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UNIT – 1 – METALLURGY

II. Answer the following questions:

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

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

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

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

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

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

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

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

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

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

5. Describe a method for refining nickel. (or) How is Ni purified by Mond process? (or) Explain the purification of Nickel. [PTA-3, FMT, HY, FRT, MAY-22, FUT-23]

- The impure nickel is heated in a stream of carbon monoxide at around 350K.
- The nickel reacts with the CO to form a highly volatile nickel tetracarbonyl.
- The solid impurities are left behind. $Ni\ (s) + 4\ CO\ (g) \longrightarrow [Ni(CO)_4]\ (g)$
- On heating the nickel tetracarbonyl around 460K, the complex decomposes to give pure metal. $[Ni(CO)_4]\ (g) \longrightarrow Ni\ (s) + 4\ CO\ (g)$

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

- This method is based on the principle of fractional crystallization. The impure metal is melted and allowed to solidify, the impurities will prefer to remain in the molten region, ie; impurities are more soluble in the melt than in the solid-state metal.
- In this process, the impure metal is taken in the form of a rod. One end of the rod is heated using a mobile induction heater, melting the metal on that portion of the rod.

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+ When the heater is slowly moved to the other end pure metal crystallizes while impurities will move on to the adjacent molten zone formed due to the movement of the heater.

+ As the heater moves further away, the molten zone containing impurities also moves along with it.

+ This process is repeated several times by moving the heater in the same direction again and again to achieve the desired purity level.

+ This process is carried out in an inert gas atmosphere to prevent the oxidation of metals.

+ Germanium, Silicon, and gallium which are used as semiconductors are refined by this process.

7. **Using the Ellingham diagram, (A) Predict the conditions under which (i) Aluminium might be expected to reduce magnesia. (ii) Magnesium could reduce alumina.**

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

   (A) (i) Ellingham diagram for the formation of Al_2O_3 and MgO intersects around 1600K.

   + Above this temperature aluminium lines lies below the magnesium line.

   + Hence we can use aluminium to reduce magnesia above 1600K.

   (ii) In Ellingham diagram below 1600K magnesium line lies below aluminium line.

   + Hence, below 1600K magnesium can reduce alumina.

   (B) In Ellingham diagram above 1000K carbon line below the iron line.

   + Hence, it is possible to reduce Fe_2O_3 by coke at a temperature around 1200K.

8. **Give the uses of zinc. [PTA-4]**

   + Metallic zinc is used in galvanising metals such as iron and steel structures to protect them from rusting and corrosion.

   + Zinc is also used to produce die-castings in the automobile, electrical and hardware industries.

   + Zinc oxide is used in the manufacture of many products such as paints, rubber, cosmetics, pharmaceuticals, plastics, inks, batteries, textiles arid electrical equipment.

   + Zinc sulphide is used in making luminous paints, fluorescent lights and x-ray screens.

   + Brass an alloy of zinc is used in water valves and communication equipment as it is highly resistant to corrosion.

9. **Explain the electrometallurgy of aluminium. [GMQP-19, FMT-22]**

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

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

   Temperature : Above 1270 K.

   The chemical reactions involved in this process are as follows:

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

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

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

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

$$C_{(s)} + O^{2-} \text{ (melt)} \rightarrow CO + 2e^-$$
$$C_{(s)} + 2O^{2-} \text{ (melt)} \rightarrow CO_2 + 4e^-$$
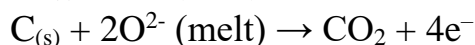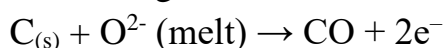
- Due to the above two reactions, anodes are slowly consumed during the electrolysis.
- The pure aluminium is formed at the cathode and settles at the bottom.
- The net electrolysis reaction can be written as follows:

$$4Al^{3+} \text{ (melt)} + 6O^{2-} \text{ (melt)} + 3C_{(s)} \rightarrow 4A_{(l)} + 3CO_{2(g)}$$
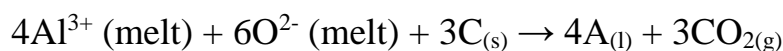
10. Explain the following terms with suitable examples. [PTA-2, SEP-20, FRT-22]

    (i) Gangue   (ii) Slag

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

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

                              Flux   *Gangue*   *Slag*
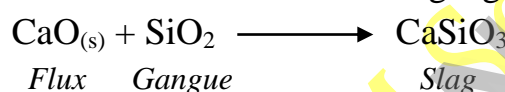
11. Give the basic requirement for vapour phase refining.

The two requirements for vapour phase refining are:

- The metal should form a volatile compound with a suitable reagent.
- The volatile compound is decomposed to give the pure metal.

12. Describe the role of the following in the process mentioned. (i) Silica in the extraction of copper. (or) What is the role of silica in extraction of copper? [FMT-22] (ii) Cryolite is the extraction of aluminium. [QY-19] (iii) Iodine in the refining of Zirconium. [QY-19] (iv) Sodium cyanide in froth floatation. [FMT-22]

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

(ii) Cryolite reduces the melting point of Al_2O_3 and increases its electrical conductivity. Aluminium is produced by the electrolytic reduction of fused alumina in the electrolytic cell. Alumina is not an electrolyte. So it is made as an electrolyte by dissolving it in the fused cryolite. The function of cryolite is to lower the fusion temperature.

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

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

13. Explain the principle of electrolytic refining with an example. (or)

How is silver purified by electrolytic refining process? [HY-19, FRT-22, JULY-22]

- Electrolytic refining is carried out in an electrolytic cell

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

        Electrolyte   : Acidified aqueous solution of salt of the metal.

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- The metal of interest dissolves from the anode, pass into the solution while the same amount of metal ions from the solution will be deposited at the cathode.
- During electrolysis, the less electropositive impurities in the anode, settle down at the bottom and are removed as anode mud.
- Electrolytic refining of silver as an example.

  Cathode : Pure silver   **Anode** : Impure silver rods

 **Electrolyte** : Acidified aqueous solution of silver nitrate.
- When a current is passed through the electrodes the following reactions will take place

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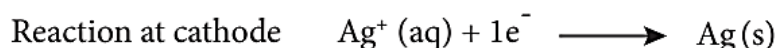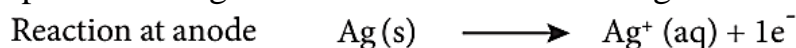
  Reaction at cathode $Ag^+(aq) + 1e^- \longrightarrow Ag(s)$
- During electrolysis, at the anode the silver atoms lose electrons and enter the solution.
- The positively charged silver cations migrate towards the cathode and get discharged by gaining electrons and deposited on the cathode.

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

- From the Ellingham diagram, it is clear that metals for which the standard free energy of formation ($\Delta fG0$) of their oxides is more negative can reduce the metal oxides for which the standard free energy of formation ($\Delta fG0$) of oxides is less negative.
- The thermodynamic factor has a major role in selecting the reducing agent for a particular reaction. Only that reagent will be preferred which will lead to a decrease in the free energy ($AG°$) at a certain specific temperature. E.g – Carbon reduce ZnO to Zn but not CO.
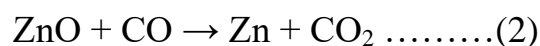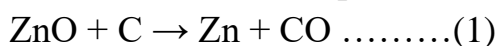
  $ZnO + C \rightarrow Zn + CO$ ....(1) $ZnO + CO \rightarrow Zn + CO_2$ ....(2)
- In the first case, there is increase in the magnitude of $\Delta S°$ while in the second case, it almost remains the same. In other words, $\Delta G°$ will have more negative value in the first case, when C is the reducing agent then in the second case when CO acts as the reducing agent.
- Therefore, C is a better reducing agent.

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

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

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

- Electrochemical principles also find applications in metallurgical process.
- The reduction of oxides of active metals such as sodium, potassium etc., by carbon is thermodynamically not feasible.
- Such metals are extracted from their ores by using electrochemical methods.
- In this technique, the metal salts are taken in a fused form or in solution form.

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✤ The metal ion present can be reduced by treating it with some suitable reducing agent or by electrolysis.

✤ Gibbs free energy change for the electrolysis process is given by the following expression

$$\Delta G° = -nFE°$$

✤ Where n is number of electrons involved in the reduction process, F is the Faraday and E° is the electrode potential of the redox couple.

✤ If E° is positive then the ΔG is negative and the reduction is spontaneous and hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive.

✤ When a more reactive metal is added to the solution containing the relatively less reactive metal ions, the more reactive metal will go into the solution.

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

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

EVALUATE YOURSELF

1. **Write the equation for the extraction of silver by leaching with sodium cyanide and show that the leaching process is a redox reaction.**
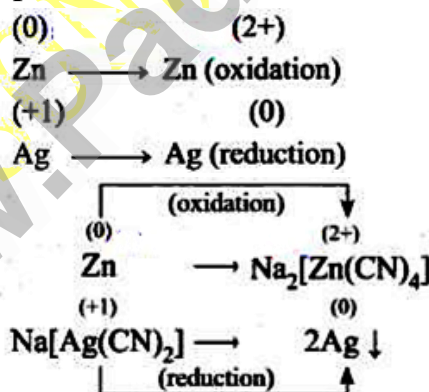
   The crushed ore of argentite (Ag_2S) is leached with sodium cyanide solution. This reaction forms sodium Argento cyanide $Na[Ag(CN)_2]$

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

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

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

   In the step 2, redox reaction take place.

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

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

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

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

   Ellingham diagram for the formation of ZnO and CO intersects around 1200K. Below this temperature the carbon line lies above zinc line. Hence ZnO is more stable than CO so the reduction is thermodynamically not feasible at this temperature range.
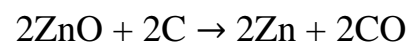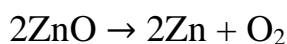
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$\Delta G° = RT \ln p_{O_2} / \text{kJmol}^{-1}O_2$
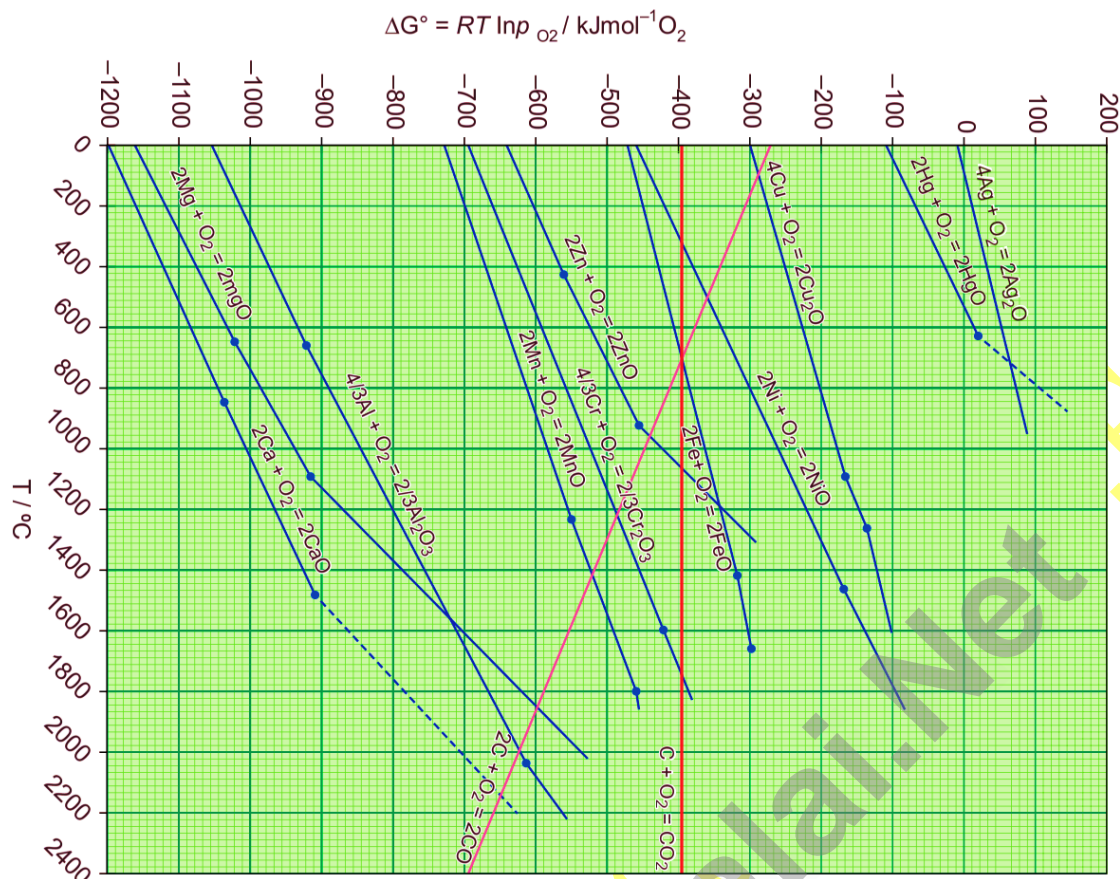
However above 1200K carbon line lies below the zinc line, hence carbon can be used as a reducing agent above 1200K.

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

Reversing (1) and adding with equation (2)

$2ZnO \rightarrow 2Zn + O_2$　　　　$2CO \rightarrow 2C + O_2$　　　　$2ZnO + 2C \rightarrow 2Zn + 2CO$
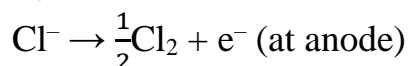
4. Metallic sodium is extracted by the electrolysis of brine (aq. NaCl). After electrolysis, the electrolytic solution becomes basic in nature. Write the possible electrode reactions.

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

The process of electrolysis involves using an electric current to bring about a chemical change and make new chemicals. In the electrolysis of brine, sodium ions migrate to the cathode, where electrons enter the melt and are reduced to sodium metal.
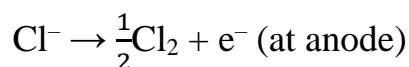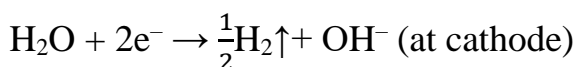
$$Na^+ + e^- \rightarrow Na \text{ (at cathode)}$$

Chloride ions migrate the other way toward the anode. They give up their electrons to the anode and are oxidised to chlorine gas.
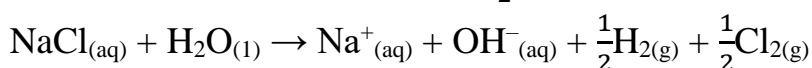
$$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^- \text{ (at anode)}$$

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

For aqueous solution of NaCl:

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

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

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

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GOVERNMENT EXAM QUESTION PAPER

1. Oxides like Ag₂O and HgO undergo self-reduction. Why? [QY-19]

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

These oxides are unstable at moderate temperatures undergo self reduction.

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

✦ Sodium ethyl xanthate acts as a collector.

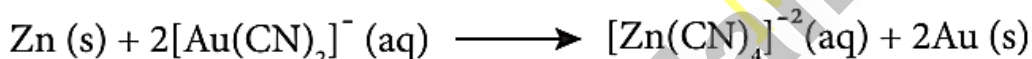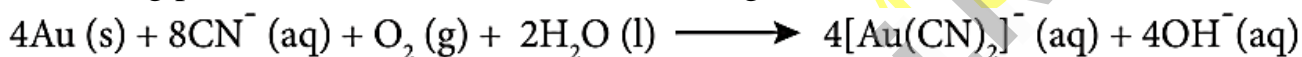✦ Sodium cyanide, Sodium carbonate are used as depressing agents in froth flotation process.

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

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

4. Explain how gold ore is leached by cyanide process. [GMQP-19, FMT-22, FUT-23]

✦ Gold is usually found in native state.

✦ The leaching process is intended to concentrate the gold metal.

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

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

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

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

✦ Gravity separation method, the ore having high specific gravity is separated from the gangue that has low specific gravity by simply washing with running water.

✦ Ore is crushed to a finely powdered form and treated with rapidly flowing current of water.

✦ During this process the lighter gangue particles are washed away by the running water.

✦ This method is generally applied to concentrate the native ore such as gold and oxide ores such as haematite (Fe_2O_3), tin stone (SnO_2)

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

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

$$2ZnS\ (s) + 2H_2SO_4\ (aq) + O_2(g) \longrightarrow 2ZnSO_4\ (aq) + 2S\ (s) + 2\,H_2O$$
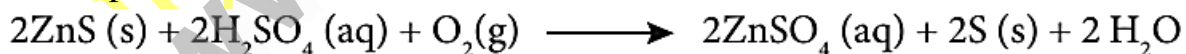
✦ In this process the insoluble sulphide is converted into soluble sulphate and elemental sulphur.

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

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

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

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

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

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in randomness. Hence, ΔS becomes negative and it makes the term, $T\Delta S$ positive in the straight line equation.

➕ The graph for the formation of carbon monoxide is a straight line with negative slope. In this case ΔS is positive as 2 moles of CO gas is formed by the consumption of one mole of oxygen gas. It indicates that CO is more stable at higher temperature.

➕ As the temperature increases, generally ΔG value for the formation of the metal oxide become less negative and becomes zero at a particular temperature. Below this temperature, ΔG is negative and the oxide is stable and above this temperature ΔG is positive. This general trend suggests that metal oxides become less stable at higher temperature and their decomposition becomes easier.

➕ There is a sudden change in the slope at a particular temperature for some metal oxides like MgO, HgO. This is due to the phase transition (melting or evaporation).

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

➕ Froth flotation method is commonly used to concentrate sulphide ores such as galena (PbS), zinc blende (ZnS) etc...

➕ In this method, the metallic ore particles which are preferentially wetted by oil can be separated from gangue.

➕ In this method, the crushed ore is suspended in water and mixed with frothing agent such as pine oil, eucalyptus oil etc.

➕ A small quantity of sodium ethyl xanthate which acts as a collector is also added.

➕ A froth is generated by blowing air through this mixture.

➕ The collector molecules attach to the ore particle and make them water repellent.

➕ As a result, ore particles, wetted by the oil, rise to the surface along with the froth.

➕ The froth is skimmed off and dried to recover the concentrated ore.

➕ The gangue particles that are preferentially wetted by water settle at the bottom.
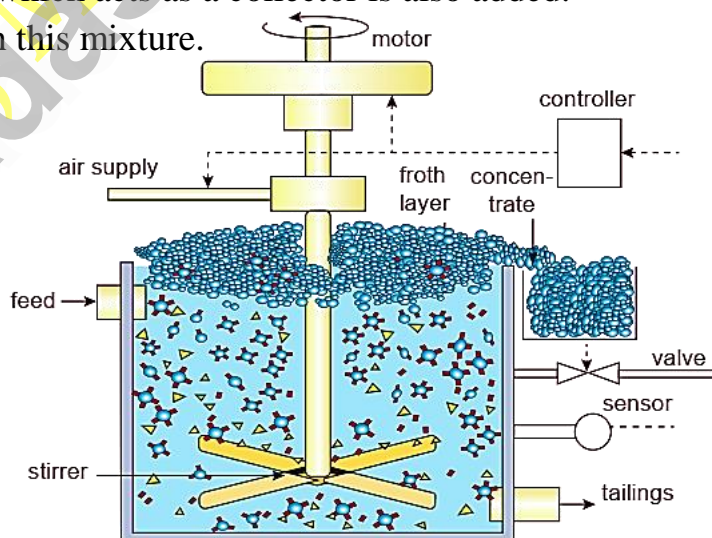
10. What is auto reduction? [HY-22, FRT-22, FRT-23]

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

$$HgS\,(s) + O_2\,(g) \longrightarrow Hg\,(l) + SO_2\uparrow$$
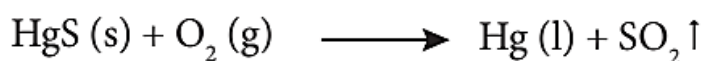
11. How are ores concentrated by magnetic separation method? [HY,FRT-22]

➕ Magnetic separation method is applicable to ferromagnetic ores and it is based on the difference in the magnetic properties of the ore and the impurities.

➕ For example tin stone can be separated from the wolframite impurities which is magnetic.

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- Similarly, ores such as chromite, pyrolusite having magnetic property can be removed from the non magnetic siliceous impurities. The crushed ore is poured on to an electromagnetic separator consisting of a belt moving over two rollers of which one is magnetic.

- The magnetic part of the ore is attracted towards the magnet and falls as a heap close to the magnetic region while the nonmagnetic part falls away from it as shown in the figure
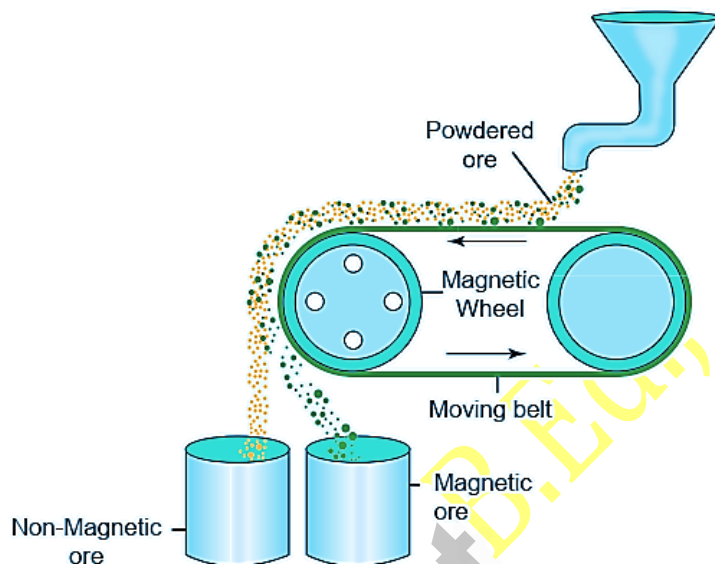
12. What is chemical leaching? [FRT-22]

- This method is based on the solubility of the ore in a suitable solvent and the reactions in aqueous solution.

- In this method, the crushed ore is allowed to dissolve in a suitable solvent, the metal present in the ore is converted to its soluble salt or complex while the gangue remains insoluble.

13. What type of oxidation process is employed for $CaCO_3$? Explain it. [FMT-22]

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

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

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

- Many heat exchangers/sinks and our day to day cooking vessels are made of aluminium.

- It is used as wraps (aluminium foils) and is used in packing materials for food items,

- Aluminium is not very strong, However , its alloys with copper, manganese, magnesium and silicon are light weight and strong and they are used in design of aeroplanes and other forms of transport.

- As Aluminium shows high resistance to corrosion, it is used in the design of chemical reactors, medical equipments, refrigeration units and gas pipelines.

- Aluminium is a good electrical conductor and cheap, hence used in electrical overhead electric cables with steel core for strength.

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

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

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

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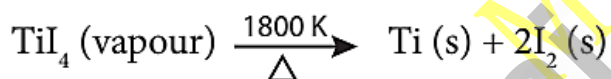
solid. The liquid melt is drained away from the other and collected. Earlier, it was used to extract antimony minerals from ore. It is also used to remove lead containing silver from copper.

17. Explain Van-Arkel method for refining Titanium. (or) Explain how Zr and Ti are refined by Van-Arkel method. [HY-22, FRT-23]
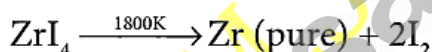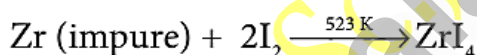
- ♣ This method is based on the thermal decomposition of metal compounds which lead to the formation of pure metals. Titanium and zirconium can be purified using this method.

- ♣ For example, the impure titanium metal is heated in an evacuated vessel with iodine at a temperature of 550 K to form the volatile titanium tetra-iodide.(TiI4). The impurities are left behind, as they do not react with iodine.

$$Ti\ (s) + 2I_2\ (s)\ \xrightarrow[\Delta]{550K}\ TiI_4\ (vapour)$$
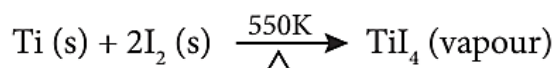
- ♣ The volatile titanium tetraiodide vapour is passed over a tungsten filament at a temperature aroud 1800 K. The titanium tetraiodide is decomposed and pure titanium is deposited on the filament. The iodine is reused.

$$TiI_4\ (vapour)\ \xrightarrow[\Delta]{1800\ K}\ Ti\ (s) + 2I_2\ (s)$$

Zirconium:

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

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

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

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

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

$$Zn\ (s) + 2[Au(CN)_2]^-\ (aq)\ \longrightarrow\ [Zn(CN)_4]^{-2}(aq) + 2Au\ (s)$$
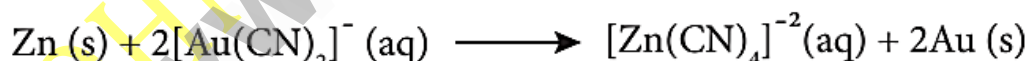
UNIT – II – P-BLOCK ELEMENTS-I | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,
UNIT – 2 – P-BLOCK ELRMENTS - I

II. Answer the following questions:

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

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

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

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

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

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

Graphite, Diamond, Fullerenes, Carbon nanotubes, Graphene.

3. Give the uses of Borax. [HY-19, AUG-21]

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

4. What is catenation? describe briefly the catenation property of carbon. [MAR, SEP20, JULY-22, FUT-23]

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

🔸 The valency of the element is greater than or equal to two. The element should have the ability to bond with itself. The self-bond must be as strong as its bond with other elements.
🔸 Kinetic inertness of catenated compound towards other molecules.
🔸 Carbon possesses all the above properties and shows catenation.
🔸 Carbon forms a wide range of compounds with itself and with other elements such as H, O, N, S and halogens.

5. Write a note on Fisher tropsch synthesis. [PTA-4, QY-22, MAR-23]

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

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

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$
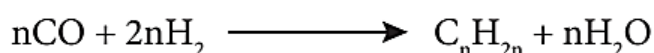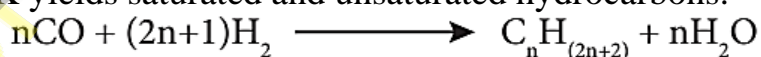
6. Give the structure of CO and CO₂.

Structure of CO:

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

$$\overset{+}{\underset{..}{C}}\!-\!\overset{..}{\underset{..}{O}}\!:^{-} \longleftrightarrow :C\!=\!\overset{..}{O} \longleftrightarrow \bar{C}\!\equiv\!\overset{+}{O}$$
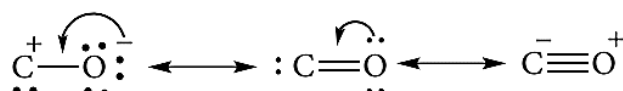
UNIT – II – P-BLOCK ELEMENTS-I | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,
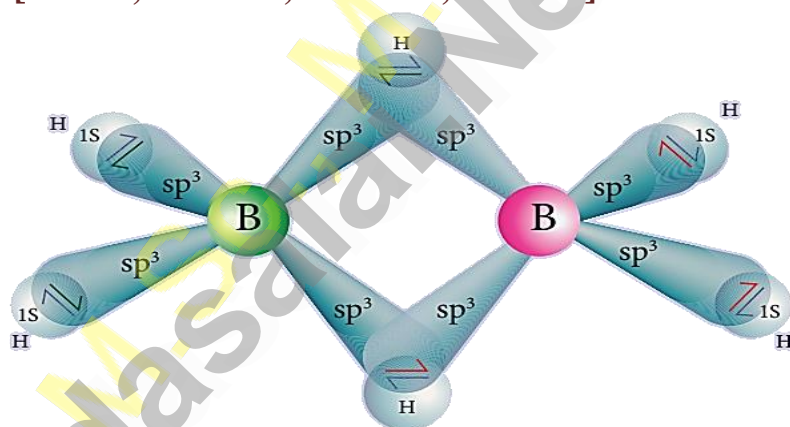
Structure of CO_2:

- Carbon dioxide has a linear structure with equal bond distance for the both C-O bonds.
- In this molecule there is two C-O sigma bond.
- In addition there is 3c-4e bond covering all the three atoms.
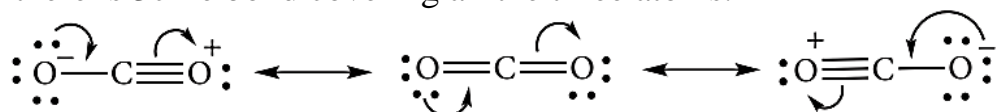
7. Give the uses of silicones. [FMT-22, HY-22, MAR-23, FUT-23]

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

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

- In diborane two BH_2 units are linked by two bridged hydrogens.
- Therefore, it has eight B-H bonds.
- However, diborane has only 12 valance electrons and are not sufficient to form normal covalent bonds.
- The four terminal B-H bonds are normal covalent bonds (two centre – two electron bond or 2c-2e bond).

- The remaining four electrons have to used for the bridged bonds, i.e. two three centred B-H-B bonds utilise two electrons each. Hence, these bonds are three centre – two electron bonds. The bridging hydrogen atoms are in a plane as shown in the figure. In dibome, the boron is sp^3 hybridised.
- Three of the four sp^3 hybridised orbitals contains single electron and the fourth orbital is empty.
- Two of the half-filled hybridised orbitals of each boron overlap with the two hydrogens to form four-terminal 2c-2e bonds, leaving one empty and one half filled hybridised orbitals on each boron.
- The Three centre – two-electron bonds, B-H-B bond formation involves overlapping the half filled hybridised orbital of one boron, the empty hybridised orbital of the other boron and the half-filled 1s orbital of hydrogen.

9. Write a short note on hydroboration. [JUN-23]

- Diborane adds on to alkenes and alkynes in ether solvent at room temperature.
- This reaction is called as hydroboration and is highly used in synthetic organic chemistry especially for anti-Markovnikov addition.
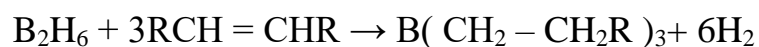
$$B_2H_6 + 3RCH = CHR \rightarrow B(CH_2 - CH_2R)_3 + 6H_2$$ **[JUN-23]**

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

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

UNIT – II – P-BLOCK ELEMENTS-I | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,

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

➕ The tendency of an element to form a cation by loosing electrons is known as an electropositive or metallic character. This character depends on the ionisation energy.

➕ Generally on descending a group the ionisation energy decreases and hence the metallic character increases.

➕ In p-block, the elements present in lower left part are metals while the elements in the upper right part are non-metals.

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

12. Complete the following reactions:

(a) $B(OH)_3 + NH_3 \rightarrow$ **[HY-22]**

(b) $Na_2B_4O_7 + H_2SO_4 + H_2O \rightarrow$

(c) $B_2H_6 + 2NaOH + 2H_2O \rightarrow$

(d) $B_2H_6 + CH_3OH \rightarrow$

(e) $BF_3 + 9H_2O \rightarrow$

(f) $HCOOH + H_2SO_4 \rightarrow$

(g) $SiCl_4 + NH_3 \rightarrow$ **[QY-19]**

(h) $SiCl_4 + C_2H_5OH \rightarrow$

(i) $B + NaOH \rightarrow$ **[QY-19]**

(j) $H_2B_4O_7 \xrightarrow{Redhot}$ **[HY-22]**

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

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

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

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

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

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

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

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

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

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

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

➕ When boric acid or borate salt is heated with ethyl alcohol in presence of concentrated H_2SO_4, an ester triethyl borate is formed.

➕ The Vapour of this ester burns with a green edged flame and this reaction is used to identify the presence of borate.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow[H_2SO_4]{Conc.} B(OC_2H_5)_3 + 3H_2O$$
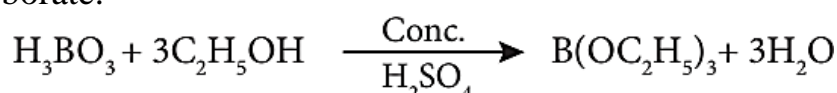
UNIT – II – P-BLOCK ELEMENTS-I | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,

14. Write a note on zeolites. [PTA-2, QY-19]

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

15. How will you convert boric acid to boron nitride? [PTA-3]

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

$$B(OH)_3 + NH_3 \xrightarrow{\Delta} BN + 3H_2O$$
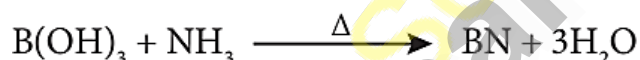
16. A hydride of 2nd period alkali metal (A) on reaction with compound of Boron (B) to give a reducing agent (C) identify A, B and C. [PTA-1, SEP-20]

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

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

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

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

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

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

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

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

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

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

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

$$CO + Fe_2O_3 \rightarrow 2Fe + 3CO_2$$
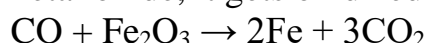
UNIT – II – P-BLOCK ELEMENTS-I | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,
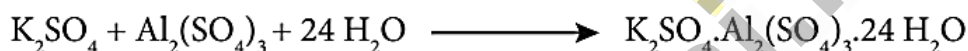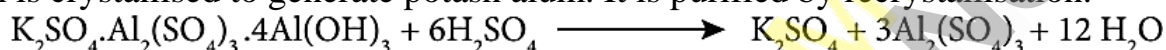
EVALUATE YOURSELF

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

➕ The group-18 consists of 6 elements, helium, neon, argon, krypton, xenon and radon. All these are gases have completely filled s and p orbitals, hence they are more stable and have least reactivity.

➕ Therefore group-18 elements are called inert gases. ns^2np^6 is the general electronic configuration of group elements.

GOVERNMENT EXAM QUESTION PAPER

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

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

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

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

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

$$K_2SO_4.Al_2(SO_4)_3.24 H_2O \xrightarrow{500 K} K_2SO_4.Al_2(SO_4)_3 + 24 H_2O$$
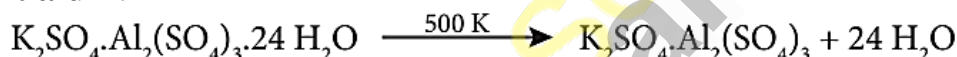
2. Although Graphite and Diamond are allotropes of carbon, graphite is soft whereas diamond is hard. Why? [QY-19]

➕ Carbon alone forms the familiar substances graphite and diamond. Both graphite and diamond are made only of carbon atoms.

➕ Graphite is very soft and slippery while Diamond is the hardest substance.

➕ While there are strong covalent bonds between carbon atoms in each layer, there are only weak forces between layers. This allows layers of carbon to slide over each other in graphite.

➕ On the other hand, in diamonds, each carbon atom is the same distance from each of its neighboring carbon atoms. they are bonded by strong covalent bonds

➕ Diamond is hard because it has four carbon atoms which form a strong covalent bond in tetrahedral structure whereas graphite is arranged in layer form through weak wander walls force hence is slippery in nature.

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

3. Give the uses of Potash alum. [QY-19]

➕ It is used for purification of water. It is also used for water proofing and textiles

➕ It is used in dyeing, paper and leather tanning industries

➕ It is employed as a styptic agent to arrest bleeding.

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

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

UNIT – II – P-BLOCK ELEMENTS-I | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,
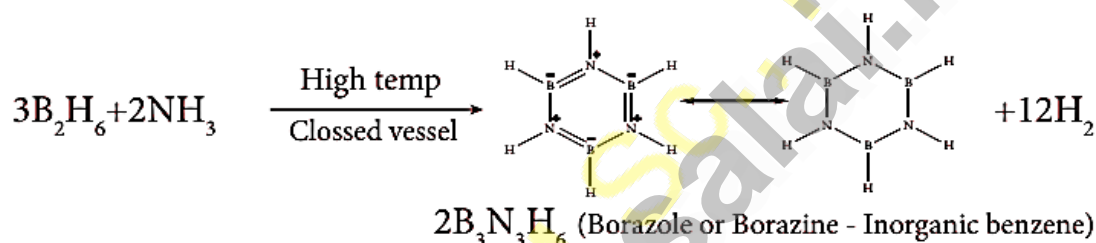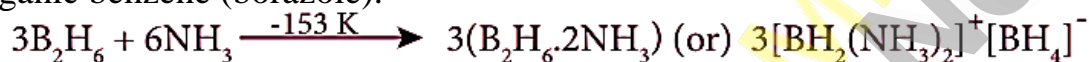
5. What are the uses of boric acid? [MAY, JULY-22]

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

6. What are fullerenes? [FMT-22]

Fullerenes are newly synthesised allotropes of carbon. Unlike graphite and diamond, these allotropes are discrete molecules such as C_{32}, C_{50}, C_{60}, C_{70}, C_{76} etc.. These molecules have cage like structures as shown in the figure. The C60 molecules have a soccer ball like structure and is called buckminster fullerene or buckyballs. It has a fused ring structure consists of 20 six membered rings and 12 five membered rings. Each carbon atom is sp^2 hybridised and forms three σ bonds & a delocalised π bond giving aromatic character to these molecules. The C-C bond distance is 1.44 Å and C=C distance 1.38 Å.

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

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

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

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

$$2B_3N_3H_6 \text{ (Borazole or Borazine - Inorganic benzene)}$$

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

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

Examples:

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

9. How does boric acid reacts with NaOH?

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

$$H_3BO_3 + NaOH \rightarrow NaBO_2 + 2H_2O$$
$$4H_3BO_3 + 2NaOH \rightarrow Na_2B_4O_7 + 7H_2O$$
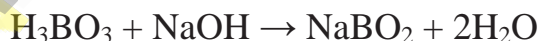
UNIT – III – P-BLOCK ELEMENTS-II | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,
UNIT – 3 – P-BLOCK ELRMENTS - II

II. Answer the following questions:

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

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

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

✤ Chalcogens are ore forming elements.

✤ Most of the ores are oxides and sulphides, therefore oxygen, sulphur and other group 16 elements are called Chalcogens.

✤ In O, S, Se, Te and Po last electron enters to p-orbital.

✤ Therefore Chalcogens belongs to p-block.

✤ Chalcogens general electronic configuration is ns^2np^4.

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

✤ The electronic configuration of Fluorine is $1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$.

✤ Fluorine the most electronegative element than other halogens and cannot exhibit any positive oxidation state.

✤ Fluorine does not have d-orbital while other halogens have d-orbitals.

✤ Therefore fluorine always exhibit an oxidation state of-1 and others in halogen family shows +1, +3, +5 and +7 oxidation states.

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

(i) OF_2 [MAR-23]	(ii) O_2F_2	(iii) Cl_2O_3	(iv) I_2O_4 [MAR-23]
(i) OF_2	(ii) O_2F_2	(iii) Cl_2O_3	(iv) I_2O_4
$+2 + 2(x) = 0$	$2(+1) + 2x = 0$	$2(x) + 3(-2) = 0$	$2(x) + 4(-2) = 0$
$+2 = -2x$	$2x = -2$	$2x = +6$	$2x = +8$
$2x = -2 \quad x = -1$	$x = -1$	$x = +3$	$x = +4$

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

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

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

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

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

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

✤ Helium is used to provide inert atmosphere in electric arc welding of metals

✤ Helium has lowest boiling point hence used in cryogenics (low temperature science).

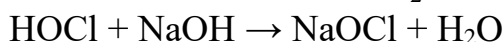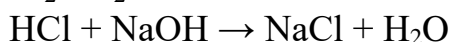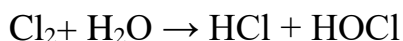✤ It is much less denser than air and hence used for filling air balloons

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

Hybridisation of iodine in IF_7 is sp^3d^3 Structure of IF_7 is pentagonal bi-pyramidal.
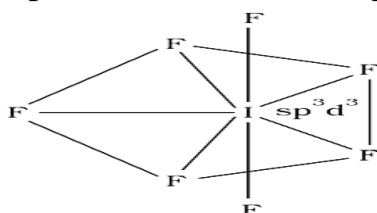
UNIT – III – P-BLOCK ELEMENTS-II | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,

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

↓ Reaction between chlorine with cold NaOH:

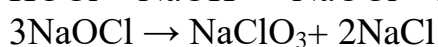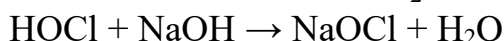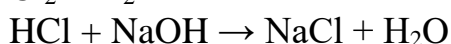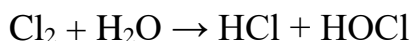$Cl_2 + H_2O \rightarrow HCl + HOCl$

$HCl + NaOH \rightarrow NaCl + H_2O$

$HOCl + NaOH \rightarrow NaOCl + H_2O$

Overall reaction

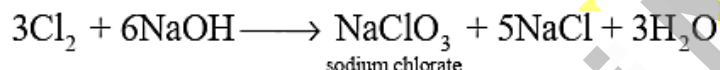$$Cl_2 + 2NaOH \longrightarrow \underset{\text{sodium hypo chlorite}}{NaOCl} + NaCl + H_2O$$

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

↓ Reaction between chlorine with hot NaOH:

$Cl_2 + H_2O \rightarrow HCl + HOCl$

$HCl + NaOH \rightarrow NaCl + H_2O$

$HOCl + NaOH \rightarrow NaOCl + H_2O$

$3NaOCl \rightarrow NaClO_3 + 2NaCl$

Overall reaction

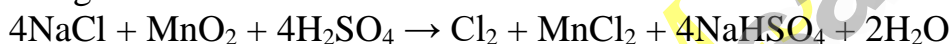$$3Cl_2 + 6NaOH \longrightarrow \underset{\text{sodium chlorate}}{NaClO_3} + 5NaCl + 3H_2O$$

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

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

↓ Chlorine is prepared by the action of cone, sulphuric acid on chlorides in presence of manganese dioxide.

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

↓ It can also be prepared by oxidising hydrochloric acid using various oxidising agents such as manganese dioxide, lead dioxide, potassium permanganate or dichromate.

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

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

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

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

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

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

$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$

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

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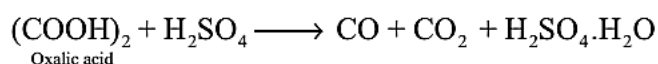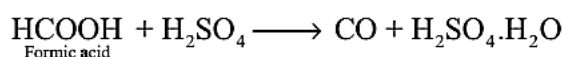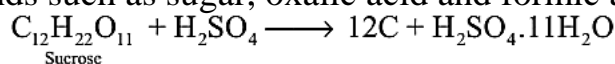
↓ It is used as a drying agent and also used in the preparation of pigments, explosives etc.

12. **Prove that sulphuric acid is a dehydrating agent (or) Give a reason to support that sulphuric acid is a dehydrating agent. [PTA1,QY,HY19, HY-22, JUN-23]**

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

↓ Hence it can be used as a dehydrating agent.

↓ When dissolved in water it forms mono ($H_2SO_4. H_2O$) and di ($H_2SO_4. 2H_2O$) hydrates and the reaction is exothermic. The dehydration property can also be illustrated by its reaction with organic compounds such as sugar, oxalic acid and formic acid.

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

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

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

UNIT – III – P-BLOCK ELEMENTS-II | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,

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

+ Due to its small size, high electro negativity, high ionisation enthalpy and absence of d-orbitals. Nitrogen exists a diatomic molecule with triple bond between the two atoms whereas other elements form single bond in the elemental state.

+ N, has a unique ability to form $p\pi - p\pi$ multiple bond whereas the heavier members of this group (15) do not form $p\pi - p\pi$ bond, because their atomic orbitals are so large and diffused that they cannot have effective overlapping.

+ N cannot form $d\pi - p\pi$ bond due to the absence of d – orbitals whereas other elements can.

14. Write the molecular formula and structural formula for the following molecules.
(a) Nitric acid   (b) dinitrogen pentoxide   (c) phosphoric acid   (d) phosphine

	Molecule	Molecular formula	Structure
a.	Nitric acid	HNO_3	
b.	Dinitorgen pentaoxide	N_2O_5	
c.	Phosphoric acid	H_3PO_4	
d.	Phosphine	PH_3	

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

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

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

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

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

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

+ Phosphine reacts with halogens to give phosphorous penta halides.
$$PH_3 + 4Cl_2 \rightarrow PCl_5 + 3HCl$$

+ Phosphine forms coordination compound with lewis acids such as boron trichloride.
$$BCl_3 + PH_3 \rightarrow [Cl_3B \leftarrow :PH_3]$$

+ Phosphine precipitates some metal from their salt solutions.
$$3AgNO_3 + PH_3 \rightarrow Ag_3P + 3HNO_3$$

18. Give a reaction between nitric acid and a basic oxide. [FUT-23]

Nitric acid reacts with bases and basic oxides to form salts and water.
$$ZnO + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2O$$
$$3FeO + 10HNO_3 \rightarrow 3Fe(NO_3)_3 + NO + 5H_2O$$

UNIT – III – P-BLOCK ELEMENTS-II | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,

19. What happens when PCl_5 is heated?

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

$$PCl_5 \xrightarrow{\triangle} PCl_3 + Cl_2$$

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

+ Fluorine has the greatest affinity for hydrogen, due to the large electro negativity difference between them, forming HF which is associated due to the hydrogen bonding.
+ Hydrofluoric acid is a weak acid are strong acids.

$$…….H\text{-}F…..H\text{-}F…..H\text{-}F……$$

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

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

+ In case of O – F bond is HOF, fluorine is most electronegative element. So its oxidation number is -1.
+ Thereby oxidation number of O is +1. Similarly in case of O – H bond is HOF. O is highly electronegative than H. So its oxidation number is -1 and oxidation number of H is +1.
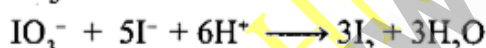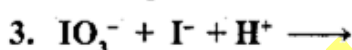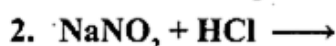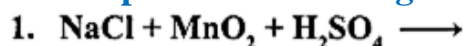+ So, Net oxidation of oxygen is $+1 + x - 1 = 0$.
+ Oxidation number of O in HOF is zero.
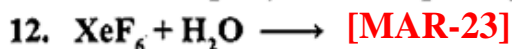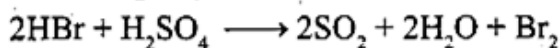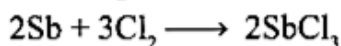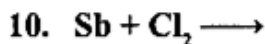
22. What type of hybridisation occur in   (i) BrF_5 (ii) BrF_3

(i) BrF_5 : BrF_5 is a AX_5 type. Therefore is has sp^3d^2 hybridisation. Hence, it has square pyramidal shape.
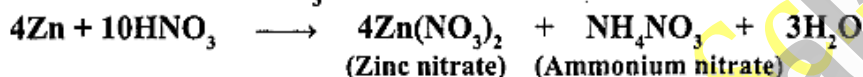
(ii) BrF_3 : BrF_3 is a AX_3 type. Therefore it has sp^3d hybridisation. Hence, it has T-shape.

23. Complete the following reactions.

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

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

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

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

5. $P_4 + NaOH + H_2O \longrightarrow$ **[MAR-23]**
   $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3 \uparrow$

6. $AgNO_3 + PH_3 \longrightarrow$ **[FUT-23]**
   $3AgNO_3 + PH_3 \longrightarrow Ag_3P + 3HNO_3$

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

8. $KClO_3 \xrightarrow{\Delta}$ **[FUT-23]**
   $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$

9. $Cu + \text{Hot Conc.} H_2SO_4 \longrightarrow$ **[MAR, FUT-23]**
   $Cu + \text{Hot Conc.} 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2 \uparrow$

UNIT – III – P-BLOCK ELEMENTS-II | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,

10. $Sb + Cl_2 \longrightarrow$

$2Sb + 3Cl_2 \longrightarrow 2SbCl_3$

11. $HBr + H_2SO_4 \longrightarrow$

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

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

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

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

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

14. $XeOF_4 + SiO_2 \longrightarrow$

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

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

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

EVALUATE YOURSELF

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

(i) **Zinc with Conc. HNO_3:**

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

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

$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$
(Zinc nitrate)   (Nitrous oxide)
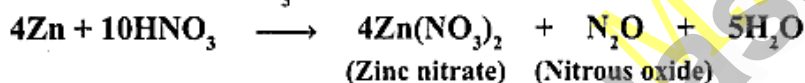
GOVERNMENT EXAM QUESTION PAPER

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

Properties of inter halogen compounds:

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

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

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

Phosphine is prepared in pure form by heating phosphorous acid.

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3 \uparrow$$
Phosphorous acid   Ortho phosphoric acid   Phosphine
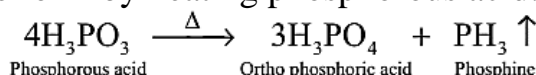
3. **How is bleaching powder prepared? [MAR-20, MAY-22]**

Bleaching powder is produced by passing chlorine gas through dry slaked lime (calcium hydroxide).
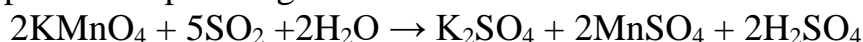
$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$
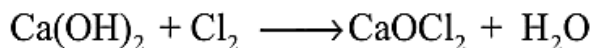
4. **SO_2 – is a reducing agent. Prove it. [SRT-22]**

+ SO_2 – It can readily be oxidised, it acts as a reducing agent. It reduces chlorine into hydrochloric acid.

UNIT – III – P-BLOCK ELEMENTS-II | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,

$$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$$
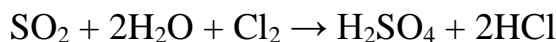
+ It also reduces potassium permanganate and dichromate to Mn^{2+}

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

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

Ammonia reacts with metallic salts to forming complexes

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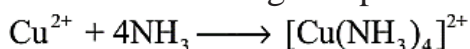
Tetraamminecopper(II)ion

(a coordination complex)

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

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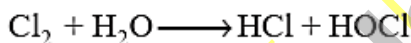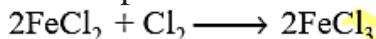+ It is used in water treatment and chemical combustion.

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

Oxidising and bleaching action: Chlorine is a strong oxidising and bleaching agent because of the nascent oxygen.
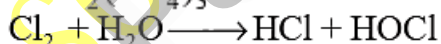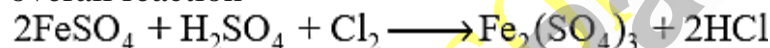
$$H_2O + Cl_2 \longrightarrow HCl + \underset{\text{Hypo chlorous acid}}{HOCl}$$

$$HOCl \longrightarrow HCl + (O)$$
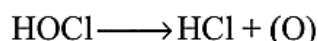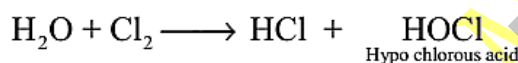
Colouring matter + Nascent oxygen → Colourless oxidation product

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

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

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

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

overall reaction

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

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

$$Na_2SO_3 + HOCl \longrightarrow Na_2SO_4 + HCl$$

overall reaction

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

$$Cl_2 + H_2S \longrightarrow 2HCl + S$$

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

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

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

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

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

(i) Sulphurous acid (H_2SO_3)
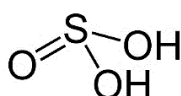
(ii) Marshall's acid or Peroxodisulphuric acid ($H_2S_2O_8$)
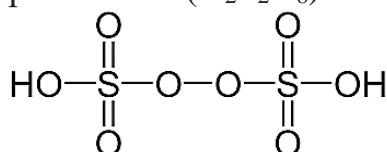
**10. Write a short note on Holmes Signal. [SEP-20, HY-22]**

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

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

In presence of water, sulphur dioxide bleaches coloured wool, silk, sponges and straw into colourless due to its reducing property.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2(H)$$

$$\underset{Coloured}{X} + 2(H) \longrightarrow \underset{Colourless}{XH_2}$$
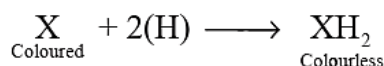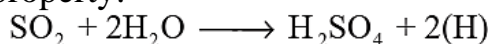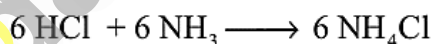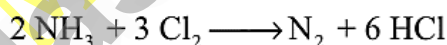
However, the bleached product (colourless) is allowed to stand in air, it is reoxidised by atmospheric oxygen to its original colour. Hence bleaching action of sulphur dioxide is temporary.

Uses:

+ Sulphur dioxide is used in bleaching hair, silk, wool etc...
+ It can be used for disinfecting crops and plants in agriculture.

Structure of sulphur dioxide:

In sulphur dioxide, sulphur atom undergoes sp2 hybridisation. A double bond arises between S and O is due $p\pi – d\pi$ overlapping.

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

(i) **NH₃ (excess) + Cl₂ → ?**
(ii) **NH₃ + Cl₂ (excess) → ?**

(i) With excess ammonia

$$2\,NH_3 + 3\,Cl_2 \longrightarrow N_2 + 6\,HCl$$

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

(ii) With excess of chlorine ammonia reacts to give nitrogen trichloride, an explosive substance.

$$2NH_3 + 6Cl_2 \longrightarrow 2NCl_3 + 6\,HCl$$

$$2NH_3(g) + HCl(g) \longrightarrow NH_4Cl\,(s)$$
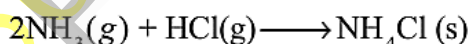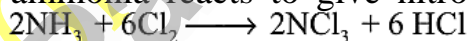
13. Explain the structure of ammonia. [SRT-22]

+ Ammonia molecule is pyramidal in shape N-H bond distance is 1.016 Å and H-H bond distance is 1.645 Å with a bond angle 107°.
+ The structure of ammonia may be regarded as a tetrahedral with one lone pair of electrons in one tetrahedral position hence it has a pyramidal shape.
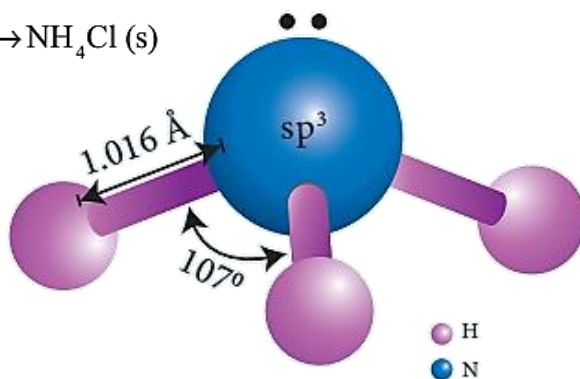
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UNIT – 4 – TRANSITION AND INNER TRANSITION ELEMENTS

II. Answer the following questions:

1. What are transition metals? Give four examples.

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

Examples: Copper, Iron, Cobalt, Nickel.

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

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

  Example:

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

3. What are inner transition elements?

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

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

Lanthanides:

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

Actinides:

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

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5. What are actinoids? Give three examples.

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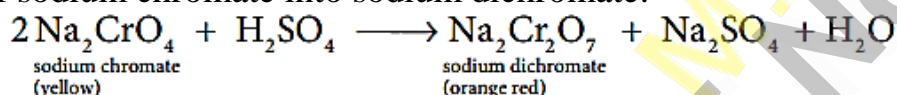+ Actinoids have general electronic configuration $[Rn]\ 5f^{0-14}\ 6d^{0-2}\ 7s^2$

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

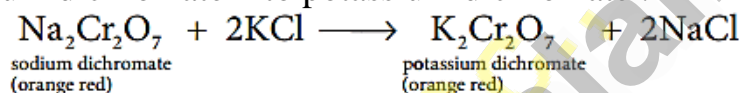## 6. Describe the preparation of potassium dichromate. [PTA-2]

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

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \xrightarrow{900 - 1000^0 C} 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2 \uparrow$$
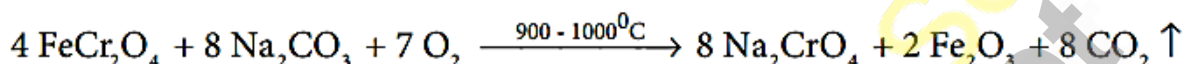
+ Conversion of sodium chromate into sodium dichromate:

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

+ Conversion of sodium dichromate into potassium dichromate :

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

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

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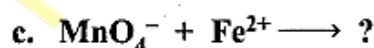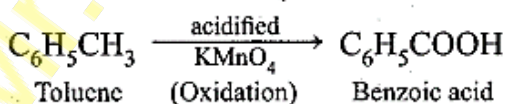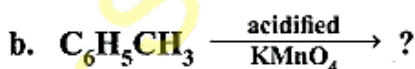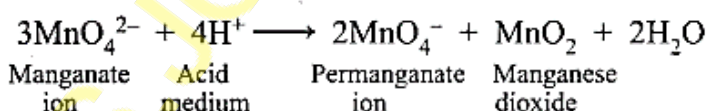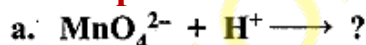
Consequences of lanthanoid contraction:

1. Basicity differences:

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

2. Similarities among lanthanoids:

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

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

8. Complete the following

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

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

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

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[\substack{\text{KMnO}_4\\\text{(Oxidation)}}]{\text{acidified}} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

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

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

Permanganate   Ferrous   (Oxidation)   Ferric
ion   ion   ion

d. $KMnO_4 \xrightarrow[\text{Red hot}]{\Delta}$?

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

Potassium   Potassium   Manganese
Permanganate   Manganate   dioxide·

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

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

Iodide ion   (Oxidation)   Iodine

f. $Na_2Cr_2O_7 + KCl \longrightarrow$?

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

Sodium dichromate   Potassium dichromate

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

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

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

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

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

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

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

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

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

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

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

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

$$\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.92\ BM$$

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

Ce (Z = 58) $\rightarrow Ce^{4+} + 4e^-$

$Ce^{4+} - 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$

$Co^{2+} - 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$.

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

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

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

- +2 oxidation state is attained by the loss of the two 4s electrons by these metals.
- Since the number of d electrons in (+2) state also increases from Ti2+ to Mn2+ the stability of +2 state increases.
- As a result d- orbital is becoming more and more half-filled which is highly stable.

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13. Which is more stable? Fe^{3+} or Fe^{2+} – explain. [QY-19, MAY-22, QY-22, SUT-23]

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

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

14. Explain the variation in $E^0_{M2+/M3+}$ 3d series.

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

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

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

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

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

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

- Ionization energy of transition element is intermediate between those of s and p block elements.
- As we move from left to right in a transition metal series, the ionization enthalpy increases as expected. This is due to increase in nuclear charge corresponding to the filling of d electrons.
- The following figure show the trends in ionisation enthalpy of transition elements.
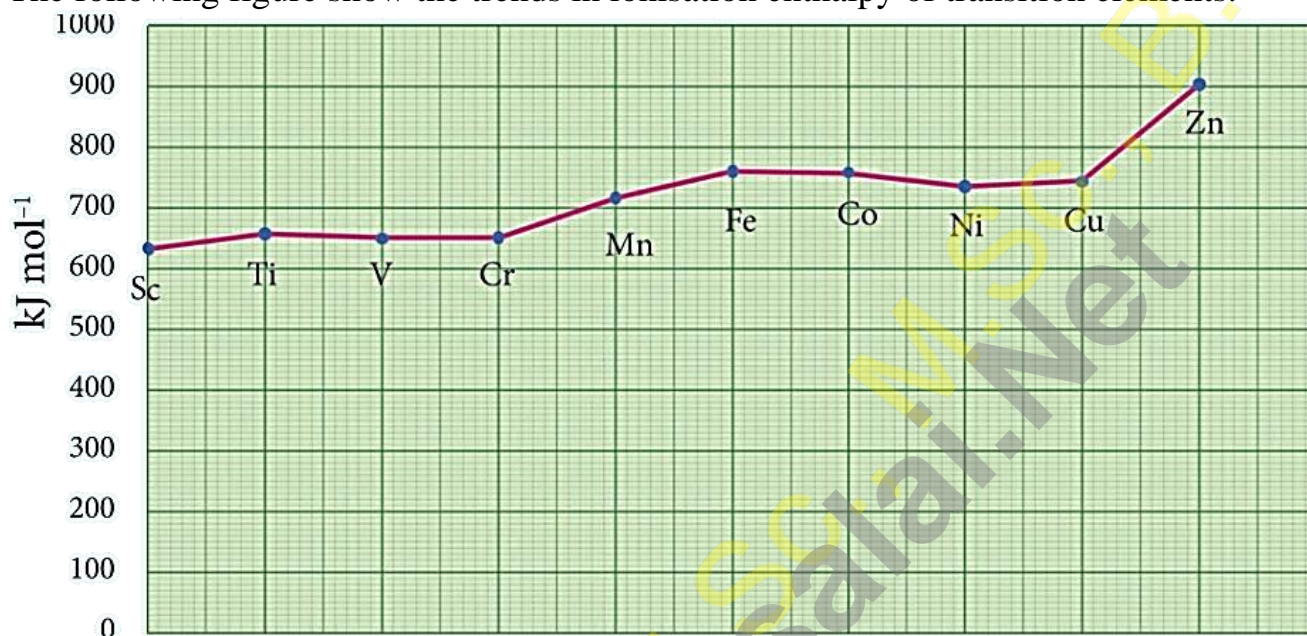
- Transition metals have smaller atomic radii and higher nuclear charger which increase the ionisation energy when compound to alkali metals.
- The first ionisation energy of 5d series of element are much higher than those of 3d and 4d series of elements.
- The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular.
- The added electron enters (n-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.
- The ionisation enthalpy values can be used to predict the thermodynamic stability of their compounds. Let us compare the ionisation energy required to form Ni^{2+} and Pt^{2+} ions.
- For Nickel, IE + IE = 737 + 1753 = 2490 kJmol^{-1}
- For Platinum, IE + IE = 864 + 1791 = 2655 kJmol^{-1}
- Since, the energy required to form Ni^{2+} is less than that of Pt^{2+}, Ni(II) compounds are thermodynamically more stable than Pt(II) compounds.

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

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

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19. Out of LU(OH)₃ and La(OH)₃ which is more basic and why? [PTA-2]

+ $La(OH)_3$ is more basic than $Lu(OH)_3$

+ As we move from Ce^{3+} to Lu^{3+}, the basic character of Lu^{3+} ions decreases.

+ Due to lanthanoid contraction the size of lanthanoid ions decreases regularly with increase in atomic size.

+ Due to the decrease in the size of Lu^{3+} ions, the ionic character of Lu – OH bond decreases, covalent character increases which results in the decrease in the basicity.

+ So actinoid show greater contraction.

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

+ Eu^{2+} Electronic configuration – $[Xe]\ 4f^7\ 5d^0\ 6s^0$

+ Ce^{2+} Electronic configuration – $[Xe]\ 4f^1\ 5d^1\ 6s^0$

+ In Eu(II), 4f subshell a half filled and 5d subshell is empty.

+ According to Aufbau principle, half filled and completely filled d (or) f orbitals are more stable than partially filled f orbitals.

+ Hence $Eu^{2+}\ [Xe]\ 4f^7\ 5d^0\ 6s^0$ is more stable than $Ce^{2+}\ [Xe]\ 4f^1\ 5d^0\ 6s^0$

21. Why do zirconium and Hafnium exhibit similar properties?

+ Zr and Hf exhibit similar properties due to lanthanoid contraction.

+ Electrons present in f subshell have poor shielding due to which with the increasing atomic number or increasing effective nuclear charge, size gets constricted.

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

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

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

+ This can be explained on the basis of the standard electrode potential values.
   $(E^0_{Cr2+/Cr} = -0.91V)$ and $(E^0_{Fe2+/Fe} = -0.44V)$

+ Thus Cr^{2+} is easily oxidised to Cr^{3+} but Fe^{2+} cannot oxidised to Fe^{3+}.

+ Cr^{2+} standard electrode potential values is more negative value.

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

$E^0_{(M2+/M)}$ value for copper metal is the sum of enthalpy changes taking place in the steps given below.
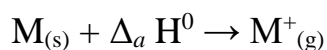
$$M_{(s)} + \Delta_a H^0 \rightarrow M^+_{(g)}$$
$$(\Delta_a H^0 = \text{Standard enthalpy of atomisation})$$
$$M^+_{(g)} + \Delta_i H^0 \rightarrow M^{2+}_{(g)}$$
$$(\Delta_i H^0 = \text{Standard ionisation enthalpy})$$
$$M^{2+}_{(g)} + \Delta_{hyd} H^0_{aq} \rightarrow M^{2+}_{(aq)}$$
$$(\Delta_{hyd} H^0 = \text{Standard hydration enthalpy})$$

Copper has a high enthalpy of atomisation (energy absorbed), but low enthalpy of hydration (energy released)

Thus $E^0_{(Cu2+/Cu)}$ is positive.

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

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

+ At the beginning of the 3d series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.

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

+ Mn^{2+} ($3d^5$) is more stable than Mn^{4+} ($3d^3$) is due to half filled stable configuration.

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

+ Cu is the only metal in the first transition series (2d series) which exhibits only +1 oxidation state most frequently.

+ It is unique in 3d series having a stable +1 oxidation state. This is because the Electronic configuration of Cu (Z = 29) is [Ar] $3d^{10}$ $4s^1$ and after losing one electron it acquires a stable $3d^{10}$ configuration.

+ So copper element only can have +1 oxidation state.

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

+ The first ionization enthalpy of chromium is lower than that of zinc. Cr (Z = 24) Electronic configuration [Ar] $3d^5$ $4s^1$.

+ In the case of Cr, first electron has to be removed easily from 4s orbital to attain the more stable half filled configuration. So Cr has lower ionization enthalpy.

+ But in the case of Zinc (Z = 30), electronic configuration [Ar] $3d^{10}$ $4s^2$.

+ The first electron has to be removed from the most stable fully filled electronic configuration becomes difficult and it requires more energy.

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

+ The melting points of the transition metals are high due to the 3d electrons being available for metallic bonding.

+ As we move from left to right along the transition metal series , melting point first increases as the number of unpaired d electrons available for metallic bonding inceases, reach a maximum value and then decreases, as the d electrons pair up and become less available for bonding.

+ For example, in the first series the melting point inceases from Scandium (m.pt 1814K) to a maximum of 2183K for vanadium, which is close to 2180K for chromium. However, manganese in 3d series and Tc in 4d series have low melting point. The maximum melting point at about the middle of transition metal series indicates that d5 configuration is favourable for strong interatomic attraction.

ELEMENTS EVALUATE YOURSELF

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

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

+ The value of the ionisation enthalpies can be used in estimating the relative stability of various transition metal compounds (or ions).

+ Formation of Pt^{4+} requires lesser energy as compared to the formation of Ni^{4+}

+ Pt^{4+} compounds are stable than Ni^{4+} compounds because the energy needed to remove 4 electrons in Pt is less than that of Ni.

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

✦ Fe (Z = 26). Electronic configuration [Ar] $3d^6 4s^2$

✦ Fe → Fe^{3+} + $3e^-$ Fe^{3+} Electronic configuration [Ar] $3d^5$. If d' orbital is half filled, it is more stable than . Fe^{2+} where it is [Ar] $3d^6$.

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

✦ Mn → Mn^{2+} + $2e^-$ By the loss of $2e^-$, Mn^{2+} is more stable due to half filled configuration.
Mn → Mn^{3+} + $3e^-$. Mn^{3+} Electronic configuration [Ar] $3d^4 4s°$.

✦ Among this Fe^{3+} is more stable than Fe^{2+} and the Mn^{2+} is more stable than Mn^{3+}.

GOVERNMENT EXAM QUESTION PAPER

1. Classify the following elements into d-block and f-block elements: [MAR-20]
　a) Tungstan　　b) Ruthenium　　c) Promethium　　d) Einsteinium

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

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

✦ Transition elements have a tendency to form coordination compounds with a species that has an ability to donate an electron pair to form a coordinate covalent bond.

✦ Transition metal ions are small and highly charged and they have vacant low energy orbitals to accept an electron pair donated by other groups. Due to these properties, transition metals form large number of complexes.

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

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

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

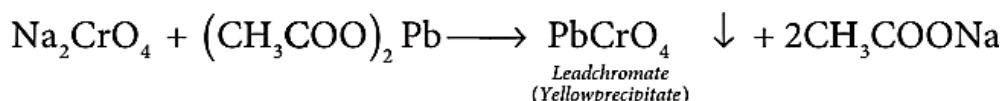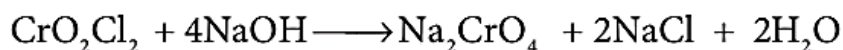Propylene → poly propylene ($TiCl_4 + Al(C_2H_5)_3$)
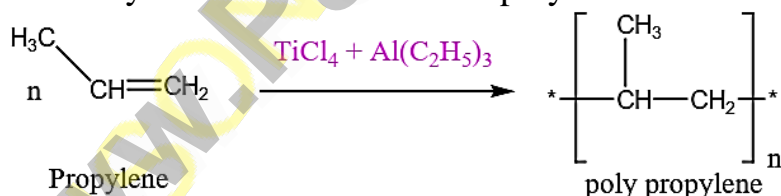
Uses: It is used for polymerisation.

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

✦ When potassium dichromate is heated with any chloride salt in the presence of Conc.H_2SO_4, orange red vapours of chromyl chloride (CrO_2Cl_2) is evolved.

✦ This reaction is used to confirm the presence of chloride ion in inorganic qualitative analysis.

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

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

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

$$Na_2CrO_4 + (CH_3COO)_2 Pb \longrightarrow PbCrO_4 \downarrow + 2CH_3COONa$$
Leadchromate
(Yellowprecipitate)

5. Explain the preparation of potassium permanganate from pyrolusite. (or) Explain the preparation of KMnO₄. [GMQ-19]

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

Conversion of MnO₂ to potassium manganate: Powdered ore is fused with KOH in the presence of air or oxidising agents like KNO_3 or $KClO_3$. A green coloured potassium manganate is formed.

$$2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\substack{potassium\ manganate \\ (Green)}}{2K_2MnO_4} + 2H_2O$$
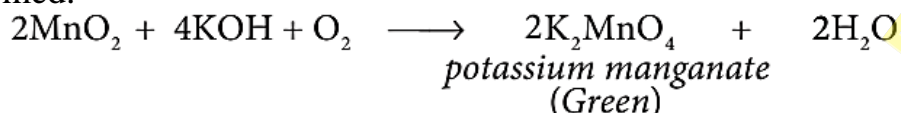
Oxidation of potassium manganate to potassium permanganate: Potassium manganate thus obtained can be oxidised in two ways, either by chemical oxidation or electrolytic oxidation.

Chemical oxidation: In this method potassium manganate is treated with ozone (O_3) or chlorine to get potassium permanganate.
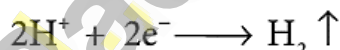
$$2MnO_4^{2-} + O_3 + H_2O \longrightarrow 2MnO_4^- + 2OH^- + O_2$$

$$2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^- + 2Cl^-$$
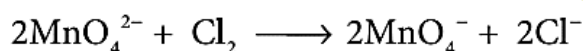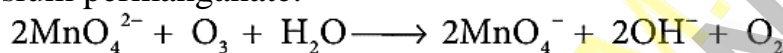
Electrolytic oxidation: In this method aqueous solution of potassium manganate is electrolyzed in the presence of little alkali.

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

$$H_2O \rightleftharpoons H^+ + OH^-$$
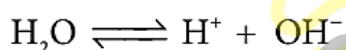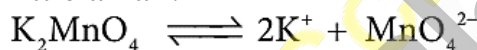
Manganate ions are converted into permanganate ions at anode.

$$\underset{Green}{2MnO_4^{2-}} \rightleftharpoons \underset{purple}{2MnO_4^-} + 2e^-$$
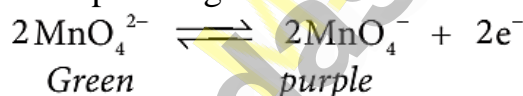
H_2 is liberated at the cathode.
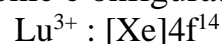
$$2H^+ + 2e^- \longrightarrow H_2 \uparrow$$

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

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

- The common oxidation state of lanthanoids is +3. In addition to that some of the lanthanoids also show either +2 or +4 oxidation states.
- Gd^{3+} and Lu^{3+} ions have extra stability, it is due to the fact that they have exactly half filled and completely filled f-orbitals respectively.their electronic c onfigurations are
  $$Gd^{3+} : [Xe]4f^7 \qquad\qquad Lu^{3+} : [Xe]4f^{14}$$
- Similarly Cerium and terbium attain $4f^0$ and $4f^7$ configurations respectively in the +4 oxidation states. Eu^{2+} and Yb^{2+} ions have exactly half filled and completely filled f orbitals respectively.
- The stability of different oxidation states has an impact on the properties of these elements. The following table shows the different oxidation states of lanthanoids.

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

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

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

8. Calculate the equivalent weight of KMnO₄ in the following reactions. [QY-19]
　a) $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$
　b) $2MnO_4^- + 10Fe^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O$

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

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

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

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

9. (i) The first ionisation energy of Chromium is less than that of Zinc. Why? [SRT-22]
　(ii) Why do 3d series transition elements possess variable oxidation states?

(i) Cr – $[Ar]3d^5 4s^2$　　　　　　　　　　　　　Zn – $[Ar]3d^{10} 4s^2$
Ionisation energy Cr is lower than that of zinc first electron has to be remove from full filled orbital and full filled electronic configuration is more stable than half filled so it require high energy to remove electron from it.

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

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

10. Explain the structure of permanganate ion. [HY-22]
Permanganate ion has tetrahedral geometry in which the central Mn7+ is sp³ hybridised.
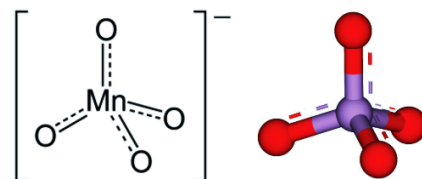
11. Give the conditions for the formation of alloys by Hume-Rothery rule. [SUT-23]

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