Intext Exercise 1

Question 1:

Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionization and electronegativity.

Solution 1:

General trends in group 15 elements

(i) Electronic configuration: All the elements in group 15 have 5 valence electrons. Their general electronic configuration is $ns^2\ np^3$.

(ii) Oxidation states: All these elements have 5 valence electrons and require three more electrons to complete their octets. However, gaining electrons is very difficult as the nucleus will have to attract three more electrons. This can take place only with nitrogen as it is the smallest in size and the distance between the nucleus and the valence shell is relatively small. The remaining elements of this group show a formal oxidation state of -3 in their covalent compounds. In addition to the -3 state, N and P also show -1 and -2 oxidation states. All the elements present in this group show +3 and +5 oxidation states. However, the stability of +5 oxidation state decreases down a group, whereas the stability of +3 oxidation state increases. This happens because of the inert pair effect.

(iii) Ionization energy and electronegativity: First ionization decreases on moving down a group. This is because of increasing atomic sizes. As we move down a group, electronegativity decreases, owing to an increase in size.

(iv) Atomic size: On moving down a group, the atomic size increases. This increase in the atomic size is attributed to an increase in the number of shells.

Question 2:

Why does the reactivity of nitrogen differ from phosphorus?

Solution 2:

Nitrogen is chemically less reactive. This is because of the high stability of its molecule, N_2. In N_2, the two nitrogen atoms form a triple bond. This triple bond has very high bond strength, which is very difficult to break, It is because of nitrogen's small size that it is able to form $p\pi$ - $p\pi$ bonds with itself. This property is not exhibited by atoms such as phosphorus. Thus, phosphorus is more reactive than nitrogen.

Intext Exercise 2

Question 3:

Discuss the trends in chemical reactivity of group 15 elements.

Solution 3:

General trends in chemical properties of group 15

(i) Reactivity towards hydrogen:
The elements of group 15 react with hydrogen to form hydrides of type EH_3, where E = N, P As, Sb, or Bi The stability of hydrides decreases on moving down from NH_3 to BiH_3.
(ii) Reactivity towards oxygen:
The elements of group 15 form two types of oxides: E_2O_3 and E_2O_5, where E = N, P, As, Sb, or Bi. The oxide with the element in the higher oxidation state is more acidic than the other. However, the acidic character decreases on moving down a group.
(iii) Reactivity towards halogens:
The group 15 elements react with halogens to form two series of salts: EX_3 and EX_5. However, nitrogen does not form NX_5 as it lacks the d-orbital. All trihalides (except NX_3) are stable,
(iv) Reactivity towards metals:
The group 15 elements react with metals to form binary compounds in which metals exhibit -3 oxidation states.

Intext Exercise 3

Question 4:
Why does NH_3 form hydrogen bond but PH_3 does not?

Solution 4:
Hydrogen bond is always formed between highly electronegative atom and H atom. Nitrogen is highly electronegative compared to phosphorus as electronegativity decreases down the group. Hence, the extent of hydrogen bonding in PH_3 is very less as compared to NH_3.

Question 5:
How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.

Solution 5:
An aqueous solution of ammonium chloride is treated with sodium nitrite.

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

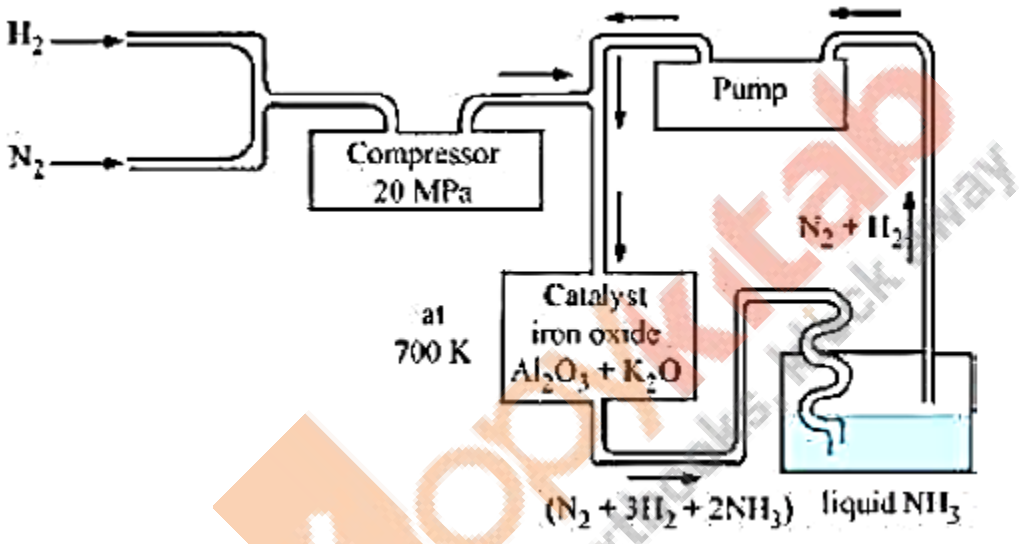
NO and HNO3 are produced in small amounts. These are impurities that can be removed on passing nitrogen gas through aqueous sulphuric acid, containing potassium dichromate.

Question 6:
How is ammonia manufactured industrially?

Solution 6:
Ammonia is prepared on a large-scale by the Haber's process.

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

The optimum conditions for manufacturing ammonia are:
(i) Pressure (around 200 ×105 Pa)
(ii) Temperature (4700 K)
(iii) Catalyst such as iron oxide with small amounts of $A1_2O_3$ and K_2O



Question 7:

Illustrate how copper metal can give different products on reaction with HNO_3.

Solution 7:

Concentrated nitric acid is a strong oxidizing agent It is used for oxidizing most metals. The products of oxidation depend on the concentration of the acid, temperature, and also on the material undergoing oxidation.

$$3Cu + 8HNO_{3(dilute)} \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

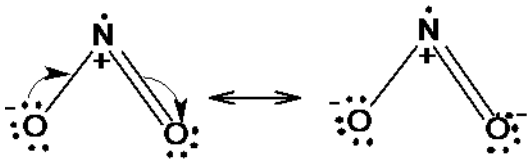
$$Cu + 4HNO_{3(conc)} \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Question 8:

Give the resonating structures of NO_2 and N_2O_5

Solution 8:

(1)



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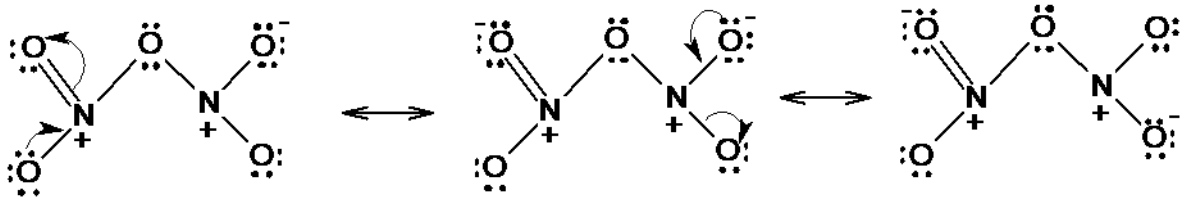


Question 9:

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 9:

Hydride NH_3 PH_3 AsH_3 SbH_3
H-M-H angle 107° 92° 91° 90°
The above trend in the H-M-H bond angle can be explained on the basis of the electronegativity of the central atom. Since nitrogen is highly electronegative, there is high electron density around nitrogen. This causes greater repulsion between the electron pairs around nitrogen, resulting in maximum bond angle. We know that electronegativity decreases on moving down a group. Consequently, the repulsive interactions between the electron pairs decrease, thereby decreasing the H-M-H bond angle.

Question 10:

Why does $R_3P = 0$ exist but $R_3N = 0$ does not (R = alkyl group)?

Solution 10:

N (unlike P) lacks the d-orbital. This restricts nitrogen to expand its coordination number beyond four. Hence, $R_3N = 0$ does not exist.

Question 11:

Explain why NH_3 is basic while BiH_3 is only feebly basic.

Solution 11:

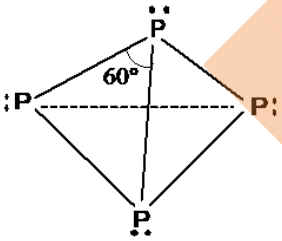
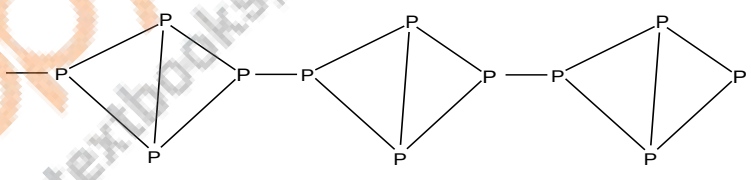
Nitrogen has a small size due to which the lone pair of electrons is concentrated in a small region. This means that the charge density per unit volume is high. On moving down a group, the size of the central atom increases and the charge gets distributed over a large area decreasing the electron density. Hence, the electron donating capacity of group 15 element hydrides decreases on moving down the group.

Question 12:
Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?

Solution 12:
Nitrogen owing to its small size has a tendency to form $p\pi - p\pi$ multiple bonds with it. Nitrogen thus forms a very stable diatomic molecule, N_2. On moving down a group, the tendency to form $p\pi - p\pi$ bonds decreases (because of the large size of heavier elements). Therefore, phosphorus (like other heavier metals) exists in the P_4 state.

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

Solution 13:

White phosphorus	**Red phosphorus**
It is a soft and waxy solid. It possesses a garlic small	It is hard and crystalline solid, without any small.
It is poisonous.	It is non-poisonous.
It is insoluble in water but soluble in carbon disulphide	It is insoluble in both water and carbon disulphide.
It undergoes spontaneous combustion in air	It is relatively less reactive
It is both solid and vapour states, it exists as a p_4 molecule. 	It exists as a chain of tetrahedral p_4 units. 

Question 14:
Why does nitrogen show catenation properties less than phosphorus**?**

Solution 14:
Catenation is much more common in phosphorous compounds than in nitrogen compounds. This is because of the relative weakness of the N-N single bond as compared to the P-P single bond. Since nitrogen atom is smaller, there is greater repulsion of electron density of two nitrogen atoms, thereby weakening the N-N single bond.

Question 15:
Give the disproportionation reaction of H_3PO_3.

Solution 15:

On heating, orthophosphorus acid (H_3PO_3) disproportionates to give orthophosphoric acid (H_3PO_4) and phosphine (PH_3) The oxidation states of P in various species involved in the reaction are mentioned below.

$$4H_3\overset{+3}{P}O_3 \longrightarrow 3H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$$

Question 16:

Can PCl_5 act as an oxidizing as well as a reducing agent? Justify.

Solution 16:

PCl_5 can only act as an oxidizing agent. The highest oxidation state that P can show is+5. In PCl_5, phosphorus is in its highest oxidation state (+5). However, it can decrease its oxidation state and act as an oxidizing agent.

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 17:

The elements of group 16 are collectively called chalcogens.

(i) Elements of group 16 have six valence electrons each. The general electronic configuration of these elements is $ns^2\ np^4$, where n varies from 2 to 6.

(ii) **Oxidation state:**

As these elements have six valence electrons $(ns^2\ np^4)$, they should display an oxidation state of -2. However, only oxygen predominantly shows the oxidation state of -2 owing to its high electronegativity. It also exhibits the oxidation state of -1 (H_2O_2), zero (O_2), and +2 (OF_2). However, the stability of the -2 oxidation state decreases on moving down a group due to a decrease in the electronegativity of the elements. The heavier elements of the group show an oxidation state of +2, +4, and +6 due to the availability of d-orbitals.

(iii) **Formation of hydrides:**

These elements form hydrides of formula H_2E, where E = O, S, Se, Te, PO. Oxygen and sulphur also form hydrides of type H_2E_2. These hydrides are quite volatile in nature.

Question 18:

Why is dioxygen a gas but sulphur a solid?

Solution 18:

Oxygen is smaller in size as compared to sulphur. Due to its smaller size, it can effectively form $p\pi - p\pi$ bonds and form O_2 (0==O) molecule. Also, the intermolecular forces in oxygen are weak van der Wall's, which cause it to exist as gas. On the other forces in oxygen are weak van der Wall's, which cause it to exist as gas. On the other hand, sulphur does not form $p\pi - p\pi$

bonds but exists as a puckered structure held together by strong covalent bonds. Hence, it is a solid.

Question 19:

Knowing the electron gain enthalpy values for $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as —141 and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having species and not O^-?
(Hint: Consider lattice energy factor in the formation of compounds).

Solution 19:

Stability of an ionic compound depends on its lattice energy. More the lattice energy of a compound, more stable it will be. Lattice energy is directly proportional to the charge carried by an ion. When a metal combines with oxygen, the lattice energy of the oxide involving O^{2-} ion is much more than the oxide involving O^- ion. Hence, the oxide having O^{2-} ions are more stable than oxides having O^-. Hence, we can say that formation of O^{2-} is energetically more favourable than formation of O^-

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Question 20:

Which aerosols deplete ozone?

Solution 20:

Freon's or chlorofluorocarbons (CFCs) are aerosols that accelerate the depletion of ozone. In the presence of ultraviolet radiations, molecules of CFCs break down to form chlorine- free radicals that combine with ozone to form oxygen.

Question 21:

Describe the manufacture of H_2SO_4 by contact process?

Solution 21:

Sulphuric acid is manufactured by the contact process. It involves the following steps:
Step (i): Sulphur or sulphide ores are burnt in air to form SO_2.

Step (ii): By a reaction with oxygen, SO_2 is converted into SO_3 in the presence of V_2O_5 as a catalyst.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$$

Step (iii):

SO_3 Produced is absorbed on H_2SO_4 to give $H_2S_2O_7$ (oleum)

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

This oleum is then diluted to obtain H_2SO_4 of the desired concentration.

In practice, the plant is operated at 2 bar (pressure) and 720 K (temperature). The Sulphuric acid thus obtained is 96-98% pure.

Question 22:

How is SO_2 an air pollutant?

Solution 22:
Sulphur dioxide causes harm to the environment in many ways:
1. It combines with water vapour present in the atmosphere to form sulphuric acid. This causes acid rain. Acid rain damages soil, plants, and buildings, especially those made of marble.
2. Even in very low concentrations, SO_2 causes irritation in the respiratory tract. It causes throat and eye irritation and can also affect the larynx to cause breathlessness.
3. It is extremely harmful to plants. Plants exposed to sulphur dioxide for a long time lose colour from their leaves. This condition is known as chlorosis. This happens because the formation of chlorophyll is affected by the presence of sulphur dioxide.

Question 23:
Why are halogens strong oxidising agents?

Solution 23:
The general electronic configuration of halogens is np^5, where n = 2-6. Thus, halogens need only one more electron to complete their octet and to attain the stable noble gas configuration. Also, halogens are highly electronegative with low dissociation energies and high negative electron gain enthalpies. Therefore, they have a high tendency to gain an electron. Hence, they act as strong oxidizing agents.

Question 24:
Explain why fluorine forms only one oxoacid, HOF

Solution 24:
Fluorine forms only one oxoacid i.e., HOF because of its high electronegativity , small size and non availability of d orbitals.

Question 25:
Explain why inspite of nearly the same electronegativity, oxygen forms hydrogen bonding while chlorine does not.

Solution 25:
Both chlorine and oxygen have almost the same electronegativity values, but chlorine rarely forms hydrogen bonding. This is because in comparison to chlorine, oxygen has a smaller size and as a result, a higher electron density per unit volume.

Question 26:
Write two uses of ClO_2

Solution 26:
Uses of ClO_2
(i) It is used for purifying water.

(ii) It is used as a bleaching agent.

Question 27:

Why are halogens coloured?

Solution 27:

Almost all halogens are coloured. This is because halogens absorb radiations in the visible region. This results in the excitation of valence electrons to a higher energy region. Since the amount of energy required for excitation differs for each halogen, each halogen displays a different colour.

F_2- yellow Cl_2- greenish yellow Br_2- red I_2- violet

Question 28:

Write the reactions of F_2 and Cl_2 with water.

Solution 28:

(i) $Cl_2 + H_2O \rightarrow \underset{\text{Hydrrolic acid}}{HCl} + \underset{\text{Hypochlorous acid}}{HOCl}$

(ii) $2F_{2(g)} + 2H_2O \rightarrow O_{2(g)} + 4HF(aq)$

Question 29:

How can you prepare Cl_2 from HCl and HCl from Cl_2? Write reasons only

Solution 29:

(i) Cl_2 can be prepared from HCl by Deacon's process. $4HCl + O_2 \xrightarrow{CaCl_2} 2Cl_2 + 2H_2O$

(ii) HCl can be prepared from Cl_2 on treating it with water.

$Cl_2 + H_2O \rightarrow \underset{\text{Hyrocloric acid}}{HCl} + \underset{\text{Hyprochlorous acid}}{HOCl}$

Question 30:

What inspired N. Bartlett for carrying out reaction between Xe and PtF_6

Solution 30:

Neil Bartlett initially carried out a reaction between oxygen and PtF_6. This resulted in the formation of a red compound, $O_2^+[PtF_6]$.

Later, he realized that the first ionization energy of oxygen $(1175kJ/mol)$ and Xe $(1175kJ/mol)$ is almost the same. Thus, he tried to prepare a compound with Xe and PtF_6. He was successful and a red-coloured compound, $Xe^+[PtF_6]^-$ was formed

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Question 31:

What are the oxidation states of phosphorus in the following:

$(i)\ H_2PO_3 (ii) PCl_3 (iii) Ca_3P_2\ (iv) NaPO_4 (v) POF_3$?

Solution 31:

Let the oxidation state of p of x.

$(i) H_3PO_3$

3 + x +3(-2) = 0

3 + x -6 = 0

X = +3

$(ii) PCl_3$

X + 3(-1) = 0

X – 3 = 0

X = + 3

$(iii)\ Ca_3P_2$

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

6 + 2x = 0

2x = 6

x = -3

$(iv)\ Na_3PO_4$

3(+1)+ x +4(-2) = 0

3+ x – 8 = 0

x – 5 = 0

x = + 5

$(v) POF_3$

x +(-2) +3(-1) = 0

x – 5 = 0

x = + 5

Question 32:

Write balanced equations for the following:

(i) $NaCl$ is heated with sulphuric acid in the presence of MnO_2.

(ii) Chlorine gas is passed into a solution of NaI in water.

Solution 32:

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

$(ii)\ Cl_2 + NaI \rightarrow 2NaCI + I_2$

Question 33:

How are xenon fluorides XeF_2, XeF_4 and XeF_6 obtained?

Solution 33:

XeF_2, XeF_4 and XeF_6 are obtained by a direct reaction between Xe and F_2. The condition under which the reaction is carried out determines the product.

$Xe_{(g)} + F_{2(g)} \longrightarrow$ $g)$

(Excess)

$Xe_{(g)} + 2F_{2(g)} \longrightarrow$ $g)$

(1:5 ratio)

$Xe_{(g)} + 3F_{2(g)} \longrightarrow$ $g)$

(1:20 ratio)

Question 34:

With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?

Solution 34:

ClO^- is isoelectronic to ClF. Also, both species contain 26 electrons in all as shown.

Total electrons

ClO^- =17+ 8+ 1= 26

In ClF =17 +9 =26

ClF Acts like a Lewis base as it accepts electrons from F to form ClF_3

Question 35:

How are XeO_3 and $XeOF_4$ prepared?

Solution 35:

(i) XeO_3 can be prepared in two ways as shown.

$6XeF_4 + 12H_2O \rightarrow 4XeO_3 + 24HF + 1O_2$

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

(ii) $XeOF_4$ can be prepared using XeF_6.

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

Question 36:

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

(i) F_2, Cl_2, Br_2, I_2 – increasing bond dissociation enthalpy.

(ii) HF, HCl, HBr, HI – increasing acid strength.

(iii) $NH_3, PH_3, AsH_3, SbH_3, BiH_3$ – increasing base strength

Solution 36:

(i) Bond dissociation energy usually decreases on moving down a group as the atomic size increases. However, the bond dissociation energy of F_2 is lower than that of Cl_2 and Br_2 This is due to the small atomic size of fluorine. Thus, the increasing order for bond dissociation energy among halogens is as follows: $I_2 < F_2 < Br_2 < Cl_2$

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

The bond dissociation energy of H-X molecules where X = F, Cl, Br, I, decreases with an increase in the atomic size. Since H-I bond is the weakest, HI is the strongest acid.

(iii) $BiH_3 \leq SbH_3 < AsH_3 < PH_3 < NH_3$

On moving from nitrogen to bismuth, the size of the atom increases while the electron density on the atom decreases. Thus, the basic strength decreases.

Question 37:

Which one of the following does not exist?

(i) XeF_4 **(ii)** NeF_2

(iii) XeF_2 **(iv)** XeF_6

Solution 37:

NeF_2 does not exist.

Question 38:

Give the formula and describe the structure of a noble gas species which is isostructural With:

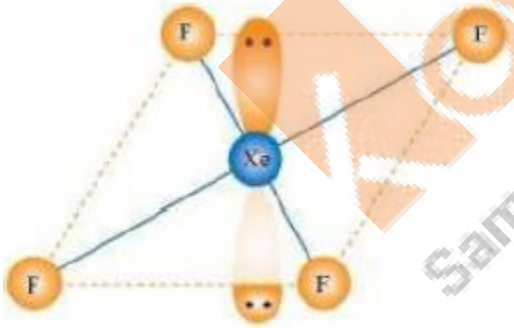
(i) ICI_4^-

(ii) IBr_2^-

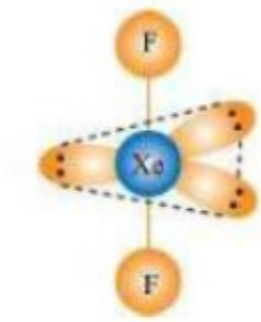
(iii) BrO_3^-

Solution 38:

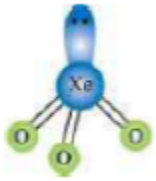
(i) XeF_4 is isostructural with ICI_4^- and has square planar geometry.



(ii) XeF_2 is isostructural to IBr_2^- and has a linear structure.



(iii) XeF_3 is isostructural BrO_3^- and has a pyramidal geometry.



Question 39:

Why do noble gases have comparatively large atomic sizes?

Solution 39:

Noble gases do not form molecules. In case of noble gases, the atomic radii correspond to van der Waal's radii. On the other hand, the atomic radii of other elements correspond to their covalent radii. By definition, van der Waal's radii are larger than covalent radii. It is for this reason that noble gases are very large in size as compared to other atoms belonging to the same period.

Question 40:

List the uses of Neon and argon gases.

Solution 40:

Uses of neon gas:

(i) It is mixed with helium to protect electrical equipment's from high voltage

(ii) It is filled in discharge tubes with characteristic colours.

(iii) It is used in beacon lights.

Uses of Argon gas:

(i) Argon along with nitrogen is used in gas-filled electric lamps. This is because Ar is more inert than N.

(ii) It is usually used to provide an inert temperature in a high metallurgical process.

(iii) It is also used in laboratories to handle air-sensitive substances.

Intext Questions

Question 1:

Why are pentahalides more covalent than trihalides?

Solution 1:

In pentahalides, the oxidation state is +5 and +3oxidation state in trihalides. Since the metal ion with a high charge has more polarizing power, pentahalides are more covalent than trihalides.

Question 2:

Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements?

Solution 2:

As we move down a group. the atomic size increases and the stability of the hydrides of group 15 elements decreases Since the stability of hydrides decreases on moving from NH_3 to BiH_3, the reducing character of the hydrides increases on moving from NH_3 to BiH_3.

Question 3:

Why is N_2 less reactive at room temperature?

Solution 3:

The two N atoms in N_2 are bonded to each other by very strong triple covalent bonds. The bond dissociation energy of this bond is very high. As a result, N_2 is less reactive at room temperature.

Question 4:

Mention the conditions required to maximize the yield of ammonia.

Solution 4:

Ammonia is prepared using the Haber s process. The yield of ammonia can be maximized under the following conditions:

(i) High pressure $(\sim 200atm)$

(ii) A temperature of $\sim$

(iii) Use of a catalyst such as iron oxide mixed with small amounts of K_2O and Al_2O_3

Question 5:

How does ammonia react with a solution of Cu^{2+}?

Solution 5:

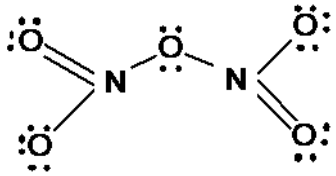
NH_3 acts as a Lewis base. It donates its electron pair and forms a linkage with metal ion.

$$\underset{Blue}{Cu^{2+}_{(aq)}} + 4NH_{3(g)} \leftrightarrow \underset{Deep\ Blue}{\left[Cu(NH_3)_4\right]^{2+}_{(aq)}}$$

Question 6:

What is the covalence of nitrogen in N_2O_5?

Solution 6:



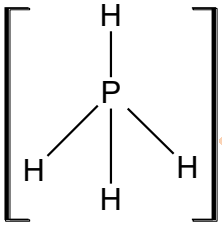
From the structure of N_2O_5 , it is evident that the covalence of nitrogen is 4.

Question 7:

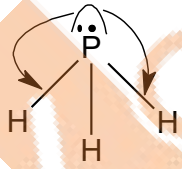
Bond angle in PH_4^+ is higher than that in PH_3. Why ?

Solution 7:

In PH_3 ,P is sp^3 hybridized. Three orbitals are involved in bonding with three hydrogen atoms and the fourth one contains a lone pair. As lone pair-bond pair repulsion is stronger than bond pair-bond pair repulsion, the tetrahedral shape associated with sp^3 bonding is changed to pyramidal. PH_3 combines with a proton to form in which the lone pair is absent. Due to PH_4^+ the absence of lone pair in PH_4^+ there is no lone pair-bond pair repulsion. Hence, the bond angle in PH_3



PH_4^+



PH_3

Question 8:

What happens when white phosphorus is heated with concentrated $NaOH$ solution in an inert atmosphere of CO_2 ?

Solution 8:

White phosphorous dissolves in boiling $NaOH$ solution (in a CO_2 atmosphere) to give phosphine, PH_3

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{phosphine}}{PH_3} + \underset{\text{Sodium hypophosphine}}{3NaH_2PO_2}$$

Question 9:

What happens when PCl_5 is heated?

Solution 9:

All the bonds that are present in PCl_5, are not similar. It has three equatorial and two axial bonds. The equatorial bonds are stronger than the axial ones. Therefore, when PCl_5, is heated strongly, it decomposes to form PCl_3

$PCl_5 \longrightarrow \quad \vdash Cl_3$

Question 10:

Write a balanced equation for the hydrolytic reaction of PCl_5, in heavy water.

Solution 10:

$PCl_5 + D_2O \rightarrow POCl_3 + 2DCl_2$

$POCl_3 + 3D_3O \rightarrow D_3PO_4 + 3DCl$

Therefore, the net reaction can be written as

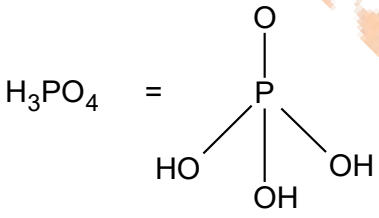
$POCl_5 + 4D_3O \rightarrow D_3PO_4 + 5DCl$

Question 11:

What is the basicity of H_3PO_4?

Solution 11:

H_3PO_4



Since there are three OH groups present in, H_3PO_4 its basicity is three i.e., it is a tribasic acid.

Question 12:

What happens when H_3PO_3 is heated?

Solution 12:

H_3PO_3 , on heating, undergoes disproportionation reaction to form PH_3 and H_3PO_4 . The oxidation numbers of P in H_3PO_3 PH_3 , and H_3PO_4 are +3, -3, and +5 respectively. As the oxidation number of the same element is decreasing and increasing during a particular reaction, the reaction is a disproportionation reaction.

$$\underset{\substack{\text{Orthophosphorous acid}\\(+3)}}{4H_3PO_3} \xrightarrow{\Delta} \underset{\substack{\text{Orthophosphoric acid}\\(+5)}}{3H_3PO_4} + \underset{\substack{\text{Phosphine}\\(-3)}}{PH_3}$$

Question 13:
List the important sources of sulphur.

Solution 13:
Sulphur mainly exists in combined form in the earth's Crust primarily as sulphates [gypsum $(CaSO_4, 2H_2O)$, Epsom salt $(MgSO_4, 7H_2O)$, baryte $BaSO_4$ and sulphides [(galena (PbS), zinc blends (ZnS), copper pyrites $(CuFeS_2)$].

Question 14:
Write the order of thermal stability of the hydrides of Group 16 elements.

Solution 14:
The thermal stability of hydrides decreases on moving down the group. This is due to a decrease in the bond dissociation enthalpy (H-E) of hydrides on moving down the group.
Therefore,

H_2O
H_2S
H_2Se
H_2Te
H_2Po

Thermal stability decreases

Question 15:
Why is H_2O a liquid and H_2S a gas?

Solution 15:
H_2O has oxygen as the central atom. Oxygen has smaller size and electronegativity as compared to sulphur. Therefore, there is extensive hydrogen bonding in H_2O , which is absent in H_2S Molecules of H_2S are held together only by weak van der Waal's forces of attraction. Hence, H_2O exists as a liquid while H2S as a solid.

Question 16:
Which of the following does not react with oxygen directly?

Zn, Ti, Pt, Fe

Solution 16:
Pt is a noble metal and does not react very easily. All other elements, Zn, Ti, Fe, are quite reactive. Hence, oxygen does not react with platinum (Pt) directly.

Question 17:
Complete the following reactions

(i) $C_2H_4 + O_2 \rightarrow$

(ii) $AAl + 3O_2 \rightarrow$

Solution 17:

(i) $\underset{Ethene}{C_2H_4} + \underset{Oxygen}{3O_4} \rightarrow \underset{Corbondioxide}{2CO_2} + \underset{Water}{2H_2O}$

(ii) $\underset{Aluminum}{4Al} + \underset{Oxygen}{3O_4} \rightarrow \underset{Alumina}{2Al_2O_3}$

Question 18:
Why does O_3 act as a powerful oxidizing agent?

Solution 18:
Ozone is not a very stable compound under normal conditions and decomposes readily on heating to give a molecule of oxygen and nascent oxygen. Nascent oxygen, being a free radical, is very reactive.

$\underset{Ozone}{O_3} \xrightarrow{\Delta} \underset{Oxygen}{O_2} + \underset{Nazcent\ Oxygen}{[O]}$

Therefore, ozone acts as a powerful oxidizing agent

Question 19:
How is O_3 estimated quantitatively?

Solution 19:
Quantitatively, ozone can be estimated with the help of potassium iodide. When ozone is made to react with potassium iodide solution buffered with a borate buffer $(pH9.2)$, iodine is liberated. This liberated iodine can be titrated against a standard solution of sodium thiosulphate. using starch as an indicator. The reactions involved in the process are given below.

$$\underset{\text{Iodide}}{2I^-} + \underset{\text{Ozone}}{O_3} \rightarrow 2OH^- + \underset{\text{Iodine}}{I_2} + O_2$$

$$I_2 + \underset{\substack{\text{Sodium}\\\text{thiosulphate}}}{2Na_2S_2O_2} \rightarrow \underset{\substack{\text{Sodium}\\\text{tetr athionate}}}{Na_2S_2O_6} + 2NaI$$

Question 20:

What happens when sulphur dioxide is passed through an aqueous solution of $Fe(III)$

Solution 20:

SO_2 acts as a reducing agent when passed through an aqueous solution containing $Fe(III)$ salt. It reduces $Fe(III)$ to $Fe(II)$ i.e., ferric ions to ferrous ions.

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

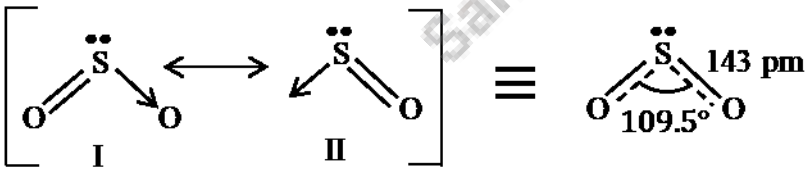
Question 21:

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 21:

The electronic configuration of S is $1s^2 2s^2 2p^2 3s^2 3p^4$

During the formation of SO_2 , one electron from 3p orbital goes to the 3d orbital and S undergoes sp^2 hybridization. Two of these orbitals form sigma bonds with two oxygen atoms and the third contains a lone pair. P-orbital and d-orbital contain an unpaired electron each. One of these electrons forms ppi- ppi bond with one oxygen atom and the other forms ppi- dpi bond with the other molecule. This is the reason SO_2 has a bent structure. Also, it is a resonance hybrid of structures I and II.



Both S-O bonds are equal in length (143 pm) and have a multiple bond character.

Question 22:

How is the presence of SO_2 detected?

Solution 22:

SO_2 is a colourless and pungent smelling gas.

It can be detected with the help of potassium permanganate solution. When SO_2 is passed through an acidified potassium permanganate solution, it decolonizes the solution.as it reduces MnO_4^- ions to Mn^{2+} ions.

$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$

Question 23:

Mention three areas in which H_2SO_4 plays an important role?

Solution 23:

Sulphuric acid is an important industrial chemical and is used for a lot of purposes. Some important uses of sulphuric acid are given below.

(i) It is used in fertilizer industry. It is used to make various fertilizers such as ammonium sulphate and calcium super phosphate.

(ii) It is used in the manufacture of pigments, paints, and detergents.

(iii) It is used in the manufacture of storage batteries.

Question 24:

Write the conditions to maximize the yield of H_2SO_4 by Contact process.

Solution 24:

Manufacture of sulphuric acid by Contact process involves three steps.

1. Burning of ores to form SO_2

2. Conversion of SO_2 to SO_3 by the reaction of the former

(V_2O_5 s used in this process as a catalyst.)

3.Absorption of SO_3 in H_2SO_4 to give oleum $(H_2S_2O_7)$

The key step in this process is the second step. In this step, two moles of gaseous reactants combine to give one mole of gaseous product. Also, this reaction is exothermic. Thus, in accordance with Le Chatelier's principle, to obtain the maximum amount of SO_3 gas, temperature should be low and pressure should be high.

Question 25:

Why is $K_{a2} << K_{a1}$ for H_2SO_4 in water?

Solution 25:

$H_2SO_{4(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{aq} + HSO_4^-; K_{a1} > 10$

$HSO_4^- + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + SO^-_{4(aq)}; K_{a2} = 1.2 \times 10^{-2}$

It can be noticed that $K_{a1} << K_{a2}$ This is because a neutral H_2SO_4 has a much higher tendency to lose a proton than the negatively charged HSO_4^-. Thus, the former is a much stronger acid than the latter.

Question 26:
Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidizing power of F_2 and Cl_2

Solution 26:
Fluorine is a much stronger oxidizing agent than chlorine. The oxidizing power depends on three factors.
1. Bond dissociation energy
2. Electron gain enthalpy
3. Hydration enthalpy
The electron gain enthalpy of chlorine is more negative than that of fluorine However, the bond dissociation energy of fluorine is much lesser than that of chlorine Also, because of its small size, the hydration energy of fluorine is much higher than that of chlorine Therefore, the latter two factors more than compensate for the less negative electron gain enthalpy of fluorine. Thus, fluorine is a much stronger oxidizing agent than chlorine.

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

Solution 27:
Anomalous behaviour of fluorine
(i) It forms only one oxoacid as compared to other halogens that form a number of oxoacids.
(ii) Ionization enthalpy, electronegativity. And electrode potential of fluorine are much higher than expected.

Question 28:
Sea is the greatest source of some halogens. Comment.

Solution 28:
Sea water contains chlorides, bromides, and iodides of Na, K, Mg, and Ca. However, it primarily contains NaCl. The deposits of dried up sea beds contain sodium chloride and carnallite, $KCl, MgCl_2, 6H_2O.$. Marine life also contains iodine in their systems. For example, sea weeds contain up-to 0.5% iodine as sodium iodide. Thus, sea is the greatest source of halogens.

Question 29:
Give the reason for bleaching action of Cl_2

Solution 29:

When chlorine reacts with water, it produces nascent oxygen. This nascent oxygen then combines with the coloured substances present in the organic matter to oxide them into colourless substances.

$Cl_2 + H_2 \rightarrow 2HCl + [O]$

Coloured substances + [O] $\rightarrow$ Oxidized colourless substance

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Question 30:

Name two poisonous gases which can be prepared from chlorine gas.

Solution 30:

Two poisonous gases that can be prepared from chlorine gas are

(i) Phosgene $(COCl_2)$

(ii) Mustard gas $(ClCH_2CH_2SCH_2CH_2Cl)$

Question 31:

Why is *ICl* more reactive than I_2 ?

Solution 31:

ICl is more reactive than I_2 because I-CI bond in *ICl* is weaker than I-I bond in I_2 .

Question 32:

Why is helium used in diving apparatus?

Solution 32:

Air contains a large amount of nitrogen and the solubility of gases in liquids increases with increase in pressure. When sea divers dive deep into the sea, large amount of nitrogen dissolves in their blood. When they come back to the surface, solubility of nitrogen decreases and it separates from the blood and forms small air bubbles. This leads to a dangerous medical condition called bends. Therefore, air in oxygen cylinders used for diving is diluted with helium gas. This is done as He is sparingly less soluble in blood.

Question 33:

Balance the following equation: $XeF_6 + H_2O \rightarrow XeO_2F_2 + HF$

Solution 33:

Balanced equation

$XeF_6 + H_2O \rightarrow XeO_2F_2 + 4HF$

Question 34:

Why has it been difficult to study the chemistry of radon?

Solution 34:

It is difficult to study the chemistry of radon because it is a radioactive substance having a half-life of only 3.82 days, compounds of radon such as RnF_2 have not been isolated. They have only been identified.