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Topic Covered p-block Elements 16.

p-BLOCK ELEMENTS

1. GROUP 13 ELEMENTS (BORON FAMILY)

1.1 Introduction

Elements of group 13 belong to p-block elements, since the last electron in them is present in the p-orbital. All these elements have three electrons in the outer most orbit: two in the s-orbital and one in the p-orbital. Thus, the electronic configuration of the outermost energy levels of these elements maybe represented as ns²np¹.

Element with At. No.		Configuration with inert gas core		
В	5	[He]2s ² 2p ¹		
AI	13	[Ne]3 s ² 3p ¹		
Ga	31	$[Ar]3d^{10}4s^24p^1$		
In	49	[Kr]4d ¹⁰ 5s ² 5p ¹		
TI	81	$[Xe]4f^{14}5d^{10}6s^{2}6p^{1}$		

Table 16.1: Electronic configuration for Group 13

1.2 Boron

Preparation:

 $Na_{2}B_{4}O_{7} + 2HCI + 5H_{2}O \longrightarrow 4H_{3}BO_{3} + 2NaCI$ $2H_{3}BO_{3} \longrightarrow B_{2}O_{3} + 3H_{2}O$ $B_{2}O_{3} + 3Mg \longrightarrow 2B + 3MgO$

Physical Properties: Low electronegativity, hard, absorbs neutrons, steel grey in color. Some dissimilarities of boron with other elements of this group are:

- (a) Boron does not form positive ions in aqueous solution and has low oxidation potential.
- (b) Boron always forms covalent compounds
- (c) Boron is non-metallic

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16.2 | p - Block Elements -

Chemical Properties

(a) Reaction with O_2 and N_2

 $4B + 3O_2 \xrightarrow{700^{\circ}C} 2B_2O_3 \qquad \qquad 2B + N_2 \xrightarrow{700^{\circ}C} 2BN$

(b) Reaction with alkalis and acids

-201-01 $2\mathsf{B} + 2\mathsf{NaOH} + 2\mathsf{H}_2\mathsf{O} \longrightarrow 2\mathsf{NaBO}_2 + 3\mathsf{H}_2 \quad 2\mathsf{B} + 3\mathsf{H}_2\mathsf{SO}_4 \xrightarrow{\text{oxidation}} 2\mathsf{H}_3\mathsf{BO}_3 + 3\mathsf{SO}_2$

(c) Boron reacts with Mg, which on hydrolysis give diborane.

 $3Mg + 2B \longrightarrow Mg_3B_2$ $Mg_3B_2 + 6HCI \longrightarrow 3MgCI_2 + B_2H_6$

(d) Reaction with silica

 $3SiO_2 + 4B \longrightarrow 2B_2O_3 + 3Si$

PLANCESS CONCEPTS

Boron has high m.p. and b.p.

Boron has a very high m. p. and b.p. because it exists as a giant covalent, polymeric structure both in solid as well as in liquid state.

B(OH), is an acid, Al(OH), is amphoteric and Tl(OH), is basic.

The electropositive or metallic character of gp. 13 elements increases from B to Tl. B being a nonmetal and thus forms an acidic hydroxide. Al forms amphoteric hydroxide and Tl, the most metallic from basic hydroxides.

Nitin Chandrol (JEE 2012, AIR 134)

1.2.1 Comparison between Boron and Aluminium

(a) Action of conc.H₂SO₄: Both react with conc. H₂SO₄ to liberate SO₂.

 $2\mathsf{B} + 3\mathsf{H}_2\mathsf{SO}_4 \longrightarrow 2\mathsf{H}_3\mathsf{BO}_3 + 3\mathsf{SO}_2 \uparrow \qquad 2\mathsf{AI} + 6\mathsf{H}_2\mathsf{SO}_4 \longrightarrow \mathsf{AI}_2(\mathsf{SO}_4)_3 + 3\mathsf{SO}_2 \uparrow + 6\mathsf{H}_2\mathsf{O}_4 \land \mathsf{AI}_2(\mathsf{SO}_4)_3 \land \mathsf{AI}_2(\mathsf{SO}_4)_3 \land \mathsf{AI}_2(\mathsf{SO}_4)_3 \land \mathsf{AI}_2(\mathsf{A}_2)_3 \land \mathsf{AI}_2(\mathsf{AI}_2)_3 \land \mathsf{AI}_2(\mathsf{AI}_2)_3 \land \mathsf{AI}_2(\mathsf{AI}_2)_3 \land \mathsf{AI}_2$

(b) Action of alkalies: Both liberate H₂.

 $2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2 \uparrow 2AI + 2NaOH + 2H_2O \longrightarrow 2NaAIO_2 + 3H_2 \uparrow$

(c) Formation of oxides: Both form oxides when heated with oxygen at high temperature.

$$4B + 3O_2 \xrightarrow{700^{\circ}C} 2B_2O_3 \qquad 4AI + 3O_2 \xrightarrow{800^{\circ}C} 2AI_2O_3$$

These oxides are amphoteric and dissolve in acids as well as in alkalies to form salts.

$B_2O_3 + 6HCI \longrightarrow 2BCI_3 + 3H_2O$	$B_2O_3 + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2O$
$AI_2O_3 + 6HCI \longrightarrow 2AICI_3 + 3H_2O$	$Al_2O_3 + 6NaOH \longrightarrow 2NaAlO_2 + H_2O$

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Chemistry | 16.3

(d) Formation of nitrides: Both, when heated with nitrogen or ammonia, form nitrides.

 $2B + N_2 \longrightarrow 2BN$ $2AI + N_2 \longrightarrow 2AIN$ $2B + 2NH_3 \longrightarrow 2BN + 3H_2$ $2AI + 2NH_3 \longrightarrow 2AIN + 3H_2$

These nitrides are decomposed by steam to from ammonia.

 $BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$ $AIN + 3H_2O \longrightarrow AI(OH)_3 + NH_3$

(e) Formation of sulphides: Both form sulphides on heating with sulphur at high temperatures. These are hydrolysed by water.

$$B_2S_3 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2S$$
$$AI_2S_3 + 6H_2O \longrightarrow 2AI(OH)_3 + 3H_2S$$

(f) Formation of chlorides: They from trichlorides by direct combination with Cl₂ or by passing Cl₂ over a heated mixture of their oxides and charcoal.

$$2B + 3CI_{2} \longrightarrow 2BCI_{3}$$

$$B_{2}O_{3} + 3C + 3CI_{2} \longrightarrow 2BCI_{3} + 3CO$$

$$2AI + 3CI_{2} \longrightarrow 2AICI_{3}$$

$$AI_{2}O_{3} + 3C + 3CI_{2} \longrightarrow 2AICI_{3} + 3CO$$

These trichlorides are covalent and are hydrolysed by water.

$$BCI_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCI$$
$$AICI_3 + 3H_2O \longrightarrow AI(OH)_3 + 3HC$$

PLANCESS CONCEPTS

• The $p\pi - p\pi$ back bonding occurs in the halides of boron but not in the halides of aluminium.

The tendency to show $p\pi - p\pi$ back bonding is maximum in boron halides and decreases very rapidly with the increase in the size of the central atom and halogen atom. "Since Al is larger in size than B, it does not show back-bonding".

• From boron to thallium, +1 oxidation state becomes more stable.

Reason: inert pair effect.

GV Abhinav (JEE 2012, AIR 329)

1.2.2 Compounds of Boron

(a) Diborane (B_2H_6)

Preparation: $4BF_3.OEt_2 + 3LiAIH_4 \xrightarrow{Et_2O} 2B_2H_6 + 3LiAIF_4 + 4Et_2O$

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16.4 | p - Block Elements

Physical Properties:

- (i) Diborane is a colourless gas (b. p. 183K). It is rapidly decomposed by water with the formation of H_3BO_3 and H_2 : $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$
- (ii) Diborane undergoes a facile addition reaction with alkenes and alkynes in ether solvents at room temperature to form organoboranes:

 $6RCH = CH_2 + B_2H_6 \longrightarrow 2B(CH_2CH_2R)_3$ (Hydroboration Reation)

(b) Boric Acid: Orthoboric acid, H₃BO₃ (commonly known as boric acid) and metaboric acid HBO₂, are two wellknown, important oxoacids of boron.

Preparation: $Na_2B_4O_7 + 2HCI + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCI$

Properties:

- (i) It is moderately soluble in water.
- (ii) On heating boric acid at 375K, metaboric acid, HBO₂ is formed. On further heating above 500K, B₂O₃ is formed.

$$H_3BO_3 \xrightarrow{375K} HBO_2 + H_2O_2$$

 $2HBO_2 \xrightarrow{500K} B_2O_3 + H_2O_3$

In solution, metaboric acid changes to orthoboric acid.

(c) Borax (Sodium tetraborate decahydrate, Na, B, O, .10H, O)

Preparation: $Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3 \downarrow$

Properties:

- (i) On heating alone, it decomposes to from NaBO₂ and B₂O₃ Na₂B₄O₇ \longrightarrow 2NaBO₂ + B₂O₃
- (ii) Borax bead Test: The formation of coloured metaborates by transition metal salts is used in the borax bead test as a qualitative analysis. The distinct colour of the bead depends on the oxidizing or reducing flame of the bunsen burner.

A cupric salt forms blue cupric metaborate in the oxidizing flame: $Na_2B_4O_7 + CuO \longrightarrow Cu(BO_2)_2 + 2NaBO_2$

In the reducing flame (ie. In presence of carbon), the coloured salt is reduced to colourless cuprous metaborate:

$$2Cu(BO_2)_2 + 2NaBO_2 + C \longrightarrow 2CuBO_2 + Na_2B_4O_7 + CO_2$$

and to metallic copper and hence the bead becomes dull red and opaque.

$$2Cu(BO)_2 + 4NaBO_2 + 2C \longrightarrow 2Cu + 2Na_2B_4O_7 + 2CO$$

Illustration 1: Show that B_2O_3 is amphoteric oxide.

Sol: Amphoteric oxide is an oxide that can behave as an acid or a base. Thus, following reactions can be written as-

$$B_2O_3 + 6HCI \longrightarrow 2BCI_3 + 3H_2O$$
$$B_2O_3 + 2NaOH \longrightarrow 2NaBO_2 + H_2O$$

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Chemistry | 16.5

Illustration 2: Boron is trivalent in nature. Explain.

(JEE MAIN)

(JEE MAIN)

Sol: Trivalency is having a valence of three or showing the presence of three valence electrons. Due to ns²np configuration it can share three electrons with other atoms.

Illustration 3: B(OH)₃ is an acid, AI(OH)₃ is amphoteric and TI(OH)₃ is basic. Explain.

Sol: The electropositive or metallic character of gp. 13 elements increases from B to Tl. B being a non-metal and thus forms an acidic hydroxide. Al forms amphoteric hydroxide and Tl, the most metallic form basic hydroxides.

Illustration 4: An inorganic compound (A) in its aqueous solution produced a white ppt. with NaOH, which dissolves in excess of NaOH. The aqueous solution of (A) also produced a white ppt. with NH_4OH which does not dissolve in excess of NH_4OH . Also, its aqueous solution produced a light yellow ppt. with $AgNO_3$ solution, soluble in dil. HNO_3 . Identify (A) (JEE ADVANCED)

Sol: The given reactions are:

(i) $AIBr_3 + 3NaOH \longrightarrow AI(OH)_3 + 3NaBr$ (A) Aluminium hydroxide (white ppt.)

$$Al(OH)_{3} + NaOH \longrightarrow NaAlO_{2} + 2H_{2}O$$
Sodium aluminate
(Soluble)

(ii) $AIBr_3 + 3NH_4OH \longrightarrow AI(OH)_3 + 3NH_4Br$

 $Al(OH)_3 + NH_4OH \longrightarrow No$ reaction and thus insoluble

(iii) $AIBr_3 + 3AgNO_3 \longrightarrow 3AgBr + Al(NO_3)$ Yellowppt.

Illustration 5: Identify A, B and C in the given reaction sequence:

(JEE ADVANCED)

$$NH_{4}CI + BCI_{3} \xrightarrow{C_{6}H_{5}CI} A \xrightarrow{NaBH_{4}} B$$

$$A \xrightarrow{CH_{3}MgBr} C$$

Sol: The product is Borazine, an inorganic compound formed here, which is isoelectronic and isostructural with benzene.

$$A = B_3N_3H_3CI_3$$
, $B = B_3N_3H_6$, $C = B_3N_3H_3(CH_3)_3$

$$3NH_4CI + 3BCI_3 - \frac{C_6H_5CI}{140 - 150^{\circ}C}$$

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16.6 | p - Block Elements

Reactions are:



Illustration 6: Aluminium vessels should not be cleaned with a cleansing agent containing washing soda. Why? (JEE ADVANCED)

Sol: Washing soda (Na₂CO₃) reacts with water to form NaOH and Al gets dissolved in caustic soda.

 $2AI+2NaOH+2H_2O \longrightarrow 2NaAIO_2 + 3H_2$ Sodium meta aluminate

Illustration 7: The $p\pi - p\pi$ back bonding occurs in the halides of boron but not in the halides of aluminium. Explain. (JEE ADVANCED)

Sol: The tendency to show $p\pi - p\pi$ back bonding is maximum in boron halides and decrease very rapidly with the increase in the size of central atom and halogen atom. Since, Al is larger in size than B and thus, does not show back bonding.

Illustration 8: Borazole or borazine is more reactive than benzene. Explain. (JEE ADVANCED)

Sol: In Borazine, B=N bonds are polar and therefore, reactivity of borazole is more than benzene which possesses non-polar C=C and C-C bonds. The more negative group attacks boron atom.

Illustration 9: From boron to thallium, +1 oxidation state becomes more stable. Explain. (JEE ADVANCED)

Sol: Inert pair effect is the tendency shown by the outermost s-electrons of the post transition elements to remain unionized or unshared. [Due to inert pair effect.]

2. GROUP 14 ELEMENTS (CARBON FAMILY)

2.1 Introduction

Carbon, silicon, germanium, tin and lead constitute the group 14 of the periodic table.

The electronic configuration of these elements are as given below.

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Chemistry | 16.7

Element	At. No	Electronic Configuration	4
С	6	1s ² , 2s ² 2p ² or [He]2s ² 2p ²	
Si	14	1s ² , 2s ² 2p ⁶ , 3s ² 3p ² or [Ne] 3s ² 3p ²	
Ge	32	1s ² , 2s ² 2p ⁶ , 3s ² 3p ⁶ , 3d ¹⁰ , 4s ² p ² or [Ar]3d ¹⁰ 4s ² 4p ²	
Sn	50	$1s^{2}, 2s^{2}2p^{6}, 3s^{2}3p^{6}, 3d^{10}, 4s^{2}4p^{6}, 4d^{10}, 5s^{2}5p^{2}$ or [Kr] $4d^{10}5s^{2}5p^{2}$	
Pb	82	$1s^{2}, 2s^{2}2p^{6}, 3s^{2}3p^{6}, 3d^{10}, 4s^{2}4p^{6}, 4d^{10}4f^{14}, 5s^{2}5p^{2}d^{10}, 6s^{2}6p^{2}$ or [Xe] 4f^{14}5d^{10}6s^{2}6p^{2}	

Table 16.2: Electronic Configuration of Group 14 Elements:

2.2 Carbon

2.2.1 Allotropes of Carbon

- (a) Crystalline form: Diamond and graphite are the two crystalline forms of carbon.
- (b) Amorphous form: Coal, Coke, Charcoal (or wood charcoal), animal charcoal (or bone black), Lamp black, Carbon black, Gas carbon and Petroleum coke are the amorphous forms of carbon.

2.2.2 Important Compounds of Carbon

(a) Carbon Monoxide (CO)

Preparation: (i) By heating oxides of heavy metals e.g. iron, zinc etc with carbon.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

 $ZnO + C \longrightarrow Zn + CO$

Two important industrial fuels-water gas and producer gas, contains carbon along with hydrogen and nitrogen, Water gas is obtained by passing steam over hot coke

$$C + H_2O \longrightarrow CO + H_2$$
(water gas)
$$2C + O_2 + 4N_2 \longrightarrow 2CO + 4N_2$$
(producer gas)

Properties: (i) It is a powerful reducing agent and reduces many metal oxides to the corresponding metal .For e.g.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$
$$CuO + CO \longrightarrow Cu + CO_2$$

Tests: (a) Burns with a blue flame

(b) A filter paper soaked in platinum or palladium chloride turns pink, green or black due to reduction of the chloride by carbon monoxide.

(b) Carbon dioxide (CO₂):

Preparation: $CaCO_3 + 2HCI \longrightarrow CaCl_2 + H_2O + CO_2$

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16.8 | p - Block Elements

Properties: (i) It turns lime water milky and the milkiness disappears when CO₂ is passed in excess.

 $Ca(OH)_{2} + CO_{2} \longrightarrow CaCO_{3} \downarrow +H_{2}O$ $CaCO_{3} + H_{2}O + CO_{2} \longrightarrow Ca(HCO_{3})_{2}$

(ii) Solid carbon dioxide or dry ice is obtained by cooling CO₂ under pressure. It passes to the solid state straight from gaseous state without liquefying (hence called dry ice).

3. Carbides: Carbon reacts with more electropositive elements to form carbides at high temperature. Types of Carbides:

- (a) Salt-like Carbides: These are the ionic salts containing either C_2^{2-} (acetylide ion) or C^{4-} (methanide ion) e. g. CaC_2 , $AI_4 C_3$, Be_2C .
- (b) **Covalent Carbides:** These are the carbides of non-metals such as silicon and boron. In Such carbides, the atoms of two elements are bonded to each other through covalent bonds. SiC is also known as Carborundum.
- (c) Interstitial Carbides: They are formed by transition elements and consist of metallic lattices with carbon atoms in the interstices. e. g. tungsten carbide WC, vanadium carbide VC.

2.3 Silicon

Extraction: Commercial form of silicon is obtained by the reduction of SiO_2 with C or CaC_2 in an electric furnace. High purity silicon is obtained either from $SiCl_4$ or from $SiHCl_3$.

Properties: Silicon is obtained by the reduction of silica. It exists in two allotropic forms:

(a) amorphous (b) crystalline

The amorphous variety is obtained by heating dry powdered silica with magnesium.

 $SiO_2 + 2Mg \longrightarrow Si + 2MgO$

The crystalline variety is obtained by heating a finely powdered sand or quartz with carbon in an electric furnace where, a small amount of iron is added to prevent the formation of carborundum (SiC)

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

Amorphous silicon is chemically more reactive than crystalline silicon. Amorphous silicon is a brownish powder. It burns brilliantly in oxygen and ignites spontaneously in fluorine.

$$Si + O_2 \longrightarrow SiO_2$$

 $Si + 2F_2 \longrightarrow SiF_4$

When amorphous silicon is strongly heated, it fuses and on cooling solidifies to the crystalline form. It forms a very hard crystalline silicon, which does not burn in oxygen but readily combines with fluorine. It dissolves in a mixture of HNO₃ and HF. When fused with alkali, it gives a silicate.

$$Na_2CO_3 + Si \longrightarrow Na_2SiO_3 + C$$

2.3.1 Silicates

A large number of silicate minerals exist in nature. Some of the important minerals are: feldspars, e.g. Albite



Figure 16.1: Differently bonded silicates

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NaAlSi₃O₈, zeolites, e.g., chabazite Ca₂[(AlO₂)₄(SiO₂)₈)H₂O], micas (muscovite)[KAl₂(Si₃AlO₁₀)(OH)₂] and asbestos [Mg(Si₂O₅)(OH)₄]. The basic structural unit in silicates is the SiO₄ tetrahedron. The SiO₄ tetrahedral can be linked in several different ways. Depending on the number of corners (0, 1, 2, 3 or 4) of the SiO₄ tetrahedral shared, various kinds of silicates, single or double chains, rings, sheet or three-dimensional networks are formed.



Normal orthosilicates (e.g. Mg_2SiO_4) contain discrete SiO_4 units. When two SiO_4 tetrahedra share a corner (common oxygen atom), we get the $(Si_2O_7)^{6-}$ unit and the silicates are called pyrosilicates. When SiO_4 units share two oxygen atoms with each other, cyclic or linear single chain silicates are formed with empirical formula $[(SiO_3)^2]_n$ as present in beryl (a mineral) $Be_3Al_2Si_6O_{18}$. A linear silicate chain is present in pyroxenes (e.g. $MgCaSi_2O_6$). If two chains are cross-linked, the resulting double stranded silicates have the composition $[(Si_4O_{11})^{6-}]_n$ and are called amphiboles. Asbestos belongs to this class. Two dimensional sheet structures are formed, three corners of each SiO_4 tetrahedron are shared as found in clays which contains $(Si_2O_5)^{2^-}$ units. When all the four corners of the SiO_4 tetrahedron are shared, 3D networks are formed, leading to different forms of silica. If in this, three-dimensional network, part of the silicon is replaced by aluminum (Al^{3^+}). This will require the incorporation of other cations (Na^+, K^+ or Ca^{2^+}) for maintaining the charge balance. The resultant 3D networks give aluminosilicates which include feldspars and zeolites. Two important man-made silicates from a practical point of view are glass and cement.

2.3.2 Silicones

These are organosilicon polymers containing Si—O—Si linkages. They may be linear, cyclic or cross-linked polymers. These are prepared from alkyl-or aryl-chlorosilanes which in turn are obtained from Grignard reagent and silicon tetrachloride.

CH ₃ MgCl	+	SiCl ₄ —	\rightarrow	CH ₃ SiCl ₃ + MgCl ₂
Methyl		Silicon		Methyl
magnesium		tetrachlorid	le	richlorosilane
Chloride				
2CH ₃ MgCl	+	SiCl ₄ –	\rightarrow	$(CH_3)_2SiCl_2 + 2MgCl_2$
				Dimethyl dichlorosilane

Preparation: Hydrolysis of the chlorides yields the corresponding silanols which polymerize by condensation by elimination of one water molecule from 2 molecules of alkyl silanols.



16.10 | p - Block Elements -

Now, since an active OH group is left at each end of the chain, polymerization continues at both the ends and thus the chain increases in length and ultimately forms a linear thermoplastic polymer.



Hydrolysis of alkyl trichlorosilane CH_3SiCl_3 gives the monomethylsilanetriol which then undergoes polymerization to a very complex cross-linked polymer.



2.3.3 Glass

Glass is a transparent or translucent amorphous supercooled solid solution of silicates and borates. The most common silicates present are those of potassium, calcium and lead, Its composition is variable as it is not a true compound. An approximate formula for ordinary glass may be given as, $R_2O.MO.6Si_2O$, where R=Na or K and M=Ca, Ba, Zn or Pb.

 SiO_2 may be replaced by Al_2O_3 , B_2O_3 , P_2O_5 . When glass is heated, it does not melt at a fixed temperature. However, it gradually softens and can be moulded into any desired shape. It is this property of glass which makes it a useful material for making articles of different shapes. Glass melts into liquid at a very high temperature.

Acidic oxides: A number of acidic oxides are useful. The choice depends upon the quality of glass to be manufactured.

- (a) **Silica:** Sand of uniform size is used, i.e., neither too fine nor too coarse. Finer variety makes the reaction violent while coarse variety slows down the reaction. It should be free from iron oxide and organic matter.
- (b) **Boron Trioxide**, B₂O₃: This is introduced in the form of boric acid or borax. It is used when a glass of low coefficient of expansion is required.
- (c) **Phosphorus pentoxide**, P_2O_5 : It is introduced in the form of calcium phosphate. It is used when opalescent glass is required.

Basic oxides: One or more of the following basic oxides are used:

Lithium, sodium, potassium, calcium, barium, magnesium, lead and zine oxides. Sodium is introduced in the form of sodium carbonate (Na_2CO_3) and carbon mixture. Potassium is added as potassium carbonate (K_2CO_3) or potassium nitrate (KNO_3). Calcium is added as $CaCO_3$ or CaO. Barium is put in as $BaCO_3$. Magnesium is added as $MgCO_3$. Lead oxide are put in such. Zinc oxide is used when heat resistance glass is to be obtained.

2.3.4 Silicon Carbide (Carborundum)

Preparation: SiC is made commercially by reducing silicon with carbon in an electric resistance furnace. SiO₂ + 3C \rightarrow SiC + 2CO

Properties: It is extremely hard and fuses with much difficulty (does not decompose below 2200°C) It resists most chemical reagents but is oxidized by a fused NaOH in contact with air.

 $SiC + 2NaOH + 2O_2 \longrightarrow Na_2CO_3 + NaSiO_3 + 2H_2O$

In SiC, carbon and silicon atoms are alternate and are each surrounded tetrahedrally. It is widely used as an abrasive for grinding, cutting and polishing.

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– Chemistry | 16.11

PLANCESS CONCEPTS

- Diamond is covalent yet its m.p. is very high. Diamond has a three dimensional polymeric structure involving very strong covalent bonds by which the atoms are held together. Hence, diamond possesses high m.p. inspite of covalent nature.
- SiF_6^{2-} is known but $SiCl_6^{2-}$ is not,

(i) Smaller size of F gives rise to less steric repulsion in SiF_6^{2-} .

(ii) Interaction of a lone pair of F with Si is stronger than that of a chlorine lone pair.

• The hydrolysis of CCl₄ is not possible but SiCl₄ is easily hydrolysed. Silicon can accomodate OH[−] ion due to the presence of 3d-subshell. whereas C-atom does not possess d-orbitals in its 2nd shell

Anand K ((JEE 2011, AIR 47))

Illustration 10: Carbon and silicon are always tetravalent but germanium and lead show divalency. Explain. (JEE MAIN)

Sol: Inert pair effect is more pronounced in Ge and Pb, as it increases down the group. This results in the divalent ionic nature of Ge and Pb.

Illustration 11: Producer gas is a less efficient fuel than water gas, why?

Sol: In water gas (CO + H_2), both components burn and evolve heat while in producer gas (CO + N_2), only CO burns, i.e., why the former has a higher calorific value and is good fuel.

Illustration 12: Diamond is the hardest substance but graphite is soft in nature. Explain. (JEE MAIN)

Sol: Diamond possesses a very big three dimensional polymeric structure involving each carbon of sp^3 -hybridized nature linked to four other neighbouring carbon atoms which makes it hardest. On the other hand, graphite has layer structure involving each carbon of sp^2 -hybridized nature having a wide separation and weak interlayer bonds and thus two adjacent layers can easily slide over the other to produce its soft nature.

Illustration 13: What happens when:

- (i) Dilute nitric acid slowly reacts with tin.
- (ii) Carbon and steam are heated.
- (iii) Red lead is treated with nitric acid.
- (iv) Iodine is added to stannous chloride.
- (v) Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia.
- (vi) Tin is treated with concentrated nitric acid.
- (vii) Lead is obtained from galena by air reduction.

Sol: (i)
$$4Sn + 10HNO_{3(dil)} \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3$$

(ii)
$$C + H_2 O \rightarrow CO + H_2$$

(Water gas)

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

(iv) $2SnCl_2 + 2I_2 \longrightarrow SnCl_4 + SnI_4$

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16.12 | p - Block Elements -

- (v) $NaCl + NH_4OH + CO_2 \longrightarrow NaHCO_3 + NH_4Cl$
- (vi) $Sn + 4HNO_{3(conc.)} \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$
- (vii) $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$
- (vii) $PbS + 2O_2 \longrightarrow PbSO_4$

Illustration 14: Indicate the principal ingredients of the following:

(i) Coal gas (ii) Producer gas (iii) Water gas.

Sol:

(i) Coal gas	H_2 +C H_4 +CO
(ii) Producer gas	CO+N ₂
(iii) Water gas	CO+H ₂

(JEE MAIN)

Illustration 15: A bluish metal (A) has a high density and readily dissolves in medium concentrated HNO_3 and liberates a gas (B) which on mixing with air turns into red coloured gas(C). Metal is little affected by dil HCl or H_2SO_4 . The solution containing bipositive ions of (A) gives red precipitate (D) when H_2S is passed in presence of saturated solution of KCl. `D' on dilution turns black forming E and F. Identify A to F. (JEE ADVANCED)

Sol: A=Pb;	B=NO;	$C = NO_2;$	$D = Pb_2SCl_2;$	E=PbS;	E=PbCl ₂
Desetters and					

Reactions are:

- (i) $3Pb+8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO \uparrow + 4H_2O$ (A) (B)Nitricoxide
- (ii) $2NO + O_2 \longrightarrow 2NO_2 \uparrow$ Nitrogendioxide(C)
- (iii) Metal is a little affected by dilute HCl or H_2SO_4 due to the formation of insoluble PbCl₂ or PbSO₄ on the surface.
- (iv) $2Pb^{2+} + H_2S + 2CI^- \longrightarrow Pb_2SCl_2 + 2H^+$ Lead sulpho chloride(D)
- (v) $Pb_2SCl_2 \longrightarrow PbS + PbCl_2$ (E)black (F)

Illustration 16: Diamond is covalent yet its m.pt. is very high. Explain.

Sol: Diamond has a three dimensional polymeric structure involving very strong covalent bonds by which the atoms are held together. Hence diamond possesses high m. pt. inspite of its covalent nature.

Illustration 17: SiF_6^{2-} is known but $SiCl_6^{2-}$ is not, why?

Sol: (i) Smaller size of F give rise to less steric repulsion in SiF_6^{2-}

(ii) Interaction of lone pair of F with Si is stronger than that of the chlorine lone pair.

Illustration 18: The hydrolysis of CCl₄ is not possible but SiCl₄ is easily hydrolysed. Explain. (JEE ADVANCED)

Sol: Silicon can accommodate OH⁻ ion in 3d-subshell whereas C-atom does not possess d-orbitals in its 2nd shell.

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- Chemistry | 16.13

3. GROUP 15 ELEMENTS (NITROGEN FAMILY)

3.1 Introduction

- N 7 P 15
- P | 15 As \ 33 ns²np³
- AS > 33 m
- Sb 51
- Bi ∫83
- (a) Electronic Configuration: ns²np³.

- (i) Atomic and Ionic Radii Covalent and ionic (in a particular state) radii increase in size, down the group.
- (b) **Ionisation Enthalpy:** Ionisation enthalpy decreases down the group due to the gradual increase in atomic size. This is due to the extra stability of half-filled p-orbitals leading to a smaller size. The order of successive ionization enthalpies, as expected is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$
- (c) Electronegativity: Decreases down the group with increasing atomic size.
- (d) **Physical Properties:** All the elements of this group are polyatomic. Dinitrogen is a diatomic gas. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids and bismuth is a metal. This is due to the decrease in ionization enthalpy and increase in atomic size. The boiling points, in general, increase from top to bottom in the group but the melting point increases up to arsenic and then decreases up to bismuth. Except nitrogen, all the elements show allotropy.

(e) Chemical Properties:

- (i) Oxidation State: The common oxidation states of these elements are -3, +3 and +5. The tendency to exhibit -3 oxidation state decreases down the group due to increase in size and metallic character. The stability of +5 oxidation state decreases down the group. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group. Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen.
- (ii) **Reactivity towards hydrogen:** All the elements of Group 15 from hydrides of the type EH_3 where E=N, P, As, Sb or Bi. Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
- (iii) **Reactivity towards oxygen:** All these elements form two types of oxides: and E₂O₅. The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group.
- (iv) Reactivity towards halogens: These elements react to form two series of halides: EX₃ and EX₅
- (v) **Reactivity towards metals:** All these elements react with metals to form their binary compounds exhibiting -3 oxidation state.

Exp. Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As_2 (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

3.1.1 Anomalous Behaviour of Nitrogen

Nitrogen differs from the rest of the members of this group due to its small size, high electronegativity, high ionization enthalpy and non-availability of d orbitals. Nitrogen has the unique ability to form $p\pi - p\pi$ multiple bonds with itself and with other elements having a small size and high electronegativity (e.g., C,O). Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form $d\pi - p\pi$ bond as the heavier elements can, for e.g., $R_3P = O$ or $R_3P = CH_2$ (R=alkyl group). Phosphorus and arsenic can form $d\pi - d\pi$ bond also with transition metals, when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

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16.14 | p - Block Elements -

3.2 Important Compounds of Nitrogen

3.2.1 Dinitrogen

Preparation:

(a) In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

 $NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$

(b) It can also be prepared by the thermal decomposition of ammonium dichromate.

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

Properties: Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.

Chemical properties:

- (a) It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia: $N_2(g) + 3H_2(g) \xrightarrow{773K} 2NH_3(g);$
- (b) Dinitrogen combines with dioxygen only at a very high temperature (at about 2000 K) to form nitric oxide, NO.

 $N_2 + O_2(g) \xrightarrow{\text{Heat}} 2NO(g)$

The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen (e.g., calcium cyanamide). It also finds use where an inert atmosphere is required (for e.g., in the iron and steel industry, inert diluent for reactive chemicals). Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

3.2.2 Ammonia

By urea: $NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3$

Decomposition of $(NH_4)_2CO_3$ gives $2NH_3 + H_2O + CO_2$

By Haber's process.

 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \Delta_f H_0 = -46.1 \text{kJmol}^{-1}$

According to Le Chatelier's principle, high pressure would favour the formation of ammonia.

Properties: Ammonia is a colourless gas with a pungent odour.

Chemical Properties: Due to hydrogen bonding, it exists in both solid and liquid states and has higher melting and boiling points than expected on the basis of its molecular mass.

Basic nature of ammonia

$$\begin{split} \mathsf{NH}_3(\mathsf{g}) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) &\longrightarrow \mathsf{NH}_4^+(\mathsf{aq}) + \mathsf{OH}^-\\ \mathsf{Cu}^{2+}(\mathsf{aq}) + 4\mathsf{NH}_3(\mathsf{aq}) &\longrightarrow [\mathsf{Cu}(\mathsf{NH}_3)_4]^{2+}(\mathsf{aq})\\ (\mathsf{blue}) & (\mathsf{deepblue}) \end{split}$$

- Chemistry | 16.15

 $\begin{array}{lll} & \mbox{Ag}^+(aq) + Cl^-(aq) & \mbox{AgCl(s)} \\ (colourless) & (whiteppt) \\ & \mbox{AgCl(s)} + 2NH_3aq & \mbox{AgCl(NH}_3)_2]Cl(aq) \\ (whiteppt) & (colourless) \end{array}$

Uses: Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) and in the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid. Liquid ammonia is also used as a refrigerant.

3.2.3 Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common preparation methods	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(l) oxide]	N ₂ O	+1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4$ $\rightarrow Fe_2(SO_4)_3 + 2NaHSO_4$ $+2H_2O + 2NO$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N ₂ O ₃	+3	$2NO + N_2O_4 \xrightarrow{250K} 2N_2O_3$	Blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO ₂	+4	$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO + O_2$	Brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N ₂ O ₄	+4	$2NO_2 \xrightarrow{cool}{Heat} N_2O_4$	Colourless solid/ liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N ₂ O ₅	+5	$2HNO_3 + P_4O_{10}$ $\xrightarrow{\text{cool}} 4HPO_3 + 2N_2O_5$	Colourless solid, acidic

Table 16.3: Oxides of nitrogen

 Table 16.4: Resonance structure and bond parameters of some oxides

Formula	Resonance Structures	Bond Parameters
N ₂ O	:N=N=Ö:↔ :N≡N−Ö:	N — N — O 113pm 119pm Linear
NO	$:N = \overleftrightarrow{O}: \leftrightarrow : N = \overleftrightarrow{O}:$	N — O 115pm
N ₂ O ₃	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c} 0 \\ \hline $

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16.16 | p - Block Elements -



- NO is paramagnetic in its gaseous state but diamagnetic in its liquid or solid state, The NO molecule has eleven valence electrons and is thus paramagnetic in nature due to unpaired electron. In solution or solid state, it forms a loose dimer in such a way that magnetic field of unpaired electrons of two molecules cancel out it behaves as diamagnetic in nature
- NF_3 is stable but NCI_3 and NI_3 are readily hydrolysed and are explosives NF_3 is not hydrolysed because neither N nor F can expand their octet by using d-orbitals. On the other hand NCI_3 and NI_3 hydrolyse violently because CI and I can expand their octet by using d-orbitals.

 $NCI_3 + 3H_2O \longrightarrow NH_3 + 3HOCI$

Vaibhav Gupta (JEE 2009, AIR 54)

3.2.4 Nitric Acid

Preparation: By Ostwald's process:

 $\begin{array}{rrr} 4NH_3(g) &+& 5O_2 \\ (from air) & \xrightarrow{Pt/Rh \ gauge \ catalyst \ }} 4NO(g) + 6H_2O(g) \end{array}$

 $2NO(g) + O_2(g) = 2NO_2(g)$ $3NO_2(g) + H_2O(1) \rightarrow 2HNO_3(aq) + NO(g)$

NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4

Properties: It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K). Laboratory grade nitric acid contains ~68% of the HNO₃ by mass and has a specific gravity of 1.504.

Chemical reaction of HNO₃ with metal and non-metals:

 $\begin{aligned} HNO_{3}(aq) + H_{2}O(I) \to H_{3}O^{+}(aq) + NO_{3}^{-}(aq) \\ 3Cu + 8HNO_{3}(dil) \to 3Cu(NO_{3})_{2} + 2NO + 4H_{2}O \\ Cu + 4HNO_{3}(conc.) \to Cu(NO_{3})_{2} + 2NO_{2} + 2H_{2}O \\ 4Zn + 10HNO_{3}(dil) \to 4Zn(NO_{3})_{2} + 5H_{2}O + N_{2}O \end{aligned}$

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- Chemistry | 16.17

$$\begin{split} &Zn + 4HNO_3(conc.) \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2 \\ &I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O \\ &C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2 \\ &S_8 + 48HNO_3 \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O \\ &P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O \end{split}$$

Brown Ring Test: The familiar brown ring test for nitrates depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown coloured complex. The test is usually carried out by adding a dilute ferrous sulphate solution to an aqueous solution containing nitrate iron, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in solution.

3.3 Phosphorus

3.3.1 Types of Phosphorous

(a) Yellow or white phosphorous (b) Red Phosphorous

White P: (a) White P exists as discrete P, molecules. It has tetrahedral geometry. Bond angle is 60° instead of 109°. With this bond angle, white P is associated with the strain accounting for its less stability and greater reactivity.

(b) Ignition temp of white P is 30°C i.e. it is highly reactive and when it undergoes ignition, it releases a large amount of energy which is emitted in the form of light, termed as Fluorescence.

Red P: (a) Formed from white P by breakage of one P - P bond and so chain of P_A

molecules is formed.

(b) Long Chain of P_4 , molecules are formed and when compared with white P, red P has more density, less reactivity with breakage of P – P bond, strain of P_4 decreases

(c) Ignition temp of red P is above 230°C

Black P: (a) Exists in a hexagonal form like graphite.

(b) It is least reactive and has maximum density.

(c) Black P exists as a solid of high density.

(d) It is a good conductor of electricity.

Uses:

- (a) Phosphorous is largely used in the matches industry.
- (b) White phosphorous is used as a rat poison.

3.3.2 Some Important Compounds of Phosphorous

(a) Phosphorus Trichloride: $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_4 + 2S_2Cl_2$

Properties: It is a colourless oily liquid and hydrolyses in the presence of moisture.

 $\mathsf{PCI}_3 + \mathsf{3H}_2\mathsf{O} \to \mathsf{H}_3\mathsf{PO}_3 + \mathsf{3HCI}$



C

Pyramidal

(c) Black Phosphorous

Figure 16.3: a Red



Figure 16.4: b Black

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16.18 | p - Block Elements -

(b) Phosphorus Pentachloride

 $\begin{array}{l} \textbf{Preparation:} \quad \begin{array}{l} \mathsf{P}_4 + 10\mathsf{Cl}_2 \rightarrow 4\mathsf{PCl}_5 \\ \mathsf{P}_4 + 10\mathsf{SO}_2\mathsf{Cl}_2 \rightarrow 4\mathsf{PCl}_5 + 10\mathsf{SO}_2 \end{array}$

Note: In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown. The three equatorial P-Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.

Properties: PCl₅ is a yellowish white powder and in moist air, it hydrolyses to POCl₃ and finally gets converted to phosphoric acid.

 $PCI_{5} + H_{2}O \rightarrow POCI_{3} + 2HCI$ $POCI_{3} + 3H_{2}O \rightarrow H_{3}PO_{4} + 3HCI$ $PCI_{5} \xrightarrow{heat} PCI_{3} + CI_{2}$



Note: In the solid state it exists as an ionic solid, $[PCI_4]^+[PCI_6]^-$ in which the cation, $[PCI_4]^+$ is tetrahedral and the anion, $[PCI_6]^-$ octahedral.

3.3.3 Oxoacids of Phosphorus

Name	Formula	Oxidation state of Phosphorous	Characteristic bonds and their number	Preparation
Hypophosphorous	H ₃ PO ₂	+1	One P-OH	white P_4 + alkali
(phosphinic)		S	Two P-H	
			One P=O	
Orthophosphorous	H ₃ PO ₃	+3	Two P-OH	$P_2O_3 + H_2O$
(Phosphonic)		0	One P-H P-O-P	
			One P=O	
Pyrophosphorous	H ₄ P ₂ O ₅	+3	Two P-OH	PCl ₃ + H ₃ PO ₃
			Two P-H	
			Two P=O	
Hypophosphoric	$H_4P_2O_6$	+4	Four P-OH	red P_4 + alkali
			Two P=O	
			One P-P	
Orthophosphoric	H ₃ PO ₄	+5	Three P-OH	$P_4O_{10} + H_2O$
			One P=O	
Pyrophosphoric	H ₄ P ₂ O ₇	+5	Four P-OH	heat phosphoric
			Two P=O	acid
			One P-O-P	
Metaphosphoric	(HPO ₃) _n	+5	Three P-OH	Phosphorus acid
			Three P=O	+Br ₂ , heat in a sealed tube
			Three P-O-P	

Table 16.5: Oxoacids of Phosphorus



Chemistry | 16.19



Illustration 23: NO is paramagnetic in gaseous state but diamagnetic in liquid or solid state, why? (JEE MAIN)

Sol: The NO molecule has eleven valence electrons and thus, paramagnetic in nature due to the unpaired electron. In solution or solid state, it forms a loose dimer in such a way that the magnetic field of unpaired electrons of two molecules cancel out and it behaves as diamagnetic in nature.

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Illustration 24: Which among P_4O_{10} , Cl_2O_7 , I_2O_5 has the greatest affinity for water?

(JEE ADVANCED)

(JEE ADVANCED)

Sol: P_4O_{10} , one of the most powerful dehydrating agents known. Cl_2O_7 is the product of dehydration of $HClO_4$ by P_4O_{10} . $12HClO_4 + P_4O_{10} \longrightarrow 6Cl_2O_7 + 4H_3PO_4$ Also, I_2O_5 is obtained by heating HIO_3 and thus, it cannot have too great affinity for water.

Illustration 25: Describe the action of heat on the following compounds:

- (i) Ammonium nitrate
- (iii) Ammonium Chloride
- (v) Ammonium dichromate
- (vi) Orthophosphoric acid

(iv) A mixture of NaNO₂ and NH₄Cl

(ii) Ammonium nitrite

- (viii) Hypophosphorous acid
- (ix) Copper nitrate

(vii) Phosphorous acid

(x) Silver Nitrate

Sol: (i)
$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

(ii)
$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

(iii)
$$NH_4CI \longrightarrow NH_3 + HCI$$

(iv)
$$NaNO_2 + NH_4CI \longrightarrow N_2 + NaCI + 2H_2O$$

(v)
$$(NH_4)_2 Cr_2 O_7 \longrightarrow N_2 + Cr_2 O_3 + 4H_2 O_3$$

- (vi) $2H_3PO_4 \xrightarrow{205^{\circ}C} H_4P_2O_7 + H_2O$
- $H_{3}PO_{4} \xrightarrow{600^{\circ}C} HPO_{3} + H_{2}O$ $4H_{3}PO_{4} \xrightarrow{\text{Red heat}} P_{4}O_{10} + 6H_{2}O$
- $4\Pi_3 PO_4 \longrightarrow P_4 O_{10} + 0\Pi_2 C_{10}$
- (vii) $4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$
- (viii) $2H_3PO_2 \longrightarrow H_3PO_4 + PH_3$

(ix)
$$2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + C$$

(x) $2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$

Illustration 26: What happens when an aqueous solution of hydrazine reacts with:

- (i) An aqueous solution I_2 .
- (ii) An alkaline solution of copper sulphate.
- (iii) An aqueous alkaline solution of potassium ferricyanide.
- (iv) An ammoniacal solution of silver nitrate.

Sol: (i)
$$N_2H_4 + 2I_2 \longrightarrow N_2 + 4HI$$

(ii) $N_2H_4 + 2CuSO_4 + 4KOH \longrightarrow N_2 + 2Cu + 2K_2SO_4 + 4H_2O$
(iii) $4K_3[Fe(CN)_6] + 4KOH + N_2H_4 \longrightarrow 4K_4[Fe(CN)_6] + 4H_2O + N_2$
(iv) $N_2H_4 + 2NH_4OH + 2AgNO_3 \longrightarrow N_2 + 2Ag + 2NH_4NO_3 + 2H_2O$

(JEE ADVANCED)

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- Chemistry | 16.21

Illustration 27: An inorganic compound (A) when heated decomposes completely to give only two gases (B) and (C). (B) is a neutral gas, fairly soluble in water and itself decomposes on heating to two different gases (D) and (E).

(A) When warmed with NaOH gives another gas (F) which turns mercurous nitrate paper black. After sometime, the gas (F) ceases to evolve, however its supply is restored by treating residual solution with aluminium powder. Identify (A) to (F) and give necessary equations. (JEE ADVANCED)

Sol: $NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$ (A) (B) (C) $2N_2O \longrightarrow N_2 + O_2$ (B) (D) (E) $NH_4NO_3 + NaOH \longrightarrow NaNO_3 + NH_3 + H_2O$ (A) $AI + NaOH + H_2O \longrightarrow NaAIO_2 + 3H$ $NaNO_3 + 8H \longrightarrow NaOH + NH_3 + 2H_2O$ $2NH_3 + Hg_2(NO_3)_2 + 2H_2O \longrightarrow Hg_2(OH)_2 + 2NH_4NO_3$ (F) Black

Illustration 28: NF₃ is stable but NCl₃ and NI₃ are readily hydrolysed and are explosives. Explain. (JEE ADVANCED)

Sol: NF₃ is not hydrolysed because neither N nor F can expand their octet by using d-orbitals. On the other hand, NCl₂ and NI₃ hydrolyse violently because Cl and I can expand their octet by using their d-orbitals. $NCI_3 + 3H_2O \longrightarrow NH_3 + 3HOCI$

4. GROUP 16 ELEMENTS (OXYGEN FAMILY)

4.1 Introduction

These are called chalcogen. Because these are ore forming elements {Chalco=ore}

0 S

- ns^2np^4 (electronic configuration table) Se
- Te Ро
- (a) Electronic Configuration: ns²np⁴
- (b) Atomic and lonic Radii: Due to the increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atom is, however, exceptionally small.
- (c) Electron Gain Enthalpy: Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However, from sulphur onwards the value again becomes less negative up to polonium.
- (d) Physical Properties: Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life= 13.8 days).

The melting and boiling points increase with an increase in atomic number down the group.

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16.22 | p - Block Elements -

4.1.1 Anomalous Behaviour of Oxygen

Due to its small size and high electronegativity, strong hydrogen bonding is observed in H₂O and not in H₂S,

- (a) **Reactivity with hydrogen:** All the elements of Group 16 form hydrides of the type H₂E (E=O, S, Se, Te, Po). Their acidic character increases from H₂O to H₂Te. The increase in acidic character can be explained in terms of a decrease in bond enthalpy for the dissociation of H-E bond down the group. Owing to the decrease in enthalpy for the dissociation of H-E bond, down the group, the thermal stability of hydrides also decreases from H₂O to H₂Po. All the hydrides except water possess reducing property and this character increases from H₂S to H₂Te.
- (b) **Reactivity with oxygen:** All these elements from oxides of the EO_2 and EO_3 types where E=S, Se, Te or Po.
- (c) Reactivity towards the halogens: Elements of group 16 form a large number of halides of the type, EX_6 , EX_4 and EX_2 where E is an element of the group and X is a halogen. The stability of the halides decreases in the order $F^- > CI^- > Br^- > I^-$.

4.2 Dioxygen

Preparation: Dioxygen can be obtained in the laboratory by the following ways:

(a) By heating oxygen containing salts such as chlorates, nitrates and permanganates.

$$2\text{KCIO}_{3} \xrightarrow[\text{Meat}]{} 2\text{KCI} + 3\text{O}_{2}$$

- (b) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide. $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
- (c) On a large scale, it can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

Properties: Dioxygen is a colourless and odourless gas. Its solubility in water is to the extent of 3.08 cm³ in 100 cm³ water at 293 K which is just sufficient for the vital support of marine and aquatic life.

Some of the reactions of dioxygen with metals, non-metals and other compounds are given below:

$$\begin{aligned} &2\text{Ca} + \text{O}_2 \rightarrow 2\text{CaO} \\ &4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3 \\ &\text{P}_4 + 5\text{O}_2 \rightarrow \text{P}_4\text{O}_{10} \\ &\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \\ &2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2 \\ &\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \end{aligned}$$

Some compounds are catalytically oxidized. For e.g.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$
$$2HCI + O_2 \xrightarrow{CuCI_2} 2CI_2 + 2H_2O$$

4.3 Sulphur

- (a) **Rhombic sulphur (** α **-sulphur):** This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS₂. It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in CS₂.
- (b) Monoclinic sulphur (β -sulphur): This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling. Till a crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of β -sulphur are formed. It is stable above 369 K and

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205.7 pm

S

S

S

102.2

(b)

transforms into α -sulphur below it. Its m.p. is 393 K and specific gravity 1.98. It is soluble in CS₂. Conversely, α -sulphur is stable below 369 K and transforms into β -sulphur above this temperature. At 369 K both the forms are stable. This temperature is called transition temperature. Both rhombic and monoclinic sulphur have S₈ molecules. These S₈ molecules are packed to give different crystal structures.



Figure 16.8: Forms of Sulphur

4.3.1 Sulphur Dioxide

Preparation: When sulphur is burnt in air or oxygen to form SO_2 $(S(s)+O_2(g) \rightarrow SO_2(g))$

Properties: Sulphur dioxide is a colourless gas with pungent smell and is highly soluble in water.

Structure of SO₂ molecules



The molecule of SO_2 in angular. It is a resonance hybrid of the two canonical forms.

Uses: Sulphur dioxide is used (i) in refining petroleum and sugar (ii) in bleaching wool and silk and (iii) as an anti-chlor, disinfectant and preservative. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide.

4.3.2 Oxoacids of Sulphur

Sulphur forms a number of oxoacids such as





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16.24 | p - Block Elements -

4.3.3 Sulphuric Acid

Manufacture: Sulphuric acid is one of the most important industrial chemicals worldwide. Sulphuric acid is manufactured by the Contact Process which involves three steps:

- (a) Burning of sulphur or sulphide ores in air to generate SO_2
- (b) Conversion of SO₂ to SO₃ by the reaction with oxygen in the presence of a catalyst (V_2O_5), and
- (c) Absorption of SO_3 in H_2SO_4 to give Oleum ($H_2S_2O_7$). 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).

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g); \Delta_r H = 196.6 \text{ kJ mol}^{-1}$$

Manufacture of Sulphuric Acid: The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum. Dilution of oleum with water gives 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.

 $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (Oleum). The sulphuric acid obtained by Contact process is 96-98% pure.

Properties: Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. It dissolves in water with the evolution of a large quantity of heat. While preparing sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into water with constant stirring. The chemical reaction of sulphuric acid is as a result of the following characteristics: (a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidizing agent.

 $H_2SO_4(aq) + H_2O(I) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$; $K_{a1} = very large(K_{a1} > 10)$

(M = Metal)

 $HSO_4^{-}(aq) + H_2O(I) \rightarrow H_3O^{+}(aq); K_{a_2} = 1.2 \times 10^{-2}$

Chemical Reactions:

 $2MX + H_2SO_4 \rightarrow 2HX + M_2SO_4 (X = F, Cl, NO_3)$

 $C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$ $Cu + 2H_2SO_4 \text{ (conc.)} \rightarrow CuSO_4 + SO_2 + 2H_2O$

 $3S+2H_2SO_4$ (conc.) $\rightarrow 3SO_2 + 2H_2O_2$

 $C + 2H_2SO_4(conc.) \rightarrow CO_2 + 2SO_2 + 2H_2O_2$

PLANCESS CONCEPTS

- Among H_2O , HCland NH_3 , H_2O has the highest boiling point and HCl the lowest. H_2O is capable of showing more stronger H-bonding than NH_3 , while HCl has no H-bonding. The b.p. order is $H_2O > NH_3 > HCl$.
- H₂S acts only as a reducing agent while SO₂ can act both as a reducing agent and oxidizing agent. S in SO₂ has a oxidation state of +4. It lies between the minimum oxidation state (-2) and maximum oxidation (+6) of S. Thus, S in SO₂ can show an increase in its oxidation number (i.e., act as a reductant) or can show a decrease in its oxidation number (i.e., it acts as an oxidant). On the other hand, in H₂S, S is in -2 oxidation state and can only increase its oxidation state to act as a reductant.

GV Abhinav (JEE 2012, AIR 329)

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Chemistry | 16.25

(JEE MAIN)

Illustration 29: What are the oxidation states of S in the following compounds:

(a) PbS (b)
$$SO_2$$
 (c) SF_6 (d) $Na_2S_2O_3$ (e) H_2SO_3

Sol: (a) -2, (b) +4, (c) +4, (d) +2, (e) +4

Illustration 30: H₂S acts only as reducing agent while SO₂ can act both as reducing agent and oxidising agent. Explain. (JEE MAIN)

Sol: S in SO₂ has oxidation state +4. It lies between the minimum oxidation state (-2) and maximum oxidation state (+6) of S. Thus S in SO_2 can show an increase in its ox. no. (i.e., act as reductant) or can show a decrease in its ox. no. (i.e., act as oxidant). On the other hand, in H_2S , S is in -2 oxidation state and can only increase its oxidation state to act as reductant.

Illustration 31: Nitric acid cannot be used to prepare H₂S. Explain.

Sol: Nitric acid is an oxidizing agent. It will oxidise H₂S.

 $H_2S + 2HNO_3 \rightarrow 2NO_2 + S + 2H_2O$

Illustration 32: Among H_2O , HCl and NH_3 , H_2O has the highest boiling point and HCl the lowest. (JEE MAIN)

Sol: H₂O is capable of showing more stronger H-bonding than NH₃, while HCl has no H-bonding. The b.p. order is $H_2O > NH_3 > HCI$

Illustration 33: Conc. H_2SO_4 cannot be used for drying up H_2S . Explain (JEE MAIN)

Sol: Conc. H_2SO_4 oxidises H_2S to S and thus cannot be used as for drying up H_2S .

 $H_2SO_4 + H_2S \rightarrow 2H_2O + SO_2 + S$

Illustration 34: Ozone destroys a mercury meniscus. Why?

Sol: Ozone oxidises Hg to mercury suboxide which starts sticking to glass and loses its mobility. Hence, Hg loses its meniscus in contact with ozone. However, it can be regained by the action of H_2O_2 .

$$2Hg + O_3 \rightarrow Hg_2O + O_2$$

Illustration 35: KMnO₄ should not be dissolved in conc. H_2SO_4 . Explain.

Sol: $KMnO_4$ forms explosive covalent compound, Mn_2O_7 with conc. H_2SO_4

 $2KMnO_4 + H_2SO_{4(conc)} \rightarrow K_2SO_4 + Mn_2O_7 + H_2O_7$

However it can be dissolved in dil. H_2SO_4 to give nascent oxygen, if it is to be used as an oxidant

Illustration 36: SO₂ acts as bleaching agent. Explain.

Sol: SO₂ in presence of water is oxidized to H₂SO₄ liberating nascent hydrogen, which reduces/bleaches the colouring matter.

 $SO_2 + 2H_2O \rightarrow H_2SO_4 + 2[H]$

Colouring matter + 2[H] \rightarrow Colourless compound

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(JEE MAIN)

Illustration 37: An acidified $K_2Cr_2O_7$ paper turns green when exposed to SO_2 . Explain. (JEE ADVANCED)

Sol: SO_2 reduces $K_2Cr_2O_7$ to green chromium sulphate. $3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$ Green

Illustration 38: A white turbidity is obtained by passing H₂S in aqueous solution of SO₂ Why? (JEE ADVANCED)

Sol: Aqueous solution of SO₂ and H₂S undergoes redox changes to produce colloidal sulphur as white turbidity. 2H₂S + H₂SO₃ \rightarrow 3H₂O + 3S (Colloidal sulphur)

5. GROUP 17 ELEMENTS (HALOGEN FAMILY)

5.1 Introduction

Named because they are sea - salts forming elements.

```
F
Cl
Br \ns<sup>2</sup>np<sup>5</sup>
I
At
```

General Properties:

```
(a) State and Nature
```

- (i) F and Cl are Gas
- (ii) Br: Liquid
- (iii) I, At is solid
- (iv) All are non metallic. But non metallic character decreases down the group.
- (v) I has metallic lustre on heating and undergoes sublimation.
- (b) Atomic Radii, Ionic Radii, B.P. and M.P., Density: All these characters increase down the group
- (c) Ionization Potential and Electronegativity: Decreases down the group

(d) Electron Affinity (E.A)

```
From F to CI \rightarrow E.A increases.
```

Due to the availability of a vacant d-orbital in Cl and then E.A. decreases

- So, order is CI > F > Br > I.
- (e) Valency and Oxidation State:
 - (i) $ns^2 np^5$
 - (ii) Valency = 1

If halogens combines with more E.N. elements, then O.S. =+1.

(iii) For Cl, Ground State:

Valency = 1

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Chemistry | 16.27



(f) Bond Energy: F – F bond dissociation energy is less than that of CI-CI and Br-Br. It is due to larger inter electronic (electron-electron) repulsion between the non-bonding electrons in the 2p orbitals of fluorine atom than in the 3p orbitals of chlorine atoms.

F-F CI-CI Br-Br I-I

38 kcal/mol 57 kcal/mol 45.5 kcal/mol 35.6 kcal/mol Cl₂ > Br₂ > F₂ > I

5.1.1 Oxidising Power

The electron affinity, or tendency to gain electrons reaches a maximum at chlorine. Oxidation may be regarded as the removal of electrons so that an oxidizing agent gains electrons.

Thus halogens act as oxidizing agents.

The strength of an oxidizing agent (i.e. oxidation potential) depends upon several energy terms and is represented by following diagram.

$$\frac{1}{2}X_{2}(s) \xrightarrow{\frac{1}{2}\text{Heat}}_{\text{Fusim}} \xrightarrow{\frac{1}{2}} X_{2}(1) \xrightarrow{\frac{1}{2}\text{heat}}_{\text{Evaporation}} \xrightarrow{\frac{1}{2}} X_{2}(g) \xrightarrow{\frac{1}{2}\text{heat}}_{\text{Dissociation}} X(g) \xrightarrow{\text{Electron}}_{\text{affinity}} X^{-}(g) \xrightarrow{\text{h eat of}}_{\text{hydration}} X^{-}(hydrated)$$

The heat of fusion, evaporation and dissociation are positive and electron affinity and heat of hydration are negative. The net energy (E) required for oxidizing reaction is given by-

$$E_{(net)} = \frac{1}{2}H_{f} + \frac{1}{2}H_{v} + \frac{1}{2}H_{d} - E.A. - H_{(hyd)}$$

Element $E_{out}(kcal)$

$$\begin{array}{cccc} F_2 & & -186.5 \\ CI_2 & & -147.4 \\ Br_2 & & -136.4 \\ I_2 & & -122.4 \end{array}$$

Thus oxidizing powers decrease on descending in group VII. Fluorine is a strong oxidising agent as seen in the reaction given below where oxygen in water has been oxidised. The oxidation of H_2O by Cl_2 is thermodynamically possible but since the energy of activation is high, this reaction does not occur.

$$F_2 + H_2O \rightarrow 2H^+ + 2F^- + \frac{1}{2}O_2$$

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

lodine is even weaker where the free energy change indicates that for oxidation of water, it needs a supply of energy.

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16.28 | p - Block Elements -

Chemical Properties

(a) Reaction with H_2

- (i) All halogens reacts with H_2 to form hydrogen halides. $H_2 + X_2 \rightarrow 2HX$
- (ii) Reactivity of Halogens F > Cl > Br > I
- (iii) HCl, HBr, HI acts as reducing agent.
- (b) Reaction with H₂O
 - (i) H_2O acts as reducing agent only with fluorine. $2F_2 + 2H_2O \rightarrow 4HF + O_2$
 - (ii) $H_2O + I_2 \rightarrow No$ Reaction.

(c) Displacement reaction

(i) $F_2 + 2NaX \rightarrow 2NaF + X_2 \{X = CI, Br, I\}$

$$CI_2 + 2NaX \rightarrow 2NaCI + X_2$$
 {X = Br₂, I₂}

So order of displacement $[F_2 > Cl_2 > Br_2 > I_2]$

- (ii) If Halogen is in -ve O.S., then it is replaced by more **E.N.** element.
- (iii) If Halogen is +ve O.S., then it is replaced by less E.N. element.
- (d) Reaction with metals: Metal halides are formed F > CI > Br > I
- (e) Reaction with non-metals: Non-metallic halides are formed. Eg. NF₃, PCl₃ etc.
- (f) Reaction with NH,
 - (i) $3F_2 + NH_3 \rightarrow NF_3 + 3HF$
 - (ii) $3Cl_2 + NH_3 \rightarrow NCl_3 + 3HCl$
- (g) Reaction with NaOH
 - (i) F_2 +NaOH (dil.) \rightarrow 2NaF + OF₂ + H₂O
 - (ii) $2F_2 + 4NaOH (conc.) \rightarrow 4NaF + 2H_2O + O_2$
- (h) Formation of oxides
 - (i) No oxides of F because of its maximum E.N. character.
 - (ii) Rest form

X ₂ O	X ₂ O ₃	X ₂ O ₅	X ₂ O ₇
g. +1	+3	+5	+7
Cl ₂ O	Cl_2O_3	Cl_2O_5	Cl ₂ O ₇

(iii) All these oxides are acidic

(iv) Acidity decreases down the group and maximum active oxide is Cl_2O_7

(i) Formation of oxyacids

(i) F does not form any oxyacid due to High E.N.

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- Chemistry | 16.29

sol.

(ii) Rest oxyacids are

НХО	HXO ₂	HXO ₃	HXO ₄
+1	+3	+5	+7
Hypohalous	Halous	Halic acid	Perhalic acid
acid	acid		

(j) Interhalogens

Products are obtained by uniting two halogen compounds:

 $AB AB_3 AB_5 AB_7$

Where A = less E.N. Halogen

B = More E.N. Halogen

 $\begin{array}{ccc} CIF & CIF_3 & BrF_5\\ Eg. & BrCl & BrCl_3 & ICl_5\\ & IBr & IBr_3 \end{array}$

These interhalogens have polarity because of different E.N.

Note: Abnormal behaviour of Fluorine as compared to Other Members:

 IF_7

Fluorine differs considerably from other halogens due to its-

- Small size
- High electronegativity.
- Non availability of d orbitals in its valence shell.
- Low bond dissociation energy of F F bond.
- Boiling point of HF is the highest and then it increases down the group.
- Due to hydrogen bonding, HF is a liquid while HCl, HBr and HI are gases.
- Solubility of salts

AgF is soluble in water while AgCl, AgBr and AgI are insoluble.

It combines with hydrogen explosively at a low temperature and even in the dark.

None of the other halogens combine so readily.

$$H_2 + F_2 \longrightarrow 2HF$$

(i) It liberates oxygen as well as ozone with water.

$$2H_2O + 2F_2 \longrightarrow 4HF + O_2,$$

$$3H_2O + 3F_2 \longrightarrow 6HF + O_2$$

Family Members of Halogen

(a) Fluorine (F₂)

(i) Uses: It is used in the preparation of fluorine compounds such as.

Freon: Freon – 12 i.e. CF_2CI_2 as used in refrigeration and air conditioning in place of NH_3 and SO_2 Teflon: $(-F_2C-CF_2)_n$ It is a new plastic.

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16.30 | p - Block Elements -

Chlorine (Cl₂)

(a) Preparation: By the electrolysis of brine (Aq. Solution of NaCl) in nelson cell. This is the cheapest method

NaCl \longrightarrow Na⁺ + Cl⁻ H₂O \longleftrightarrow H⁺ + OH⁻ At Cathode: $\frac{H^+ + e^- \longrightarrow H}{H + H \longrightarrow H_2}$ At anode: $\frac{Cl^- \longrightarrow Cl + e^-}{Cl + Cl \longrightarrow Cl_2}$

(b) Deacon's process:

$$4\text{HCI} + \text{O}_2 \xrightarrow[CuCl_2]{} 2\text{H}_2\text{O} + 2\text{Cl}_2$$
$$4 \quad : \quad 1$$

Chlorine gas thus obtained contains N_2 and O_2 and is used for the manufacture of bleaching powder by Hasenclever's process

(c) Uses:

(i) As a germicide and disinfectant.

(ii) Domestic antiseptic solution (NaOCl)

Bromine (Br₂)

(a) **Preparation:** (a) Bittern: Mother liquor contains about 0.25% of bromine or MgBr₂ and is known as bittern. Bittern is treated wih Chlorine gas.

 $MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$

(b) Uses: (a) It is used in preparation of ethyl bromide which is used in the manufacturing of tetraethyl lead (TEL) as an important anti – knock compound in the petroleum industry.

$$C_{2}H_{6} + Br_{2} \longrightarrow C_{2}H_{5}Br + HBr$$

$$4C_{2}H_{5}Br + 4Na - Pb \longrightarrow (C_{2}H_{5})_{4}Pb + 4NaBr + 2Pb$$

lodine (I,)

- (a) I_2 is the rarest of all the halogens. Its main source is kelp (varee).
- (b) **Properties:** (a) It is only sparingly soluble in water but readily in NaOK iodide due to formation of triiodide. KI + I₂ \longrightarrow KI₃

However, this solution behaves as a simple mixture of KI and free I₂.

Note: Tincture of iodine contains $\frac{1}{2}$ ounce I_2 , $\frac{1}{4}$ ounce KI and 1 pinch of rectified spirit.

Chemistry | 16.31

Oxidation state	Chlorine	Bromine	lodine	Name of acid	Name of salt of halogens	
+1	HCIO	HBrO	HIO	Hypohalous	Hypohalite	Stability and acidity
+3	HCIO ₂	-	-	Halous	Halite	Increases but
+5	HCIO ₃	HBrO ₃	HIO3	Halic	Halate	Oxidizing power
+7	HCIO ₄	HBrO ₄	HIO ₄	Perhalic	Perhalate	decreases

Table 16.6: Oxy acids of Halogens

Oxy Acids of Halogens:

- (a) Fluorine does not form any oxy-acids because it is more electronegative than oxygen.
- (b) Other halogens form four series of oxy acids with formulae

 $HXO \rightarrow Hypohalous$

 $\mathrm{HXO}_2 \rightarrow \mathrm{Halous}$

 $HXO_3 \rightarrow Halic$

 $HXO_4 \rightarrow Perhalic acids or Halic (I), Halic (III), Halic (V) and Halic (VII)$

- (c) Thermal stability Stability increases and oxidizing power decreases
- (d) Oxidising power-

```
CIO<sup>-</sup>
```

 \downarrow

 CIO_4^-

Hypochlorites are the strongest oxidizing agents,

(e) Relative acidity ∞ oxidation no.

 $HCIO_4 > HCIO_3 > HCIO_2 > HCIO$

Note: (i) In all these acids and salts halogen is in sp³ hybridised state.

(ii) Stronger the acid, the weaker will be its conjugate base and vice-versa.

 $ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$ (relative basic character)

Thus, CIO_4^- is the weakest base and $HCIO_4^-$ (conjugate acid of CIO_4^-) is the strongest acid.

 $CIO_4^- > CIO_3^- > CIO_2^- > CIO^-$

Relative stability of CI-O bonds

16.32 | p - Block Elements -

PLANCESS CONCEPTS

- Fluorine exhibits a covalence of one only whereas other halogens show a covalence ranging from 1 to 7. Because in fluorine vacant d-orbitals are not present and so the electron can't be unpaired by electronic excitation. On the other hand, rest all halogens show covalence from 1 to 7 by the excitation of their p-electrons to d-subshells.
- KHF_2 is well known, whereas $KHCl_2$ or $KHBr_2$ does not exist. H_2F_2 exists as dimeric molecule due to H-bonding and thus, shows dibasic nature. Hence, it gives two series of salts KHF_2 [K⁺ and F⁻.....H –F⁻] and KF [K⁺ and F⁻] whereas HCl and HBr do not show hydrogen bonding and thus formation of $KHCl_2$ or $KHBr_2$ is not possible.

Chinmay S Purandare (JEE 2012, AIR 698)

Illustration 39: Pure HI kept in a bottle acquires a brown colour after some time. Explain. (JEE MAIN)

Sol: HI is strong reducing agent and is oxidized by oxygen to I_2 . The liberated iodine is dissolved there and imparts a brown colour to the solution. $4HI+O_2 \longrightarrow 2H_2O + 2I_2$

Illustration 40: lodine dissolves more in KI solution, than in pure water. Explain (JEE MAIN)

Sol: I₂ is non-polar in nature and thus its solubility in water (a polar solvent) is less which however becomes more if KI is present due to a complex formation. I₂ + KI \longrightarrow KI₃ (soluble complex)

Illustration 41: Chlorine is a gas while iodine is a solid under ordinary conditions. Explain. (JEE MAIN)

Sol: Due to high mol. wt., Van der Waals' forces of attraction one stronger in I_2 .

Illustration 42: Fluorine exhibits a covalence of one only whereas other halogens show a covalence ranging from 1 to 7. (JEE MAIN)

Sol: Because in fluorine, vacant d-orbitals are not present and so electrons can't be unpaired by electronic excitation. On the other hand, rest all halogens show covalence from 1 to 7 by excitation of their s and p-electrons to d-subshells.

Halogens (Cl, Br, I)	ns	np	nd
Ground state		↑↓ ↑↓ ↑	
I excited state	()	↑↓ ↑ ↑	Covalence = 1
			Covalence = 3
II excited state		$\uparrow \uparrow \uparrow$	
			Covalence = 5
III excited state	() $ $	$\uparrow \uparrow \uparrow$	
			Covalence = 7

Fluorine is the most electronegative element and thus shows only negative oxidation state. Furthermore, it has 2s²2p⁵ configuration and thus shows only -1 oxidation state in order to complete its octet. Also like other halogens, it does not have vacant d-orbitals in its valence shell.

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– Chemistry | 16.33

(JEE MAIN)

(JEE ADVANCED)

(JEE ADVANCED)

Illustration 43: Fluorine is a non-metal whereas iodine shows some metallic properties as well. Explain.

Sol: Owing to small size and high I.E., F has no tendency to lose electron. I is large and has lower I.E. So, it may lose an electron.

Illustration 44: Why are halogens coloured and on moving from F_2 to I_2 , the colour of halogens becomes dark, why?

Sol: Because energy required in electronic excitation and de-excitation lies in visible region. On moving from F_2 to I_2 , the size of atom increases and so energy levels become closer and so promotion energy becomes less. So, colour deepens.

Illustration 45: Dry chlorine does not act as bleaching agent.

Sol: The bleaching action of Cl₂ is due to its reaction with H₂O to liberate nascent oxygen.

Illustration 46: lodine stains on cloths can be removed by hypo. (JEE ADVANCED)

Sol: Hypo reacts with iodine to form water soluble sodium tetrathionate and sodium iodide.

 $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

Illustration 47: Colour of KI solution containing starch turns blue when chlorine water is added to it. Explain.

Sol: Cl_2 replaces I_2 from its aqueous solution due to its higher standard reduction potential than iodine. $Cl_2 + 2KI \longrightarrow 2KCI + I_2$

Illustration 48: KHF₂ is well known, whereas KHBr₂ does not exist. Explain. (JEE ADVANCED)

Sol: H_2F_2 exists as dimeric molecule due to H_2 bonding and thus shows dibasic nature. Hence it gives two series of salts KHF_2 as $[K^+ \text{ and } F^-]$ and $KF[K^+ \text{ and } F^-]$ whereas HCl and HBr do not show hydrogen bonding and thus formation of $KHCl_2$ or $KHBr_2$ is not possible.

6. NOBLE GASES OF RARE GASES

6.1 Introduction

They occur in the atmosphere infrequently and are hence also referred to as the rare gases.

He 2 1s²

Ne 10 Ar 18

Kr 36 ns²np

Xe 54

Rn 86

All have octet configuration except He having duplet configuration.

(a) They exist in gaseous state.

(b) Rn is produced by the disintegration of radium and is radioactive itself.

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16.34 | p - Block Elements -

- (c) Ramsay discovered these gases.
- (d) The first inert gas to be discovered by Ramsay was argon.

Occurance: Group 18 of the periodic table consists of six elements – helium, neon, argon, krypton, xenon and radon which are collectively known as the Noble Gases.

All the noble gases except radon occur in the atmosphere. Their total abundance in dry air is 1% by volume of which argon is the major component. Neon, argon, krypton and xenon are obtained as by-products of liquefication of air and separation of its constitution by fractional distillation. The main commercial source of helium is natural gas. Helium is the second most abundant element in the universe (23% compared to 76% hydrogen) although its terrestrial abundance is very low. Radon is obtained as the decay product of ²²⁶Ra.

$$^{226}_{88}$$
Ra $\rightarrow ^{222}_{86}$ Rn $+ ^{4}_{2}$ He

Isolation: Except He, non-radioactive noble gases are commercially isolated from air by two methods.

- (a) **Fractional distillation of liquid air (claude's method):** Due to the difference in b.p. the various constituents of air are separated from each other.
- (b) Dewar's coconut charcoal adsorption method:
 - (i) O_2 and N_2 are removed by means of compound formation.
 - (ii) The principle of this method is that the adsorption capacity of these gases at low temperature by coconut charcoal increase with the increase in their atomic weights.
 - (iii) Thus He has the lowest and Xe has the maximum adsorption capacity.

General Properties

(a) Atomic radii, melting point and boiling point, density:

(i) All increases down the group.

- (ii) He is the only element having two boiling point i.e. 4.1 K and 2.5 K.
- (iii) It is the only element which exists in two liquid phases i.e. He and He_2 .

(b) Ionisation energy:

(i) They possess very high ionisation energy.

(ii) Ionisation energy of Xe is nearly equal to that of molecular oxygen.

- (c) Electron affinity: Due to complete octet, noble gas atoms are unable to take extra electrons.
- (d) Monatomicity: Due to very high I.E. and nearly zero E.A. noble gas atoms are not capable of combining and

their value of $\gamma = \frac{p}{r}$ is close to 1.66.

(e) Force of attraction between atoms of noble Gases:

Vander Waal's force between the atoms increases from He to Xe.

(f) **Solubility in water:** Slightly soluble in water and solubility in water increases with the increase in atomic number.

(g) Chemical nature:

(i) Noble gases are almost chemically inert.

(ii) But Kr, Xe and Rn are slightly reactive because of the radioactive nature of these gases.

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– Chemistry | 16.35

(h) Adsorption of inert gases:

- (i) Done on coconut. Gas particles are adsorbed at the surface of coconut charcoal
- (ii) Larger the size, more will be the adsorption. So, maximum adsorption of Xe at highest temp.
- (iii) First gas discovered was Argon. (Ar Lazy gas)
- (iv) The other inert gas isolated was Neon.
- (v) The other inert gas which remained a hidden gas krypton (Kryptos = Hidden)
- (vi) Then Xenon (Xenon = danger) was discovered
- (vii) Rn emits α , β , γ radiations.
- (viii) Discovery of the by Lockeyer on sun's atmosphere.

Family members of noble gases:

Noble gas compounds proved elusive for many years. The real chemistry of noble gases began in 1962 with the isolation of an orange yellow solid by Neil Bartlett from the reaction of xenon with PtF_6 . Bartlett had noticed that PtF_6 reacts with oxygen to form O_2 ⁺[PtF_6]⁻ and since the ionization enthalpies of O_2 and Xe are close to each other [Xe=1170; $O_2 = 1175 \text{ kJ mol}^{-1}$], he reasoned that PtF_6 would react with xenon to form Xe^+ [PtF_6]^{-*}. Since this exciting discovery, several other xenon compounds, mainly with the most electronegative elements-fluorine and oxygen, have been synthesised. The compounds of krypton are fewer, only the difluoride (KrF₂) has been studied in detail. Compounds of radon have not been isolated but only identified by radiotracer techniques. No true compounds of Ar, Ne or He are known.

Xenon (Xe): It is the only element that forms true compounds and that too with highly reactive elements F_2 . Xenon forms three binary fluorides, XeF_2 , XeF_4 and XeF_6 by the direct union of elements under appropriate sunlight or light from a high pressure mercury arc lamp:

 $Xe(g) + F_{2}(g) \xrightarrow{6 \ 73 \ \text{K}, \ 1 \ \text{bar}} XeF_{2}(s)$ (xenon in excess) $Xe(g) + 2F_{2}(g) \xrightarrow{8 \ 73 \ \text{K}, \ 7 \ \text{bar}} XeF_{2}(s)$ (1:5 ratio) $Xe(g) + 3F_{2}(g) \xrightarrow{5 \ 73 \ \text{K}, \ -70 \ \text{bar}} XeF_{6}(s)$ (1:20 ratio)

 XeF_2 , XeF_4 and XeF_6 are colourless solids subliming readily at 298 K. They are powerful fluorinating agents. They are readily hydrolysed by even traces of water. The hydrolysis of XeF_2 can be represented by the equation:

 $2XeF_2(s) + 2H_2O(l) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$

The structures of the three xenon fluorides can be deduced from VSEPR theory (Valence shell electron pair theory). XeF_2 and XeF_4 have linear and square planar structures, respectively. XeF_6 has seven electron pairs (6 bonding pairs and one lone pair) and would thus have a distorted octahedral structure as found experimentally in the gas phase. In the solid state, XeF_6 contains tetrameric and hexameric units in which acceptors form cationic species and fluoride ion donors form fluoroanions.

 $\begin{aligned} & XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^- XeF_4^+ \\ & SbF_5 \longrightarrow [xeF_3]^+ [SbF_6]^- XeF_6 + MF \longrightarrow M^+ [XeF_7]^- \\ & [M = Na, K, Rb \text{ or } Cs] \end{aligned}$

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(b) These compounds are not formed by He.

Uses:

- (a) Noble gases are widely used to provide inert atmospheres in metallurgical process
- (b) He is used as a cooling medium in gas cooled atomic reactions because of its high thermal conductivity, low viscosity and low density.
- (c) Liquid He is used in gas thermometers required for low temperature measurement.
- (d) Neon in neon lamps.
- (e) Neon is used in neon tubes for rectifiers, voltage regulators etc.
- (f) Argon is used in filling incandescent lamps.
- (g) Xe is used in the discharge tube for quick photography.
- (h) Rn is used in the treatment of cancer (Radiotherapy)

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— Chemistry | 16.37

PLANCESS CONCEPTS	
Noble gases have zero electron affinity. Noble gases have stable electronic config	guration. Hence, it
is difficult to add the electron	
 Atomic size of noble gases is maximum in their period. For noble gases only, Van de be obtained. For rest of the elements, covalent or Ionic radii are obtained. Van de always larger than covalent radii. 	er Waals' radii can er Waals' radii are
• Decreasing order of Xe-F bond length in XeF ₂ , XeF ₄ , XeF ₆	
$XeF_2 > XeF_4 > XeF_6$	
2.00Å 1.95Å 1.89Å	
Bond shortening may be accounted in terms of an increase in the charge on a xen	ion atom.
Vaibhav Gupta (J	IEE 2009, AIR 54)
Illustration 49: Helium and neon do not form compounds with fluorine. Explain.	(JEE MAIN)
Sol: They are chemically unreactive, owing to small size and high I.E.	
Illustration 50: Why do noble gases have zero electron affinity?	(JEE MAIN)
Sol: Noble gases have stable electronic configuration. Hence, it is difficult to add the ele electron affinity.	ectron resulting in zero
Illustration 51: Why are noble gases less reactive?	(JEE MAIN)
Sol: Due to completely filled outermost shell.	
Illustration 52: Atomic size of noble gases is maximum in their period. Explain.	(JEE MAIN)
Sol: For noble gases only Van der Waals' radii can be obtained. For rest all elements, cov obtained. Van der Waals' radii are always larger than covalent radii.	valent or ionic radii are
Illustration 53: Noble gases have maximum ionization energy in their period.	(JEE MAIN)
Sol: Due to a more effective nuclear charge which increases along the period.	
Illustration 54: The b.p. of noble gases increases with the increase in at. no. Explain.	(JEE ADVANCED)
Sol: As at. wt. increases, Van der Waals' forces of attraction becomes strong.	
Illustration 55: Why is helium molecule, (He_2) not formed?	(JEE ADVANCED)
Sol: For He ₂ , bond order is zero.	
Illustration 56. Yonon has a closed shall configuration but forms compounds with flue in-	Evolain
induction but forms compounds with fluorine	(JEE ADVANCED)
Sol: Gases and thus the outermost shell electrons of Xe are excited to d-subshell.	()
Illustration 57: Complete the following reactions.	(JEE ADVANCED)

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16.38 | p - Block Elements -



2.00 A° 1.95 A° 1.89 A°

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Chemistry | 16.39

POINTS TO REMEMBER

- Elements of group 15 exhibit two important oxidation states +3 and +5 but +3 oxidation state is formed because of inert pair effect.
- In hydrides of group V:
- Bond angle : NH₃ > PH₃ > AsH₃ > SbH₃ Basic character : NH₃ > PH₃ > AsH₃
- Boling point : NH₃ < PH₃ < AsH₃ < SbH₃ Stability : NH₃ > PH₃ > AsH₃ > SbH₃
- Reducing character : NH₃ < PH₃ < AsH₃
- Phosphorus exists as P₄ in elemental state and exists in several allotropic forms.
- The oxoacids having P-H bonds are good reducing agents.
- N₂O is called laughing gas and is obtained by heating NH₄NO₃.
- Sulphur exists as S₈ and has plucked ring structure.
- Group 16 elements are called chalcogens. These consists of O, S, Se, Te and Po.
- Allotropic forms of oxygen is O_3 , which is highly oxidising agent.
- The highest oxidation state of S is +6 in SF₆.
- In hydrides of group VI
- Bond angle : H₂O > H₂S > H₂Se > H₂Te Acidic character : H₂O < H₂S < H₂Se
- Volatility : $H_2O < H_2S > H_2Se > H_2$ Te.
- Halogens are most electronegative elements. Among these iodine has some electropositive character and exists as +1 and +3.
- Reducing Power : I⁻ > Br⁻ > Cl⁻ > F⁻
- Oxidising power: $F_2 > CI_2 > Br_2 > I_2$
- Acidic strength in water : HF < HCl < HBr < HI. HF weaker base because of its highest bond dissociation energy
- Acidic character : HClO₄ > HClO₃ > HClO₂ > HClO
- HCIO > HBrO > HIO.
- Oxidation power : HClO₄ > HClO₃ > HClO₂ > HClO
- Fluorine shows only -1 oxidation state while other halogens show variable oxidation states from +1 to +7.

JEE Main/Boards

Exercise 1

Q.1 How is ammonia manufactured industrially?

Q.2 The HNH angle value is higher than HPH, HAsH and HSbH angles. Why?

Q.3 Write main differences between the properties of white phosphorus and red phosphorus.

Q.4 Why does nitrogen show catenation properties less than phosphorus?

Q.5 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.

Q.6 Knowing the electron gain enthalpy values for $O \rightarrow O^-$ and $O \rightarrow O_2^-$ as -141 and 702kJ mol⁻¹

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16.40 | p - Block Elements -

respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^{-} ?

Q.7 Which aerosols deplete ozone?

Q.8 Describe the manufacture of H_2SO_4 by contact process?

Q.9 Why are halogens strong oxidizing agents?

Q.10 Explain why inspite of nearly the same electronegativity, nitrogen forms hydrogen bonding while chlorine does not.

Q.11 How can you prepare Cl_2 from HCl and HCl from Cl_2 ? Write reactions only.

Q.12 What are the oxidation states of phosphorus in the following:

(i) H ₃ PO ₃	(ii) PCl ₃	(iii) Ca ₃ P ₂
(iv) Na ₃ PO ₄	(v) POF ₃	

Q.13 Write balanced equation 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 Nal in water.

Q.14 How are xenon fluorides XeF₂, XeF₄ and XeF₆ obtained?

Q.15 With what neutral molecule is CIO-isoelectronic? Is that molecule a Lewis base?

Q.16 How are XeO₃ and XeOF₄ prepared?

Q.17 Why do noble gases have comparatively large atomic sizes?

Q.18 List the uses of neon.

Q.19 Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionization enthalpy and electronegativity.

Q.20 Give the formula and describe the structure of a noble gas species which is isostructural with:

(i) ICl_4^- (ii) IBr_2^- (iii) BrO_3^-

Q.21 Draw the structure of the following molecules:

(i) XeF₄ (ii) BrF₃

Q.22 Account for the following:

(i) H_2S acts only as a reducing agent but SO_2 acts both as a reducing agent as well as an oxidising agent.

(ii) SF_6 is known but SH_6 is not known.

(iii) Compounds of fluorides of oxygen and not the oxides of fluorine.

Q.23 (i) Complete the following reaction equations:

(A) $XeF_2 + PF_5 \rightarrow$

(B) $Cl_2(g) + NaOH(aq)$ (hot and conc.)

(ii) Explain the following observations:

(a) +3 oxidation state becomes more and more stable from As to Bi in the group.

(b) Sulphur in the vapour state exhibits para magnetism

Q.24 (i) Draw the structure of the following:

(a) H_3PO_2 (b) BrF_3

(ii) How would you account for the following observations:

(A) Phosphorus has a greater tendency for catenation than nitrogen.

(B) Bond dissociation energy of fluorine is less than that of chlorine.

(C) No chemical compound of helium is known.

Q.25 Explain the following:

(A) Ammonia has a higher boiling point than phosphine.

(B) Helium does not form any chemical compound.

(C) Bi (V) is a stronger oxidising agent than Sb(V).

Q.26 (i) Complete the following reaction equations.

(a) $PCI_5 + H_2O(excess) \rightarrow$

(b) $F_2 + H_2O \rightarrow$

(ii) Explain the following observations:

(a) Phosphorus has a greater tendency for catenation than nitrogen.

(b) In solution of H_2SO_4 in water, the second dissociation constant k_{a_2} , is less than first dissociation constant k_{a_1} .

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- Chemistry | 16.41

Q.27 (i) Complete the following reaction equations

(a) P_4 + NaOH + $H_2O \rightarrow$ (b) Cu + HNO₃(dilute) \rightarrow

(ii) Explain why

(a) H_2O is a liquid while, inspite of a higher molecular mass HS_2 is a gas

(b) Helium is used in diving equipment.

Q.28 PCl_s is well known while Pl_s is unknown. Why?

Q.29 Urea is better nitrogenous fertilizer than ammonium sulphate. Explain.

Q.30 HF is stored in wax coated glass bottles. Why?

 $\textbf{Q.31}~\text{KHF}_2$ is well known, whereas KHCI_2 or KHBr_2 does not exist. Explain

Q.32 Halogens are strong oxidants. Why?

Q.33 Chlorine displaces iodine from aqueous solution of KI. Why?

Q.34 Account for the following observation

(i) lodine is liberated in the reaction between KI and Cu²⁺ but chlorine is not liberated when KCI is added to Cu²⁺.

(ii) 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 catalyst used in the oxidation of SO_2 ?

Q.35 Explain the following

(i) An orange potassium dichromate paper turns green on exposure to sulphur dioxide.

(ii) Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction.

Q.36 Explain it with reason: SO_2 can function both as a reducing or oxidizing agent while SO_3 can function only as an oxidizing agent and H_2S can function as reducing agent only

Q.37 Explain why?

(i) Orthophosphoric acid is tribasic but phosphorus acid is dibasic.

(ii) It is advisable to grow a leguminous crop on a soil every three or four years

Q.38 Zinc reacts with dil. H_2SO_4 to give H_2 . It also reacts with conc. H_2SO_4 to give SO_2 . Make difference between these two reactions.

Exercise 2

Single Correct Choice Type

Q.1 $H_3PO_3 \xrightarrow{\Delta} (x) + PH_3$; is

- (A) Dehydration reaction
- (B) Oxidation reaction
- (C) Disproportionation reaction
- (D) Dephosphorylation reaction

Q.2 Which of the following species is not a pseudohalide?

(A) CNO ⁻	(B) RCOO
(C) OCN	(D) N_{3}^{-}

Q.3 First compound of inert gases was prepared by scientist Neil Barthlete in 1962. This compound is

(A) XePtF₆ (B) XeO₃ (C) XeF₆ (D) XeOF₄

Q.4 Boron forms BX_3 type of halides. The correct increasing order of Lewis-acid strength of these halides is

(A)
$$BF_3 > BCI_3 > BBr_3 > BI_3$$
 (B) $BI_3 > BBr_3 > BCI_3 > BF_3$
(C) $BF_2 > BI_3 > BCI_2 > BBr_3$ (D) $BF_2 > BCI_2 > BI_3 > BBr_3$

Q 5. The compound (SiH₃)₃N is

(A) Pyramidal and more basic than (CH₃)₃N

(B) Planar and less basic than $(CH_3)_3N$

- (C) Pyramidal and less basic than (CH₃)₃N
- (D) Planar and more basic than (CH₃)₃N

Q 6. In a molecule of phosphorus (V) oxide, there are

(A) 4P-P, 10P-O and 4P=O bonds.

(B) 12P-O and 4P=O bonds

(C) 2P-O and 4P=P bonds

(D) 6P-P, 12P-O and 4P=P bonds

Q 7. When oxalic acid reacts with conc. $H_2SO_{4'}$ two gases produced are neutral and acidic in nature respectively. Potassium hydroxide absorbs one of the two gases.

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16.42 | p - Block Elements -

The product formed during this absorption and the gas which absorbed are respectively.

(A) $K_2 CO_3$ and CO_2	(B) KHCO ₃ and CO ₂
(C) K_2CO_3 and CO	(D) KHCO $_3$ and CO

Q 8. Which of the following is the correct order of acidic strength?

(A) $Cl_2O_7 > SO_2 > P_4O_{10}$	(B) $CO_2 > N_2O_5 > SO_3$
(C) $Na_2O > MgO > Al_2O_3$	(D) $K_2O > CaO > MgO$

Q 9. $Ca+C_2 \longrightarrow CaC_2 \xrightarrow{N_2} A$ Compound (A) is used as a/an

(A) Fertilizer	(B) Dehydrating agent
(C) Oxidizing agent	(D) Reducing agent

Q 10. A gas which exists in three allotropic forms $\alpha,\beta,and \gamma$ is

(A) SO_2 (B) SO_3 (C) CO_2 (D) NH_3

Q 11. When an inorganic compound reacts with SO₂ in aqueous medium, produces (A). (A) on reaction with Na₂CO₃, gives compound (B) which with sulphur, gives a substance (C) used in photography. Compound C is

(A) Na_2S (B) $Na_2S_2O_7$ (C) Na_2SO_4 (D) $Na_2S_2O_3$

Q 12. Borax is actually made of two tetrahedral and two triangular units joined together and should be written as: $Na_2[B_4O_5(OH)_4].8H_2O$. Consider the following statements about borax:

(a) Each boron atom has four B-O bonds

(b) Each boron atom has three B-O bonds

(c) Two boron atoms have four B-O bonds while other two have three B-O bonds.

(d) Each boron atom has one -OH groups

Select correct statement(s)

(A) a, b (B) b, c (C) c, d (D) a, c

Q.13 When a compound X reacts with ozone in aqueous medium, a compound Y is produced. Ozone also reacts with Y and produces compound Z. Z acts as an oxidizing agent, then X, Y and Z will be

(A) X = HI, $Y = I_2$ and $Z = HIO_3$ (B) X = KI, $Y = I_2$ and $Z = HIO_3$ (C) X = KI, $Y = I_2$ and $Z = HIO_4$ (D) X = HI, $Y = I_2$ and $Z = HIO_4$

Previous Years' Questions

Q.1 Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives (2004)

	(1989)
Q.2 In the extraction of a	aluminium the electrolyte is.
(C) Al ³⁺ + 3Cl ⁻	(D) Al ₂ O ₃ + 6HCl
(A) [Al(OH) ₆] ³⁻ +3HCl	(B) [Al(H ₂ O) ₆] ³⁺ + 3Cl ⁻

(A) Fused cryolite with feldspar

- (B) Fused cryolite with fluorspar
- (C) Pure alumina in molten cryolite
- (D) Pure alumina with bauxite and molten cryolite

Q.3 Boron cannot form which one of the following anions. (2011)

(A) BF_6^3 (B) BH_4^- (C) $B(OH)_4^-$ (D) BO_2^-

Q.4 Heating an aqueous solution of aluminium chloride to dryness will give (2005)

(A) $AICI_3$ (B) AI_2CI_6 (C) AI_2O_3 (D) $AI(OH)CI_2$

Q.5 The structure of diborane (B_2H_6) contains. (2009)

- (A) Four 2c-2e bonds and two 3c-2e bonds
- (B) Two 2c-2e bonds and four 3c-2e bonds
- (C) Two 2c-2e bonds and two 3c-3e bonds
- (D) Four 2c-2e bonds and four 3c-2e bonds

Q.6 The stability of dihalides of Si, Ge, Sn and Pb increases steadily in sequence (2007)

- (A) $GeX_2 \ll SiX_2 \ll SnX_2 \ll PbX_2$ (B) $SiX_2 \ll GeX_2 \ll PbX_2 \ll SnX_2$ (C) $SiX_2 \ll GeX_2 \ll SnX_2 \ll PbX_2$
- (D) $PbX_2 \ll SnX_2 \ll GeX_2 \ll SiX_2$

Q.7 In silicon dioxide,

(2005)

(A) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms

(B) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bounded to two silicon atoms

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– Chemistry | 16.43

(C) Silicon atom is bonded to two oxygen atoms

(D) There are double bonds between silicon and oxygen atoms

Q.8 In which of the following arrangements the sequence is not strictly according to the property written against it. **(2009)**

(A) $CO_2 < SiO_2 < SnO_2 < PbO_2$: Increasing oxidizing power

(B) HF < HCl < HBr < HI: Increasing acid strength

(C) $NH_3 < PH_3 < AsH_3 < SbH_3$: Increasing basic strength

(D) B < C < O < N: Increasing first ionization enthalpy

Q.9 The percentage of p-character in the orbitals forming P-P bonds in P_4 is (2007)

(A) 25 (B) 33 (C) 50 (D) 75

Q.10 Which of the following statement is wrong (2011)

(A) The stability of hydrides increase from NH_3 to BiH_3 in group 15 of the periodic table

(B) Nitrogen cannot form $d\pi - p\pi$ bond

(C) Single N – N bond is weaker than the single P - P bond

(D) N_2O_4 has two resonance structure

Q.11 What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid

(2003)

(A) Cr^{3+} and $Cr_2O_7^{2-}$ are formed

(B) $Cr_2O_7^{2-}$ and H_2O are formed

(C) CrO_4^{2-} is reduced to +3 state of Cr

(D) CrO_4^{2-} is oxidized to +7 state of Cr

Q.12 In case of nitrogen, NCl_3 is possible but not NCl_5 while in case of phosphorous, PCl_3 as well as PCl_5 are possible. It is due to (2004)

(A) Availability of vacant d-orbital in P but not in N

(B) Lower electronegativity of P than N

(C) Lower tendency of H bond formation in P than N

(D) Occurrence of P in solid while N in gaseous state at room temperature

Q.13 What may be expected to happen when phosphine gas is mixed with chlorine gas (2003)

(A) The mixture only cools down

- (B) PCl₃ and HCl are formed and the mixture warms up
- (C) PCl₅ and HCl are formed and mixture cools down
- (D) PCl₃ and Cl₂ is formed with warming up

Q.14 Which of the following statements regarding sulphur is incorrect? (2011)

(A) S_2 molecule is paramagnetic

(B) The vapour at 200° C consists mostly of S₈ rings

(C) At 600° C, the gas mainly consists of S₂ molecules

(D) The oxidation state of sulphur is never less than +4 in its compounds

Q.15 The correct order of the thermal stability of hydrogen halides (H - X) is (2010)

(A) HI > HBr > HCl > HF (B) HF > HCl > HBr > HI

(C) HCL < HF < HBr < HI (D) HI > HCl < HF < HBr

Q.16 Identify the incorrect statement among the following (2007)

(A) Ozone reacts with SO_2 to give SO_3

(B) Silicon reacts with NaOH_(aq) in the presence of air to give Na₂SiO₃ and H₂O

(C) Cl_2 reacts with excess of NH_3 to give N_2 and HCl

(D) Br_2 reacts with hot and strong NaOH solution to give NaBr, NaBrO₄ and H₂O

Q.17 Which one of the following reactions of Xenon compounds is not feasible? (2009)

- (A) $XeO_3 + 6HF \rightarrow XeF_6 + 3H_2O$
- (B) $3XeF_4 + 6H_2O \rightarrow 2Xe + XeO_3 + 12HF + 1.5O_2$
- (C) $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$
- (D) $XeF_6 + RbF \rightarrow Rb[XeF_7]$

Q.18 The number of hydrogen atom(s) attached to phosphorus atom in hypophosphorous acid is (2005)

- (A) Zero (B) Two
- (C) One (D) Three

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16.44 | p - Block Elements -

Q.19 The decreasing bond angles from $NH_3(106^\circ)$ to $SbH_3(101^\circ)$ down group-15 of the periodic table is due to **(2006)**

(A) Increasing bp-bp repulsion

(B) Increasing p-orbital character in sp^3

(C) Decreasing lp-bp repulsion

(D) Decreasing electronegativity

Q.20 In XeF₂, XeF₄, XeF₆, the number of lone pairs on Xe is respectively (2002)

(A) 2, 3, 1	(B) 1, 2, 3				
(C) 4, 1, 2	(D) 3, 2, 1				

Q.21 Which one of the following statements regarding helium is incorrect? (2004)

(A) It is used to produce and sustain powerful superconducting magnets

(B) It is used as a cryogenic agent for carrying out experiments at low temperatures

(C) It is used to fill gas balloons instead of hydrogen because it is lighter and non-inflammable

(D) It is used in gas-cooled nuclear reactors

Q.22 Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. The explanation for it is that (2003)

(A) Concentrated hydrochloric acid emits strongly smelling HCl gas all the time

(B) Oxygen in air reacts with the emitted HCl gas to form a cloud of chlorine gas

(C) Strong affinity of HCl gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke

(D) Due to strong affinity for water, concentrated hydrochloric acid pulls moisture of air towards itself. This moisture forms droplets of water and hence the cloud.

Q.23 Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar? (2013)

(A) Ca < S < Ba < Se < Ar
(B) S < Se < Ca < Ba < Ar
(C) Ba < Ca < Se < S < Ar
(D) Ca < Ba < S < se < Ar

Q.24 Which one of the following properties is **not** shown by NO? (2014)

(A) It combines with oxygen to form nitrogen dioxide

(B) It's bond order is 2.5

(C) It is diamagnetic in gaseous state

(D) It is a neutral oxide

Q.25 Assertion: Nitrogen and Oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen. (2015)

Reason: The reaction between nitrogen and oxygen requires high temperature.

(A) Both assertion and reason are correct, and the reason is the correct explanation for the assertion

(B) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion

(C) The assertion is incorrect, but the reason is correct

(D) Both the assertion and reason are incorrect

Q.26 The species in which the N atom is in a state of sp hybridization is: (2016)

(A) NO_2^+ (B) NO_2^- (C) NO_3^- (D) NO_2

Q. 27 The pair in which phosphorous atoms have a formal oxidation state of + 3 is : (2016)

(A) Orthophosphorous and pyrophosphorous acids

(B) Pyrophosphorous and hypophosphoric acids

(C) Orthophosphorous and hypophosphoric acids

(D) Pyrophosphorous and pyrophosphoric acids

- Chemistry | 16.45

JEE Advanced/Boards

Exercise 1

Q.1 Arrange the following in the order of property indicated for each set:

(i) $F_{2'} Cl_{2'} Br_{2'} l_2$ – increasing bond dissociation enthalpy.

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

(iii) NH₃, PH₃, AsH₃, SbH₃, BiH₃ – increasing base strength.

Q.2 Which one of the following does not exists?

(i) XeOF₄ (ii) NeF₂ (iii) XeF₂ (iv) XeF₆

Q.3 Complete the following chemical equations:

(i) $Ca_3P_2(s) + H_2O(\ell) \rightarrow \dots$ (ii) $Cu^{2+}(aq) + NH_3(aq) \rightarrow \dots$ (excess)

Q.4 A solution of ferric chloride acidified with HCl is unaffected when hydrogen is bubbled through it, but gets reduced when zinc is added to some acidified solution. Why?

Q.5 Aqua-regia dissolves noble metals in it. Explain.

Q.6 Pure PH₃ does not burn in air, but impure sample of PH₃ burns in air. Why?

Q.7 Precipitation of second group sulphides in qualitative analysis is carried out with H_2S in presence of HCl and not nitric acid. Why?

Q.8 KMnO₄ should not be dissolved in conc. H_2SO_4 . Why?

Q.9 Account for the following observations

(i) Bleaching of flowers by Cl_2 is permanent, while by SO₂ it is temporary.

(ii) The brown colour of an acidified dilute solution of iodine in aqueous potassium iodide is intensified by the addition of a nitrite but is discharged by the addition of a sulphite.

Q.10 Explain the following



Silver nitrate solution when treated with a very dilute solution of hypo gives black precipitate but when it is treated with a concentrated solution of hypo it does not form any ppt.

Q.11 Explain it with reason

(i) Concentrated nitric acid turns yellow in sunlight.

(ii) Nitrous oxide supports combustion more vigorously than air.

Q.12 Explain why?

(i) Yellow phosphorous is kept under water but not the red phosphorous.

Q.13 What happens when(Give relevant equation)

(i) Hypophosphorous acid is heated.

(ii) Sodium iodate is treated with sodium bisulphite solution.

(iii) Chlorine gas is passed through dry and aqueous SO_2 gas.

(iv) Potassium dichromate and concentrated hydrochloric acid are heated together.

Q.14 Brief it with relevant equation

(i) A few drops of bismuth oxide solution in conc. HCl are added to excess of water.

(ii) lodine is added to a solution of potassium lodide.

(iii) Hydriodic acid is added to copper sulphate solution.

(iv) Hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide.

Q.15 Explain it (Give relevant equation)

(i) Sulphur dioxide is bubbled through aq. Solution of $CuSO_4$ in presence of potassium thiocyanate.

(ii) Ozone is treated with ethylene.

(iiii) Sulphur is boiled with caustic soda solution.

16.46 | p - Block Elements -

Exercise 2

Single Correct Choice Type

Q.1 Which is incorrectly matched

(A)
$$CsBr_3 \rightarrow Cs^+ + Br_3^-$$

(B)
$$I_4O_9 \rightarrow I^{3+} + (IO_3^{-})_3$$

- (C) $AgBrO_3 \rightarrow Ag^+ + BrO_3^-$
- (D) $I_2O_4 \rightarrow IO_2^- + IO_2^-$

Q.2 An orange solid (X) on heating, gives a colourless gas (Y) and a only green residue (Z). Gas (Y) on treatment with Mg, produces a white solid substance.....

(A) Mg_3N_2 (B) MgO (C) Mg_2O_3 (D) $MgCI_2$

Q.3 An inorganic salt (A) is decomposed at about 523 K to give products (B) and (C). Compound (C) is a liquid at room temperature and is neutral to litmus paper while oxide (B) on burning with white phosphorous, given a dehydrating agent (D).

Compounds (A), (B), (C) and (D) will be identified as

(A) NH₄NO₃, N₂O, H₂O, P₂O₅

(B) NH₄NO₂, K₂O, P₂O₂

(C) CaCO₃ CaO. H₂O, CaCl₂

(D) CaCO₃, CaO, H₂O, Ca(OH)₂

Q.4 An inorganic compound (A) made of two most occurring elements into the earth crust, having a polymeric tetra-headral network structure. With carbon, compound (A) produces a poisonous gas (B) which is the most stable diatomic molecule. Compounds (A) and (B) will be

(A) $SiO_{2'} CO_2$ (B) $SiO_{2'}CO$ (C) SiC,CO (D) $SiO_{2'}N_2$

Q.5 A sulphate of a metal (A) on heating evolves two gases (B) and (C) and an oxide

(D) Gas (B) turns $K_2Cr_2O_7$ paper green while gas (C) forms a trimer in which there is no S-S bond. Compound (D) with HCl, forms a Lewis base (E) which exists as a dimer. Compounds (A), (B), (C), (D) and (E) are respectively

(A) FeSO₄, SO₂, SO₃, Fe₂O₃, FeCl₃
(B) Al₂(SO₄)₃, SO₂, SO₃, Al₂O₃, FeCl₃
(C) FeS, SO₂, SO₃, FeSO₄, FeCl₃

(D) FeS, SO₂, SO₃, Fe₂(PO₄)₃, FeCl₂

Q.6 A tetra-atomic molecule (A) on reaction with nitrogen (I) oxide, produces two substances (B) and (C). (B) is a dehydrating agent in its monomeric gas which shows almost inert behaviour. The substances (A) and (B) and (C) respectively will be

(A) P ₄ , P ₄ O ₁ , N ₂	(B)P ₄ , N ₂ O ₅ , N ₂	\mathbf{C}
(C)P ₄ , P ₂ O ₃ , Ar	(D)P ₄ ,P ₂ O ₃ , H ₂	N.

Q.7 Which one of the following compounds on strong heating evolves ammonia gas?

(A) (NH ₄) ₂ SO ₄	(B) HNO ₃
(C) (NH ₄) ₂ Cr ₂ O ₇	(D) NH ₃ NO ₃

Q.8 The correct order of acidic strength of oxy-acids of chlorine is

(A) $HCIO < HCIO_2 < HCIO_3 < HCIO_4$ (B) $HCIO_4 < HCIO_3 < HCIO_2 < HCIO$ (C) $HCIO > HCIO_4 > HCIO_3 > HCIO_2$

(D)
$$HCIO_4 < HCIO_2 > HCIO_3 > HCIO_4$$

Q.9 Concentrated HNO₃ reacts with iodine to give

(A) HI (B) HOI (C) HOIO, (D) HOIO,

Q.10 Conc. H_2SO_4 cannot be used to prepare HBr from NaBr because it

- (A) Reacts slowly with NaBr
- (B) Oxides HBr
- (C) Reduces HBr
- (D) Disproportionates HBr

Q.11	Com	ιροι	und (X) is	CH ₂	/	COC)н _	P_4) ₁₀ ,	150°C	××
-		'	·		e ₂		coc	ЭН				- //

- (A) Malonic acid (B) Carbon suboxide
- (C) Tartaric acid (D) Acetic acid

Q.12 Molecular shapes of $SF_{4'}$ CF₄ and XeF₄ are

(A) The same, with 2, 0 and 1 lone pairs of electrons respectively

(B) The same, with 2, 0 and 1 lone pairs of electrons respectively

(C) The different, with 0, 1 and 2 lone pairs of electrons respectively

(D) The different, with 1, 0 and 2 lone pairs of electrons respectively

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— Chemistry | 16.47

Q.13 When $AgNO_3$ is heated strongly, the products formed are

(A) NO and NO ₂ (B) NO ₂ and O ₂

(C) NO_2 and N_2O	(D) NO and O_2
-----------------------	------------------

Q.14 $HNO_3 + P_4O_{10} \longrightarrow HPO_3 + A$; the product A is (A) N_2O (B) N_2O_3 (C) NO_2 (D) N_2O_5

Q.15 $B(OH)_3 + NaOH \longrightarrow NaBO_2 + Na[B(OH)_4] + H_2O$

How can these reaction is made to proceed in forward direction?

(A) Addition of cis 1, 2 diol (B) Addition of borax

(C) Addition of trans 1, 2 diol (D) Addition of Na₂HPO₄

Comprehension Type

Paragraph 1: Read the following short write-up and answer the questions at the end of it.

The name 'silica' covers an entire group of minerals, which have general formula SiO_2 , the most common of which is quartz. Quartz is a framework silicate with SiO_4 tetrahedra arranged is spirals. The spirals can turn in a clockwise or anticlockwise direction- a feature that results in there being two mirror images, optically active, varieties of quartz.

Q.16 The following pictures represent various silicate anions. Their formulae are respectively:



Q.17 Si $_{3}O_{9}^{6-}$ (having three tetrahedral) is represented



(D) None of these

Q.18 The silicate anion in the mineral kinoite is a chain of three SiO_4 tetrahedra that share corners with adjacent tetrahedral. The mineral also contains Ca^{2+} ions, Cu^{2+} ions, and water molecules in 1:1:1 ratio mineral is represented as:

(A) CaCuSi ₃ O ₁₀ . H ₂ O	(B) CaCuSi ₃ O ₁₀ . 2H
(C) $Ca_2Cu_2Si_3O_{10}.2 H_2O$	(D) None of these

Paragraph 2: There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH₃, and PH₃. Phosphine is a flammable gas and is prepared from white phosphorus.

Q.19 Among the following, the correct statement is

(A) Phosphorus have no biological significance in humans.

(B) Between nitrates and phosphates, phosphates are less abundant in earth's crust.

(C) Between nitrates and phosphates, nitrates are less abundant in earth's crust.

(D) Oxidation of nitrates is possible in soil.

Q.20 Among the following, the correct statement is

(A) Between NH₃ and PH₃, NH₃ is a better electron donor because the lone pair of electrons occupies spherical sp³ orbital and is less directional

(B) Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is more directional

(C) Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is more directional

(D) Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies spherical sp^3 orbital and is less directional

Q.21 PH₃ as one of the products. This is a

(A) Dimerization reaction.

- (B) Disproportionation reaction
- (C) Condensation reaction

(D) Precipitation reaction

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16.48 | p - Block Elements -

Assertion Reasoning Type

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following responses:

(A) If both (A) and (R) are true and (R) is correct explanation of (A) $% \left(A\right) =0$

(B) If both (A) and (R) are true but (R) is not correct explanation of (A)

(C) If (A) is true but (R) is false

(D) If (A) is false but (R) is true

Q.22 Assertion: Borax bead test is applicable only to coloured salt.

Reason: In borax bead test, coloured salts are decomposed to give coloured metal meta borates.

Q.23 Assertion: Conc. H_2SO_4 cannot be used to prepare pure HBr from NaBr

Reason: It reacts slowly with NaBr.

Q.24 Assertion: Silicones are very inert polymers.

Reason: Both Si-O and Si-C bond energies are very high.

Q.25 Assertion: Chlorine gas disproportionates in hot and conc. NaOH solution.

Reason: NaCl and NaOCl are formed in the above reaction.

Multiple Correct Choice Type

Q.26 The correct statement(s) related to allotropes of carbon is/are

(A) Graphite is the most stable allotropes of carbon and having a two dimensional sheet like structure of hexagonal rings of carbon (sp²).

(B) Diamond is the hardest allotrope of carbon and having a three dimensional network structure of C (sp³)

(C) Fullerene (C_{60}) is recently discovered non-crystalline allotrope of carbon having a football like structure.

(D) Vander waal's force of attraction acts between the layers of graphite 6.14 A away from each other.

Q.27 $Al_2(SO_4)_3 + NH_4OH \longrightarrow X$, then

- (A) X is a white coloured compound(B) X is insoluble in excess of NH4OH
- (C) X is soluble in NaOH
- (D) X cannot be used as an antacid.

Q.28 Which of the following is/are correct for group 14 elements?

(A) The stability of dihalides are in the order $CX_2 < SiX_2$ < $GeX_2 < SnX_2 < PbX_2$

(B) The ability to form $p\pi - p\pi$ multiple bonds among themselves increases down the group.

(C) The tendency for catenation decreases down the group.

(D) They all form oxides with the formula MO_2 .

Q.29 $2NO_2 \leftrightarrow \rightarrow N_2O_4$ The dimerization of NO_2 is accompanied with

(A) Decrease in paramagnetism

- (B) Change in colour
- (C) Increase in temperature

(D) Increase in paramagnetism

Q.30 $C(OH)_4$ is unstable because a carbon atom cannot hold more than one –OH groups but $Si(OH)_4$

is stable compound because

- (A) C-O bond energy is low.
- (B) C-O bond energy is high.
- (C) Si-O bond energy is low.
- (D) Si-O bond energy is high.

Q.31 Which of the following statements is/are correct regarding inter-halogen compound ABx types?

- (A) x may be 1, 3, 5 and 7
- (B) A is more electronegative halogen than B
- (C) FBr₃ cannot exists

(D) the structure of CIF_3 and IF_7 show deviation from normal structures and could be explained on the basis of VSEPR theory.

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– Chemistry | 16.49

Q.32 Select correct statement(s)

(A) Borax is used as buffer

(B) 1 M borax solution reacts with equal volumes of 2M HCl solution

(C) Titration of borax can be made using methyl orange as the indicator.

(D) Coloured bead obtained in borax-bead test contains metaborate.

Q.33 Select correct statement about B₂H₆

(A) Bridging groups are electron-deficient with 12 valence electrons

(B) It has 2c-2e B-H bonds

(C) It has 3c-2e B-H-B bonds

(D) All above are correct statements.

Match the Columns

Q.34 Match the following

Column I	Column II
(A) $Bi^{3+} \rightarrow (BiO)^+$	(p) Heat
(B) $[AIO_2]^- \rightarrow Al(OH)_3$	(q) Hydrolysis
(C) $\text{SiO}_4^{4-} \rightarrow \text{Si}_2\text{O}_7^{6-}$	(r) Acidification
(D) $(B_4O_7^{2-}) \rightarrow [B(OH)_3]$	(s) Dilution by water

Previous Years' Questions

Q.1 H₃BO₃ is

(2003)

(A) Monobasic acid and weak Lewis acid

- (B) Monobasic and weak Bronsted acid
- (C) Monobasic and strong Lewis acid
- (D) Tribasic and weak Bronsted acid

Q.2 $B(OH)_3 + NaOH \longrightarrow NaBO_2 + Na[B(OH)_4] + H_2 O$ How can one proceed this reaction in the forward direction? (2006)

(A) Addition of cis 1, 2 diol

(B) Addition of borax

(C) Addition of trans 1, 2 diol

(D) Addition of Na₂HPO₄

Q.3 In the reaction, $2X + B_2H_6 \longrightarrow [BH_2 (X)_2]^+[BH_4]^-$, the amine (s) X is (are) (2009)

(A) NH ₃	(B) CH ₃ NH ₂
(C) (CH ₃) ₂ NH	(D) (CH ₃) ₃ N

Read the following questions and answer as per the direction given below:

(a) Statement-I is true; statement-II is true; statement-II is the correct explanation of statement-I.

(b) Statement-I is true; statement-II is true; statement-II is not the correct explanation of statement-I.

(c) Statement-I is true; statement-II is false.

(d) Statement-I is false; statement-II is true.

Q.4 Statement-I: In water, orthoboric acid behaves as a weak monobasic acid.

Statement-II: In water, orthoboric acid acts as a proton donor. (2007)

Q.5 Statement-I: Between SiCl₄ and CCl₄, only SiCl₄ reacts with water.

Statement-II: SiCl₄ is ionic and CCl₄ is covalent. (2001)

Q.6 The two types of bonds present in B_2H_6 are covalent and (1994)

Q.7 Extra pure N_2 can be obtained by heating (2011)

(A) NH ₃ with Cu	IO (B) NH ₄ NO ₃
(C) $(NH_{4})_{2}Cr_{2}O_{7}$	(D) $Ba(N_3)_2$

Q.8 The reaction of P_4 with X leads selectively to P_4O_6 . The X, is (2009)

(A) Dry O₂

(B) A mixture of O_2 and N_2

(C) Moist O₂

(D) O_2 in the presence of aqueous NaOH

Q.9 The set with correct order of acid strength is (2001)

(A) $HCIO < HCIO_2 < HCIO_3 < HCIO_4$

- (B) $\text{HCIO}_4 < \text{HCIO}_3 < \text{HCIO}_2 < \text{HCIO}$
- (C) $HCIO < HCIO_4 < HCIO_3 < HCIO_2$
- (D) $HCIO_4 < HCIO_2 < HCIO_3 < HCIO_3$

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(1989)

(1998)

16.50 | p - Block Elements -

Q.10 Nitrogen (I) oxide is produced by

(A) Thermal decomposition of NH_4NO_3

(B) Disproportionation of N_2O_4

(C) Thermal decomposition of NH_4NO_2

(D) Interaction of hydroxylamine and nitrous acid

Q.11 White phosphorus (P_4) has

(A) Six P—P single bonds

(B) Four P—P single bonds

(C) Four lone pairs of electrons

(D) PPP angle of 60°

Paragraph: The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6. XeF₄ reacts violently with water to give XeO₃. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell. (2007)

Q.12 Argon is used in arc welding because of its

(A) Low reactivity with metal

(B) Ability to lower the melting point of metal

(C) Flammability

- (D) High calorific value
- Q.13 The structure of XeO₃ is

(A) Linear (B) Planer (C) Pyramidal (D) T-shaped

Q.14 XeO₄ and XeO₆ are expected to be

(A) Oxidizing (B) Reducing

(C) Unreactive (D) Strongly basic

Q.15 White phosphourus on reaction with NaOH gives PH_3 as one of the products. This is a (2008)

(A) Dimerisation reaction

(B) Disproportionation reaction

(C) Condensation reaction

(D) Precipitation reaction

Q.16 All the compounds listed in column I react with water. Match the result of the respective with the appropriate option listed in column II. (2010)

Column I	Column II
(A) (CH ₃) ₂ SiCl ₂	(p) Hydrogen halide formation
(B) XeF ₄	(q) Redox reaction
(C) Cl ₂	(r) Reacts with glass
(D) VCl ₂	(s) Polymerization
	(t) O ₂ formation

Q.17 The basicity of phosphorus acid (H₃PO₃) is (1990)

Q.18 Among the following, the number of compounds than can react with PCI_5 to give $POCI_3$ is $O_2, CO_2, SO_2, H_2SO_4, P_4O_{10}$ (2011)

Q.19 Extra pure N₂ can be obtained by heating (2011)

(A) NH_3 with CuO (B) NH_4NO_3 (C) $(NH_4)Cr_2O_7$ (D) $Ba(N_3)_2$

Q.20 The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are respectively (2012)

(A) Redox reaction ; 3 and 5

(B) Redox reaction; +3 and +5

(C) Disproportionation reaction ; -3 and + 5

(D) Disproportionation reaction ; 3 and + 3

Q.21 Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is (2012)

(A) Cl_2O (B) Cl_2O_7 (C) ClO_2 (D) Cl_2O_6

Q.22 With respect to graphite and diamond, which of the statement(s) given below is (are) correct? (2012)

(A) Graphite is harder than diamond.

(B) Graphite has higher electrical conductivity than diamond.

(C) Graphite has higher thermal conductivity than diamond.

(D) Graphite has higher C - C bond order than diamond.

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- Chemistry | 16.51

Q.23 Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen ? (2012)

(A) HNO ₂ ,NO,NH ₄ Cl,N ₂	(B) HNO ₃ ,NO,N ₂ NH ₄ Cl
(C) HNO ₃ ,NH ₄ Cl,NO,N ₂	(D) NO, HNO ₃ , NH ₄ Cl, N ₂

Q.24 Concentrated nitric acid, upon long standing, turns yellow – brown due to the formation of (2013)

(A) NO (B) NO_2 (C) N_2O (D) N_2O_4

Q.25 The correct statement(s) about O₃ is(are) (2013)

(A) O-O bond lengths are equal

(B) Thermal decomposition of O_3 is endothermic

(C) O_3 is diamagnetic in nature

(D) O_3 has a bent structure

Q.26 The product formed in the reaction of SOCl₂ with white phosphorous is **(2014)**

(A) PCl_3 (B) SO_2Cl_2 (C) SCl_2 (D) $POCl_3$

Q.27 Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is (2014)



Q.28 Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is (2015)

Q.29 The correct statement(s) regarding, (i) HCIO, (ii) HCIO₂, (iii) HCIO₃, and (iv) HCIO₄, is (are) (2015)

(A) The number of CI = O binds in (ii) and (iii) together is two

(B) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three

(C) The hybridizatiob of Cl in (iv) is sp

(D) Amongst (i) to (iv), the strongest acid is (i)

Q.30 Among the triatomic molecules/ions $BeCl_2, N_3^-, N_2O, NO_2^+, O_3, SCl_2, |Cl_2, I_3^-$ and XeF_2^- the total number of linear molecule(s)/ion(s) where the hybridization of the central atom does not have contribution from the d-orbital (s) is

[Atomic number : S = 16, Cl = 17, l = 53 and Xe = 54] (2015)

Q.31 The increasing order of atomic radii of the
following Group 13 elements is(2016)(A) Al < Ga < In < Tl</td>(B) Ga < Al < In < Tl</td>

(C) AI < In < Ga < TI (D) AI < Ga < TI < In

Q.32 The crystalline form of borax has (2016) (A) Tetranuclear $\left[B_4O_5(OH)_4\right]^{2-}$ unit

(B) All boron atoms in the same plane

(C) Equal number of $\, sp^2 \, and \, \, sp^3 \,$ hybridized boron atoms

(D) One terminal hydroxide per boron atom

Q.33 The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10} (2016)

(A) Can also be prepared by reaction of P₄ and HNO₃

(B) Is diamagnetic

(C) Contains one N-N bond

(D) Reacts with Na metal producing a brown gas



16.52 | p - Block Elements -

PlancEssential Questions

JEE Main/Boards

J	EE	Adv	/an	ced	/Bc	bar	ds
		AU	an	CCU		Jai	us

Exerci	se 1		Exercis	se 1	
Q.12	Q.22	Q.23	Q.3	Q.9	Q.13
Q.34	Q.36	Q.37	Q.14	Q.16	S
Exerci	se 2		Exercis	se 2	\mathbf{O}
Q.7	Q.12		Q.1	Q.3	Q.11
Previo	ous Years'	Questions	Q.15 0.29	Q.27 0.30	Q.28 Q.32
Q.1	Q.8	Q.12	Q.33	S	U
Q.14	Q.21		Previo	us Years'	Questions
			Q,3	Q.5	Q.6

Answer Key							
JEE Main/Boards							
Exercise 2	19						
Single Correct Ch	oice Type						
Q.1 C	Q.2 B	Q.3 A	Q.4 B	Q.5 B	Q.6 B		
Q.7 A	Q.8 A	Q.9 A	Q.10 B	Q.11 D	Q.12 C		
Q.13 A							
Previous Year	s' Questions						
Q.1 D	Q.2 C	Q.3 A	Q.4 C	Q.5 A	Q.6 C		
Q.7 A	Q.8 C	Q.9 D	Q.10 A	Q.11 B	Q.12 A		
Q.13 C	Q.14 D	Q.15 B	Q.16 D	Q.17 A	Q.18 B		
Q.19 D	Q.20 D	Q.21 C	Q.22 B	Q. 23 C	Q.24. C		
Q.25 A	Q.26 A	Q.27 A					

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- Chemistry | 16.53

JEE Adva	nced/Bo	ards			
Exercise 2					
Single Correct	Choice Type				
Q.1 D	Q.2 B	Q.3 A	Q.4 B	Q.5 A	Q.6 A
Q.7 A	Q.8 A	Q.9 C	Q.10 B	Q.11 B	Q.12 D
Q.13 B	Q.14 D	Q.15 A			
Comprehensio	n Type			ć	Q
Q.16 B	Q.17 B	Q.18 C	Q.19 C	Q.20 C	Q.21 B
Assertion Reas	oning Type			5	
Q.22 A	Q.23 C	Q.24 A	Q.25 C	0	
Multiple Correc	ct Choice Type	,	C		
Q.26 A, B	Q.27 A, B, C	Q.28 A, C, D	Q.29 A, B	Q.30 A, D	Q.31 A, C
Q.32 A, B, C, D	Q.33 B, C				
Match the Colu	ımns		\mathbf{C}		
Q.34 $A \rightarrow q$, s; B	$B \rightarrow r; C \rightarrow r; D$	\rightarrow q, r			
Previous Yea	ars' Questic	ons			
Q.1 A	Q.2 A	Q.3 A, B, C	Q.4 C	Q.5 C	Q.6 Banana Bond
Q.7 D	Q.8 B	Q.9 A	Q.10 A, D	Q.11 A, C, D	Q.12 A
Q.13 C	Q.14 A	Q.15 B	Q.16 A \rightarrow p, s	;; B → p, q, r, t; C	\rightarrow p, q, t: D \rightarrow p
Q.17 B	Q.18 D	Q.19 D	Q.20 C	Q.21 A	Q.22 B, C, D
Q.23 B	Q.24 B	Q.25 A, C, D	Q.26 A	Q.27 C	Q.28 6
Q.29 B, C	Q.30 D	Q.31 B	Q.32 A, C, D	Q.33 B, D	
NNN	3				

16.54 | p - Block Elements -

Solutions

JEE Main/Boards

Exercise 1

Sol 1: Ammonia is manufactured industrially by using Haber's process.

 $N_2(g) + 3H_2(g) \xrightarrow{Fe/Mo} 2NH_3(g)$

2. In NH_3 , N is sp³ hybridised and one lone pair of electrons is present on N atom. Due to long pair – bond pair repulsions, the H-atoms are pushed closer and the bond angles decrease from 109° to 107°. In HPH or HAsH or HSbH, the central atom uses only pure p-atomic orbital in the bond formation. As p-atomic orbitals are mutually perpendicular to each other, the bond angle is close to 90°

Sol 2: On moving down the group, size of central atom increases and its electronegativity decreases. As a result, bond pairs lie away from central atom resulting in decreases in bond angle.

Sol 3:

White phosphorus	Red phosphorus
(i) It consist of discrete P_4 tetrahedral.	(i) It consists of polymer of P_4 tetrahedral units
(ii) It glows in dark and is soluble in CS_2	(ii) It does not glow in the dark and is insoluble in CS_2
(iii) It is highly reactive due to strained P_4 tetrahedral	(iii) It is much less reactive due to polymerization
(iv) It dissolves in NaOH to give PH ₃	(iv) It is insoluble in NaOH

Sol 4: The bond dissociation energy of N-N bond is less than that of P-P due to strong lone pair-lone pair repulsions.

Sol 5: (i) Electronic configuration:

 ${}_{8}O = [He]2s^{2}2p^{4}; {}_{16}DS = [Ne]3s^{2}3p^{4};$ ${}_{34}Se = [Ar]3d^{10}4s^{2}2p^{4}$ ${}_{52}Te = [Kr]4d^{10}5s^{2}2p^{4}$ and ${}_{84}Po = [Xe]4f^{14}5d^{10}6s^{2}6p^{4}$ All these elements have same $ns^2 np^4$ (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, at the maximum they can show an oxidation state + 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 state 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.e., 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 1s-orbital of hydrogen to form hybrids of the general formula EH_2 i.e., $H_2 O$, $H_2 S$, $H_2 Se$, $H_2 Te$ and $H_2 Po$. Therefore, on the basis of formation of hydride of the general formula, EH_2 , these elements are justified to be placed in group 16 of the periodic table.

Sol 6: Although the formation of O^{2-} from O is endothermic but still almost all elements form oxides and this is due to high lattice energy of the oxides. This is due to small size and high charge of O^{2-} .

Sol 7: Aerosols such as chlorofluorocarbons (CFCs), i.e., feron $(CCl_2 F_2)$ depletes the O₃ layer by supplying Cl free radicals which convert O₃ to O₂ as shown below:

$$Cl_{2}CF_{2}(g) \xrightarrow{hv} \bullet Cl(g) + \bullet CCIF_{2}(g)$$

$$\bullet Cl(g) + O_{3}(g) \longrightarrow CIO \bullet (g) + O_{2}(g)$$

$$CIO \bullet (g) + \bullet O(g) \longrightarrow \bullet Cl(g) + O_{2}(g)$$

Sol 8: Sulphuric acid is manufactured by the Contact Process which involves three steps:

(i) Burning of sulphur or sulphide ores in air to produce SO₂.

(ii) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5). and

(iii) absorption of SO₃ in H_2SO_4 to give oleum ($H_2S_2O_7$).

The SO₂ produced is purified by removing dust and other impurities such as arsenic compounds.

- Chemistry | 16.55

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).

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g); \Delta_r H^\circ = -196.6 \text{ kJ mol}^{-2}$$

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 the 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 oleum with water gives H_2SO_4 of the desired concentration.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

(Oleum)

The sulphuric acid obtained by contact process is 96-98% pure.

Sol 9: Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy, halogens have a strong tendency to accept electrons and thus get reduced.

$$X + e^{-} \longrightarrow X^{-}$$

Thus, halogens act as strong oxidising agents. Their oxidising power, however, decreases from F_2 to I_2 .

Sol 10: 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 on oxygen atom is much higher than that on chlorine atom. Hence, oxygen forms hydrogen bonds while chlorine does not though both have approx. The same electronegativity.

Sol 11: HCl can be oxidized to Cl_2 by a number of oxidising agents like MnO₂, KMnO₄ and K₂CrO₇

 $MnO_2 + 4HCI \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

 Cl_2 can be reduced to HCl by reaction of H_2 in the presence of diffused sunlight.

 $H_2 + CI_2 \xrightarrow{\text{Diffused sunlight}} 2HCI$

Sol 12: Let the oxidation state of P be x.

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

x -1

(ii) P Cl_3 : x + 3(-1) = 0 or x = +3

(iii)
$$\overset{+2}{Ca}_{3} \overset{x}{P_{2}} \therefore 3(+2) + 2 \times x = 0 \text{ or } x = -3$$

(iv) $\overset{+1}{Na}_{3} \overset{x}{P} \overset{-2}{O_{4}} \therefore 3(+1) + x + 4(-2) = 0 \text{ or } x = +5$
(v) $\overset{x}{P} \overset{-2}{O} \overset{-1}{F_{3}} \therefore x + 1(-2) + 3(-1) = 0 \text{ or } x = +5.$

Sol 13: Cl₂ is produced

 $Cl_2(g) + 2NaI(aq)$

$$[NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl] \times 4$$

$$4HCl + MnO_2 \longrightarrow MNCl_2 + Cl_2 + 2H_2O$$

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + Cl_2 + 2H_2O$$
(ii) Cl₂ being an oxidising agent oxidises Nal to l₂.

 $\sim 2NaCl(aq) + I_2(s)$

Sol 14: These xenon fluorides are prepared by direct reaction between Xe and F_2 under different conditions as shown below:

$$\begin{array}{c} Xe(g) + F_2(g) & \xrightarrow{673K,1 \text{ bar}} XeF_2(s) \\ excess) & Xe(g) + 2F_2(g) & \xrightarrow{873K,7 \text{ bar}} XeF_4(s) \\ (1:5 \text{ ration}) & Xe(g) + 3F_2(g) & \xrightarrow{573K,60-70 \text{ bar}} XeF_6(s) \\ (1:20 \text{ ration}) & \end{array}$$

Sol 15: Replace O⁻(9 electrons) in CIO⁻ by F (9 electrons). The resulting neutral molecule is CIF. Since CIF can combine further with F to form $CIF_{3'}$ so, CIF is a Lewis base.

Sol 16: Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3

$$\begin{split} & 6\mathsf{XeF}_4 + 12\mathsf{H}_2\mathsf{O} \longrightarrow & 4\mathsf{Xe} + 2\mathsf{XeO}_3 + 2\mathsf{4HF} + \mathsf{3O}_2 \\ & \mathsf{XeF}_6 + \mathsf{3H}_2\mathsf{O} \longrightarrow & \mathsf{XeO}_3 + \mathsf{6HF} \end{split}$$

In contrast, partial hydrolysis of XeF₆ gives XeOF₄

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

Sol 17: Noble gases have only van der Waals' radii while others have covalent radii. Van der Waals' radii are larger than covalent radii. Hence, noble gases have comparatively large atomic sizes.

Sol 18: Uses of Neon:

(i) Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes.

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16.56 | p - Block Elements -

(ii) Neon bulbs are used in botanical gardens and in green houses.

(iii) Neon is used in voltage regulators and indicators.

Sol 19: Electronic configuration: The valence shell electronic configuration of these elements are ns² np³. The s-orbital in these elements is completely filled and p-orbitals are half-filled, making their electronic configuration extra stable.

Oxidation states: The common oxidation states of these elements are -3 , +3, and + 5. The tendency to exhibit -3 oxidation, state decreases down the group due to increase in size and metallic character. In fact last member of the group, bismuth hardly forms any compounds in -3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterized Bi (v) compound is BiF_3 The stability of +5 oxidation state decreases and that of +3 oxidation state increases (due to inert pair effect) down the group. Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen.

Phosphorus also shows +1 and +4 oxidation states in some oxoacids.

Atomic size: Covalent and ionic (in a particular state) radii increases in size 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 the presence of completely filled d and /or f orbitals in heavier members.

Ionization Enthalpy: Ionization enthalpy decreases down the group due to gradual increases in atomic size. Because of the extra stable half-filled p-orbitals electronic configuration and smaller size, the ionization enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionization enthalpies as expected is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$.

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

I in ICI_4^{-} has four bond pairs and two lone pairs. Therefore, according to VSEPR theory, it should be square planar as shown.

Here, ICI_{4}^{-} has $(7+4\times7+1) = 36$ valence electrons. A noble gas species having 36 valence electrons is XeF_{4} (8 + 4 × 7 = 36). Therefore, like ICI_{4}^{-} , XeF_{4} is also square planar.





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 $22(7+2\times7+1)$ valence electrons. A noble gas species having 22 valence electrons is XeF_2^{-} (8+2×7 = 22). Thus, like IBr_2^{-} , XeF_2^{-} is also linear:



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 should be pyramidal. Here, BrO⁻₃ has $26(7+3\times6+1=26)$ valence electrons. A noble gas species having 26 valence electrons is XeO₃ ($8+3\times6+1=26$). Thus, like BrO⁻₃, XeO₃ is also pyramidal.

Sol 21: XeF,



Sol 20: (i) Structure of ICl



Square planar

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– Chemistry | 16.57

BrF₃



T-Shaped

Sol 22: (i) The minimum oxidation number (O.N.) of S is -2 while its maximum O.N. is +6 In SO₂, the O. N. is +4, here, it can not only increase its O.N. by losing electrons but also reduce its O.N. by gaining electrons. Thus, it acts both as a reducing agent as well as an oxidising agent. In contrast, in H_2S , S has an O.N. of -2. Thus, it can only increase its O.N by losing electrons and hence acts only as a reducing agent.

(ii) Fluorine being the strongest oxidising agent oxidises sulphur to its maximum oxidation state of +6 and thus forms SF_6 In contrast H_2 being a very weak oxidising agent cannot oxidise S to its maximum oxidation state of +6 and hence does not form SH_6

(iii) This is because fluorine is more electronegative than oxygen.

Sol 23: (i) (a) $XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$:

(b) $2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 + O_2$

(ii) (a) +3 oxidation state becomes more stable from As to Bi in the group due to inert pair effect. The reluctance of the s electrons to take part in the chemical bonding due to which the lower oxidation state become more stable on descending down the group of p-block elements is known as inert pair effect.

(b) Sulphur in vapour state exhibits paramagnetic behaviour because it forms S_2 molecules like O_2 which contains two unpaired electrons.

Sol 24: (ii) (a) Because P-P bond is stronger than N-N bond.

(b) $p\pi - p\pi$ bonding is available in case of fluorine whereas in case of chlorine, $d\pi - p\pi$ is seen.

(c) Ionization energy is quite high.

```
Sol 25: (ii) a Hydrogen bonding in NH<sub>3</sub>
```

(b) same as 24(c).

(c) Due to Due to the inert pair effect, Sb and Bi are more stable in +3 oxidation state as compared to the +5 state. But due to the presence of f orbital electrons in Bi, its +3 is more stable than Sb(+3). That is why, Bi(V) tends to achieve Bi(III) state (i.e. reduction of Bi) for greater stability easily as compared to the Sb. since Bi (V) is undergoing self reduction, hence it is a stronger oxidising agent then Sb(V).

Sol 26:

(i) (a)
$$PCl_5 + H_2OH \rightarrow Cl + H_3PO_4$$

(b)
$$F_2 + H_2 O \rightarrow HF + O_2$$

(ii) (a) Presence of d-orbitals in P.

(b) Formation of bisulfate anion (HSO_4^-) by loss of one proton gives a bigger Ka₁.

Sol 27: (i) (a) $P_4 + 4NaOH + 2H_2O \rightarrow 2PH_3 + 2Na_2HPO_3$ (b) $3Cu + 8HNO_3$ (dilute) $\rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$

(ii)(a) Oxygen has small size and more electronegativity in comparison to sulphur and thus H_2O molecules exists as associated molecule to form liquid state because of H-bonding. H_2S doesnt not show H-bonding and thus exists as unassociated molecules to have gaseous state.

ii) (b) Deep sea divers can remain at depth only for controlled periods and must come up slowly and even remain at specified depths to avoid the bends. When ordinary air is used for diving the oxygen in the air is used up by the body but the nitrogen builds up to a new equilibrium state at the higher pressure required at great depths. The excess nitrogen would then come out of tissues and form bubbles (like the fizz in a opened can of soda) in the blood causing the bends and great pain with possible death. During controlled decompression the helium would also diffuse out of tissues and the lungs more easily than nitrogen avoiding the bends.

Sol 28: In PCl_5 , due to small size and high electronegativity of Cl, hybridisation is possible. But in PI_5 , hybridisation is restricted due to large size and less electronegativity.

Sol 29: Urea releases nitrogen readily as compared to ammonium sulphate and moreover, urea contains the highest percentage of nitrogen.

Sol 30: HF has a corrosive action on glass.

16.58 | p - Block Elements -

Sol 31: H_2F_2 exists as dimeric molecule due to H-bonding and thus shows dibasic nature. Hence it gives two series

of salts KHF_2 as $\left[K^+andF^-....H-F^-\right]$ and $KF\left[K^+andF^-\right]$ whereas HCl and HBr do not show hydrogen bonding and thus formation of $KHCl_2$ or $KHBr_2$ is not possible.

Sol 32: Halogens have variable oxidation states, +1, +3, +5 and +7.

Sol 33: Chlorine can displace iodine sinc its above I in the group.

Sol 34: (i) Ionization energy of Cl is greater than Iodine. Thus I_2 can be readily displaced.

ii) SO_2 is obtained by burning sulphur in air.

 $S + O_2 \rightarrow SO_2$

The SO_2 so obtained is impure. Dust present in sulphur is removed by allowing the gas to expand, when some dust settles, as well as by passing through electrostatic precipitators and finally washing with water. The moistened gas is now treated with conc.H₂SO₄ to dry SO₂ and H₂SO₄ is kept in use until its concentration falls to 94%.

The SO_2 so obtained then catalytically converted to SO_3

 $2SO_2 + O_2 \xrightarrow[]{ finely divided Pt deposited on MgSO_4 } or Fe_2O_3 & CuO \\ or Pt-silicagel \\ Or Pt-$

Sol 35: (i)

 SO_2 reduces $K_2Cr_2O_7$ to green chromium sulphate.

$$3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

ii) Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2S \uparrow
foul odour

Sol 36: The oxidation number of sulphur in sulphur dioxide is +4 which lies between its maximum value (+6) and minimum value (-2). Hence sulphur dioxide can both be oxidized and reduced and SO_2 can act both as a reducer and oxidizer respectively

As oxidizer

$$2H_2S^{-2} + SO_2 = 3S^{+} 2H_2O$$

AS reducer-

$$I_2^0 + SO_2 + 2H_2O = 2HI + H_2SO_4$$

 $2K \stackrel{+5}{S}O_3 + 5\stackrel{+4}{S}O_2 + 4H_2O \rightarrow I_2 + 4H_2\stackrel{+6}{S}O_4 + K_2SO_4$

Sulphur is placed below oxygen in the same group in the periodic table.

Thus H₂S acts as a reducing agent only.

Sol 37: (i) H_3PO_4 , orthophosphoric acid, can be written $O = P(OH)_3$. It has three acidic protons (attached to

oxygen) and is therefore tribasic. But Phosphorus acid, H_3PO_3 , is diprotic (readily ionizes two protons), not triprotic as might be suggested by the formula.

ii) to restore the fertility of the soil. These plants have the ability to fix atmospheric nitrogen to form nitrogen compounds through the help of certain bacteria present in their root. These nitrogen compounds go into the soil and make it more fertile.

Sol 38:
$$Zn + H_2SO_4(dil) \longrightarrow ZnSO_4 + H_2$$

 $Zn + conc, H_2SO_4 \longrightarrow ZnSO_4 + SO_2 + 2H_2C$

Exercise 2

Single Correct Choice Type

Sol 1: (C) $H_3PO_2 \xrightarrow{\Lambda} (X) + PH_3$;

Disproportionation reaction

Sol 2: (B) (b) **Pseudohalogen molecules:** (meaning"fake" halogens) are inorganic molecules of the general forms Ps–Ps or Ps–X, where Ps is a **pseudohalogen group** such as cyanide, cyanate, thiocyanate and others, and X is a "true" halogen.

Sol 3: (A) Fact.

Sol 4: (B) (b) Depends on the sizes of the halogens

Sol 5: (B) (b) It has a lone pair in 2p orbital which is transferred to the empty d-orbital of Si atom resulting $d\pi$ -p π bonding.





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– Chemistry | 16.59

Sol 7: (A)

 $\begin{array}{l} H_2C_2O_4 + H_2SO_4 \rightarrow H_2O + CO + CO_2 \\ KOH + CO_2 \rightarrow K_2CO_3 + H_2O \end{array}$

Sol 8: (A) Acidic strengths increases as electronegativity of atom increases So, $Cl_2O_7 > SO_2 > P_4O_{10}$

Sol 9: (A)
$$CaC_2 + N_2 \rightarrow \underbrace{CaCN_2}_{Calcium \ cyanamide} + C$$

Sol 10: (B) Fact.

Sol 11: (D) Self explanatory

Sol 12: (C)



Sol 13: (A) $KI + O_3 + H_2O \rightarrow I_2 + KOH + O_2$

Previous Years' Questions

Sol 1: (D)
$$Al_2Cl_6 + 12H_2O \Rightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^{-1}$$

Sol 2: (C) Fact.

Sol 3: (A) Boron does not have d orbitals in its valence shell and so, maximum covalency of Boron cannot exceed 4. So, its cannot form BF_6^{-3} .

Sol 4: (C)
$$Al_2Cl_66H_2O \longrightarrow Al_2O_3 + 6HCl + 3H_2O_3$$







Sol 6: (C) Stability of dihalides increases down the group.

Sol 8: (C) Down the group, acidic character increases.

Sol 9: (D) In P_4 , P_7 P bond is sp³ hybridised

 \therefore % p character = 75

Sol 10: (A) Down the group, stability of hydrides decreases.

Sol 11: (B) $K_2Cr_2O_7 + HNO_3(dil) \rightarrow Cr_2O_7^{-2} + 2k^+ + 2H_2O$ excess $Cr_2O_7^{-2} \& H_2O$ are formed.

Sol 12: (A) Nitrogen does not have vacant d-orbitals.

Sol 13: (C)
$$PH_3 + 4Cl_2 \rightarrow PCl_5 + 3HCl$$

Sol 14: (D) a) $S \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^4$
 $S_2 = \text{total } 32 \text{ e}^-$
 $\sigma(2s)^2 \sigma^*(2s)^2 \dots \left[\pi(3p_x)^2\right] \left[x(3p_y)^2\right]$
 $\left[\pi(3p_2)^2\right] \left[x^*(3p_x)^1\right] \left[\pi^*(3p_y)^1\right]$
b) Vapour at 200 - S_8

c) Vapour at 600 - S₂

d) Oxidation state of S in S_2 is O.

Sol 15: (B) HF > HCl > HBr > HI (Thermal stability).

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16.60 | p - Block Elements -

Sol 16: (D) $Br_2 + NaOH(not) \rightarrow NaBr + NaBrO_4 + H_2O$

Sol 17: (A) $XeF_6 + H_2O \rightarrow XeO_3 + 6HF$

Reaction is not reversible.



Sol 19: (D) Decrease in Electronegativity down the group causes decreases in bond angles.

Sol 20: (D) $XeF_2 \rightarrow 3\ell p, 2BP$

 $XeF_4 \rightarrow 2\ell p, 4BP$

 $XeF_6 \rightarrow 1\ell p, 6BP$



Sol 21: (C) Helium is twice as heavy as hydrogen, its lifting power is 92% of that of hydrogen. Helium has the lowest melting and boiling point of any element which makes liquid helium an ideal coolant for many extremely low temperature application such as super conducting magnet and cryogenic research where temperature close to absolute zero are needed.

Sol 22: (B) HCl is a gas.

Sol 24: (C) NO is paramagnetic in gaseous state and diamagnetic in solid state.

Sol 25: (A) $N_2 + O_2 \longrightarrow 2NO$

 $\Delta G = \Delta H - T \Delta S$

 $\Delta H \& \Delta S$ As are positive.

So reaction is thermodynamically favourable at high temperature.

Sol 26: (A) O = N = Osp hybridisation

Sol 27: (A) Phosphorus acid series contain phosphorus in the oxidation state (+ III).



JEE Advanced/Boards

Exercise 1

Sol 1: (i) $I_2 < F_2 < Br_2 < CI_2$ (ii) HF < HCl < HBr < H -l (iii) BiH₃ < SbH₃ < AsH₃ < PH₃ < NH₃

Sol 2: NeF₂ does not exist.

Sol 3: (i)
$$Ca_3P_2 + H_2O \rightarrow Ca(OH)_2 + PH_3$$

(ii) $Cu^{2+}(aq) + NH_3(aq) \rightarrow Cu(NH_3)_4^{+2}$ excess Deepblue complexion

Sol 4: Reaction of Zinc and HCl produces nascent hydrogen which is more reactive than molecular hydrogen.

Sol 5: Aquaregia is a mixture of 1 part conc. HNO_3 and 3 part conc. HCl. The mixture liberate nascent chlorine which dissolves noble metals.

Sol 6: The impurity in PH_3 is P_2H_4 , the liquid hydride present in phosphine catches fire as soon as it contact with air and forms vortex rings of smoke.

Sol 23: (C) Factual.

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Chemistry | 16.61

Sol 7: The chlorides, nitrates and sulphates are soluble while the sulfides are insoluble.

Sol 8: Mn_2O_7 is formed in the reaction between $KMnO_4$ and $H_2SO_4.Mn_2O_7$ is unstable and explosive in nature.

Sol 9: (i) Bleaching by SO_2 takes place du to reduction, since SO_2 liberates nascent hydrogen. The colours are restored by the oxidation of colourless substance by air.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$

 $Colour + 2[H] \xrightarrow{Air} Colourless$

On the other hand Cl_2 acts as bleaching agent due to oxidation and permanent.

 $Cl_2 + H_2O \longrightarrow 2HCI + [O]$

(ii) Nitrite oxidizes iodide ion to iodine and thus liberated iodine gets dissolved in KI

solution to intensity its colour. On the other hand, sulphites are themselves oxidized by I_2 of solution and thus, reducing I_2 to discharge the colour of solution.

Sol 10: (i)
$$2Ag^+ + SO_3^{2-} \rightarrow Ag_2SO_3 \downarrow$$

 $Ag_2SO_3 + SO_3^{2-}(excess) \rightarrow 2[Ag(SO_3)]^-(soluble)$

Sol 11: (i) Nitric acid in its pure form is colorless. The color changes to brownish-yellow due to the presence of nitrogen dioxide (NO_2) . This nitrogen dioxide usually forms when bottles containing nitric acid reacts with oxygen in the air to form nitrogen dioxide which remains dissolved in the acid to give this particular colour.

(ii) N_2O is better source of oxygen than air because air has oxygen about 1/5 of its volume. While N_2O on decomposition produces oxygen about 1/3 volume.

Sol 12: (i) Yellow phosphorus is quite reactive in air and very unstable burns in air whereas Red Phosphorus is very stable and less reactive.

Sol 13: (i) $3H_3PO_2 = PH_3 + 2H_3PO_3;$ $4H_3PO_3 = PH_3 + 3H_3PO_4$ (ii) $IO_3^- + 3HSO_3^- \rightarrow I^- + 3HSO_4^-$

(iii)
$$SO_2 + CI_2 \rightarrow SO_2CI_2$$

(iv)
$$K_2Cr_2O_7 + 14 \underset{conc.}{HCl} \rightarrow 2K^+ + 2Cr^{3+} + 8Cl^- + 7H_2O(l) + 3Cl_2(g)$$

Sol 14: (i)

Bismuth oxide +HCl + excess water \rightarrow ppt / turbidity Bi³⁺(aq.) + Cl⁻(aq.) + 3H₂ O(l) \rightleftharpoons BiOCl \downarrow +2H₃O^{\oplus}(aq).

(ii)
$$\underset{(aq.)}{KI} + I_2 \rightarrow KI_3(aq.)$$

Through this reaction, iodine is used in redox titrations.

(iii)
$$4HI + CuSO_4 \rightarrow CuI_4^{2-}$$

(aq.) copper tetraiodate comple

(iv) $2H_2S + SO_2 \rightarrow 3S + 2H_2O$

Sol 15: (i)
$$CuSO_4 + KSCN \rightarrow CuSCN + K_2SO_4$$

(ii)
$$O_3 + CH_2 = CH_2 - CH_2$$

(iii) $6NaOH + 4S \rightarrow Na_2S_2O_3 + Na_2S + Na_2SO_3$

Exercise 2

Single Correct Choice Type

Sol 1: (D)
$$I_2O_4 \longrightarrow IO^+ + IO_3^-$$

Sol 2: (B)

$$\begin{array}{c} 4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2 \uparrow \\ \text{orange solid} \\ (X) \\ (Z) \\ \hline \\ Mg \\ White solid \end{array}$$

Sol 3: (A)

$$NH_4NO_3 \xrightarrow{A} N_2O_{(B)} + 2H_2O(Neutral to litmus paper)$$

 $N_2O \xrightarrow{White phosphorous} P_2O_5$

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16.62 | p - Block Elements -

Sol 4: (B) SiO₂ has tetrahedral network structure.

$$SiO_2 + 3C \longrightarrow 2CO + SiC$$

Sol 5: (A)

$$FeSO_{4} \xrightarrow{\Lambda} SO_{2}^{+4} + SO_{3} + Fe_{2}O_{3}$$

$$SO_{2} \xrightarrow{K_{2}Cr_{2}O_{7}} Cr^{+3} (Green)$$

$$SO_{3} \xrightarrow{K_{2}Cr_{2}O_{7}} FeCl_{3}$$

Sol 6: (A) $P_4 + 10NO \longrightarrow P_4O_{10} + 5N_2$ Dehydrating agent

Sol 7: (A) $(NH_4)_2 SO_4 \xrightarrow{\Delta} NH_3 + H_2O + SO_3$

Sol 8: (A) More the no.of oxygen atoms increase, acidic strength increases.

Sol 9: (C)
$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O_3$$

Sol 10: (B) $2HBr + H_2SO_4(conc.) \longrightarrow Br_2 + SO_2 + 2H_2O_2$ HBr gets oxidised to Br_2

Sol 11: (B)

$$HOOC - CH_2 - COOH \xrightarrow{150^{\circ}C}_{P_4O_{10}} O = C = C = C = O + 2H_2C$$
Malonicacid Carbonsuboxide Tricarbon dioxide

Sol 12: (D)



Sol 13: (B) When $AgNO_3$ is heated strongly it decomposes to give metallic silver.

$$2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 + O_2$$

Sol 14: (D) $4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$

Sol 15: (A) Addition of Cis-1,2-diol converts boric acid into a strong complex, so as to prevent hydrolysis of complex & make it strong enough to be titrated with NaOH.

Comprehension Type

Sol 16: (B) 40^{-} atoms with 1 Si atom So, SiO₄⁻⁴ 20^{-} atoms are shared between 3 tetrahedral 3 Si atoms with 10 oxygen atoms Si₃O₁₀⁻⁸.

Sol 17: (B) (B) will be the structure.

Sol 18: (C) Anion will be Si₃O₁₀⁻⁸.

So compound will be Ca₂ Cu₂ Si₃O₁₀.2H₂O

Sol 19: (C) Due to greater solubility and nature to be prone to microbial action, nitrates are less abundant is earth's crust.

Sol 20: (C) NH_3 is better electron donor because the lone pair of electrons occupies sp³-orbital and is more directional.

Sol 21: (B) White phosphorus on reaction with NaOH gives PH_3 as one of the product in disproportionation reaction.

 $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$

Assertion Reasoning Type

Sol 22: (A) Reason is correct explanation of assertion. Coloured salts decompose to give. Coloured meta borates. So borax bead fast is applicable to coloured salt.

Sol 23: (C) H_2SO_4 is a stronger oxidizing agent than both $Br_2 \& I_2$.

Sol 24: (A) Reason is correct explanation of Assertion. Bond energy of Si-O & Si-C are very high which make then inert.

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– Chemistry | 16.63

Sol 25: (C)

 $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$ (conc. & hot)

Multiple Correct Choice Type

Sol 26: (A, B) Fact.

Sol 27: (A, B, C)

$$Al_2(SO_4)_3 + NH_4OH \longrightarrow Al(OH)_3$$

 \downarrow
(a) White coloured
(b) Insoluble in NH_4OH
(c) Soluble in $NaOH$

Sol 28: (A, C, D) Stability of dihalides increase down the group.

Ability of forming $p\pi - p\pi$ multiple bonds decreases down the group.

They all form oxides (MO_2) .

Sol 29: (A, B) NO_2 is paramagnetic, but N_2O_4 is diamagnetic.

 NO_2 is brown and $\mathrm{N}_2\mathrm{O}_4$ is colourless.

Sol 30: (A, D) C – O bond energy is less than SiO bond energy.

Sol 31: (A, C) IF₃, IF₅, IF₇, BrCl

B is more Electronegative than A

FBr₃ does not exist.

There is no deviation in structure of CIF_3 and IF_7 .

Sol 32: (A, B, C, D) Fact.

Sol 33: (B, C)

Match the Columns

Sol 34:
$$A \rightarrow q$$
, s; $B \rightarrow r$; $C \rightarrow r$; $D \rightarrow q$, r
A. $Bi^{3+} + H_2O \longrightarrow BiO^+ + 2H^+$ thus (q) and (s)
B. $AlO_2^- + H_3O^+ \longrightarrow Al(OH)_3 \downarrow$ thus (r)
C. $2SiO_4^{4-} + 2H^+ \longrightarrow Si_2O_7^{6-}$ thus (r)
D. $B_4 O_7^{2-} \xrightarrow{H^+} B(OH)_3$
 $B_4 O_7^{2-} \xrightarrow{H_2O} B(OH)_3$. Thus, (q) are (r)

Previous Years' Questions

Sol 1: (A) Orthoboric acid is a weak, monobasic, Lewis acid.



 $p\pi$ - $p\pi$ back-bonding between 'B' and 'O' decreases acid strength greatly:



Sol 2: (A) Orthoboric acid is a very weak acid, direct neutralization does not complete. However, addition of cis-diol allow the reaction to go to completion by forming a stable complex with $[B(OH)_{4}]^{-}$ as:



Sol 3: (**A**, **B**, **C**) Diborane ($B_2 H_6$) undergo unsymmetric cleavage with NH₃, primary and secondary amine while tertiary amine brings about symmetrical cleavage of B_2H_6 as:

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16.64 | p - Block Elements -



Sol 4: (C) Orthoboric acid is a weak, monobasic, Lewis acid and the poor acidic character is due to $p \pi - p \pi$ back bondings as



Back bonding decreases electron deficiency decreases electron its Lewis acid strength.

Sol 5: (C) SiCl₄ reacts with water due to vacant dorbitals available with Si as:



No such vacant d-orbitals are available with carbon, hence CCl_4 does not react with water. Otherwise, both $SiCl_4$ and CCl_4 are covalent.

Sol 6: Three centred two electron bonds.



Azide salt of barium can be obtained in purest form as well as the decomposition product contain solid Ba as by product along with gaseous nitrogen, hence no additional step of separation is required. Other reactions are:

$$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$$

$$2NH_3 + 3CuO \xrightarrow{Heat} 3Cu + 3H_2O + N_2$$

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

Sol 8: (B) In limited supply of oxygen, phosphorus is oxidized to its lower oxide P_4O_6 while excess of oxygen gives $P_4O_{10}A$ mixture of O_2 and N_2 is used for controlled oxidation of phosphorus into P_4O_6 .

Sol 9: (A) Amongst oxyacids of a given halogen, higher the oxidation number of halogen, stronger the acid. Hence,

 $HOCI < HCIO_2 < HCIO_3 < HCIO_4$.

Sol 10: (A, D)

 $NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$ $NH_2OHHCl + NaNO_2 \longrightarrow NaCl + 2H_2O + N_2O$ However, NH_4NO_2 on heating gives N₂.

Sol 11: (A, C, D) The structure of P₄ is



It has six P-P single bonds. There are four lone pairs of electrons on four phosphorus. P-P-P bond angle are 60.

Sol 12: (A) Ar, being inert, provide inert atmosphere in arc welding, and prevent from undesired oxidation.

Sol 13: (C) Xe is sp³ hybridised with one lone pair. Hence, molecule of XeO₃ has pyramidal shape.

$$0 = : X_e: = 0$$
$$\parallel 0$$

Sol 14: (A) Both XeF_4 and XeF_6 are strong oxidising agent.

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- Chemistry | 16.65

Sol 15: (B) White phosphorus undergo disproportionation in alkaline medium.

$$P_4 + NaOH \longrightarrow PH_3 + NaH_2PO_2$$

Sol 16:
$$A \rightarrow p$$
, s; $B \rightarrow p$, q, r, t; $C \rightarrow p$, q, t; $D \rightarrow p$



 $\begin{aligned} & 3XeF_4 + 6H_2O \rightarrow XeO_3 + 2Xe + 12HF + CI\frac{3}{2}O_2 \\ & Cl_2 + H_2O \rightarrow HCI + HOCI \rightarrow HCI + \frac{1}{2}O_2 \\ & VCl_5 + H_2O \rightarrow VOVCl_3 + 2HCI \end{aligned}$

Sol 17: (B) $H_3PO_3[O = PH(OH)_2]$ is a dibasic acid.

Sol 18: (D)
$$PCl_5 + SO_2 \rightarrow POCl_3 + SOCl_2$$

 $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

 $6PCI_5 + P_4O_{10} \rightarrow 10POCI_3$

Sol 19: (D)
$$(NH_4)_2 Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$$

$$\rm NH_4\rm NO_3 \rightarrow \rm N_2\rm O + \rm H_2\rm O$$

 $3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O$

 $Ba(N_3)_2 \rightarrow 3N_2 + Ba$ (pure nitrogen)

Sol 20: (C) P_4 (white) +NaOH+3H₂O \rightarrow PH₃ + 3NaH₂PO₂ PH₃ has - 3 and NaH₂PO₃ has +5.

Sol 21: (A) Bleaching powder contains salt HCI It is obtained by adding H_2O to Cl_2O

Sol 22: (B, C, D) Graphite is sp² hybridized and contains Vander Wall Force. While diamond is sp³ hybridized.

Sol 23: (B) $HNO_3 \rightarrow +5$ $NO \rightarrow +2, N_2 = 0$ $NH_4CI \rightarrow -3$

Sol 24: (B) $4HNO_3 \xrightarrow{Sunlight} 4NO_2 + 2H_2O + O_2$

Sol 25: (A, C, D) Exothermic.

Sol 26: (A)
$$SOCI_2 + P_4 \longrightarrow PCI_3 + SO_2 + S_2CI_2$$

Sol 27: (C) $XeF_6 + 3H_2O \rightarrow XeO_3 + 3H_2F_2$
 $XeO_3 + OH^- \rightarrow HXeO_4^-$
 $2HXeO_4^- + 2OH^- \rightarrow XeO_6^{-4} + Xe + 2H_2O + O_2$

Sol 28: $B_2H_6 + 6MeOH \rightarrow 2B(OMe)_2 + 6H_2$

Diborane reacts with methanol to give hydrogen and trimethoxyborate ester.



$$CI - Be - CI \qquad -1 + 1 - 1 \qquad N \equiv N \rightarrow O \qquad O = N = 1$$

Linear(sphybridisation)

Sol 31: (B) Ga < Al < In < Tl

On moving down the group, atomic radii increases except Ga to poor screening effect.

Sol 32: (A, C, D)



Sol 33: (B, D) $4HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4HPO_3$

$$\mathrm{P_4} + \mathrm{20HNO_3} \rightarrow \mathrm{4H_3PO_4} + \mathrm{20NO_24H_2O}$$

$$\begin{array}{c} O = \underset{\bigcirc}{N-O-N} = O \text{ is diamagnetic} \\ \downarrow \\ O \\ O \\ N_2O_5 + Na \longrightarrow NaNO_3 + NO_2 \uparrow \end{array}$$

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