NCERT Solutions for Class 12 Chemistry

Chapter 7 The p Block Elements

INTEXT Questions

Question 1.
Why are pentahalides more covalent than trihalides?
Solution:
Higher the positive oxidation state of central atom, more will be its polarising power which, in turn, increases the covalent character of bond formed between the central atom and the other atom.

Question 2.
Why is BiH_3 the strongest reducing agent amongst all the hydrides of group 15 element?
Solution:
Because BiH_3 is the least stable among the hydrides of group 15.

Question 3.
Why is N_2 less reactive at room temperature?
Solution:
Because of strong pπ – pπ overlap resulting into the triple bond. N = N due to which the bond dissociation energy of N_2 is very high rendering it less reactive.

Question 4.
Mention the conditions required to maximise the yield of ammonia.
Solution:
$N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta_f H = -46.1$ kj mol^{-1}
In accordance with Le Chatelier's principle high pressure and low temperature would favour formation of ammonia. The optimum conditions for the production of ammonia are a pressure of about 200 atm, a temperature of about 700K and use of a catalyst such as iron oxide with small amount of K_2O and Al_2,O_3 as promoters.

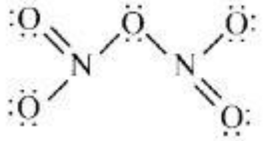
Question 5.
How does ammonia react with a solution of Cu^{2+}?
Solution:
NH_3 in the form of solution reacts with Cu^{2+} to form a complex with deep blue colour.

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons \underset{\text{(deep blue)}}{[Cu(NH_3)_4]^{2+}_{(aq)}}$$

Question 6.
What is the covalence of nitrogen in N_2O_5?
Solution:

From the structure of N_2O_5, it is evident that covalence of nitrogen is four.

N_2O_5 :



Question 7.
Bond angle in PH_4^+ is higher than in PH_3. Why?
Solution:
Both are sp^3 hybridised. In PH_4^+ all the four orbitals are bonded whereas in PH_3 there is a lone pair of electrons on P, which is responsible for lone pair-bond pair repulsion in PH_3 reducing the bond angle to less than 109° 28′.

Question 8.
What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2?
Solution:
When white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2, phosphine gas is liberated.

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{Phosphine}}{PH_3} + 3NaH_2PO_2$$

Question 9.
What happens when PCl_5 is heated?
Solution:
On heating PCl_5 sublimes and is converted to PCl_3 on stronger heating.

$$PCl_5 \xrightarrow{\text{heat}} PCl_3 + Cl_2$$

Question 10.
Write a balanced equation for the hydrolytic reaction of PCl_5 in heavy water.
Solution:
$PCl_5 + D_2O \rightarrow POCl_3, + 2DCl$

Question 11.
What is the basicity of H_3PO_4?
Solution:
Three P – OH groups are present in the molecule of H_3PO_4. Therefore, its basicity is three.

Question 12.
What happens when H_3PO_3 is heated?
Solution:
On heating phosphorous acid dispropotionates to give orthophosphoric acid and

phosphine.
$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

Question 13.
List the important sources of sulphur.
Solution:
Combined sulphur exists as sulphates, such as gypsum, epsom, baryte and sulphides such as galena, zinc blende, copper pyrites, etc. Traces of sulphur occur as hydrogen sulphide in volcanoes. Few organic materials like eggs, proteins, garlic, onion, mustard, hair and wool contain sulphur. 0.03 – 0.1% sulphur is present in the earth's crust.

Question 14.
Write the order of thermal stability of the hydrides of group 16 element.
Solution:
$H_2O > H_2S > H_2Se > H_2Te$

Question 15.
Why is H_2O a liquid and H_2S a gas?
Solution:
Because of small size and high electronegativity of oxygen, molecules of water are highly associated through hydrogen bonding resulting in its liquid state.

Question 16.
Which of the following does not react with oxygen directly? Zn,Ti, Pt, Fe.
Solution:
Platinum does not react with oxygen directly

Question 17.
Complete the following reactions :

1. $C_2H_4 + O_2 \rightarrow$
2. $4Al + 3\ O_2 \rightarrow$

Solution:

1. $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
2. $4Al + 3O_2 \rightarrow 2Al_2O_3$

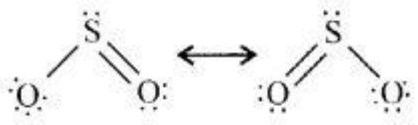
Question 18.
Why does O_3 act as a powerful oxidising agent?
Solution:
Due to the ease with which ozone liberates nascent oxygen atoms, it acts as a powerful oxidising agent.
$O_3 \rightarrow O_2 + O$

Question 19.
How is O_3 estimated quantitatively?
Solution:
When ozone reacts with an excess of KI solution buffered with a borate buffer (pH = 9.2), iodine is liberated which can be titrated against standard solution of sodium thiosulphate. This is used as a method of estimation of ozone quantitatively.

Question 20.
What happens when sulphur dioxide is passed through an aqueous solution of Fe(lll) salt?
Solution:
When sulphur dioxide is passed through an aqueous solution of ferric ions, ferric ions are reduced to ferrous ions.

$$Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

Question 21.
Comment on the nature of two S — O bonds formed in SO_2 molecule. Are the two S — O bonds in this molecule equal?
Solution:
Both the S—O bonds are covalent and have equal strength due to resonating structures.



Question 22.
How is the presence of SO_2 detected?
Solution:
Presence of SO_2 is detected by bringing a paper dipped in acidified potassium dichromate near the gas. If the paper turns green, it shows the presence of SO_2 gas.

$$\underset{\text{(Orange)}}{K_2Cr_2O_7} + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + \underset{\text{(Green)}}{Cr_2(SO_4)_3} + H_2O$$

Question 23.
Mention three areas in which H_2SO_4 plays an important role.
Solution:

1. In manufacture of fertilisers.
2. In manufacture of pigments, paints and dyestuff intermediates.
3. In detergent industry

Question 24.
Write the conditions to maximise the yield of H_2SO_4 by Contact process.
Solution:
The key step in the manufacture of sulphuric acid is oxidation of SO_2 to SO_3 in

presence of V_2O_5 catalyst.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3, \ \Delta H = -196.6 \text{ kJ mol}^{-1}$$

The reaction is exothermic and reversible. Hence, low temperature and high pressure are the favourable conditions for maximum yield of SO_3. In practice a pressure of 2 bar and temperature of 720 K is maintained.

Question 25.
Why is $K_{a2} \ll K_{a1}$ for H_2SO_4 in water?
Solution:
H_2SO_4 is a very strong acid in water largely because of its first ionisation to H_3O^+ and HSO_4^- The ionisation of HSO_4^- to H_3O^+ and SO_4^{2-} is very very small. That is why, $K_{a2} \ll K_{a1}$.

Question 26.
Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidising power of F_2 and Cl_2.
Solution:
Fluorine is a better oxidising agent than chlorine because $E°_{F2/F-}$ is higher than $E°_{Cl2/Cl-}$ It is mainly due to low bond dissociation energy, high hydration energy and lower electron gain enthalpy, non-availability of d-orbitals in valence shell, that results in higher reduction potential of F_2 than chlorine.

Question 27.
Give two examples to show the anomalous behaviour of fluorine.
Solution:

1. Ionisation enthalpy, electro-negativity and electrode potential are higher for fluorine than the expected trends of other halogen.
2. Fluorine does not show any positive oxidation state except in HOF.

Question 28.
Sea is the greatest source of some halogens. Comment.
Solution:
Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium but sodium chloride being the maximum makes sea water saline. Various sea weeds contain upto 0.5% iodine.

Question 29.
Give the reason for bleaching action of Cl_2.
Solution:
Chlorine bleaches by oxidation $Cl_2 + H_2O \rightarrow HCl + HOCl \rightarrow HCl + [O]$
The nascent oxygen reacts with dye to make it colourless.

Question 30.
Name two poisonous gases which can be prepared from chlorine gas.
Solution:
$COCl_2$ (phosgene), CCl_3NO_2 (tear gas)

Question 31.
Why is ICI more reactive than I2?
Solution:
In general, interhalogen compounds are more reactive than halogens due to weaker X-X' bonding than X-X bond. Thus, ICI is more reactive than I_2.

Question 32.
Why is helium used in diving apparatus?
Solution:
A mixture of helium and oxygen does not cause pain due to very low solubility of helium in blood as compared to nitrogen.

Question 33.
Balance the following equation :
$XeF_6 + H_2O \rightarrow XeO_2F_2 + 4HF$
Solution:

Question 34.
Why has it been difficult to study the chemistry of radon?
Solution:
Radon is radioactive with very short half-life which makes the study of chemistry of radon difficult.

NCERT Exercises

Question 1.
Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.
Solution:
The valence shel 1 electronic configuration of group 15 elements is ns2np3. Due to half- filled p-orbitals, these elements have extra stability associated with them.

The common oxidation states of these elements are – 3, +3 and +5. The tendency to exhibit -3 oxidation state decreases down the group. The stability of +5 state decreases and that of +3 state increases down the group due to inert pair effect.

The size of group 15 elements increases down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to presence of completely filled d and or f orbitals in heavier members.

Down the group, ionisation enthalpy decreases due to increase in atomic size. Due to stable half-filled configuration, they have much greater value than that of group 14 elements.

The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.

Question 2.
Why does the reactivity of nitrogen differ from phosphorus?
Solution:
Nitrogen has a unique ability to form pπ – pπ multiple bonds with itself and with other elements having small size and high electronegativity. Consequently, its bond enthalpy is very high and reactivity is less. Another factor which affects the chemistry of N is the absence of d-orbitals in its valence shell. As a result, not only the covalency of N is restricted to four, it can also not form dn – pn bonds. P on the other hand, does not form pn – pn bonds and hence it only forms a P – P single bond, which can easily be broken. Also, phosphorus has vacant d-orbitals and can form dn – dn bond with transition metals to form compounds which can act as ligands.

Question 3.
Discuss the trends in chemical reactivity of group 15 elements.
Solution:
Nitrogen has very low reactivity due to unavailability of vacant d-orbital and high bond dissociation energy of N ≡ N bond.

(a) Hydrides : General formula for hydrides is MH_3, e.g., NH_3, PH_3, ASH_3, SbH_3, BiH_3. All these hydrides are covalent in nature and have pyramidal structure (sp^3 hybridized).

Property	Down the group	Reason
Basic strength of MH_3	decreases	The size of central atom increases, electron density decreases.
Thermal stability of MH_3	decreases	The size of the central atom increases, its tendency to form stable $M-H$ bonds decreases.
Reducing character	increases	The stability of hydrides decreases, thus the reducing character increases.
Melting and boiling point	increases (except in N)	NH_3 has high melting point and boiling point than PH_3 due to hydrogen bonding. As the molecular size increases van der Waals forces increases.

(b) Halides – Elements of group 15 form two types of halides viz. trihalides and pentahalides. The halides are predominantly basic (Lewis bases) in nature and have lone pair of electrons (central atom is sp3 hybridized). The pentahalides are thermally less stable than the trihalides.

Property	Gradation	Reason
Stability of trihalides of nitrogen	$NF_3 > NCl_3 > NBr_3$	Large size difference between N and the halogens
Lewis base strength	$NF_3 < NCl_3 < NBr_3 < NI_3$	Decreasing electronegativity of halogens
Bond angle among the halides of phosphorus	$PF_3 < PCl_3 < PBr_3 < PI_3$	Due to decreased bond pair-bond pair repulsion

(c) Oxides – All the elements of this group form two types of oxides ie., M_2O_3 and M_2O_5 and are called trioxides and pentoxides

Property	Gradation	Reason
Acidic strength of trioxides	$N_2O_3 > P_2O_3 > As_2O_3$	Electronegativity of central atom decreases
Acidic strength of pentoxide	$N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5 > Bi_2O_5$	Electronegativity of central atom decreases.
Acidic strength of oxides of nitrogen	$N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$	Oxidation state of central atom increases

Stability of pentoxide	P_2O_5 > As_2O_5 > Sb_2O_5 > N_2O_5 > Bi_2O_5	Stability of oxides of a higher oxidation state *i.e.*, M_2O_5 decreases with increasing atomic number

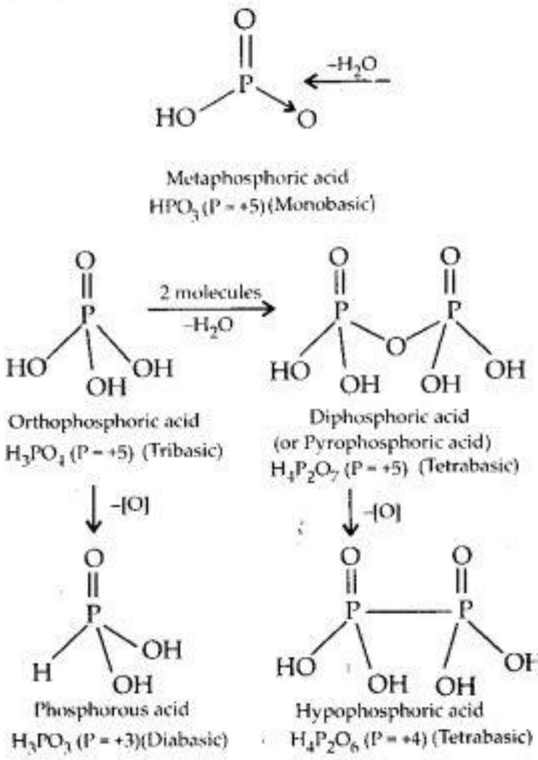
(d) Oxoacids – The elements of this group form a number of oxoacids out of which those of N and P are more common.

Oxoacids of N :

Formula (Name)	Ox. state of N
$H_2N_2O_2$ (Hyponitrous acid)	+1
HNO_2 (Nitrous acid)	+3
HNO_3 (Nitric acid)	+5

Oxo-acids of P :

Formula (Name)	Ox. state	Basicity
H_3PO_3 (Phosphorous acid)	+3	2
H_3PO_4 (Orthophosphoric acid)	+5	3
HPO_3 (Metaphosphoric acid)	+5	1
$H_4P_2O_6$ (Hypophosphoric acid)	+4	4
$H_2P_2O_7$ (Pyrophosphoric acid)	+5	4



Question 4.
Why does NH_3 form hydrogen bond but PH_3 does not?
Solution:
Hydrogen bond is formed between electronegative atom and hydrogen atom. Nitrogen is an electronegative atom and electronegativity decreases down the group so PH_3 cannot form H – bond.

Question 5.
How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.
Solution:
In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl_{(aq)} + NaNO_{2(aq)} \rightarrow N_{2(g)} + 2H_2O_{(l)} + NaCl_{(aq)}$$

Small amounts of NO and HNO_3 are also formed in this reaction. These impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate. It can also be obtained by the thermal decomposition of ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

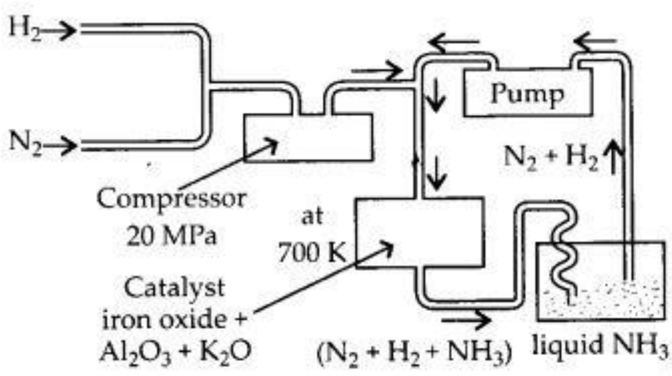
Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

$$Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba + 3N_2$$

Question 6.
How is ammonia manufactured industrially?
Solution:
Industrially ammonia is manufactured by Haber's process.

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \quad \Delta_f H° = -46.1 \text{ kJ/mol}$$

In accordance with Le-Chatelier's principle, high pressure and low temperature would favour the formation of ammonia. The optimum conditions for production of ammonia are a pressure of 200 × 105 Pa (about 200 atm), a temperature of -700 K and the use of a catalyst such as iron-oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.



The manufacture of ammonia

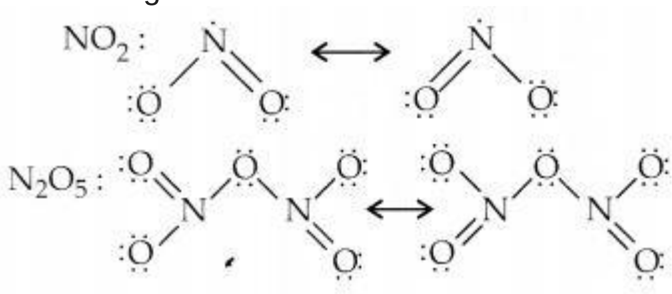
Question 7.
Illustrate how copper metal can give different products on reaction with HNO_3.
Solution:
acid is a strong oxidising agent and attacks most metals. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation. Copper with . cold dil. HNO_3 forms nitric oxide (NO).

$$\underset{\text{(Cold, dil.)}}{3Cu + 8HNO_3} \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Copper with hot conc. HNO_3 forms nitrogen dioxide (NO_2).

$$\underset{\text{(Hot conc.)}}{Cu + 4HNO_3} \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Question 8.
Give the resonating structures of NO_2 and N_2O_5.
Solution:
Resonating structures



Question 9.
The HNH angle value is higher than HPH, HAsH and HSbH angles. Why?
[Hint : Can be explained on the basis of sp^3 hybridisation in NH_3 and only s-p bonding between hydrogen and other elements of the group].
Solution:
The actual bond angles are

NH_3	PH_3	AsH_3	SbH_3
106.5°	93.5°	91.5°	91.3°

The decreased bond angle in other hydrides can be explained by the fact that the sp^3 hybridisation becomes less and less distinct with increasing size of the central atom i.e., pure p-orbitals are utilised in M-H bonding.

Question 10.
Why does $R_3P = O$ exist but $R_3 N = O$ does not (R = alkyl group)?
Solution:
In $R_3 N = O$, covalency required is five. The maximum covalency of nitrogen is four as it does not possess d-orbitals in the valence shell i.e., it cannot extend its valency beyond four. On the other hand, other members have d-orbitals and can utilise these orbitals to show covalency of five or six e.g., $R_3P = O$, PCl_5, $[SbF6]^-$ etc. These can form dπ – pπ bonds.

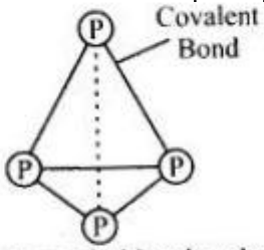
Question 11.
Explain why NH_3 is basic while BiH_3 is only feebly basic.
Solution:
The basic character decreases from NH_3 to BiH_3. The basic nature is due to the presence of lone pair of electrons on the central atom. NH_3 is the strongest electron pair donor due to its small size as the electron density of the electron pair is concentrated over a small region. As the size increases the electron density gets diffused over a large region and hence the ability to donate the electron pair (basic nature) decreases.

Question 12.
Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?
Solution:
Nitrogen is diatomic gaseous molecule at ordinary temperature due to its ability to form pπ – pπ multiple bonds. The molecule has one σ and two π – bonds.
Phosphorus exists as discrete tetratomic tetrahedral molecules as these are not capable of forming multiple bonds due to repulsion between non-bonded electrons of the inner core.

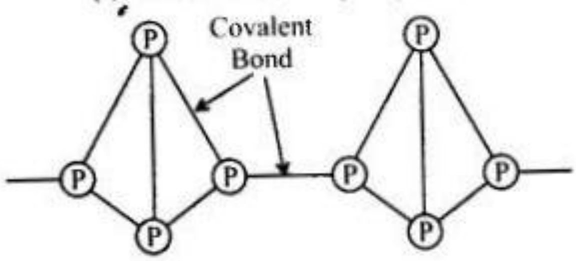
Question 13.
Write main differences between the properties of white phosphorus and red phosphorus.
Solution:

Property	White Phosphorus	Red Phosphorus
(i) State	Translucent	Brittle substance (crystalline)
(ii) Colour	White, gets yellowish on exposure to light	Red
(iii) Odour	Garlic like odour	Odourless
(iv) Hardness	Soft like wax and can be cut by knife	Hard
(v) Poisonous nature	Poisonous	Non-poisonous
(vi) Solubility	Soluble in CS_2	Insoluble in CS_2
(vii) Chemiluminescence	Glows in dark	Does not glow in dark
(viii) Density	1.80	2.10
(ix) Reactivity	Very reactive	Less reactive
(x) Action of chlorine	Burns readily in Cl_2 forming PCl_3 and PCl_5	Combines with Cl_2 only on heating forming first PCl_3 and then PCl_5.

Structure of white and red phosphorus are given below :



(i) Structure of white phosphorus



(ii) Structure of red phosphorus

Question 14.
Why does nitrogen show catenation properties less than phosphorus?
Solution:
The single N-N bond is weaker than the single P-P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen.

Question 15.
Give the disproportionation reaction of H_3PO_3.
Solution:
The acids in +3 oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states, e.g., phosphorous acid on heating disproportionates to give orthophosphoric acid and phosphine.
$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

Question 16.
Can PCl_5 act as an oxidising as well as a reducing agent? Justify.
Solution:
The oxidation state of P in PCl_5 is +5. As P has five electrons in its valence shell, it cannot increase its oxidation state beyond +5 by donating electrons, therefore, PCl_5 cannot act as a reducing agent. However, it can decrease its oxidation number from +5 to +3 or some lower value, so, PCl_5 acts as an oxidising agent. For example, it oxidises Ag to AgCl, Sn to $SnCl_4$.

$$\overset{0}{2Ag} + \overset{+5}{PCl_5} \longrightarrow \overset{+1}{2AgCl} + \overset{+3}{PCl_3}$$
$$\overset{0}{Sn} + \overset{+5}{2PCl_5} \longrightarrow \overset{+4}{SnCl_4} + \overset{+3}{2PCl_3}$$

Question 17.
Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.
Solution:
(i) Electronic configuration :
$_{8}O = [He]2s^2 2p^4$; $_{16}S = [Ne]3s^2 3p^4$;
$_{34}Se = [Ar]3d^{10} 4s^2 4p^4$
$_{52}Te = [Kr]4d^{10} 5s^2 5p^4$ and $_{84}Po = [Xe]4f^{14} 5d^{10} 6s^2 6p^4$
All these elements have same ns^2np^4 (n = 2 to 6) valence shell electronic configuration and hence are justified to be placed in group 16 of the periodic table.

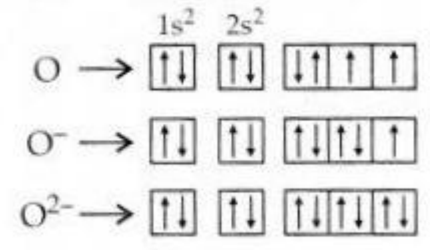
(ii) Oxidation states : They need two more electrons to form dinegative ions by acquiring the nearest noble gas configuration. So, the minimum oxidation state of these elements should be -2. Oxygen predominantly and sulphur to some extent being electronegative show an oxidation state of -2. Since these elements have six electrons in the valence shell, therefore, the maximum oxidation state they can show is, + 6. Other positive oxidation states shown by these elements are +2 and +4. Although, oxygen due to the absence of d-orbitals does not show oxidation states of +4 and +6. Thus, on the basis of minimum and maximum oxidation states, these elements are justified to be placed in the same group i.c., group 16 of the periodic table.

(iii) Formation of hydrides : All the elements complete their respective octets by sharing two of their valence electrons with ls-orbilal of hydrogen to form hydrides of the general formula EH_2 i.c., H_2O, H_2S, H_2Se, H_2Te and H_2Po. Therefore, on the basis of formation of hydrides of the general formula, EH2, these elements are justified to be placed in group 16 of the periodic table.

Question 18.
Why is dioxygen a gas but sulphur a solid?
Solution:
Oxygen atom has the tendency to form multiple bonds (pπ – pπ interaction) with other oxygen atom on account of small size while this tendency is missing in sulphur atom. The bond energy of oxygen-oxygen double bond (0 = 0) is quite large (about three times that of oxygen-oxygen single bond, O – O = 34.9 kcal mol^{-1}) while sulphur-sulphur double bond (S = S) is not so large (less than double of sulphur-sulphur single bond, S – S = 63.8 kcal mob1). As a resul —O—O—O— chains are less stable as compared to O = O molecule while —S—S—S— chains are more stable than S = S molecule. Therefore, at room temperature, while oxygen exists as a diatomic gas molecule, sulphur exists as S_8 solid.

Question 19.
Knowing the electron gain enthalpy values for O → O^- and O → O^{2-} as -141 and 702 kJ mol^{-1} respectively, how can you account for the formation of large number of oxides having O^{2-} species and not O^- ?
Hint : Consider lattice energy factor in the formation of compound.
Solution:

This can be explained with the help of electronic configuration.



As O^{2-} has most stable configuration amongst these. So, formation of O^{2-} is much more easier. In solid state, large amount of energy (lattice enthalpy) is released to form divalent O^{2-} ions. It is greater lattice enthalpy of O^{2-} which compensates for the high energy required to remove the second electron.

Question 20.
Which aerosols deplete ozone?
Solution:
CFC – Chlorofluorocarbon (freons) : These compounds commonly known as freons are introduced into the atmosphere from aerosol sprays and refrigerating equipments. They undergo photochemical decomposition and destroy ozone as shown by the following sequence of reactions.

$$CF_2Cl_2 \xrightarrow{h\nu} {}^{\bullet}CF_2Cl + Cl^{\bullet} \text{ (free radical)}$$
$$CFCl_3 \xrightarrow{h\nu} {}^{\bullet}CFCl_2 + Cl^{\bullet}$$
$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$
$$ClO^{\bullet} \xrightarrow{\text{slow}} Cl^{\bullet} + {}^{\bullet}O$$
$$ClO^{\bullet} + {}^{\bullet}O \longrightarrow Cl^{\bullet} + O_2$$

Question 21.
Describe the manufacture of H_2SO_4 by Contact process?
Solution:
Sulphuric acid is manufactured by the Contact process which involves three steps :

1. burning of sulphur or sulphide ores in air to generate SO_2.
2. conversion of SO_2 to SO_3 by the reaction with oxygen in the presr nee of a catalyst (V_2O_5), and
3. absorption of SO_3 in H_2SO_4 to give oleum ($H_2S_2O_7$).

A flow diagram for the manufacture of sulphuric acid is shown in the figure. The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds. The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

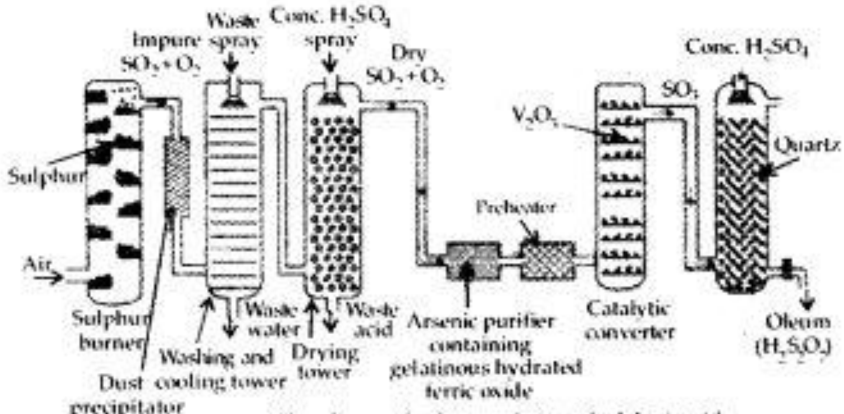
$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$$
$$\Delta_r H^{\ominus} = -196.6 \text{ kJ mol}^{-1}$$

The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow.

In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K. The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum. Dilution of oleum with water give H_2SO_4 of the desired concentration. In the industry, two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.

$$SO_3 + H_2SO_4 \rightarrow \underset{\text{(Oleum)}}{H_2S_2O_7}$$

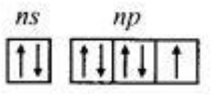
The sulphuric acid obtained by Contact process is 96 – 98% pure.



Flow diagram for the manufacture of sulphuric acid

Question 22.
How is SO_2 an air pollutant?
Solution:
SO_2 present in atmosphere combines with water to give sulphuric acid.
$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$
This is called acid rain. Acid rain causes extensive damage to building and statues made of marble, limestone, etc. due to its reaction to give CaSO4.
$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$
This way SO_2 acts as pollutant.

Question 23.
Why are halogens strong oxidising agents?
Solution:
General electronic configuration of halogen is



It will easily accept one electron to fulfill its shell. This easily acceptance of electron makes halogens strong oxidising agents.

Question 24.
Explain why fluorine forms only one oxoacid, HOF.
Solution:
Due to high electronegativity and absence of d orbitals, F does not form oxoacids such as HOFO, $HOFO_2$ and $HOFO_3$ in which the oxidation state of F is +3, +5 and +7. It just forms one oxoacid, i.e., HOF in which the oxidation state of F is + 1.

Question 25.
Explain why inspite of nearly the same electronegativity, oxygen forms hydrogen bonding while chlorine does not.
Solution:
Although O and Cl have about the same electronegativity, yet their atomic size (covalent radii) are much different: O = 66 pm and Cl = 99 pm. Thus, electron density per unit volume of oxygen atom is much higher than that of chlorine atom. Hence, oxygen forms hydrogen bonds while chlorine does not though both have approx, the same electronegativity.

Question 26.
Write two uses of ClO_2.
Solution:
ClO_2 is a powerful oxidising agent. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

Question 27.
Why are halogens coloured?
Solution:
All halogens are coloured because of absorption of radiations in visible region which results in the excitation of outer electrons to higher level. By absorbing different quanta of radiation, they display different colours as
$F_2 \rightarrow$ yellow
$Cl_2 \rightarrow$ greenish yellow
$Br_2 \rightarrow$ red
$I_2 \rightarrow$ violet

Question 28.
Write the reactions of F_2 and Cl_2 with water.

Solution:
Fluorine reacts vigorously with water and oxidises water to oxygen.
$$2H_2O + 2F_2 \rightarrow 4HF + O_2$$
Chlorine dissolves in water to form chlorine water. It slowly reacts with the water to form a mixture of hydrochloric acid and hypochlorous acid.
$$H_2O + Cl_2 \rightarrow HCl + HOCl$$
Hypochlorous acid is very unstable. In presence of sunlight, it decomposes to give HCl and nascent oxygen.
$$HOCl \xrightarrow{h\upsilon} HCl + O$$
This oxygen is responsible for oxidising and bleaching properties of chlorine.

Question 29.
How can you prepare Cl_2 from HCl and HCl from Cl_2? Write reactions only.
Solution:
Preparation of chlorine by Deacon's process : By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ at 723 K
$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$
Preparation of HCl :
Cl_2 can be reduced to HCl by reaction of H_2 in the presence of diffused sunlight.
$$H_2 + Cl_2 \xrightarrow[\text{Sunlight}]{\text{Diffused}} 2HCl$$

Question 30.
What inspired N. Bartlett for carrying out reaction between Xe and PtF_6?
Solution:
Neil Bartlett observed that PtF_6 reacts with O_2 to yield an ionic solid, $O_2^+PtF_6^-$. Here, O_2 gets oxidised to O_2^+ by PtF_6. Since the first ionisation enthalpy of Xe(1170 kJ mol^{-1}) is fairly close to that of O_2 molecule (1175 kJ mol^{-1}), Bartlett thought that PtF_6 should also oxidise Xe. When Xe and PtF_6 were mixed, a rapid reaction took place and a red solid with the formula, $Xe^+PtF_6^-$ was obtained.
$$Xe + PtF_6 \xrightarrow{278\ K} Xe^+[PtF_6]^-$$

Question 31.
What are the oxidation states of phosphorus in the following :

1. H_3PO_3
2. PCl_3
3. Ca_3P_2
4. Na_3PO_4
5. POF_3?

Solution:

Let the oxidation state of P be x.

(i) $\overset{+1}{H_3}\overset{x}{P}\overset{-2}{O_3}$ $\therefore 3(+1) + x + 3(-2) = 0$ or $x = +3$

(ii) $\overset{x}{P}\overset{-1}{Cl_3}$ $\therefore x + 3(-1) = 0$ or $x = +3$

(iii) $\overset{+2}{Ca_3}\overset{x}{P_2}$ $\therefore 3(+2) + 2 \times x = 0$ or $x = -3$

(iv) $\overset{+1}{Na_3}\overset{x}{P}\overset{-2}{O_4}$ $\therefore 3(+1) + x + 4(-2) = 0$ or $x = +5$

(v) $\overset{x}{P}\,\overset{-2}{O}\,\overset{-1}{F_3}$ $\therefore x + 1(-2) + 3(-1) = 0$ or $x = +5$.

Question 32.

Write balanced equations for the following :

1. NaCl is heated with sulphuric acid in the presence of MnO_2.
2. Chlorine gas is passed into a solution of NaI in water.

Solution:

(i) $MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + O$

$[NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl] \times 2$

$2HCl + O \rightarrow H_2O + Cl_2$

$2NaCl + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$

(ii) Cl will replace I

$2NaI_{(aq)} + Cl_{2(g)} \rightarrow 2NaCl_{(aq)} + I_{2(s)}$

Question 33.

How are xenon fluorides XeF_2, XeF_4 and XeF_6 obtained?

Solution:

Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.

$$\underset{\text{(xenon in excess)}}{Xe_{(g)}} + F_{2(g)} \xrightarrow[\text{1 bar}]{\text{673 K}} XeF_{2(s)}$$

$$\underset{\text{(1 : 5 ratio)}}{Xe_{(g)} + 2F_{2(g)}} \xrightarrow[\text{7 bar}]{\text{873 K}} XeF_{4(s)}$$

$$\underset{\text{(1 : 20 ratio)}}{Xe_{(g)} + 3F_{2(g)}} \xrightarrow[\text{60-70 bar}]{\text{573 K}} XeF_{6(s)}$$

Question 34.
With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?
Solution:
Replace O^- (9 electrons) in ClO^- by F (9 electrons). The resulting neutral molecule is ClF. Since ClF can combine further with F to form ClF_3, so, ClF is a Lewis base.

Question 35.
How are XeO_3 and $XeOF_4$ prepared?
Solution:
Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24\,HF + 3O_2$

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

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

$XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

Question 36.
Arrange the following in the order of property indicated for each set :

1. F_2, Cl_2, Br_2, I_2 – increasing bond dissociation enthalpy.
2. HF, HCl, HBr, HI – increasing acid strength.
3. NH_3, PH_3, ASH_3, SbH_3, BiH_3 – increasing base strength.

Solution:

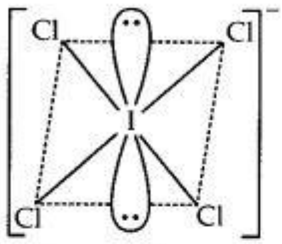
1. $I_2 < Br_2 < F_2 < Cl_2$
2. HF < HCl < HBr < HI
3. $NH_3 > PH_3 > AsH_3 >$ SbH, $> BiH_3$

Question 37.
Which one of the following does not exist?
(i) $XeOF_4$
(ii) NeF_2
(iii) XeF_2
(iv) XeF_6
Solution:
(ii) Amongst all noble gases, only Xe (except KrF_2) forms compounds.

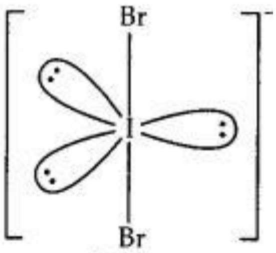
Question 38.
Give the formula and describe the structure of a noble gas species which is isostructural with :

1. ICl^-_4
2. IBr^-_2
3. $Br0^-_3$

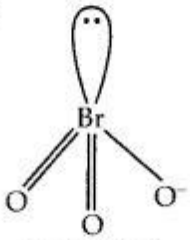
Solution:
(i) Structure of ICl_4^- : I in ICl_4^- has four bond pairs and two lone pairs. Therefore, according to VSEPR theory, it should be square planar as shown.
Here, ICl_4^- has $(7 + 4 \times 7 + 1) = 36$ valence electrons. A noble gas species having 36 valence electrons is
$XeF_4 (8 + 4 \times 7 = 36)$. Therefore, like ICl_4^-, XeF_4 is also square planar.
(ii) Structure of IBr_2^- : I in IBr_2^- has two bond pairs and three lone pairs. So, according to VSEPR theory, it should be linear.
Here, IBr_2^- has 22 $(7 + 2 \times 7 + 1)$ valence electrons.
A noble gas species having 22 valence electrons is XeF_2 $(8 + 2 \times 7 = 22)$.
Thus, like IBr_2^-, XeF_2 is also linear :



Square planar



Linear



Pyramidal

(iii) Structure of BrO_3^- : The central atom Br has seven electrons. Four of these electrons form two double bonds or coordinate bonds with two oxygen atoms while the fifth electron forms a single bond with O^- ion. The remaining two electrons form one lone pair. Hence, in all there are three bond pairs and one lone pair around Br atom in BrO_3^- Therefore, according to VSEPR theory, BrO_3^- s should be pyramidal.

Here, BrO_3^- has 26(7 + 3 × 6 + 1 = 26) valence electrons. A noble gas species having 26 valence electrons is XeO_3 (8 + 3 × 6 = 26). Thus, like BrO_3^-, XeO_3 is also pyramidal.

Question 39.
Why do noble gases have comparatively large atomic sizes?
Solution:
The atomic radii of noble gases are by far the largest in their respective periods. This is due to the reason that noble gases have only van der Waals radii while others have cova lent radii, van der Waals radii, by definition are larger than covalent radii.

Question 40.
List the uses of neon and argon gases.

Solution:
Uses of neon :

- Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes.
- Glow of different colours ‘neon signs’ can be produced by mixing neon with other gases.
- Neon bulbs and used in botanical gardens and in green houses.

Uses of argon:

- Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes such as arc welding of metals and alloys. In the laboratory, it is used for handling substance which are air sensitive.
- It is used in filling incandescent and fluorescent lamps where its presence retards the sublimation of the filament and thus increases the life of the lamp.
- It is also used in “neon signs” for obtaining lights of different colours.

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