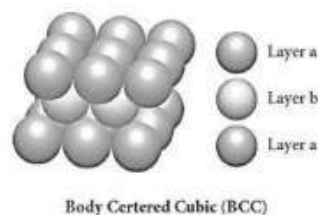
#### (i) AAAA type

- ✓ It 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, so that any unit cell of such arrangement as simple cubic structure .
- ✓ 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 of the sphere in simple cubic arrangement is 6.



#### ii) ABAB.. Type

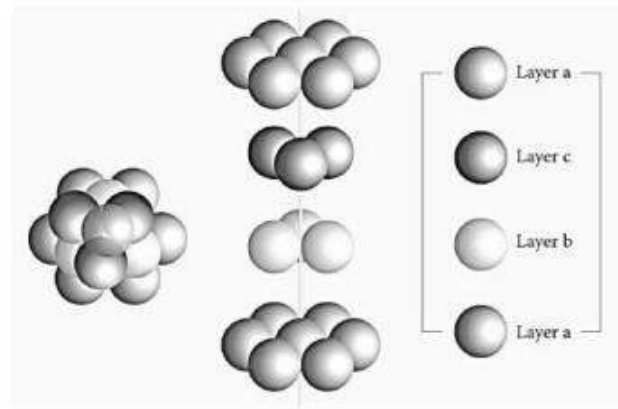
- ✓ In this arrangement, the spheres in the first layer ( A type ) are slightly separated and the second layer is formed by arranging the spheres in the depressions between the spheres in layer A .
- ✓ The third layer is a repeat of the first.
- ✓ This pattern ABABAB is repeated throughout the crystal.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



#### iii) ABCABC type arrangement

- ✓ In this arrangement, the first layer is formed by arranging the spheres as in the case of two dimensional ABAB arrangements.
- ✓ The spheres of second row fit into the depression of first row. This is layer 'a'.
- ✓ The second layer is formed by placing the spheres in the depressions of the first layer. This is layer 'b'.
- ✓ There are two types of voids x and y.
- ✓ Wherever a sphere of second layer (b) is above the void (x) of the first layer (a), a tetrahedral void is formed. This constitutes four spheres – three in the lower (a) and one in the upper layer (b). When the centers of these four spheres are joined, a tetrahedron is formed.

- ✓ At the same time, the voids (y) in the first layer (a) are partially covered by the spheres of layer (b), now such a void in (a) is called an octahedral void.
- ✓ The third layer may be placed over the second layer in such a way that all the spheres of the third layer fit in octahedral voids. This arrangement of the third layer is different from other two layers (a) and (b), and hence, the third layer is designated (c). If the stacking of layers is continued in abcabcabc... pattern, then the arrangement is called cubic close packed (ccp) structure.



- ✓ In ccp arrangements, the coordination number of each sphere is 12 – six neighbouring spheres in its own layer, three spheres in the layer above and three spheres in the layer below.

### 13. Why ionic crystals are hard and brittle?

- ✓ Only strong forces can change the relative position of its constituent ions, so they are hard
- ✓ In ionic compounds the ions are rigidly held in a lattice because the positive and negative ions are strongly attracted to each other and difficult to separate.
- ✓ But the brittleness of a compound is how easy it is to shift the position of atoms or ions in a lattice

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

The spheres are touching along the leading diagonal of the cube

In  $\triangle ABC$

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

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

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

In  $\triangle ABC$

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

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

$$AC = \sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3a^2} = \sqrt{3}a$$

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

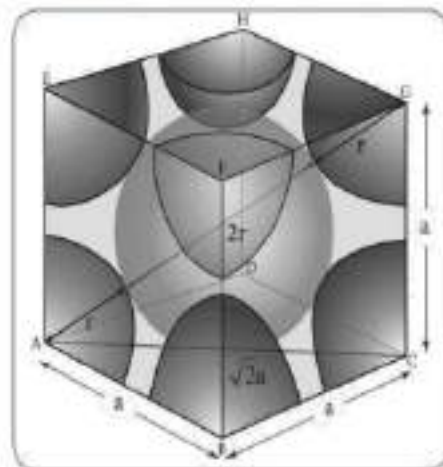
$$\text{Volume of the sphere with radius 'r'} = \frac{4}{3} \pi r^3$$

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

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

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

$$= 2 \times \frac{\sqrt{3}}{16} \pi a^3 = \frac{\sqrt{3} \pi a^3}{8}$$





$$\begin{aligned} \text{Packing fraction} &= \frac{\text{Total volume occupied by sphere in a unit cell}}{\text{volume of unit cell}} \times 100 \\ &= \frac{\left(\frac{\sqrt{3}\pi a^3}{8}\right)}{(a)^3} \times 100 \\ &= \sqrt{3} \times 3.14 \times 12.5 = 1.732 \times 3.14 \times 12.5 = 68\% \end{aligned}$$

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

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

The two dimensional coordination number of a molecule in square close packed layer is 4

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

- ✓ The number of nearest neighbour that surrounding a particle in a crystal is called coordination number.
- ✓ The coordination number of atoms in a bcc structure is 8.

**17. An element has bcc structure with a cell edge of 288 pm, the density of the element is 7.2 gcm<sup>-3</sup>. How many atoms are present in 208g of the element?**

**Given :** a = 288 pm    ρ = 7.2 gcm<sup>-3</sup>

$$\begin{aligned} \text{Volume of the unit cell} &= a^3 = (288 \text{ pm})^3 \\ &= (288 \times 10^{-10} \text{ cm})^3 \\ &= 2.39 \times 10^{-23} \text{ cm}^3 \end{aligned}$$

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

$$7.2 \text{ gcm}^{-3} = \frac{2M}{(2.39 \times 10^{-23} \text{ cm}^3) \times (6.023 \times 10^{23} \text{ mol}^{-1})}$$

$$M = \frac{7.2 \text{ g} \times 14.33 \text{ cm}^3 \text{ mol}^{-1}}{2} = 51.42 \text{ gmol}^{-1}$$

51.42 g of the element contains 6.023 × 10<sup>23</sup> atom

$$\begin{aligned} 208 \text{ g of the element will contain} &= \frac{6.023 \times 10^{23} \times 208}{51.42} \text{ atoms} \\ &= 24.17 \times 10^{23} \text{ atoms} \end{aligned}$$

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

let 'a' is the edge of the cube and 'r' is the radius of atom.

**Given :** r = 125 pm

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

Sub the value of 'r' we get,

$$\begin{aligned} a &= 2 \times 1.414 \times 125 \text{ pm} \\ &= 354 \text{ pm (approximately)} \end{aligned}$$

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

**Given :** Concentration of  $\text{SrCl}_2 = 10^{-2}$  mole%

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

Number of moles of NaCl = 100 – moles of  $\text{SrCl}_2$

Moles of  $\text{SrCl}_2$  is very negligible as compare to total moles.

Number of moles of NaCl = 100

$$\begin{aligned} \text{1 mole of NaCl is dopped with } \text{SrCl}_2 &= \frac{10^{-2}}{100} \text{ moles} \\ &= 10^{-4} \text{ mole of SrCl}_2 \end{aligned}$$

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

$$1 \text{ mole} = 6.023 \times 10^{23} \text{ particles}$$

$$\begin{aligned} \text{So, cation vacancies per mole of NaCl} &= 10^{-4} \times 6.023 \times 10^{23} \\ &= 6.023 \times 10^{19} \text{ vacancies} \end{aligned}$$

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

**Given :**  $\rho = 2.48 \text{ g cm}^{-3}$

Since it is face centered number of unit cell = 4 , Molar mass of KF =  $58.8 \text{ g mol}^{-1}$

$$\begin{aligned} a^3 &= \frac{nM}{\rho N_A} \\ &= \frac{4 \times 58.8}{2.48 \times 6.023 \times 10^{23}} \\ a^3 &= 1.57 \times 10^{-22} \text{ cm}^3 \end{aligned}$$

$$V = (\text{Edge length})^3 = a^3$$

$$\text{Edge length} = \sqrt[3]{V} = \sqrt[3]{1.57 \times 10^{-22}} = 538 \text{ pm}$$

$$d = \frac{a}{\sqrt{2}}$$

$$d = \frac{538}{1.414}$$

$$d = 380.12 \text{ pm}$$

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

**Given :**  $\rho = 10 \text{ g cm}^{-3}$      $a = 100 \text{ pm}$     Mass = 1 g

No of atoms in fcc unit cell = 4

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

$$\text{Number of atoms in 1g of crystal} = \frac{Z \times M}{\rho a^3} = \frac{4 \times 1}{10^{-24}} = 4 \times 10^{23} \text{ atoms}$$

22. Atoms X and Y form bcc crystalline structure. Atom X is present at the corners of the cube and Y

is at the center of the cube. What is the formula of the compound?

The atom at the corner makes a contribution of  $\frac{1}{8}$  to the unit cell (X)

The atom at the center makes a contribution of 1 to the unit cell (Y)

$$\begin{aligned} \text{Thus, number of atoms X per unit cell} &= \text{Number of atoms} \times \text{Contribution per unit cell} \\ &= 8 \text{ (at the corners)} \times \frac{1}{8} \text{ atoms per unit cell} \\ &= 1 \end{aligned}$$

$$\begin{aligned} \text{Thus, number of atoms Y per unit cell} &= \text{Number of atoms} \times \text{contribution per unit cell} \\ &= 1 \text{ (at the body centre)} \times 1 \\ &= 1 \end{aligned}$$

Thus, the formula of the given compound is XY.

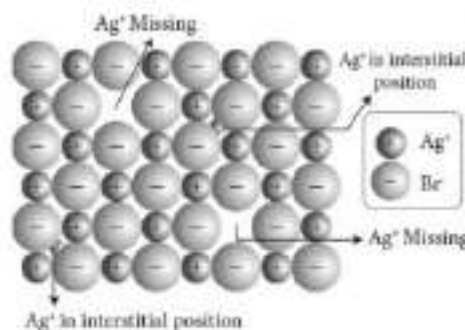
23. Sodium metal crystallizes in bcc structure with the edge length of the unit cell  $4.3 \times 10^{-8}$  cm. calculate the radius of sodium atom.

Given :  $a = 4.3 \times 10^{-8}$  cm.

$$\begin{aligned} \text{For bcc } r &= \frac{\sqrt{3}}{4} a \\ &= \frac{\sqrt{3}}{4} \times 4.3 \times 10^{-8} \text{ cm.} \\ &= 1.786 \times 10^{-8} \text{ cm} \end{aligned}$$

24. Write a note on Frenkel defect.

- ✓ Frenkel defect arises due to the dislocation of ions from its crystal lattice.
- ✓ The ion which is missing from the lattice point occupies an interstitial position. This defect is shown by ionic solids in which cation and anion differ in size.
- ✓ Unlike Schottky defect, this defect does not affect the density of the crystal.
- ✓ For example AgBr, in this case, small  $\text{Ag}^+$  ion leaves its normal site and occupies an interstitial position as shown in the figure.





## UNIT – 7 CHEMICAL KINETICS

### 1. Define average rate and instantaneous rate.

#### Average rate

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

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

It may be defined as the change in concentration of a reactant or product of a chemical reaction at a given instant.

$$\text{Instantaneous reaction rate} = \frac{d[I_2]}{dt}$$

Where  $d[I_2]$  = small change in concentration of iodine  
and  $dt$  = small change in time

### 2. Define rate law and rate constant.

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



The rate expression for this reaction is

$$\text{Rate} \propto [\text{A}]^x [\text{B}]^y$$

Rate =  $k [\text{A}]^x [\text{B}]^y$  (where  $k$  is a proportionality constant called rate constant)

### 3. Derive integrated rate law for a zero order reaction $\text{A} \rightarrow \text{product}$

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



The rate law can be written as,

$$\begin{aligned} \text{Rate} &= k[\text{A}]^0 \\ -\frac{d[\text{A}]}{dt} &= k(1) \quad (\because [\text{A}]^0 = 1) \\ -d[\text{A}] &= k dt \end{aligned}$$

Integrate the above equation between the limits of  $[\text{A}_0]$  at zero time and  $[\text{A}]$  at some later time 't',

$$\int_{[\text{A}_0]}^{[\text{A}]} d[\text{A}] = k \int_0^t dt$$

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

$$[\text{A}_0] - [\text{A}] = kt$$

$$k = \frac{[A_0] - [A]}{t}$$

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

$$\text{ie., } [A] = -kt + [A_0]$$

$$y = c + mx$$

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

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

The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value. For a first order reaction, the half life is a constant i.e., it does not depend on the initial concentration.

The rate constant for a first order reaction is given by

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

$$\text{at } t = t_{1/2} ; [A] = \frac{[A_0]}{2}$$

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

$$k = \frac{2.303}{t_{1/2}} \log 2$$

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

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

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

**Elementary reaction:**

Each and every single step in a reaction mechanism is called an elementary reaction.

Differences between order and molecularity:

S.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) fractional (or) integer	It is always a whole number, cannot be zero or a fractional number.
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.**

When a reaction occurs in a sequence of elementary steps, the overall reaction rate is governed by whichever one of those steps is the slowest. The **rate-determining step** is the slowest step in the sequence of steps in a reaction mechanism.

The decomposition of hydrogen peroxide catalysed by  $I^-$ :



It is experimentally found that the reaction is first order with respect to both  $H_2O_2$  and  $I^-$ , which indicates that  $I^-$  is also involved in the reaction. The mechanism involves the following steps.

**Step:1**



**Step : 2**



Overall reaction is



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



7. Describe the graphical representation of first order reaction.

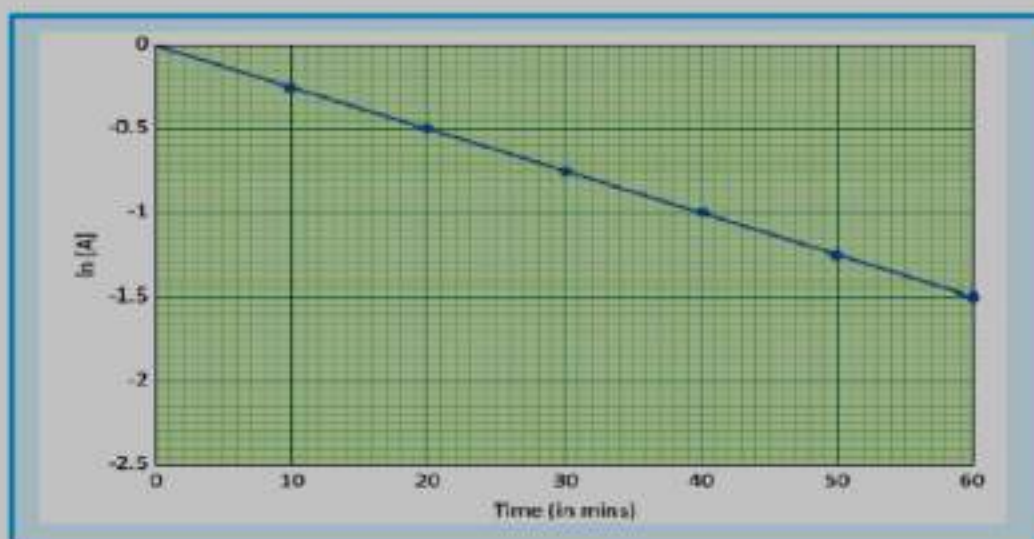


Fig: 7.3 A plot of  $\ln[A]$  Vs  $t$  for a first order reaction,  $A \longrightarrow \text{product}$  with initial concentration of  $[A] = 1.00 \text{ M}$  and  $k = 2.5 \times 10^{-2} \text{ min}^{-1}$ .

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

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

Equation (2) can be written in the form  $y = mx + c$  as below

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

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

$$\Rightarrow y = c + mx$$

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

8. Write the rate law for the following reactions.

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

$$\text{Rate} = k [A]^{3/2} [B]^0$$

(b) A reaction that is second order in  $\text{NO}$  and first order in  $\text{Br}_2$ .

The reaction



$$\text{Rate} = k [\text{NO}]^2 [\text{Br}_2]$$

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

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

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

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

(i) Concentration of [L] is quadrupled

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

$$[L] = [4L]$$

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

$$\text{Rate} = k [A]^2 [B] 4^{3/2} [L]^{3/2} \quad \{4^{(3/2)}\} = (4 \times 4 \times 4)^{1/2} = (64)^{1/2} = 8$$

$$\text{Rate} = k8 [A]^2 [B] [L]^{3/2}$$

Rate is increased by 8 times

(ii) Concentration of both [A] and [B] are doubled. The rate law for a reaction of A,

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

$$[A] = [2A], [B] = [2B]$$

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

$$\text{Rate} = k4 [A]^2 2 [B][L]^{3/2}$$

$$\text{Rate} = 8k [A]^2 [B] [L]^{3/2} \quad \text{Rate is increased by 8 times}$$

(iii) Concentration of [A] is halved

$$[A] = [A/2]$$

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

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

Rate is decreased by  $\frac{1}{4}$  times

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

$$[A] = [A/3], [L] = [4L]$$

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

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

$$\text{Rate} = (1/9)k [A]^2 [B] 4^{3/2} [L]^{3/2} \quad \{4^{(3/2)}\} = (4 \times 4 \times 4)^{1/2} = (64)^{1/2} = 8$$

$$\text{Rate} = (8/9)k [A]^2 [B] [L]^{3/2} \quad \text{Rate is decreased by } 8/9 \text{ times}$$

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

For a second order reaction

$$\text{Rate} = k[A]^2$$

$$K = \text{Rate}/[A]^2 ; \quad (7.5 \times 10^{-3} / (0.05)^2) (\text{mol L}^{-1} \text{ S}^{-1}) / (\text{mol L}^{-1})^2$$

$$\text{Rate constant } k = (7.5 \times 10^{-3}) / (5 \times 10^{-2})^2$$

$$= 3 \text{ mol}^{-1} \text{ L}^1 \text{ S}^{-1}$$

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

$$\text{Rate } k = [x]^{3/2}[y]^{1/2}$$

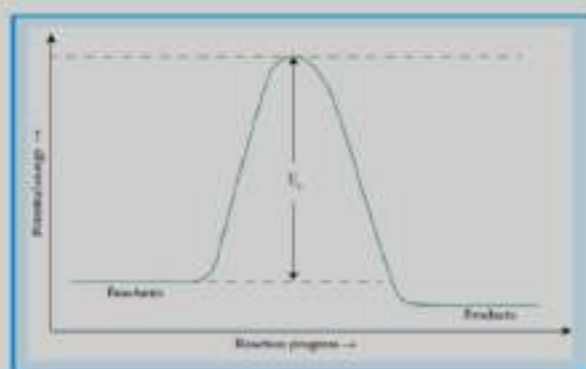
$$\text{Order} = (3/2) + (1/2)$$

Overall order = 2. The reaction with respect to z is Zero order

13. Explain briefly the collision theory of bimolecular reactions.

### Collision theory :

Collision Theory chemical reactions occur as a result of collisions between the reacting molecules. Let us understand this theory by considering the following reaction.



If we consider that, the reaction between  $A_2$  and  $B_2$  molecules proceeds through collisions between them, then the rate would be proportional to the number of collisions per second.

Rate  $\propto$  number of molecules colliding per litre per second (collision rate)

The number of collisions is directly proportional to the concentration of both  $A_2$  and  $B_2$ .

$$\text{Collision rate} \propto [A]^2[B]^2$$

Collision rate =  $Z[A]^2[B]^2$  Where, Z is a constant.

The collision rate in gases can be calculated from kinetic theory of gases. For a gas at room temperature (298K) and 1 atm pressure, each molecule undergoes approximately  $10^9$  collisions per second, i.e., 1 collision in  $10^{-9}$  second. Thus, if every collision resulted in reaction, the reaction would be complete in  $10^{-9}$  second. In actual practice this does not happen. It implies that all collisions are not effective to lead to the reaction.

In order to react, the colliding molecules must possess a minimum energy called activation energy. The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.

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

$$F = e^{-E_a/RT}$$

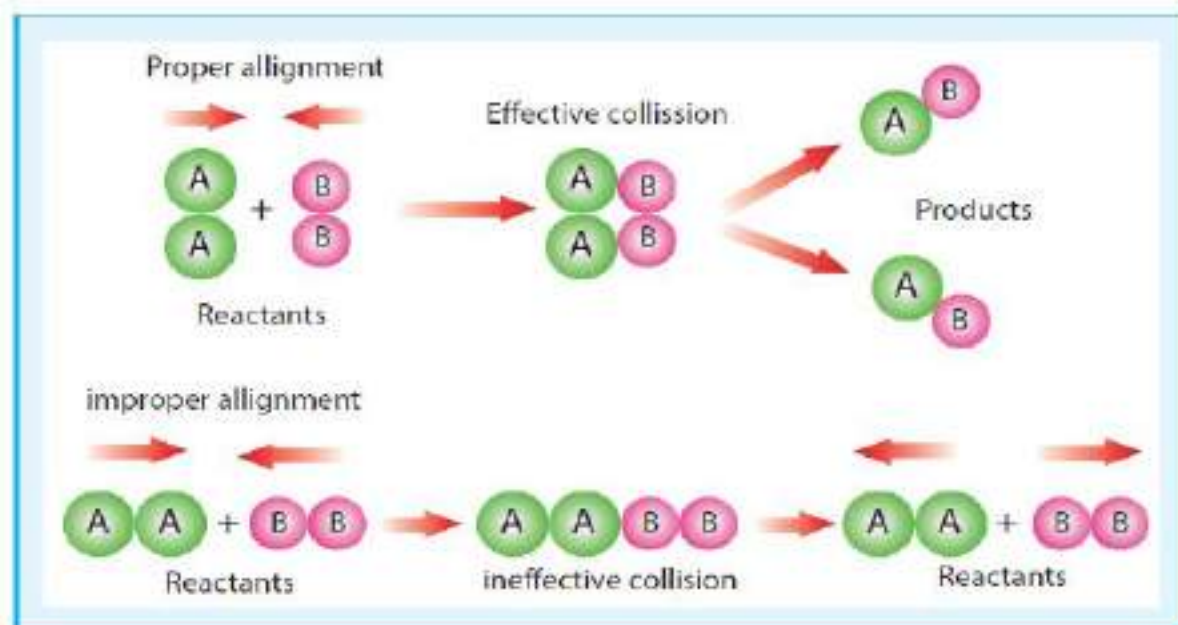
To understand the magnitude of collision factor (f), Let us calculate the collision factor (f) for a reaction having activation energy of  $100 \text{ kJ mol}^{-1}$  at 300K.



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

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

Thus, out of  $10^{18}$  collisions only four collisions are sufficiently energetic to convert reactants to products. This fraction of collisions is further reduced due to orientation factor i.e., even if the reactant collide with sufficient energy, they will not react unless the orientation of the reactant molecules is suitable for the formation of the transition state.



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

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

$$\Rightarrow \text{Rate} = p \times f \times \text{collision rate}$$

$$\text{i.e., Rate} = p \times e^{-E_a/RT} \times Z [A_2] [B_2] \dots (1)$$

As per the rate law,

$$\text{Rate} = k [A_2] [B_2] \dots (2)$$

Where  $k$  is the rate constant

On comparing equation (1) and (2), the rate constant  $k$  is \*

$$k = p Z e^{E_a/RT}$$

#### 14. Write Arrhenius equation and explains the terms involved.

$$k = A e^{-E_a/RT}$$

Where  $A$  the frequency factor,

$R$  the gas constant,  $E_a$  the activation energy of the reaction and,

$T$  the absolute temperature (in K)

15. The decomposition of  $\text{Cl}_2\text{O}_7$  at 500K in the gas phase to  $\text{Cl}_2$  and  $\text{O}_2$  is a first order reaction. After 1 minute at 500K, the pressure of  $\text{Cl}_2\text{O}_7$  falls from 0.08 to 0.04 atm. Calculate the rate constant in  $\text{s}^{-1}$

$$K = 2.303/t \log[A_0]/[A]$$

$$K = 2.303/ 60 \text{ sec} \log[0.08]/[0.04]$$

$$K = 2.303/ 60 \text{ sec} \log 2$$

$$= \frac{(2.303 \times 0.3030)}{60} = 1.153 \times 10^{-2} \text{ S}^{-1}$$

17. Explain pseudo first order reaction with an example.

**Pseudo first order reaction:**

Kinetic study of a higher order reaction is difficult to follow, for example, in a study of a second order reaction involving two different reactants; the simultaneous measurement of change in the concentration of both the reactants is very difficult. To overcome such difficulties, A second order reaction can be altered to a first order reaction by taking one of the reactant in large excess, such reaction is called pseudo first order reaction. Let us consider the acid hydrolysis of an ester,



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

Now, we can define  $k [\text{H}_2\text{O}] = k'$ ; Therefore the above rate equation becomes

$$\text{Rate} = k' [\text{CH}_3 \text{COOCH}_3]$$

Thus it follows first order kinetics.

18. Identify the order for the following reactions

(i) Rusting of Iron : Zero order Reaction

(ii) Radioactive disintegration of  ${}_{92}\text{U}^{238}$  : First order reaction

(iii)  $2\text{A} + 3\text{B} \longrightarrow \text{products}$ ; rate  $k = [\text{A}]^{1/2} [\text{B}]^2$  order =  $(\frac{1}{2} + 2) = 2.5$

19. A gas phase reaction has energy of activation  $200 \text{ kJ mol}^{-1}$ . If the frequency factor of the reaction is  $1.6 \times 10^{13} \text{ s}^{-1}$ . Calculate the rate constant at 600 K. ( $e^{-40.09} = 3.8 \times 10^{-18}$ ).

$$k = A e^{-E_a/RT} \quad A = 1.6 \times 10^{13} \text{ s}^{-1} \quad T = 600 \text{ K} \quad R = 8.314 \text{ JKmol}^{-1}$$

$$E_a = 200 \text{ kJ mol}^{-1} = 200 \times 10^3 \text{ J mol}^{-1} \quad e^{-40.09} = 3.8 \times 10^{-18}$$

$$K = A e^{-E_a/RT}$$

$$1.6 \times 10^{13} \times e^{-\left(\frac{200 \times 10^3}{8.314 \text{ JK}^{-1} \times 600}\right)}$$

$$= 1.6 \times 10^{13} \times 3.8 \times 10^{-18}$$

$$K = 6.08 \times 10^{-5}$$

20. For the reaction  $2x + y \longrightarrow L$  find the rate law from the following data.

[x] (min)	[y] (min)	rate (M s <sup>-1</sup> )
0.2	0.02	0.15
0.4	0.02	0.30
0.4	0.08	1.20

$$\text{Rate} = k [X]^n [Y]^m$$

$$0.15 = k [0.2]^n [0.02]^m \text{-----(1)}$$

$$0.30 = k [0.4]^n [0.02]^m \text{-----(2)}$$

$$1.20 = k [0.4]^n [0.08]^m \text{-----(3)}$$

$$(3)/(2)$$

$$\frac{1.2}{0.3} = \frac{k [0.4]^n [0.08]^m}{k [0.4]^n [0.02]^m}$$

$$4 = (4)^m$$

$$m=1$$

$$(2)/(1)$$

$$\frac{0.30}{0.15} = \frac{k [0.4]^n [0.02]^m}{k [0.2]^n [0.02]^m} = 2 = (2)^n$$

$$n=1$$

$$\text{Rate} = k [X]^n [Y]^m$$

$$= \frac{0.15}{[0.2]^1 [0.02]^1}$$

$$K = 37.5 \text{ mol}^{-1} \text{L s}^{-1}$$

21. How do concentrations of the reactant influence the rate of reaction?

**Concentration of the reactants:**

The rate of a reaction increases with the increase in the concentration of the reactants. The effect of concentration is explained on the basis of collision theory of reaction rates. According to this theory, the rate of a reaction depends upon the number of collisions between the reacting molecules. Higher the concentration, greater is the possibility for collision and hence the rate



## 22. How do nature of the reactant influence rate of reaction.

A chemical reaction involves breaking of certain existing bonds of the reactant and forming new bonds which lead to the product. The net energy involved in this process is dependent on the nature of the reactant and hence the rates are different for different reactants.

Let us compare the following two reactions that you carried out in volumetric analysis.

- 1). Redox reaction between ferrous ammonium sulphate (FAS) and  $\text{KMnO}_4$
- 2). Redox reaction between oxalic acid and  $\text{KMnO}_4$

The oxidation of oxalate ion by  $\text{KMnO}_4$  is relatively slow compared to the reaction between  $\text{KMnO}_4$  and  $\text{Fe}^{2+}$ . In fact heating is required for the reaction between  $\text{KMnO}_4$  and Oxalate ion and is carried out at around  $60^\circ\text{C}$ .

The physical state of the reactant also plays an important role to influence the rate of reactions. Gas phase reactions are faster as compared to the reactions involving solid or liquid reactants.

23. The rate constant for a first order reaction is  $1.54 \times 10^{-3} \text{ s}^{-1}$ . Calculate its half life time.

$$t_{1/2} = 0.6932 / 1.54 \times 10^{-3} \text{ s}^{-1}$$
$$= 450 \text{ seconds}$$

24. The half life of the homogeneous gaseous reaction  $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$  which obeys first order kinetics is 8.0 minutes. How long will it take for the concentration of  $\text{SO}_2\text{Cl}_2$  to be reduced to 1% of the initial value?

We know that,  $k = \frac{0.693}{t_{1/2}}$

$$k = \frac{0.693}{8.0} \text{ minutes} = 0.087 \text{ minutes}^{-1}$$

For a first order reaction,

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

$$t = \frac{2.303}{0.087 \text{ min}^{-1}} \log \left( \frac{100}{1} \right)$$

$$t = 52.93 \text{ min.}$$

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?

$$t_{1/2} = \frac{0.693}{K}$$

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{60} = 0.0115 \text{ s}^{-1}$$

$$K = 0.0115 \text{ s}^{-1}.$$

For time 3 mins (180 Sec)

$$K = \frac{2.303}{t} \log \frac{[a_0]}{[a]}$$

$$\therefore 0.0115 = \frac{2.303}{t} \log \frac{[a_0]}{[a]}$$

$$\log = \frac{[a_0]}{[a]} 0.014$$

$$\frac{[a_0]}{[a]} = \text{antilog}(0.014)$$

$$\frac{[a_0]}{[a]} = \text{antilog}(0.014)$$

$$\frac{[a_0]}{[a]} = 1.0327$$

% of the reactant left after 3 min

$$\frac{[a]}{[a_0]} \times 100 = \frac{1}{4} = 25\%$$

**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?**

Let  $A=100\text{ M}$ ,  $[A_0] - [A] = 20\text{ M}$ ,

For the zero order reaction

$$K = \left( \frac{[A_0] - [A]}{t} \right)$$

$$K = \left( \frac{20\text{ M}}{20\text{ min}} \right) = 1\text{ M min}^{-1}$$

Rate constant for a reaction =  $1\text{ M min}^{-1}$

To calculate the time for 80% of completion

$k = 1\text{ M min}^{-1}$ ,  $[A_0] = 100\text{ M}$ ,

$[A_0] - [A] = 80\text{ M}$ ,  $t = ?$

Therefore,

$$t = \left( \frac{[A_0] - [A]}{k} \right) = \left( \frac{80\text{ M}}{1\text{ M min}^{-1}} \right) = 80\text{ min}$$

**27. The activation energy of a reaction is  $22.5\text{ k Cal mol}^{-1}$  and the value of rate constant at  $40^\circ\text{C}$  is  $1.8 \times 10^{-5}\text{ s}^{-1}$ . Calculate the frequency factor, A.**

Here, we are given that

$$E_a = 22.5\text{ kcal mol}^{-1} = 22500\text{ cal mol}^{-1}$$

$$T = 40^\circ\text{C} = 40 + 273 = 313\text{ K}$$

$$k = 1.8 \times 10^{-5}\text{ sec}^{-1}$$

Substituting the values in the equation.

$$\log A = \log k + \left( \frac{E_a}{2.303RT} \right)$$

$$\log A = \log(1.8 \times 10^{-5}) + \left( \frac{22500}{2.303 \times 1.987 \times 313} \right)$$

$$\log A = \log(1.8)(-5) + (15.7089)$$

$$\log A = 10.9642$$

$$A = \text{antilog}(10.9642)$$

$$A = 9.208 \times 10^{10} \text{ collisions } s^{-1}$$

**28. Benzene diazonium chloride in aqueous solution decomposes according to the equation  $C_6H_5N_2Cl \rightarrow C_6H_5Cl + N_2$ . Starting with an initial concentration of  $10 \text{ g L}^{-1}$ , the volume of  $N_2$  gas obtained at  $50^\circ\text{C}$  at different intervals of time was found to be as under:**

t (min):	6	12	18	24	30	$\infty$
Vol. of $N_2$ (ml)	19.3	32.6	41.3	46.5	50.4	58.3

For a first order reaction

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

$$k = \frac{2.303}{t} \log \left( \frac{V_\infty}{V_\infty - V_1} \right)$$

In the present case,  $V_\infty = 58.3 \text{ ml}$ .

The value of  $k$  at different time can be calculated as follows.

**29. From the following data, show that the decomposition of hydrogen peroxide is a reaction of 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.

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

$$k = \left( \frac{2.303}{t} \right) \log \left( \frac{V_0}{V_t} \right)$$

In the present case,  $V_0 = 46.1 \text{ ml}$ . The value of  $k$  at each instant can be calculated as follows:

$t(\text{min})$	$V_t$	$k = \left( \frac{2.303}{t} \right) \log \left( \frac{V_0}{V_t} \right)$
10	29.8	$k = \frac{2.303}{20} \log \left( \frac{46.1}{29.8} \right) = 0.0436 \text{ min}^{-1}$
20	19.3	$k = \frac{2.303}{20} \log \left( \frac{46.1}{19.3} \right) = 0.0435 \text{ min}^{-1}$

Thus, the value of  $k$  comes out to be nearly constant. Hence it is a reaction of the first order.

$t(\text{min})$	$V_1$	$V_\infty = V_1$	$\frac{2.303}{t} \log \left( \frac{V_0}{V_0 - V_1} \right)$
6	19.3	$58.3 - 19.3 = 39.0$	$k = \frac{2.303}{6} \log \left( \frac{58.3}{39} \right) = 0.0670 \text{ min}^{-1}$
12	32.6	$58.3 - 32.6 = 25.7$	$k = \frac{2.303}{12} \log \left( \frac{58.3}{25.7} \right) = 0.0683 \text{ min}^{-1}$
18	41.3	$58.3 - 41.3 = 17.0$	$k = \frac{2.303}{18} \log \left( \frac{58.3}{17} \right) = 0.0685 \text{ min}^{-1}$
24	46.5	$58.3 - 46.5 = 11.8$	$k = \frac{2.303}{24} \log \left( \frac{58.3}{11.8} \right) = 0.0666 \text{ min}^{-1}$

**30. A first order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?**

For the first order reaction

$$k = \left(\frac{2.303}{t}\right) \log\left(\frac{a}{a-x}\right)$$

$$\text{when } x = \left(\frac{40}{100}\right) a = 0.4a$$

$$t = 50m$$

$$\therefore k = \left(\frac{2.303}{50}\right) \log\left(\frac{a}{a-0.4a}\right)$$

$$k = \left(\frac{2.303}{50}\right) \log\left(\frac{1}{0.6}\right)$$

$$= 0.010216 \text{min}^{-1}$$

$$t = ? \text{ when } x = 0.8 a$$

$$\text{From above } K = 0.010216 \text{min}^{-1}$$

$$\therefore t = \left(\frac{2.303}{0.010216}\right) \log\left(\frac{a}{a-0.8a}\right)$$

$$\left(\frac{2.303}{0.010216}\right) \log\left(\frac{1}{0.2}\right) = 157.58 \text{ min}$$

The time at which the reaction will be 80% complete is 157.58 min.