Fill Ups of The p-Block Elements

Fill in the Blanks

Q.1. The lowest possible oxidation state of nitrogen is (1980)

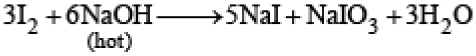
Ans. –3

Solution. –3;

Q.2. Iodine reacts with hot NaOH solution. The products are NaI and .... (1980)

Ans. $NaIO_3$

Solution. $NaIO_3$



$$3I_2 + \underset{(hot)}{6NaOH} \longrightarrow 5NaI + NaIO_3 + 3H_2O$$

Q.3. .... is a weak acid. (HF, HCl, HI) (1981 - 1 Mark)

Ans. HF

Solution. HF; HF is the weakest of the three, because the ionisation (i.e. acidic character) of HX is a multistep process and when its DH, heat of ionisation, is calculated it comes out to be the minimum. This is due to the strong H – F bond, large heat of hydration (because of H-bonding) and low value of electron affinity of F-atom.

Q.4. The increase in the solubility of iodine in an aqueous solution of potassium iodide is due to the formation of .... (1982 - 1 Mark)

Ans. KI_3

Solution. KI_3; complexes are more soluble in water as compared to normal salts. [$KI+I_2 \rightarrow KI_3$]

Q.5. Hydrogen gas is liberated by the action of aluminium with concentrated solution of .... (1987 - 1 Mark)

Ans. Sodium hydroxide

Solution. Sodium hydroxide;

$Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$

Q.6. .... phosphorus is reactive because of its highly strained tetrahedral structure. (1987 - 1 Mark)

Ans. white/ yellow

Solution. white/ yellow; NOTE : In white phosphorus, each phosphorus atom is linked to the other three atoms by covalent bonds. PPP bond angle is 60°, due to which the molecule remains under strain and hence is active in nature.

Q.7. .... acid gives hypo .... ion. (1988 - 1 Mark)

(hydrobromic, hypobromous, perbromic, bromide, bromite, perbromate)

Ans. hypobromous, bromide

Solution. Hypobromous; bromite. $HBrO \rightleftharpoons H^+ + BrO^-$

Q.8. Sulphur acts as .... agent in vulcanization of rubber.
(1989 - 1 Mark)

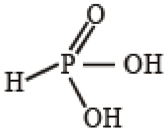
Ans. cross -linking

Solution. Cross-linking;

Q.9. The basicity of phosphorous acid (H_3PO_3) is .... (1990 - 1 Mark)

Ans. two

Solution. **two;**



[It contains two replaceable hydrogens.]

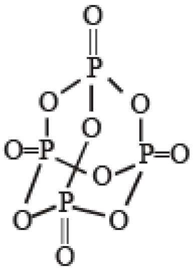
Q.10. The hydrolysis of alkyl substituted chlorosilan es gives ....

Ans. silicones

Solution. Silicones;

Q.11. In P_4O_{10}, the number of oxygen atoms bonded to each phosphorus atom is .... (1992 - 1 Mark)

Ans. 4



Solution. four.

In each P atom is linked to 4 oxygen atoms

Q.12. The lead chamber process involves oxidation of SO_2 by atomic oxygen under the influence of .... as catalyst. (1992 - 1 Mark)

Ans. Nitric oxide

Solution. Nitric oxide. [NO]

The mixture containing SO_2, air and nitric oxide, when treated with steam, sulphuric acid is formed.

$$2SO_2 + \underbrace{O_2 + 2H_2O}_{\text{Air}} + \underset{\text{(Catalyst)}}{[NO]} \rightarrow 2H_2SO_4 + [NO]$$

Q.13. The hydrolysis of trialkylchlorosilane R_3SiCl, yields .... (1994 - 1 Mark)

Ans. Trialkyl chlorosilanol

Solution. Trialkyl chlorosilanol; The hydrolysis of R_3SiCl, yields $R_3Si(OH)$ which condenses to give $R_3Si – O – SiR_3$

$$R_3\,Si\,O - \boxed{H + H - O} - Si\,R_3 \longrightarrow R_3 - Si - O - Si - R_3$$

Q.14. One recently discovered allotrope of carbon (e.g., C_{60}) is commonly known as........... (1994 - 1 Mark)

Ans. fullerene

Solution. Fullerene

Q.15. Solubility of iodine in water is greatly increased by the addition of iodide ions because of the formation of .... (1994 - 1 Mark)

Ans. I^-_3 complex ion

Solution. I^-_3 complex ion $I_2 + I^- \longrightarrow I_3^-$

Q.16. A liquid which is permanently supercooled is frequently called a .... (1997 - 1 Mark)

Ans. glass

Solution. glass

Q.17. Compounds that formally contain Pb^{4+} are easily reduced to Pb^{2+}. The stability of the lower oxidation state is due to .... (1997 - 1 Mark)

Ans. inert-pair effect

Solution. inert-pair effect ; When ns^2 electrons of outermost shell do not participate in bonding it is called inert pair and the effect is called inert pair effect.

True / False of The p-Block Elements

Q.1. Red phosphorus is less volatile than white phosphor us because the former has a tetrahedral structure. (1982 - 1 Mark)

Ans. F

Solution. False : Red phosphorus is polymeric substance. It exist as chains of P_4 tetrahedra linked together. Therefore, it is less volatile than white phosphorus.

Q.2. When PbO_2 reacts with a dilute acid, it gives hydrogen peroxide. (1982 - 1 Mark)

Ans. F

Solution. False : PbO_2 is a dioxide and it does not give hydrogen peroxide when it reacts with a dilute acid.

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

Q.3. Carbon tetrachloride burns in air when lighted to give phosgene. (1983 - 1 Mark)

Ans. F

Solution. False : CCl4 gives phosgene with superheated steam

$CCl_4 + H_2O \rightarrow COCl_2 + 2HCl$

Q.4. Dil. HCl oxidizes metallic Fe to Fe^{2+}. (1983 - 1 Mark)

Ans. T

Solution. True : $Fe + 2HCl \rightarrow FeCl_2 + H_2$ [In $FeCl_2$, Fe is in +2 state.]

Q.5. In aqueous solution chlorine is a stronger oxidizing agent than fluorine. (1984 - 1 Mark)

Ans. F

Solution. False : Since halogens have high electron affinities, they easily pick up electrons from other substances. Hence halogens are oxidising agents. The oxidising power decreases from fluorine to iodine. Since fluorine is the strongest oxidising agent it will oxidise any of the other halide ions in solution or when dry. Similarly, Cl_2 will displace Br– and I– ions from their solutions and Br_2 will displace I– ions.

NOTE : In general, a halogen of low atomic number will oxidise the halide ion of higher atomic number.

Q.6. The H-N-H bond angle in NH_3 is greater than the H-As-H bond angle is AsH_3. (1984 - 1 Mark)

Ans. T

Solution. True : NOTE : The central element in the metal hydrides of group 15 elements is although in sp3 hybrid state, the H – M – H bond angle is less than the normal tetrahedral bond angle of 109º 28'; e.g. the bond angle, H – N – H in NH_3 is 106º 45'.

This is due to greater repulsion between a lone pair and a bond pair of electrons than between the two bond pairs of electrons.

The decrease in bond angle from 106º 45' in ammonia to about 90º in AsH_3 can be explained by the fact that in the latter case sp^3 hybridisation becomes less and less distinct with the increasing size of their electron clouds, i.e., pure p orbitals (instaed of sp^3 hybrid orbitals) are used for M – H bonding and the lone pair of electrons is present in spherical s-orbital.

Q.7. Carbon tetrachloride is inflammable. (1985 - ½ Mark)

Ans. F

Solution. False : because of its high thermal stability. CCl_4 is most stable as compared to other tetrachloride's of the group.

Q.8. Graphite is better lubricant on the moon than on the earth. (1987 - 1 Mark)

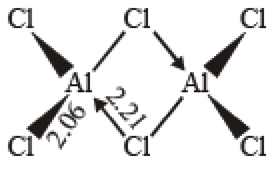
Ans. T

Solution. True : Graphite is better lubricant on the moon than on the earth because of lack of gravitation pull on the moon, where friction is already less than earth.

Q.9. All the Al–Cl bonds in Al_2Cl_6 are equivalent. (1989 - 1 Mark)

Ans. F

Solution.



Structure of Al_2Cl_2

Bond distance between aluminium-chlorine bond forming bridge is greater (2.21 Å) than the distance between aluminium-chlorine bond present in the end (2.06 Å).

Q.10. Nitric oxide, though an odd electron molecule, is diamagnetic in liquid state. (1991 - 1 Mark)

Ans. T

Solution. True : The molecule of NO has eleven valence electrons (5 due to N and 6 due to O). It is impossible for all of them to be paired, hence the nitric oxide molecule contains an odd electron which makes gaseous nitric oxide paramagnetic.

NOTE : In the liquid and solid states, nitric oxide is polymerised to a dimer which is diamagnetic.

Q.11. Diamond is harder than graphite. (1993 - 1 Mark)

Ans. T

Solution. True : In diamond, each carbon atom is in sp^3 hybridised state and is linked to four other neighbouring carbon atoms held at the corners of a regular tetrahedron by covalent bonds.

Owing to very strong covalent bonds by which the atoms are held together, diamond is the hardest substance known. Graphite has a two dimensional sheet like structure and carbon in sp^2 hybridised state is attached to three other carbon atoms by three s bonds forming a hexagonal planar structure. Due to wide separation and weak interlayer bonds, the two adjacent layers can easily slide over each other; hence graphite is soft.

Q.12. The tendency for catenation is much higher for C than for Si. (1993 - 1 Mark)

Ans. T

Solution. True : The property of catenation in carbon is due to the fact that in carbon atom, the number of valence electrons (4) is equal to the number of valence orbitals (one 2s + three 2p).

Hence carbon in the tetravalent state is fully saturated, i.e., it has neither any vacant orbital nor any lone pair of electrons on its atom due to which the C – C bond is extremely stable.

NOTE : The reason for greater tendency of carbon for catenation than silicon may further be explained by the fact that the C – C bond energy is approximately of the same magnitude as the energies of the bond between C and other elements.

On the other hand, the Si – Si bond is weaker than the bonds between silicon and other elements.

Q.13. HBr is a stronger acid than HI because of hydrogen bonding. (1993 - 1 Mark)

Ans. F

Solution. False : None amongst, HBr and HI, HI exhibit hydrogen bonding. HI is a stronger acid than HBr because of its higher dissociation constant, K_a. HI has a stronger tendency to release protons to water molecules and hence is a stronger acid.

Subjective Problems of The p-Block Elements (Part -1)

Q.1. Account for the following. Limit your answer to two sentences
(i) Hydrogen bromide cannot be prepared by action of concentrated sulphuric acid or sodium bromide.
(ii) When a blue litmus paper is dipped into a solution of hypochlorous acid, it first turns red and then later gets decolourised. (1979)

Solution. (i) HBr is a reducing agent and it reduces H_2SO_4 to SO_2.

(ii) Acids turn blue litmus red, so HClO also turns blue litmus red. The colour of litmus is decolourised because HClO is also a strong oxidising agent.

Q.2. Write balanced equation involved in the preparation of
(i) Anhydrous aluminium chloride from alumina.
(ii) Bleaching powder from slaked lime.
(iii) Tin metal from cassiterite
(iv) Chlorine from sodium chloride.
(v) Nitric oxide from nitric acid.

Solution.

(i) $$\underset{\text{Alumina}}{Al_2O_3} + 3C + 3Cl_2 \longrightarrow \underset{\substack{\text{Aluminium}\\ \text{chloride}}}{2AlCl_3} + 3CO$$

(ii) $$\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \longrightarrow \underset{\substack{\text{bleaching}\\ \text{powder}}}{CaOCl_2} + H_2O$$

(iii) $$\underset{\text{Cassiterite}}{SnO_2} + 2C \longrightarrow \underset{\text{Tin}}{Sn} + 2CO$$

(iv) $$\underset{\substack{\text{Sodium}\\ \text{chloride}}}{2NaCl} + MnO_2 + 2H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

(v) $$3Cu + \underset{\text{Nitric acid}}{8HNO_3} \longrightarrow \underset{\text{Nitric oxide}}{2NO} + 3Cu(NO_3)_2 + 4H_2O$$

Q.3. State with balanced equations, what happens when :
(i) Tin is treated with moderately concentrated nitric acid.
(ii) Aluminium is reacted with hot concentrated caustic soda solution

Solution.

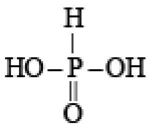
(i) $Sn + 4HNO_3 \longrightarrow \underset{\text{Metastanic acid}}{H_2SnO_3} + 4NO_2 + H_2O$

(ii) $2Al + 2NaOH + 2H_2O \longrightarrow \underset{\text{Sod. aluminate}}{2NaAlO_2} + 3H_2$

Q.4. Give structural formula for the following :
(i) Phosphorous acid, H_3PO_3 (1981 - 1 Mark)
(ii) Pyrophosphoric acid, $H_4P_2O_7$ (1981 - 1 Mark)

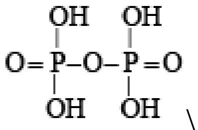
Solution.

(*i*)



$$HO-\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{P}}-OH$$

(*ii*)



$$O=\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}=O$$

\

Q.5. Complete the following equations (no balancing is needed)

(*i*) $HCO_3^- + Al^{3+} \longrightarrow Al(OH)_3 + ...$ (1981 - 1 Mark)

(ii) $AlBr_3 + K_2Cr_2O_7 + H_3PO_4 \longrightarrow K_3PO_4 + AlPO_4 + H_2O$ +....+.... (1981 - 1 Mark)

Solution.

(*i*) $HCO_3^- + Al^{3+} \rightarrow Al(OH)_3 + CO_3^{2-}$

(*ii*) $AlBr_3 + K_2Cr_2O_7 + H_3PO_4$
$\rightarrow K_3PO_4 + AlPO_4 + H_2O + Br_2 + Cr^{3+}$

Q.6. Give reasons for the following :

(i) Carbon acts as an abrasive and also as a lubricant. (1981 - 1 Mark)

(ii) Sulphur melts to a clear mobile liquid at 119ºC, but on further heating above 160ºC, it becomes viscous. (1981 - 1 Mark)

(iii) In the preparation of hydrogen iodide from alkali iodides, phosphoric acid is preferred to sulphuric acid (1982 - 1 Mark)

(iv) Orthophosphate or acid, H_3PO_4, is tribals but phosphorous acid, H_3PO_3, is dibasic. (1982 - 1 Mark)

(v) A bottle of liquor ammonia should be cooled before opening the stopper. (1983 - 1 Mark)

(vi) Solid carbon dioxide is known as dry ice. (1983 - 1 Mark)

(vii) Anhydrous HCl is a bad conductor of electricity but aqueous HCl is a good conductor; (1985 - 1 Mark)

(viii) Graphite is used as a solid lubricant; (1985 - 1 Mark)

(ix) Fluorine cannot be prepared from fluorides by chemical oxidation. (1985 - 1 Mark)

(x) The mixture of hydrazine and hydrogen peroxide with a copper(II) catalyst is used as a rocket propellant. (1987 - 1 Mark)

(xi) Orth phosphorus acid is not tribasic acid. (1987 - 1 Mark)

(xii) The molecule of magnesium chloride is linear whereas that of stannous chloride is angular. (1987 - 1 Mark)

(xiii) Valency of oxygen is generally two whereas sulphur shows valency of two, four and six. (1988 - 1 Mark)

(xiv) H_3PO_3 is a dibasic acid. (1989 - 1 Mark)

(xv) Phosphine has lower boiling point than ammonia. (1989 - 1 Mark)

(xvi) Ammonium chloride is acidic in liquid ammonia solvent. (1991 - 1 Mark)

(xvii) The hydroxides of aluminium and iron are insoluble in water. However, NaOH is used to separate one from the other. (1991 - 1 Mark)

(xviii) Bond dissociation energy of F_2 is less than that of Cl_2. (1992 - 1 Mark)

(xix) Sulphur dioxide is a more powerful reducing agent in an alkaline medium than in acidic medium. (1992 - 1 Mark)

(xx) The experimentally determined N – F bond length in NF_3 is greater than the sum of the single covalent bond radii of N and F. (1995 - 2 Marks)

(xxi) Mg_3N_2 when reacted with water gives off NH_3 but HCl is not obtained from $MgCl_2$ on reaction with water at room temperature. (1995 - 2 Marks)

(xxii) $(SiH_3)_3N$ is a weaker base than $(CH_3)_3N$. (1995 - 2 Marks)

Solution. (i) Carbon exists in various allotropic forms like diamond, graphite, coal, etc. Diamond consists of a three dimensional structure of sp_3 hybridised carbon atoms bonded through very strong covalent bonds. It makes it hard and useful as an abrasive.

Graphite, on the other hand, is made up of a two dimensional sheet like structure made of sp_2 hybridised carbon atoms. These layers of carbon atoms are held together by relatively weak van der Waal's forces and can, therefore, slip over one another imparting lubricating properties to graphite.

(ii) Sulphur consists of S8 rings held together by weak van der Waal's forces. As sulphur melts at 119ºC, these van der Waal's forces are overcome and S8 rings slip and roll over one another giving rise to a clear mobile liquid. Above 160ºC, the S8 rings begin to open up and form long chains which gets tangled with each other, thereby gradually increasing the viscosity.

(iii) NOTE : HI cannot be prepared by heating hydrogen iodide with conc. H_2SO_4 because it is a strong reducing agent and reduces H_2SO_4 to SO_2 and is itself oxidised to iodine.

$H_2SO_4 + 2HI \rightarrow SO_2 + I_2 + 2H_2O$

Hence HI is prepared by heating iodides with conc. phosphoric acid.
$3KI + H_3PO_4 \rightarrow K_3PO_4 + 3HI$

(iv) In H_3PO_4 and H_3PO_3 the P atom is attached to 3 and 2 OH groups respectively. The H atom of these P – OH bonds are invisible. This clearly shows that H_3PO_4 is tribasic and H_3PO_3 is dibasic.

(v) Liquor ammonia possesses high vapour pressure at room temperature and thus before opening a bottle of liquor ammonia, it should be cooled to lower the pressure of NH_3 inside the bottle, otherwise NH_3 will bump out of the bottle.

(vi) Solid CO_2 is technically known as dry ice because it sublimes without leaving any stain on surface.

(vii) Anhydrous HCl, being a non - polar covalent compound, is a bad conductor however an aqueous solution of HCl is ionised (Fajan's rule) to give H^+ and Cl^- ions and is a good conductor.

(viii) In graphite, out of four valence electrons, only three form covalent bonds (sp^2 hybridisation) with three other carbon atoms. This forms hexagonal rings as sheets of one atom thickness. These sheets are held together by weak attractive forces. One electron of each carbon atom is free and this enables these thin sheets to slide over one another. For this reason graphite is a soft material with lubricating properties.

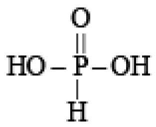
(ix) The standard reduction potential of fluorine is highest and thus it cannot be oxidized by any reagent

$$\left(\frac{1}{2}\right) F_2 + e \longrightarrow F^-;\ E^\circ_{RP} = \text{maximum}$$

(x) The mixture of N2H4 and H_2O_2 (in presence of Cu (II) catalyst) is used as a rocket propellant because the reaction is highly exothermic and large volume of gases are evolved, which can propel a rocket.

$$\underset{\text{Hydrazine}}{N_2H_4} + \underset{\substack{\text{Hydrogen}\\ \text{peroxide}}}{2H_2O_2} \xrightarrow{Cu(II)} N_2(g)\uparrow + 4H_2O(g)\uparrow$$

(xi) Orth phosphorus acid is a dibasic acid a s it has 2–OH groups in its formula:



$$HO-\overset{\overset{O}{||}}{\underset{\underset{H}{|}}{P}}-OH$$

(xii) In $MgCl_2$, Mg is sp hybridised while in $SnCl_2$, Sn is sp^2 hybridised (hence the molecule is angular).

(xiii) **NOTE :** Oxygen is the 2nd most electronegative element after the fluorine and thus invariably show negative oxidation state.

Further more, it has $2s^22p^4$ configuration and thus requires only two electrons to complete its octet to show –2 oxidation state. Although sulphur also possess ns^2np^4 configuration but due to availability of d-orbitals in their outer most shell –2, +2, +4, +6 oxidation state are also shown. Oxygen, however, shows only –2 oxidation state due to non-availability of d-orbitals in its outermost shell.

(xiv) NOTE : H_3PO_3 is a dibasic acid because it contains two OH groups in its molecule.

In the two P–OH bonds, the hydrogen is ionisable. [For structure see part (xi)]

(xv) NOTE : As compared to P, N atom has higher electronegativity and small size and shows H-bonding.

Thus ammonia molecule show association where as phosphine does not.

(xvi) It is due to self ionization of NH_3, the reaction is

$$2NH_3 \rightarrow NH_4^+ + NH_2^-$$

Thus on addition of NH_4Cl the concentration of NH^+_4 radical increases and therefore NH_4Cl acts as an acid in liquid NH_3.

(xvii) In excess of NaOH the hydroxide of Al becomes soluble due to the formation of meta-aluminate.

(xviii) The repulsive forces between fluorine atoms are high due to its small size and high electronegativity. It makes dissociation of F – F bond easy. So bond dissociation energy of F_2 is less than Cl_2

(xix) The reducing nature of SO_2 is represented as

$$SO_2 + 2OH^- \rightarrow SO_4^{2-} + 2H^+ + 2e^-$$

Hence with the increase of OH^- (alkalinity) the forward reaction is favoured.
(xx) Nitrogen and fluorine both are small and have high electron density, they repel the bonded pair of electrons leading to larger bond length than expected.
(xxi) N^{3-} being smaller in size and high charge present on it make it more susceptible to hydrolysis:

$$N^{3-} + 3H_2O \rightarrow NH_3 + 3OH^-$$

Cl^- being a weak conjugate base does not undergo hydrolysis. $MgCl_2$ is stronger electrolyte and so it is not hydrolysed.

(xxii) In $(SiH_3)_3N$, lone pair of electrons on nitrogen is involved in pπ – dπ back bonding, while in $(CH_3)_3N$ no such pπ – dπ back bonding is possible because of absence of d orbitals in carbon so $(CH_3)_3N$ is more basic than $(SiH_3)_3N$.

Q.7. State with balanced equations what happens when :

(i) White phosphorous (P_4) is boiled with a strong solution of sodium hydroxide in an inert atmosphere. (1982/87 - 1 Mark)

(ii) Sodiumiodate is treated with sodium bisulphite solution. (1982 - 1 Mark)

(iii) Dilute nitric acid is slowly reacted with metallic tin. (1987 - 1 Mark)
(iv) Potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid. (1987 - 1 Mark)

(v) Iodate ion reacts with bisulphite ion to liberate iodine. (1988 - 1 Mark)

(vi) Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide. (1988 - 1 Mark)

(vii) Hypophosphorous acid is heated. (1989 - 1 Mark)

(viii) Sodium bromate reacts with fluorine in presence of alkali.
(1989 - 1 Mark)

(ix) Sodium chlorate reacts with sulphur dioxide in dilute sulphuric acid medium. (1989 - 1 Mark)

(x) Write balanced equations for the preparation of crystalline silicon from $SiCl_4$. (1990 - 1 Mark)

(xi) Write balanced equations for the preparation of phosphine from CaO and white phosphorus. (1990 - 2 Marks)

(xii) Write balanced equations for the preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide. (1990 - 1 Mark)

(xiii) Aqueous solution of sodiumnitrate is heated with zinc dust and caustic soda solution. (1990 - 1 Mark)

(xiv) Sodium iodate is added to a solution of sodium bisulphite.
(1990 - 1 Marks)

(xv) Sodium nitrite is produced by absorbing the oxides of nitrogen in aqueous solution of washing soda. (1991 - 1 Mark)

(xvi) Nitrogen is obtained in the reaction of aqueous ammonia with potassium permanganate. (1991 - 1 Mark)

(xvii) Elemental phosphorus reacts with conc. HNO_3 to give phosphoric acid. (1991 - 1 Mark)

(xviii) Sulphur is precipitated in the reaction of hydrogen sulphide with sodium bisulphite solution. (1991 - 1 Mark)

(xix) Phosphorus is treated with concentrated nitric acid. (1997 - 1 Mark)

OR

Manufacture of phosphoric acid from phosphorus. (1997 - 1 Mark)

(xx) Reaction of aluminium with aqueous sodium hydroxide. (1997 - 1 Mark)

(xxi) Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. (1997 - 2 Marks)

(xxii) $P_4O_{10} + PCl_5 \rightarrow$ (1998 - 1 Mark)

(xxiii) $SnCl_4 + C_2H_5Cl + Na \rightarrow$ (1998 - 1 Mark)

Solution. (i) Phosphine gas (PH_3) is evolved when white phosphorous is boiled with aqueous NaOH or alcoholic solution of potassium hydroxide.

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{Sod. Hypophosphite}}{NaH_2PO_2} + PH_3\uparrow$$

(ii) This is a method used to prepare I_2.

$5NaHSO_3 + 2NaIO_3 \rightarrow 3NaHSO_4 + 2Na_2SO_4 + I_2 + H_2O$

(*iii*) $4Sn + \underset{\text{(dilute)}}{10HNO_3} \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$

(*iv*) $2KMnO_4 + 3H_2SO_4$
$\rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$
$5H_2C_2O_4 + 5[O] \rightarrow 10CO_2\uparrow + 5H_2O$

(*v*) $2IO_3^- + 5HSO_3^- \rightarrow I_2 + H_2O + 3HSO_4^- + 2SO_4^{2-}$

(*vi*) $4P + 10HNO_3 + H_2O \rightarrow 5NO + 5NO_2 + 4H_3PO_4$

(*vii*) $2H_3PO_2 \xrightarrow{\text{Heat}} \underset{\text{Phosphine}}{PH_3} + H_3PO_4$

(*viii*) $NaBrO_3 + F_2 + 2NaOH \rightarrow NaBrO_4 + 2NaF + H_2O$
(*ix*) $NaClO_3 + SO_2 + 10H^+ \rightarrow NaCl + S + 5H_2O$

(*x*) $3SiCl_4 + \underset{\text{(molten)}}{4Al} \xrightarrow{\Delta} 4AlCl_3\uparrow + 3Si$

(*xi*) $15CaO + 4P_4 \xrightarrow{\Delta} 5Ca_3P_2 + 3P_2O_5\uparrow$
$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3\uparrow\,] \times 5$
$\overline{15CaO + 4P_4 + 30H_2O \rightarrow 15Ca(OH)_2 + 3P_2O_5 + 10PH_3\uparrow}$
(*xii*) $CaSO_4 + 2NH_3 + CO_2 + H_2O \rightarrow CaCO_3\downarrow + (NH_4)_2SO_4$

(*xiii*) $NaNO_2 + 6H \xrightarrow{Zn/NaOH} NaOH + NH_3 + H_2O$
(*xiv*) $2NaIO_3 + 5NaHSO_3 \rightarrow 2Na_2SO_4 + 3NaHSO_4 + I_2 + H_2O$
(*xv*) $Na_2CO_3 + NO + NO_2 \rightarrow 2NaNO_2 + CO_2$
(*xvi*) $4KMnO_4 + 2H_2O \rightarrow 4MnO_2 + 4KOH + 3O_2$
$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

(*xvii*) $P_4 + 20HNO_3 \xrightarrow[\text{catalyst}]{I_2 \text{ as}} 4H_3PO_4 + 20NO_2 + 4H_2O$

(*xviii*) $2H_2S + NaHSO_3 + H^+ \rightarrow 3S\downarrow + 3H_2O + Na^+$

(*xix*) $[2HNO_3 \rightarrow H_2O + 2NO_2 + [O]] \times 10$

$$P_4 + 10[O] \rightarrow P_4O_{10}$$

$$\underline{P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4}$$
$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

(*xx*) $2Al + 2NaOH + 6H_2O \rightarrow \underset{\substack{\text{Sodium} \\ \text{meta-aluminate}}}{2NaAlO_2} + 2H_2O + 3H_2O$

(*xxi*) $Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + \underset{\text{(foul odour)}}{3H_2S\uparrow}$

Foul odour, on damping of Al_2S_3 is due to formation of H_2S gas, which smells like rotten eggs.

(*xxii*) $P_4O_{10} + 6PCl_5 \rightarrow 10POCl_3$

(*xxiii*) $SnCl_4 + 2C_2H_5Cl + Na \rightarrow C_4H_{10} + Na_2[SnCl_6]$

Q.8. Show with equation s h ow the following compound is prepared (equations need not be balanced) sodium thiosulphate from sodium sulphite.
(1982 - 1 Mark)

Solution. By boiling Na_2SO_3 solution with powder of sulphur in absence of air sodium thiosulphate is prepared. Unreacted S is removed, filtrate is evaporated to give crystals of sod. This sulphate.

$$\mathbf{Na_2SO_3 + S \rightarrow Na_2S_2O_3}$$

Q.9. Give balanced equations for the extraction of aluminium from bauxite by electrolysis. (1982 - 2 Marks)

Solution. Extraction of aluminium from bauxite:

$4AlF_3 + (\textit{from cryolite}) \rightleftharpoons 4Al^{3+} + 12F^-$

At cathode : $4Al^{3+} + 12e^- \rightarrow 4Al$

At anode : (i) $12F^{-} \rightarrow 6F_2 + 12e^{-}$

(ii) $2Al_2O_3 + 6F_2 \rightarrow 4AlF_3 + 3O_2$

Q.10. State the conditions under which the following preparation is carried out. Give the necessary equations which need not be balanced : Alumina from aluminium. (1983 - 1 Mark)

Solution.

$$Al + NaOH \xrightarrow{aq.} NaAlO_2$$

$$\xrightarrow{2H_2O} Al(OH)_3 \xrightarrow{heat} Al_2O_3\,(\text{Alumina})$$

Q.11. Write down the resonance structures of nitrous oxide. (1985 - 2 Marks)

OR

Write the two resonance structures of N_2O that satisfy the octet rule. (1990 - 1 Mark)

Solution. N_2O has two principal resonance structures :

$${}^{-}:\ddot{N}=\overset{+}{N}=\ddot{O}: \longleftrightarrow :N\equiv\overset{+}{N}-\underset{..}{\ddot{O}}:^{-}$$

Q.12. Write down the balanced equations for the reactions when:
(i) a mixture of potassium chlorate, oxalic acid and sulphuric acid is heated; (1985 - 1 Mark)

(ii) Ammonium sulphate is heated with a mixture of nitric oxide and nitrogen dioxide. (1985 - 1 Mark)
Solution. (i) $KClO_3 + 2H_2C_2O_4 + H_2SO_4 \rightarrow KHSO_4 + HCl + 6CO_2 + 3H_2O$

(ii) $(NH_4)_2SO_4 + NO + NO_2 \rightarrow 2N_2 + 3H_2O + H_2SO_4$

Q.13. What happens when :

(i) hydrogen sulphide is bubbled through an aqueous solution of sulphur

dioxide. (1985 - 1 Mark)

(ii) tin is treated with concentrated nitric acid. (1985 - 1 Mark)

(iii) Pb_3O_4 is treated with nitric acid. (1985 - 1 Mark)

Solution. (i) H_2S oxidises into S,

$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$

(ii) $\underset{\text{conc.}}{Sn + 4HNO_3} \rightarrow \underset{\text{meta stannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$

(iii) $Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O + PbO_2\downarrow$

Q.14. Arrange the following in :

(i) increasing bond strength (1986 - 1 Mark)
HCl, HBr, HF, HI

(ii) HOCl, $HOClO_2$, $HOClO_3$, HOClO in increasing order of thermal stability. (1988 - 1 Mark)

(iii) CO_2, N_2O_5, SiO_2, SO_3 in the order of increasing acidic character. (1988 - 1 Mark)

(iv) Increasing order of extent of hydrolysis :
CCl_4, $MgCl_2$, $AlCl_3$, PCl_5, $SiCl_4$ (1991 - 1 Mark)

Ans. (i) $HI < HBr < HCl < HF$,

(ii) $HOCl < HOClO < HOClO_2 < HOClO_3$

(iii) $SiO_2 < CO_2 < N_2O_5 < SO_3$,

(iv) $CCl_4 < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$

Solution.

(i) $HI < HBr < HCl < HF$

The strength of H–X bond decreases from HF to HI.

The larger is H–X bond length, lower is the bond energy, lesser is the bond strength.

(ii) HOCl < HOClO < $HOClO_2$ < $HOClO_3$ As the number of oxygen atoms increase, the -ve charge dispersal becomes more and more from Cl atom due to more electronegativity of oxygen atom and thus lesser is the charge on Cl atom, more will be its stability.

(iii) $SiO_2 < CO_2 < N_2O_5 < SO_3$.
Among oxides of the non-metals, the acidic strength increases with oxidation state. Hence SO_3 (O.S. of S = +6) is most acidic followed by N_2O_5 (O.S. of N = +5) and CO_2 and SiO_2 (O.S. of C and Si = +4). Further CO_2 is more acidic than SiO_2 because of small size of C-atom.

(iv) Since carbon has no d-orbital, it cannot extend its coordination number beyond four, its halides are not attacked (hydrolysed) by water. On the other hand, silicon have vacant d-orbitals to which water molecules can coordinate and hence their halides are hydrolysed by water.

NOTE : Increasing order of extent of hydrolysis

$CCl_4 < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$

Q.15. Mention the products formed in the following :
(i) Chlorine gas is bubbled through a solution of ferrous bromide. (1986 - 1 Mark)
(ii) Iodine is added to a solution of stannous chloride. (1986 - 1 Mark)
(iii) Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride. (1986 - 1 Mark)

Solution.

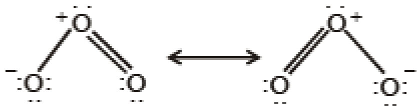
(*i*) $2FeBr_2 + 3Cl_2 \rightarrow 2FeCl_3 + 2Br_2$
(*ii*) $2SnCl_2 + 2I_2 \rightarrow SnCl_4 + SnI_4$

(*iii*) $SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow H_2SO_4$

$H_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2HCl$

Q.16. Write the two resonance structures of ozone which satisfy the octet rule. (1991 - 1 Mark)

Solution. The two resonating structures of ozone are :



Q.17.

$PbS \xrightarrow[\text{air}]{\text{heat in}} A + PbS \xrightarrow{B}$ **Pb + SO_2; Identify A and B. (1991 - 2 Marks)**

Ans. [A]-PbO, [B]-heat in the absence of air

Solution.

$$3PbS \xrightarrow[\text{air}]{\text{heat in}} \underset{(A)}{2PbO} + PbS$$

$$\xrightarrow{\text{heat in the absence of air (B)}} 3Pb + SO_2$$

Q.18. Complete and balance the following chemical reactions :

(i) Red phosphorus is reacted with iodine in presence of water. (1992 - 1 Mark)

$P + I_2 + H_2O \rightarrow$ .... + ...

(ii) Anhydrous potassium nitrate is heated with excess of metallic potassium.

(1992 - 1 Mark)

$KNO_3(s) + K(s) \rightarrow$ .... + ...

(iii) $NH_3 + NaOCl \rightarrow$ .... + ... (1993 - 1 Mark)

(iv) $Sn + 2KOH + 4H_2O \rightarrow$ .... + ...

Solution.(i) $2P + 3I_2 + 6H_2O \rightarrow 2H_3PO_4 + 6HI$

(ii) $2KNO_3 + 10K \rightarrow 6K_2O + N_2$

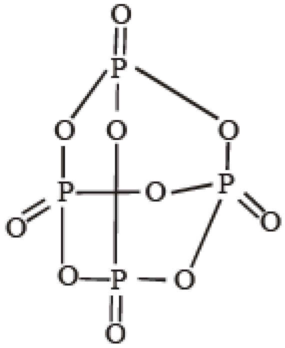
(iii) $2NH_3 + NaOCl \rightarrow \underset{\text{Hydrazine}}{H_2N.NH_2} + NaCl + H_2O$

(iv) $Sn + 2KOH + 4H_2O \rightarrow K_2Sn(OH)_6 + 2H_2$

Q.19. Draw the structure of P_4O_{10} and identify the number of single and double P—O bonds. (1996 - 3 Marks)

Ans. 12, 4

Solution.



Number of P – O single bonds = 12
Number of P – O double bonds = 4

Q.20. Gradual addition of KI solution to $Bi(NO_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions. (1996 - 2 Marks)

Solution. At first $Bi(NO_3)_3$ hydrolyses to give nitric acid which, being an oxidising agent, oxidises potassium iodide liberating free iodine responsible for dark brown precipitate. Iodine dissolves in excess of potassium iodide forming soluble KI_3 imparting yellow colour to solution

$$\begin{array}{l}
Bi(NO_3)_3 + H_2O \longrightarrow [Bi(OH)(NO_3)_2] + HNO_3 \\
NO_3^- + 4H^+ + 3e^- \longrightarrow NO_2 + 2H_2O\,] \times 2 \\
\qquad\quad 2I^- \longrightarrow I_2 + 2e^-\,] \times 3 \\
\hline
2NO_3^- + 8H^+ + 6I^- \longrightarrow 2NO + 4H_2O + \underset{\text{(dark brown ppt)}}{3I_2\downarrow}
\end{array}$$

$$KI + I_2 \longrightarrow \underset{\text{(Yellow solution)}}{KI_3}$$

Q.21. Complete the following chemical equations:
(a) $KI + Cl2 \rightarrow$
(b) $KCIO_3 + l_2 \rightarrow$

Justify the formation of the products in the above reactions. (1996 - 2 Marks)

Solution. $2KI + Cl_2 \rightarrow 2KCl + I_2$
Since Cl_2 is more powerful oxidising agent than I_2, Cl_2 is able to displace I^- to form I_2.

$$2I^- \rightarrow I_2 + 2e^-, \qquad E^\circ = +0.54\,V \qquad ...(i)$$

$$Cl_2 + 2e^- \rightarrow 2Cl^- \qquad E^\circ = 1.36V \qquad ...(ii)$$

On subtracting eq. (i) from eq. (ii), we get

$$Cl_{2(g)} + 2I^-_{(aq)} + \rightarrow 2Cl^-_{(aq)} + I_{2(s)} \quad E^\circ = 0.82V$$

(b) $2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl2$.

Here ClO_3^- is more powerful oxidising agent than

IO_3^-, so Cl is displaced by I.

$$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O,\ E^\circ = 1.195V \quad ...(i)$$

$$2ClO_3^- + 12H^+ + 10e^- \rightarrow Cl_2 + 6H_2O, E^\circ = 1.47V \ ..(ii)$$

On subtracting eq. (i) from eq. (ii), we get

$$2ClO_3^- + I_2 \rightarrow 2IO_3^- + Cl_2 \qquad E^\circ = 0.275V$$

Subjective Problems of The p-Block Elements (Part -2)

Q.22. A soluble compound of a poisonous element M, when heated with Zn/H_2SO_4 gives a colourless and extremely poisonous gaseous compound N, which on passing through a heated tube gives a silvery mirror of element M. Identify M and N. (1997 - 2 Marks)

Ans. M = As,N = AsH_3

Solution.

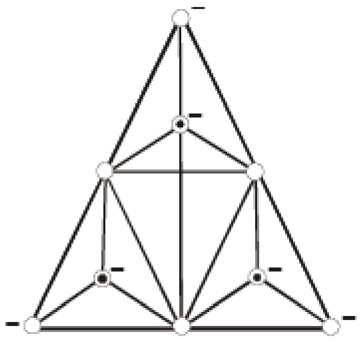
$$AsCl_3 + 6H \xrightarrow{Zn/H_2SO_4} \underset{(N)}{AsH_3} + 3HCl$$

$$2AsH_3 \xrightarrow{\Delta} \underset{(M)}{2As} + 3H_2 \uparrow$$

Hence $M = As;\ N = As\,H_3$

Q.23. Draw the structure of a cyclic silicate, $(Si_3O_9)^{6-}$ with proper labelling. (1998 - 4 Marks)

Solution. In cyclic $Si_3O_9^{6-}$, three tetrahedral of SiO_4^{2-} are joined together sharing two oxygen atoms per tetrahedron.



Dark circle represents Si and open circle represents oxygen atom/ion

Structure of $Si_3O_9^{6-}$;

Q.24. Thionyl chloride can be synthesized by chlorinating SO_2 using PCI_5. Thionyl chloride is used to prepare anhydrous ferric chloride starting from its hexahydrated salt.
Alternatively, the anhydrous ferric chloride can also be prepared from its hexahydrated salt by treating with 2, 2 – dimethoxypropane. Discuss all this using balanced chemical equations. (1998 - 6 Marks)

Solution.

$$SO_2 + PCl_5 \rightarrow \underset{\text{Thionyl chloride}}{SOCl_2} + POCl_3$$

$$FeCl_3 . 6H_2O + 6SOCl_2 \rightarrow FeCl_3 + 12HCl + 6SO_2$$

$$FeCl_3 . 6H_2O + 6CH_3 - C(OCH_3)_2 - CH_3$$
$$\rightarrow FeCl_3 + 12CH_3OH + 6CH_3COCH_3$$

Q.25. Reaction of phosphoric acid with $Ca_5(PO_4)_3F$ yields a fertilizer "triple superphosphate". Represent the same through balanced chemical equation. (1998 - 2 Marks)

Solution.

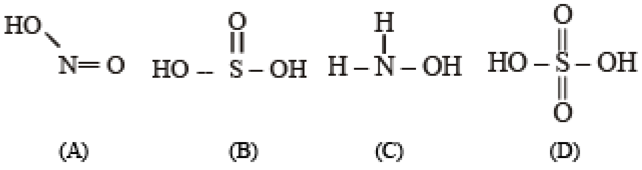
$$7H_3PO_4 + Ca_5(PO_4)_3F \rightarrow \underset{\text{Triple superphosphate}}{5Ca(H_2PO_4)_2} + HF$$

Q.26. In the following equation, (1999 - 6 Marks)
$A + 2B + H_2O \rightarrow C + 2D$
($A = HNO_2$, $B = H_2SO_3$, $C = NH_2OH$). Identify D. Draw the structures of A, B, C and D.

Solution. The reaction is

$$\underset{(A)}{HNO_2} + \underset{(B)}{2H_2SO_3} + H_2O \rightarrow \underset{(C)}{NH_2OH} + \underset{(D)}{2H_2SO_4}$$

The structures of A, B, C and D are as follows.

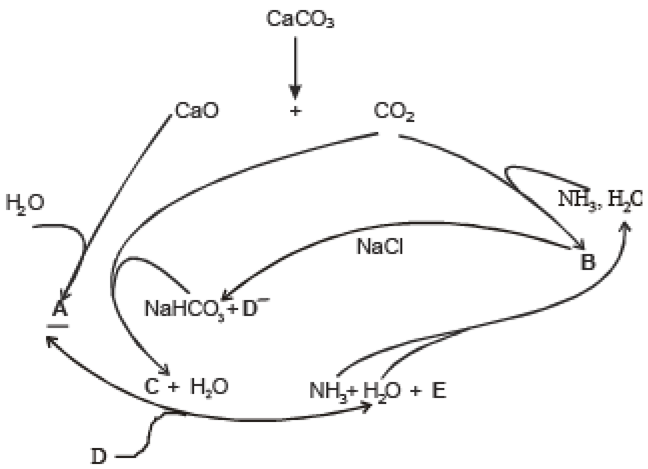


Q.27. In the contact process for industrial manufacture of sulphuric acid some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of SO_2? (1999 - 4 Marks)

Solution: Sulphur trioxide produced in the contact process is absorbed by sulphuric acid forming $H_2S_2O_7$. It is not dissolved in water as it gives a dense fog of sulphuric acid particles.

The catalyst used in the contact process is vanadium pentoxide.

Q.28. The Haber process can be represented by the following scheme;



Identify A, B, C, D and E. **(1999 - 5 Marks)**

Ans. $\underset{A}{Ca(OH)_2}, \underset{B}{NH_4HCO_3}, \underset{C}{Na_2CO_3}, \underset{D}{NH_4Cl}, \underset{E}{CaCl_2}$

Solution. In such a case

A = $Ca(OH)_2$, B = NH_4HCO_3, C = Na_2CO_3, D = NH_4Cl and E = $CaCl_2$

$$CaO + H_2O \longrightarrow \underset{(A)}{Ca(OH)_2}$$

$$NH_3 + CO_2 + H_2O \longrightarrow \underset{\text{Sod. Bicarbonate(B)}}{NH_4HCO_3}$$

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + \underset{\text{Amm. chloride(D)}}{NH_4Cl}$$

$$2NaHCO_3 \xrightarrow{\Delta} \underset{\text{Sod. carbonate (C)}}{Na_2CO_3} + H_2O + CO_2$$

$$Ca(OH)_2 + 2NH_4Cl \longrightarrow \underset{(E)}{CaCl_2} + \underset{\substack{\text{can be}\\\text{used again}}}{2NH_3} + 2H_2O$$

Q.29. Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction (2000 - 2 Marks).

Solution. More electronegative halogen displaces lesser electronegative halogen from its halide. Thus,

$Cl_2 + 2KBr$ (or 2 KI) $\rightarrow 2KCl + Br_2$ (or I_2)

Q.30. Draw the molecular structures of XeF_2, XeF_4 and XeO_2F_2 indicating the location of lone pair(s) of electrons. (2000 - 3 Marks)

Solution. TIPS/Formulae :

Use the formula

H (hydridisation) $H = \frac{1}{2}(V + M - C + A)$ where

V = number of electron in valence shell of central atom

M = number of monovalent atoms surrounding the central atom

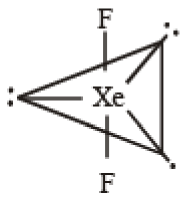
C = Charge on cation

A = Charge on anion

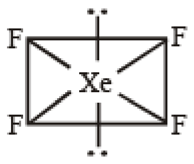
XeF_2 : $H = \frac{1}{2}(8+2-0+0) = 5$ Hence hybridisation is sp3d, and thus its structure is linear.

XeF, : $H = \frac{1}{2}(8+4-0+0) = 6$, Hence hybridisation is sp^3d^2. and thus its structure is square planar.

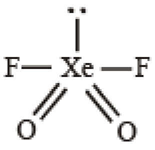
XeO_2F_2 : $H = \frac{1}{2}(8+2-0+0) = 5$, Hence hybridisation is sp^3d. and shape is see saw.



XeF_2



XeF_4



XeO_2F_2

Q.31. Give reason(s) why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus as a tetratomic molecule. (2000 - 2 Marks)

Solution. Elemental nitrogen exists as a diatomic molecule because nitrogen can form pπ - pπ multiple bonds which is not possible in case of phosphorus due to repulsion between non-bonded electrons of the inner core. There is no such repulsion in case of smaller nitrogen atoms as they have only $1s^2$ electrons in their inner core.

Q.32. Compound (X) on reduction with $LiAlH_4$ gives a hydride (Y) containing 21.72% hydrogen along with other products. The compound (Y) reacts with air explosively resulting in boron trioxide. Identify (X) and (Y). Give balanced reactions involved in the formation of (Y) and its reaction with air.
Draw the structure of (Y). (2001 - 5 Marks)

Ans. BCl_3 or BBr_3, B_2H_6

Solution. Since B_2O_3 is formed by reaction of (Y) with air, (Y) therefore should be

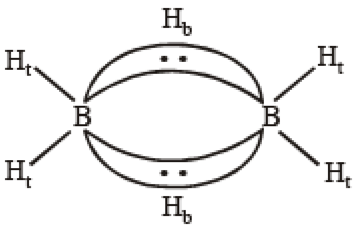
B_2H_6 in which % of hydrogen is 21.72. The compound (X) on reduction with

$LiAlH_4$ gives B_2H_6. Thus it is boron trihalide. The reactions are shown as:

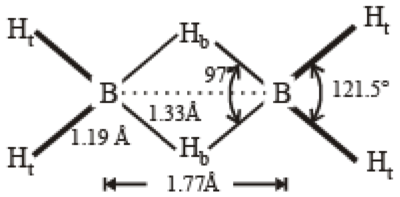
$$\underset{(X)}{4BX_3} + 3LiAlH_4 \longrightarrow \underset{(Y)}{2B_2H_6} + 3LiX + 3AlX_3 \qquad (X = Cl \text{ or } Br)$$

$$\underset{(Y)}{B_2H_6} + 3O_2 \longrightarrow B_2O_3 + 3H_2O + \text{heat}$$

Structure of B_2H_6 is as follows:



or



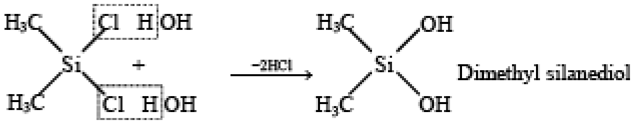
Thus the diborane molecule has four two-centre- two -electron bonds (2c – 2e bonds) also called usual bonds and two three-centre-two -electron bonds (3c – 2e) also called banana bonds. Hydrogen attached to usual and banana bonds are called H_t (terminal H) and H_b (bridged H) respectively.

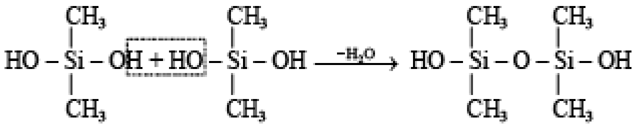
Q.33. Starting from $SiCl_4$, prepare the following in steps not exceeding the number

given in parentheses (give reactions only):
(i) Silicon (1)
(ii) Linear silicone containing methyl groups only (4)
(iii) Na_2SiO_3 (3)

Solution. (i) $SiCl_4 + 2Mg(\text{or } Zn) \rightarrow Si + 2MgCl_2$ (or $ZnCl_2$)

(ii) $SiCl_4 + 2CH_3MgCl \rightarrow (CH_3)_2SiCl_2 + 2MgCl_2$





$$HO-\overset{CH_3}{\underset{CH_3}{Si}}-OH + HO-\overset{CH_3}{\underset{CH_3}{Si}}-OH \xrightarrow{-H_2O} HO-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-OH$$

Polymerisation continues on both ends to give linear silicone.

(iii) $SiCl_4 + 2Mg \longrightarrow Si + 2MgCl_2$

$Si + Na_2CO_3 \longrightarrow Na_2SiO_3 + C$

$SiCl_4 + 4H_2O \longrightarrow Si(OH)_2 + 4HCl$

$Si(OH)_2 \xrightarrow{\text{heat}} SiO_2 + 2H_2O$

$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$

Q.34. Write balanced equations for the reactions of the following compounds with water : (2002 - 5 Marks)
(i) Al_4C_3
(ii) CaNCN
(iii) BF_3
(iv) NCl_3
(v) XeF_4

Solution.

(i) $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4 \uparrow$

(ii) $CaNCN + 3H_2O \longrightarrow CaCO_3 \downarrow + 2NH_3$

Ammonia formed dissolves in water to form NH_4OH

$$CaNCN + 5H_2O \longrightarrow 2NH_4OH + CaCO_3 \downarrow$$

(iii) $4BF_3 + 3H_2O \longrightarrow 3HBF_4 + B(OH)_3$

(iv) $NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$

(v) $3XeF_4 + 6H_2O \longrightarrow XeO_3 + 2Xe + \frac{3}{2}O_2 + 12HF$

Q.35. How is boron obtained from borax? Give chemical equations with reaction conditions. Write the structure of B_2H_6 and its reaction with HCl. (2002 - 5 Marks)

Solution. NOTE : When hot con centrated HCl is added to borax ($Na_2B_4O_7.10H_2O$) the sparingly soluble H_3BO_3 is formed which on subsequent heating gives B_2O_3 which is reduced to boron on heating with Mg, Na or K

$Na_2B_4O_7$ (anhydrous) + 2HCl(hot, conc.)

$\rightarrow 2NaCl + H_2B_4O_7$

$$H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3 \downarrow$$

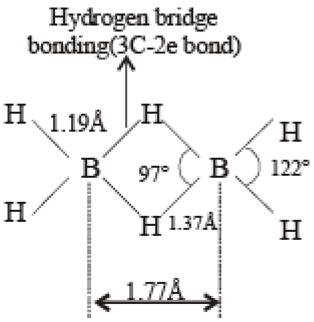
$$2H_3BO_3 \xrightarrow{\text{strong heating}} B_2O_3 + 3H_2O$$

$$B_2O_3 + 6K \longrightarrow 2B + 3K_2O \text{ or}$$

$$B_2O_3 + 6Na \longrightarrow 2B + 3Na_2O \text{ or}$$

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

Structure of B_2H_6



$B_2H_6 + HCl \rightarrow B_2H_5Cl + H_2$

[NOTE : Normally this reaction takes place in the presence of Lewis acid ($AlCl_3$)]

Q.36. Write down reactions involved in the extraction of Pb. What is the oxidation number of lead in litharge? (2003 - 2 Marks)

Ans. O.N. of Pb in PbO is +2

Solution.

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
$$PbS + 2O_2 \longrightarrow PbSO_4$$
$$PbS + 2PbO \longrightarrow 3Pb + SO_2$$
$$PbS + PbSO_4 \longrightarrow 2Pb + 2SO_2$$

Q.37. Identify the following:

$$Na_2CO_3 \xrightarrow{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow[\Delta]{\text{Elemental S}} C \xrightarrow{I_2} D$$

Also mention the oxidation state of S in all the compounds.

Ans. $\underset{A}{NaHSO_3\,(OS=+4)}, \underset{B}{Na_2SO_3\,(OS=+4)}, \underset{C}{Na_2S_2O_3\,(OS=-2)}, \underset{D}{Na_2S_4O_6\,(OS=+2.5)}$

Solution.

$$Na_2SO_3 + S \rightarrow \underset{(C)}{2Na_2S_2O_3}$$

$$2Na_2S_2O_3 + I_2 \rightarrow \underset{(D)}{2Na_2S_4O_6} + 2NaI$$

Oxidation states of 'S' are : + 4 in (A) , (+ 6) in B and + 2 in (C), + 2.5 in (D)

Q.38. AlF_3 is insoluble in anhydrous HF but it becomes soluble in presence of little amount of KF. Addition of boron trifluoride to the resulting solution causes reprecipitation of AlF_3.

Explain with balanced chemical equations. (2004 - 2 Marks)

Solution. HF is weakly dissociated, while KF is highly dissociated giving a high concentration of F– which leads to the formation of soluble AlF_6^{3-}.

$AlF_3 + 3\,KF \rightarrow K_3[AlF_6]$

Since BF_3 is more acidic than AlF_3, it pulls out F– from AlF_6^{3-} reprecipitating AlF_3.

$$K_3[AlF_6]+3BF_3 \rightarrow 3KBF_4+AlF_3\downarrow$$

Q.39. How many grams of CaO are required to neutralize 852 gm of P4O10 ? Draw structure of P_4O_{10} molecule. (2005 - 2 Marks)

Ans. 1008 g

Solution.

$$6\,CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$$

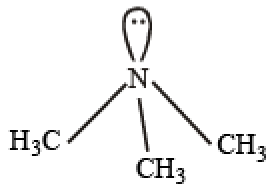
$$\text{Moles of } P_4O_{10} = \frac{852}{284} = 3$$

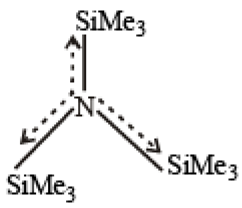
Moles of CaO = 3 × 6 = 18; wt. of CaO = 18 × 56 = 1008 g

For structure of P_4O_{10} : See question 20 of this section.

Q.40. Write the structures of $(CH_3)_3$ N and $(Me_3Si)_3$ N . Are they isostructural? Justify your answer. (2005 - 2 Marks)

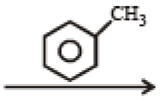
Solution. $(CH_3)_3$ N and $(Me_3Si)_3$ N are not isostructural, the former is pyramidal while the latter is trigonal planar. Silicon has vacant d orbitals which can accommodate lone pair of electrons from N (back bonding) leading to planar shape.





Q.41.

$$(B) \xleftarrow{NaBr+MnO_2} (A) \xrightarrow{Conc.HNO_3} (C)$$



(D) (explosive product)

Ans. $\underset{A}{\text{Conc. } H_2SO_4}, \underset{B}{Br_2}, \underset{C}{NO_2^+}, \underset{D}{\text{TNT}}$

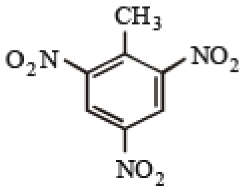
Solution.

A. Conc. H_2SO_4

B. Br_2

C. NO_2^+

D.



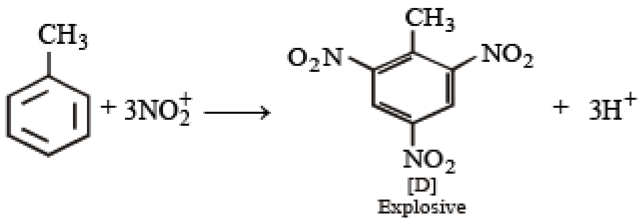
TNT

Reactions involved are

$$\underset{[A]}{2\,NaBr + 2\,H_2SO_4} + MnO_2$$

$$\longrightarrow Na_2SO_4 + MnSO_4 + \underset{\substack{[B] \\ \text{Brown fumes} \\ \text{and pungent smell}}}{Br_2 \uparrow} + 2\,H_2O$$

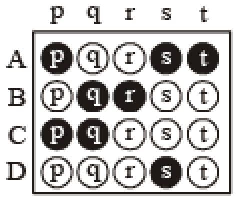
$$H_2SO_4 + HNO_3 \longrightarrow HSO_4^- + \underset{[C]}{NO_2^+} + H_2O$$



Match the Following, Integer Value of The p-Block Elements

Match the Following

DIRECTIONS (Q. 1 to 3) : Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:
If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.



Q.1. Match gases under specified conditions listed in Column I with their properties/laws in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

Column I	**Column II**
(A) Explosive	**(p) NaN_3**
(B) Artificial gem	**(q) Fe_3O_4**
(C) Self reduction	**(r) Cu**
(D) Magnetic material	**(s) Al_2O_3**
	(t) Pb(N3)2
	(u) Fe2O3
	(v) Cu
	(w) SiC

Ans. (A)-t; (B)-s; (C)-v; (D)-u

Solution. (A)-(t), Pb(N3)2 is an explosive

(B)-(s), Al_2O_3 is used to prepare artificial gun

(C)-(v), Extraction of copper involves self-reduction process.

(D)-(u), Fe_2O_3 is a magnetic material.

Q.2. Match the following :

	Column I		Column II
(A)	$Bi^{3+} \longrightarrow (BiO)^+$	(p)	Heat
(B)	$[AlO_2]^- \longrightarrow Al(OH)_3$	(q)	Hydrolysis
(C)	$[SiO_4]^{4-} \longrightarrow [Si_2O_7]^{6-}$	(r)	Acidification
(D)	$[B_4O_7]^{2-} \longrightarrow [B(OH)_3]$	(s)	Dilution by water

Ans. (A)-q; (B)-s; (C)-p; (D)-r

Solution. (A)-(q), Bi^{3+} hydrolyses to yield BiO^+ ion

(B)-(s), AlO_2^- on dilution yields a white ppt. of $Al(OH)_3$

(C)-(p), When heated $(SiO_4)^{4-}$ changes to $(Si_2O_7)^{6-}$

(D)-(r), When acidified $(B_4O_7)^{2-}$ gives $B(OH)_3$ (or H_3BO_3)

Q.3. Match each of the diatomic molecules in Column I with its property/properties in Column II.

Column I	Column II
(A) B_2	**(p) Paramagnetic**
(B) N_2	**(q) Undergoes oxidation**
(C) O^-_2	**(r) Undergoes reduction**
(D) O_2	**(s) Bond order $\geq$ 2**
	(t) Mixing of 's' and 'p' orbital

Ans. (A)-p, r, t; (B)-s, t ; (C)-p, q, r ; (D)-p, r, s

Solution.

(A) B_2 $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^1 = \pi 2p_z^1$

Bond order = 1 Paramagnetic

(B) N_2 $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2 = \pi 2p_z^2$

Bond order = 3 Diamagnetic

(C) O_2^- $\sigma 1s^2, \sigma^* 1s^2; \sigma 2s^2 . \sigma^* 2s^2; \sigma 2p_x^2, \pi 2p_y^2$

$$= \pi 2p_z^2, \pi^* 2p_y^2 = \pi^* 2p_z^1$$

Bond order = 1.5 Paramagnetic

(D) O_2 $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2$

$$= \pi 2p_z^2, \pi^* 2p_y^1 = \pi^* 2p_z^1$$

Bond order = 2 Paramagnetic

DIRECTIONS (for Q. 4) : Following question has matching lists. The codes for the lists have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

Q.4. The unbalanced chemical reactions given in List I show missing reagent or condition (?) which are provided in List II. Match List I with List II and select the correct answer using the code given below the lists

	List I		List II
P.	$PbO_2 + H_2SO_4 \xrightarrow{?} PbSO_4 + O_2 +$ other product	1.	NO
Q.	$Na_2S_2O_3 + H_2O \xrightarrow{?} NaHSO_4 +$ other product	2.	I_2
R.	$N_2H_4 \xrightarrow{?} N_2 +$ other product	3.	Warm
S.	$XeF_2 \xrightarrow{?} Xe +$ other product	4.	Cl_2

Codes :

	P	Q	R	S
(a)	4	2	3	1
(b)	3	2	1	4
(c)	1	4	2	3
(d)	3	4	2	1

Ans. (d)

Solution.

(P)

$$2PbO_2 + 2H_2SO_4 \xrightarrow{\text{Warm}} 2PbSO_4 + 2H_2O + O_2$$

(Q)

$$Na_2S_2O_3 + 5H_2O + 4Cl_2 \longrightarrow 2NaHSO_4 + 8HCl$$

(R) $N_2H_4 + 2I_2 \longrightarrow N_2 + 4HI$

(S) $XeF_2 + 2NO \longrightarrow Xe + 2NOF$

Integer Value Correct Type

Q.1. The coordination number of Al in the crystalline state of $AlCl_3$ is (2009)

Ans. 6

Solution. Coordination number of Al is 6. It exists in ccp lattice with 6 coordinate layer structure.

Q.2. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is (2010)

Ans. 3

Solution. Total cationic charge = Total anionic charge

$2n + 6 + 24 = 36 \Rightarrow n = 3$

Q.3. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is (2011)

Ans. 5

Solution. $3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$

Q.4. Among the following, the number of compounds than can react with PCl_5 to give $POCl_3$ is (2011)

O_2, CO_2, SO_2, H_2O, H_2SO_4, P_4O_{10}

Ans. 4

Solution. $PCl_5 + SO_2 \longrightarrow POCl_3 + SOCl_2$

$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$

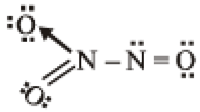
$PCl_5 + H_2SO_4 \longrightarrow POCl_3 + SO_2Cl_2 + 2HCl$

$6PCl_5 + P_4O_{10} \longrightarrow 10POCl_3$

Q.5. The total number of lone pairs of electrons in N_2O_3 is (JEE Adv. 2015)

Ans. 8

Solution.



Number of lone pairs = 8

Q.6. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is (JEE Adv. 2015)

Ans. 6

Solution. $3B_2H_6 + 18CH_3OH \rightarrow 6B(OCH_3)_3 + 18H_2$