

P- Block Elements

CHAPTER 07

INTRODUCTION

The right side of the periodic table having group number 13, 14, 15, 16, 17 and 18 are known as p – block elements. These elements have 3, 4, 5, 6, 7 and 8 electrons in their outer most shell, respectively. The last electron of these groups' elements occupies the position in p – sub shell that is why are added as p – block elements. Their general configuration is ns^2np^{1-6} .

Some important properties of p-block

1) Electron affinity

Electron affinity increase from left to right along the period amongst the p – block elements and it decreases from top to bottom. But group 15 is having exceptionally low values of electron affinity and is due to extra stability because of the presence of exactly half-filled orbital in their valence shell. Similarly, elements of group 18 (noble gases) have zero affinities due to presence of complete octet which provides then stability.

2) Metallic Character

The metallic character is governed by

- (i) Size of atoms and
- (ii) Ionization energy.

The elements having bigger size and low ionization energy has a greater metallic character. After combining both above mentioned factors we observe that the elements with above two properties are located in left corner of p – block and strong non – metallic elements are located at right corner and a diagonal strip of elements separates thus two, having in between properties are called as metalloids.

3) Oxidation state

The p – block elements show variety of oxidation states both positive and negative. Some of the p – block elements show different oxidation state due to inert – pair effect, where their lower oxidation state is more predominant.

Sr. No.	Property	Along period (left to right)	Along group (top to bottom)
1.	Atomic radii	Decreases	Increases
2.	Ionization potential	Increases	Decreases
3.	Electron affinity	Increases	Decreases
4.	Electro negativity	Increases	Decreases
5.	Metallic character	Decreases	Increases
6.	Oxidizing property	Increases	Decreases
7.	Reducing property	Decreases	Increases

GENERAL TRENDS IN PHYSICAL PROPERTIES OF GROUP-15 ELEMENTS

Sr. No.	Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
1.	Configuration	[He]2s ² 2p ³	[Ne]3s ² 3p ³	[Ar]4s ² 4p ³	[Kr]5s ² 5p ³	[Xe]6s ² 6p ³
2.	Common oxidation state	-3, +3, +5	-3, +3, +5	+3, +5	+3, +5	+3
3.	Atomic radius (pm)	70	110	120	140	150
4.	First ionization energy (KJ/mol)	1012	1012	947	834	703
5.	Electronegativity	3.0	2.1	2.0	1.9	1.9

CHEMICAL PROPERTIES OF GROUP 15 ELEMENTS

As we move down the group there is a decrease in covalent character.



Nitrogen is chemically less reactive, due to high stability of its molecule, N₂ in which two nitrogen atoms are combined through triple covalent bonds (N ≡ N) from which one is sigma (σ) and two are pie (π) bonds, thus posses high bond strength (941.4 KJ mol⁻¹).

Nitrogen has one special feature that it can form pπ - pπ multiple bonds with itself, carbon and oxygen due to its small size. In phosphorus rather pπ - pπ, dπ - pπ is found as in POX₃.

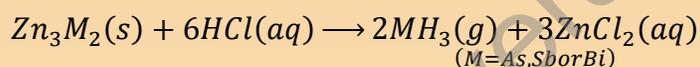
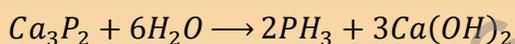
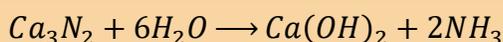
1. Hydrides

All elements of this group form gaseous hydrides of the type MH_3 . The stability however decreases down the group for these hydrides.

NH_3	PH_3	AsH_3	SbH_3	BiH_3
Ammonia	Phosphine	Arsine	Stibine	Bismuthine

All the hydrides are strong reducing agents and reacts with metal ions to give phosphides, arsenide's or antimonides. Phosphine and other hydrides of heavier members of this groups are highly poisonous.

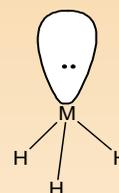
Formation of Hydrides



Beside these, N_2H_4 another hydride of nitrogen can be prepared by the action of NH_3 and sodium hypochlorite. $NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$

Structure of Hydrides

In these entire hydrides central atom assumes sp^3 hybrid state forming four sp^3 hybrid orbitals. Bond angle of $H - M - H$ decreases down the group. Down the group thermal stability also decreases.



It is because of decrease in $M - H$ bond strength due to increase in the size of central atom. These hydrides behave as reducing agents. And down the group reducing power increases. Boiling point of hydrides increases from PH_3 to BiH_3 but NH_3 has exceptionally high B.P. due to presence of intermolecular hydrogen bonding. The hydrides of group 15, due to availability of lone pair on central atom act as Lewis bases. The basic character decreases down the group. This is due to the decrease in density of electron on the central atom down the group as the volume of central atom increases down the group.

Ammonia (NH_3) : Nitrogen forms three different hydrides with hydrogen

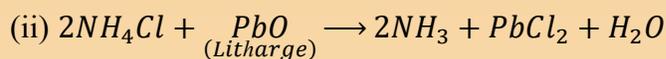
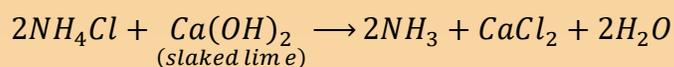
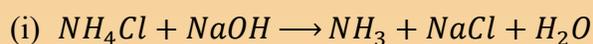
- (i) NH_3
- (ii) Hydrazine, NH_2NH_2
- (iii) Hydrazoic acid, N_3H

Ammonia (NH₃) is one of the very important hydrides found in traces in atmosphere. The atmospheric ammonia is formed by the bacterial decomposition of nitrogenous matter of plants and animals.

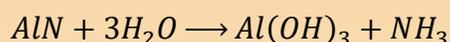
It was isolated in 1774 by Priestley by the action of ammonium chloride and lime.

It was named alkaline air. Berthelot, in 1788, pointed out that ammonia is a compound of nitrogen and hydrogen. IN 1800, Davy established its formula NH₃.

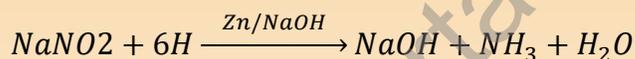
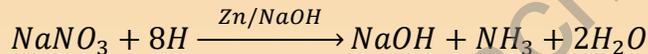
Preparations



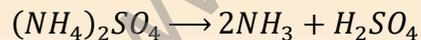
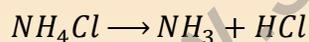
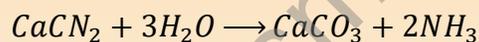
(iii) By reacting nitrides with water, ammonia is obtained



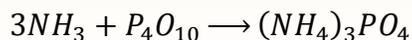
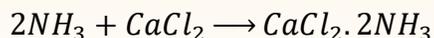
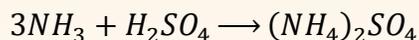
(iv) By reduction of nitrates and nitrites with Zn and caustic soda



(v) By hydrolysis of calcium cyanamide



For drying of NH₃ gas, the common dehydrating agents like sulphuric acid or CaCl₂ or P₂O₅ cannot be used as these react with ammonia and hence it is cleared by quick lime (CaO).



Manufacture of NH₃

(i) Haber's process

This is the most important industrial method discovered by *Fritz Haber*. This method involves the direct combination of nitrogen and hydrogen according to the following reaction

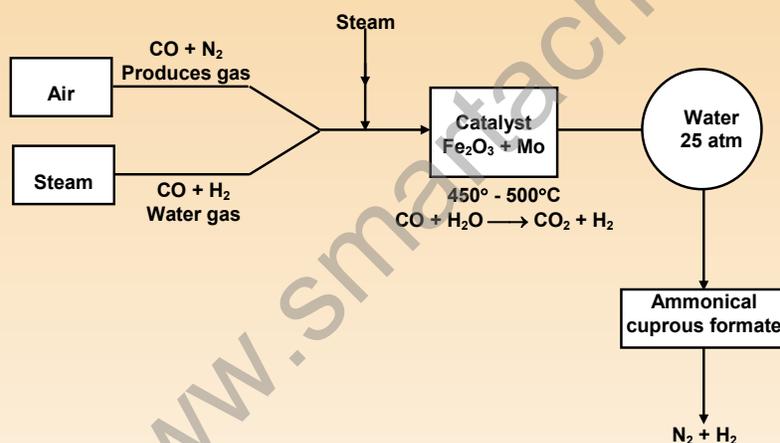


- (a) High pressure: Usually a pressure of 200 atmosphere is applied.
- (b) Low temperature: The working temperature of 450 – 550°C is maintained.
- (c) Catalyst: In order to speed up the reaction, a catalyst is used.

The following catalysts have been proposed for this purpose.

- (i) Finely divided iron with some molybdenum as a promoter.
- (ii) Finely divided nickel and soda lime deposited over pumice stone.
- (iii) Finely divided osmium or uranium.

Process : Nitrogen is obtained through liquification followed by fractional evaporation of liquid air. Hydrogen is obtained by electrolysis of water.



Uses of Ammonia

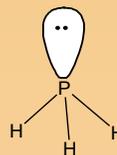
1. Liquid ammonia is used in refrigeration.
2. Aqueous NH₃ is used in qualitative as well as quantitative analysis in laboratory.
3. In manufacture of nitric acid (Ostwald's process), sodium bicarbonate (solvay process) and ammonium compounds. Ammonium sulphate, ammonium calcium phosphate.
4. Calcium ammonium nitrate, etc. are used as fertilizers. Ammonium nitrate is used in certain explosives.
5. It is used as a cleaning agent for removing grease.
6. Ammonia is also used in the manufacture of urea which is an excellent fertilizer of nitrogen.

Structure

NH_3 is a covalent molecule in which nitrogen is in sp^3 hybridisation state.

But due to presence of one lone pair it acquires pyramidal structure.

The bond angle is 107.1° not $109^\circ 28'$ due to lp – bp repulsion.

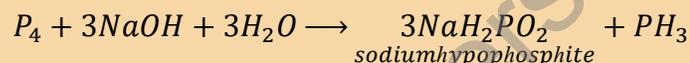


Phosphine (PH_3)

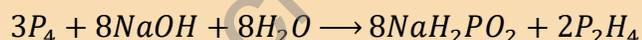
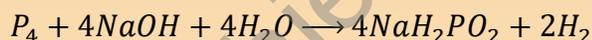
It is the hydride of phosphorous and was discovered by Gengembre in 1783.

Laboratory Preparation

It is prepared by boiling yellow phosphorous with a concentrated solution of sodium hydroxide in an inert atmosphere.

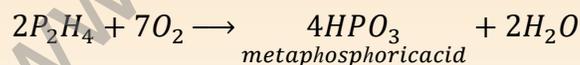


Phosphorus also forms P_2H_4 , beside PH_3 .



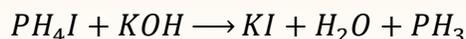
A concentrated solution of NaOH is taken in a round bottom flask. Few pieces of yellow phosphorous are dropped in to it. Coal gas, oil gas or carbon dioxide is then bubbled through the flask to displace the air from the apparatus.

The flask is then heated. PH_3 is evolved. It is driven out along with a current of inert gas. As soon as the bubbles of gas come in contact with air, they catch fire spontaneously forming rings of smoke known as vortex rings. This combustion is due to the presence of highly inflammable phosphorous dihydride (P_2H_4)



P_2H_4 can be removed from phosphine by the following methods

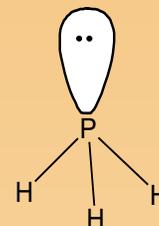
- (i) By passing the evolved gas through a freezing mixture which condenses P_2H_4 .
- (ii) By passing the gas through HI . PH_3 is absorbed forming phosphonium iodide. This on treatment with caustic potash gives pure phosphine.



Structure of phosphine

Phosphine is a covalent molecule. It has pyramidal structure like ammonia.

The bond angle H—P—H is 93° .



Uses

- For making Holme's signals.
- For making smoke screens.
- For making metallic phosphides.

2. Halides

Two types of halides are available for this group. One is MX_3 and another is MX_5 type.

MX_3 : NCl_3 , PCl_3 , $AsCl_3$, $SbCl_3$ and $BiCl_3$

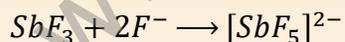
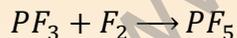
MX_5 : PCl_5 , $AsCl_5$, $SbCl_5$

(a) Tri halides

- All trihalides are covalent except BiF_3 which is ionic.
- Like hydrides these trihalides have pyramidal structure and a central atom is sp^3 hybridized.
- These trihalides can be easily hydrolysed by water except NX_3 .



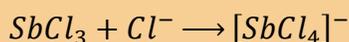
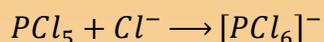
- The trihalides of P, As and Sb act as Lewis acids and combine with Lewis bases.



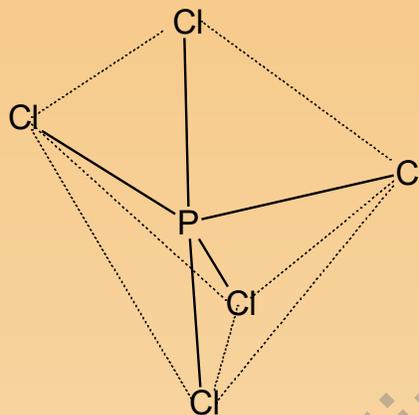
(b) Penta halides

In this central atom attains sp^3d hybridization and forms five covalent bonds with five chlorine atoms.

Penta halides have less thermal stability as compared to trihalides. All penta halides act as Lewis acids.



PCl_5 exists as molecule in gaseous state but in solid it exists as $[PCl_4]^+[PCl_6]^-$ and is ionic in nature. PBr_5 , PI_5 also exist in the ionic form in solid state.



3. Oxides

The elements of group 15 combines with oxygen directly or indirectly to form different types of oxides.

Oxidation state of central atom	N	P	As	Sb	Bi
+5	N_2O_5	P_4O_{10}	As_2O_5	Sb_2O_5	Bi_2O_5
+4	N_2O_4 , NO_2	P_4O_8	-	-	-
+3	N_2O_3	P_4O_6	As_2O_3	Sb_2O_3	Bi_2O_3
+2	NO	-	-	-	-
+1	N_2O	-	-	-	-

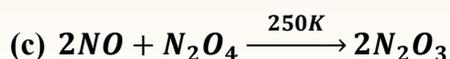
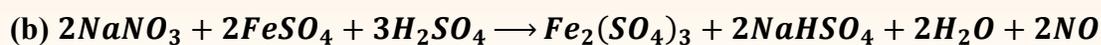
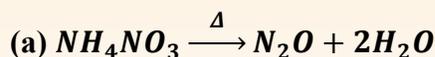
Nature of oxides

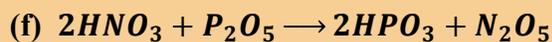
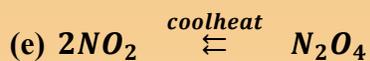
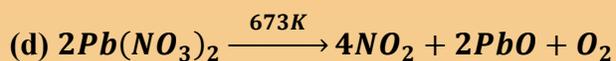
All the oxides of nitrogen and phosphorus are strongly acidic in nature (except NO and N_2O); oxides of arsenic are weakly acidic; oxides of antimony are amphoteric and oxides of bismuth are weakly basic. This can be explained on the basis of increase in size of central atom. In lower element oxides, atom has small size and it can more strongly pull the electron pair between

O-H bond in water and thus helps in release of H^+ ions.

Formation of oxides

1. Formation of oxides of nitrogen





Oxyacid's

Oxides of N, P and As when dissolves in water to form oxy acids. Oxy acids of Sb and Bi are not stable.

Some important oxy acids:

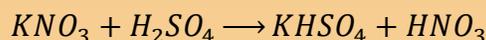
Element	Formula of the oxyacid	Name of the oxyacid	Oxidation state of element in oxyacid
Nitrogen	H ₂ N ₂ O ₂	Hyponitrous acid	+1
	HNO ₂	Nitrous acid	+3
	HNO ₃	Nitric acid	+5
Phosphorus	H ₃ PO ₂	Hypo phosphorus acid	+1
	H ₃ PO ₃	Phosphorus acid	+3
	H ₃ PO ₄	Phosphoric acid	+5
	(HPO ₄) _n	Phosphoric acid	+5
	H ₄ P ₂ O ₇	Metaphosphoric acid Pyrophosphoric acid	+5
Arsenic	H ₃ AsO ₃	Arsenious acid	+3
	H ₃ AsO ₄	Arsenic acid	+5
Sb & Bi	No stable acid		

Oxyacid's of Nitrogen HNO₃, Nitric acid

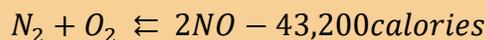
Nitric acid is also known as aqua fortis (meaning strong water) which was given by alchemists.

Methods of preparation

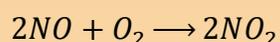
(a) Laboratory preparation



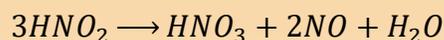
(b) Birkeland Eyde process



The formation of nitric oxide is favored by high temperature thus it is maintained at $3000^\circ C$. The nitric oxide is cooled to $1000^\circ C$ as to prevent its decomposition. Nitric oxide further combines with O_2 .

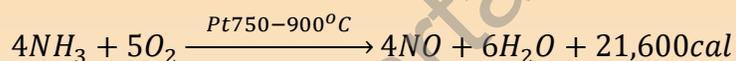


The vapours then passed through water when nitric acid is produced.

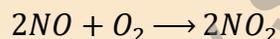


(c) Ostwald's process (Modern process)

In this process the nitric acid is formed first when NH_3 and air passed over platinum gauze at $750 - 900^\circ C$.



The nitric oxide is then oxidized to NO_2 by air which is cooled to $50^\circ C$ and absorbed in water.

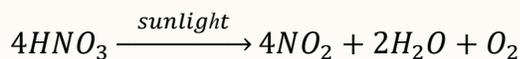


Fuming nitric acid

When NO_2 is dissolved in conc. nitric acid it forms fuming nitric acid. It is brown in colour. It is obtained by distilling concentrated HNO_3 with a little starch.

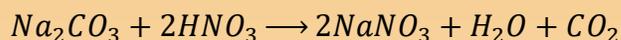
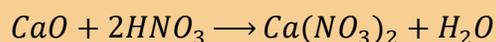
Physical properties

HNO_3 is colorless fuming with pungent smell soluble in water. Nitric acid usually acquires yellow color due to its decomposition by sunlight into NO_2 .

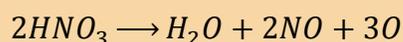
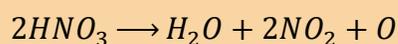


Chemical properties

(a) It is very strong acid and exhibit usual properties of acids.



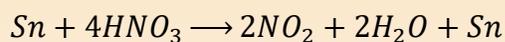
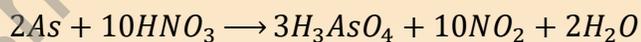
(b) Oxidising agent



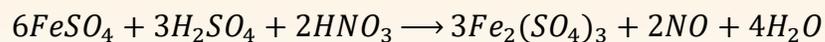
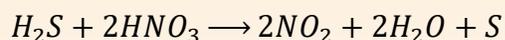
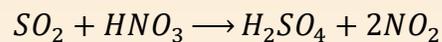
(i) Oxidation of non – metals



(ii) Oxidation of metalloids

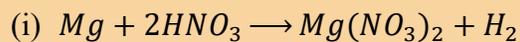
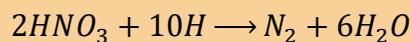
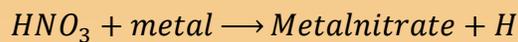


(iii) Oxidation of compounds



In this reaction NO is absorbed by ferrous sulphate and a dark brown ring of nitroso ferrous sulphate is formed. This is the *brown ring test* for nitrates.

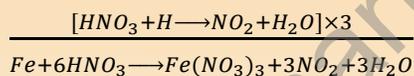
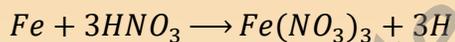
(c) Action on metals



Iron with dil. HNO_3

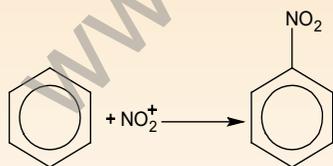
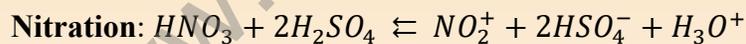


Iron with conc. HNO_3

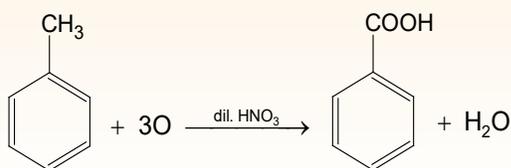


conc. Ferric nitrate

(d) Action on organic compounds



Oxidation

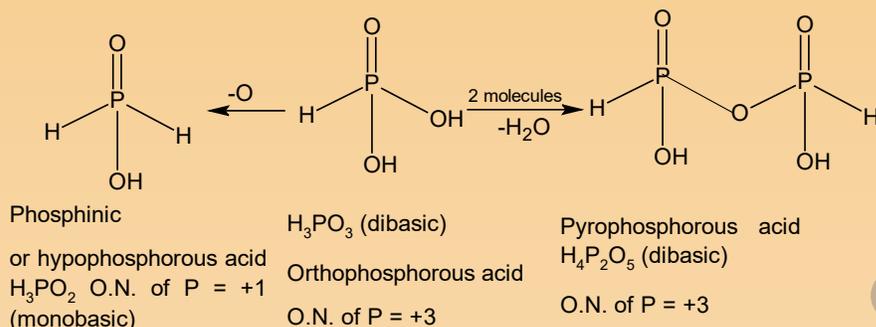


Oxyacids of phosphorus

Phosphorus forms two series of oxyacids namely; phosphorus acid and phosphoric acid.

(a) Phosphorus acid series

The series consists of p atom exhibiting oxidation state of +3. They act as reducing agents.



Special Note

- ✓ *Meta* is used for acid obtained by loss of H_2O molecule.
- ✓ *Pyro* is used for the acid obtained from two molecules with a loss of H_2O .
- ✓ *Hypo* is used for the acid having lower oxygen content than the parent acid.

GENERAL TRENDS IN PHYSICAL PROPERTIES OF GROUP-16 ELEMENTS (OXYGEN FAMILY)

Sr. No	Property	Oxygen	Sulfur	Selenium	Tellurium	Polonium
1.	Configuration	$[\text{He}]2s^22p_4$	$[\text{Ne}]3s^23p_4$	$[\text{Ar}]4s^24p^4$	$[\text{Kr}]5s^25p^4$	$[\text{Xe}]6s^26p_4$
2.	Common oxidation state	-2	-2, +4, +6	+4, +6	+4, +6	
3.	Atomic radius (pm)	66	104	116	143	167
4.	First ionization energy (KJ/mol)	1314	1000	941	869	812

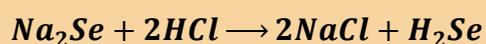
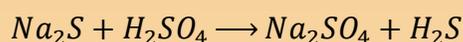
CHEMICAL PROPERTIES OF GROUP 16 ELEMENTS

The group 16 elements show a lot of variation in their chemical behaviours. Both O and S are reactive but reactivity decreases down the group and oxygen reacts with almost all the elements.

1. Hydrides

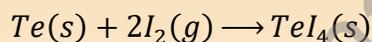
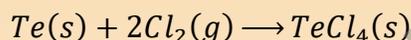
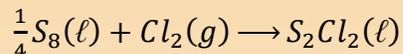
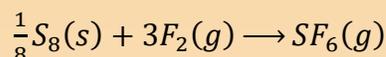
The elements of group 16 form volatile hydrides such as H_2O , H_2S , H_2Se , H_2Te and H_2Po .

H_2O can be prepared by heating H_2 in oxygen while other hydrides may be obtained by the action of acids on metal sulphides, selenoids and fluorides, e.g.



2. Halides

The elements of group 16 form many kinds of halides from which di, tetra and hexa halides are common. These halides can be obtained by direct interaction of chalcogens to halogen atoms.



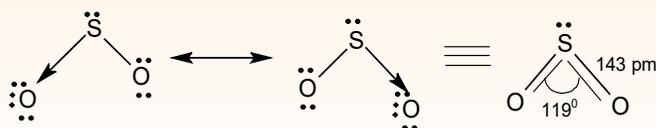
Oxygen and sulphur form a number of halides. eg. ClO_2 , OF_2 , I_2O_5 , Cl_2O_7 , S_2Cl_2 , SF_4 , SF_6 etc.

3. Oxides

This group elements form a number of oxides.

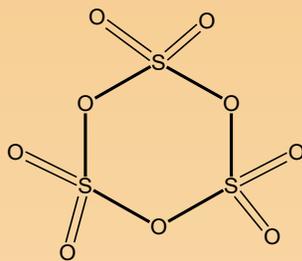
- All elements (except Se) form monoxide.
- All elements form dioxide with formula MO_2 , SO_2 is a gas, SeO_2 is a volatile solid.

While TeO_2 and PoO_2 are non-volatile crystalline solids.

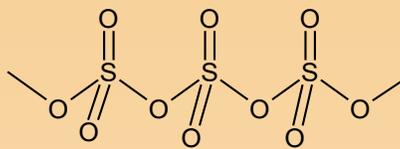


(iii) All the elements of this group form MO_3 type trioxides. The best known trioxide is SO_3 .

In solid state it can exist either as a cyclic trimer, $(SO_3)_3$ or as a linear chain cross-linked into sheets. Selenium trioxide is a cyclic tetramer whereas TeO_2 is a solid with network structure.



Cyclic trimer of SO_3 (S)



Linear chains of SO_3 (S)

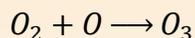
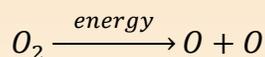
OZONE (O_3)

Ozone was first observed through a rotten smell by Van Marum in 1758 which was confirmed by Schonbein in 1840. Sorrel established its formula, O_3 , and pointed out that the ozone is an allotrope of oxygen.

Ozone prevents the living world from the harmful radiations (UV) coming from sun. Its layer lies 12 to 15 miles above earth's surface. Near earth's surface it is decomposed by dust particles.

Preparation of ozone

Ozone is prepared in laboratory by passing silent electric discharge through dry oxygen. By passing the electric current some of the oxygen molecules dissociate and then atomic oxygen combines with oxygen molecules to form ozone.



The mixture thus obtained contains 5 – 10% ozone by volume and the mixture is called as ozonised oxygen.

The apparatus used for this purpose is known as ozoniser.

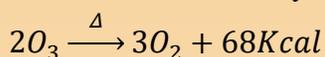
Physical properties

- i. It is having characteristic rotten smell with pale blue color.
- ii. It can be liquefied into pale blue liquid at -112.4°C . If we reach at -249.7°C , it converts into violet black crystals.
- iii. It is heavier than air.
- iv. **Solubility:** It is slightly soluble in water but more soluble in turpentine oil, glacial acetic acid or carbon tetrachloride.
- v. It causes headache and nausea when inhaled in small amount.

Chemical properties

(a) Decomposition

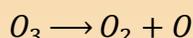
It is unstable and easily decomposes into oxygen at 300°C .



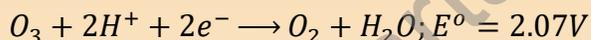
MnO_2 , platinum black, silver, lead dioxide, etc., decompose ozone at ordinary temperature, i.e. they catalyze its decomposition.

(b) Oxidising nature

It acts as a strong oxidising agent due to the ease with which it can liberate nascent oxygen. The potential equation is

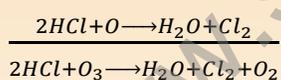
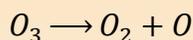


The oxidation potential in acidic medium is $+2.07\text{ V}$.

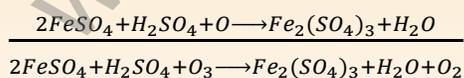
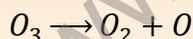


Examples

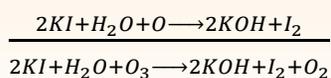
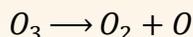
- (i) It oxidises HCl into Cl_2 , HBr into Br_2 and HI into iodine.



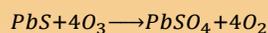
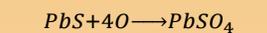
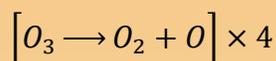
- (ii) Acidified ferrous sulphate into ferric sulphate



- (iii) It liberates iodine from neutral KI solution.

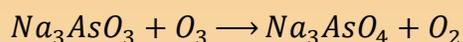
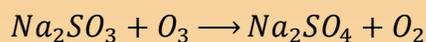
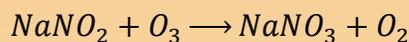


(iv) Lead sulphide (black) is oxidised to lead sulphate (colorless).

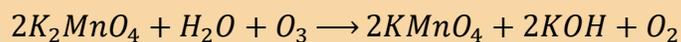


Similarly, CuS, ZnS and CdS are oxidised to corresponding sulphates.

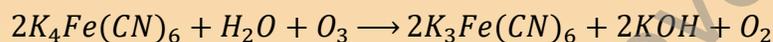
(v) It oxidise nitrites into nitrates, sulphite into sulphates, arsenates to arsenates, manganate to permanganate and ferrocyanide to ferricyanide.



sodium sodium
arsenate arsenate.

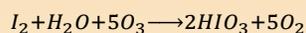
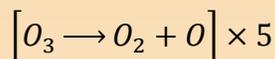


Potassium potassium
manganate permanganate



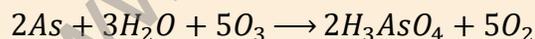
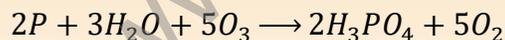
Potassium Potassium
Ferrocyanide ferricyanide

(vi) Moist iodine is oxidised to iodic acid

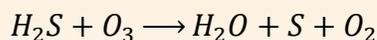


Iodic acid

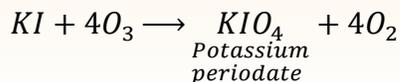
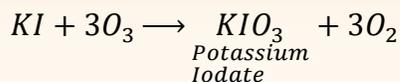
Similarly moist Sulphur, phosphorus and arsenic are oxidised to their corresponding oxyacid's.



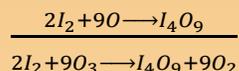
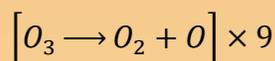
(vii) H_2S is oxidised to sulphur



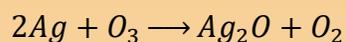
(viii) Alkaline KI is oxidised to potassium iodate and periodate.



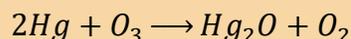
(ix) Dry iodine is oxidised to yellow powder, I_4O_9 .



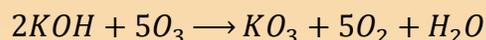
(x) Silver metal is blackened due to alternate oxidation of the metal and reduction of oxide.



(xi) Mercury in the presence of ozone is oxidised to suboxide which dissolves in mercury. It starts sticking to glass and loses mobility. Hence, mercury loses its meniscus in contact with ozone. This is known as tailing of mercury.

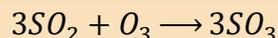


(xii) Ozone reacts with KOH and forms potassium ozonide, KO_3 , which is an orange colored solid and contains paramagnetic O_3^- ion.

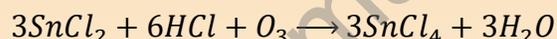


In all above reactions, oxygen is evolved. There are few reactions in which whole of the oxygen are used up in the process of oxidation.

1. Oxidises SO_2 to SO_3

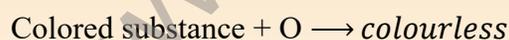


2. Acidified stannous chloride is oxidised to stannic chloride.



(c) **Bleaching property**

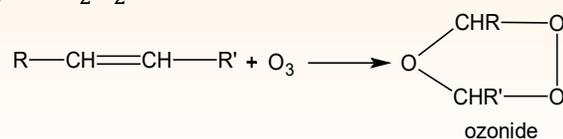
It acts as a good bleaching agent due to release of nascent oxygen.

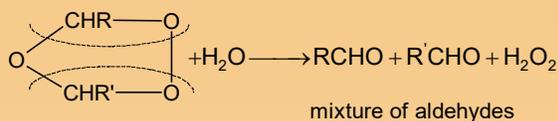


It bleaches oil, ivory, flour, starch, waxes wood pulp etc.

(d) **Formation of ozonide**

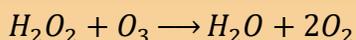
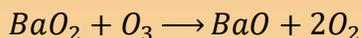
Ozone forms ozonide when reacts with unsaturated organic compounds containing double bond. The ozonide break to form carbonyl compounds when heated with water. This process is called ozonolysis. H_2O_2 is evolved in most of the cases.





(e) Reaction with peroxide

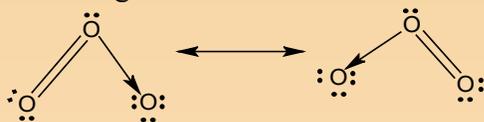
Reaction of ozone with peroxide results in their mutual reduction with the liberation of oxygen.



Structure of ozone



The bond length is intermediate between that for a single bond (1.48 \AA in H_2O_2) and for a double bond (1.21 \AA in O_2). Ozone is, therefore, considered to be a resonance hybrid of the following two forms.



Tests of ozone

- ✓ It has a strong rotten smell.
- ✓ Metallic mercury loses its fluidity in contact with O_3 .
- ✓ It turns an alcoholic solution of benzidine brown.
- ✓ It turns an alcoholic solution of tetramethyl base violet.
- ✓ It turns starch – iodide paper blue.

4. oxyacid's

The important oxyacid's of S, Se and T are given in the table.

Sulphur	Selenium	Tellurium
Sulphureous acid H_2SO_3 .	Selenious acid H_2SeO_3	Tellurous acid
Sulphureous acid H_2SO_4	Selenic acid H_2SeO_4	H_2TeO_3 .
Peroxomonosulphuric acid H_2SO_5 (Caro's acid)		Telluric acid H_2TeO_4 .
Peroxodisulphuric acid $\text{H}_2\text{S}_2\text{O}_8$ (Marshall's acid)		
Thio sulphuric acid $\text{H}_2\text{S}_2\text{O}_3$		
Dithionic acid $\text{H}_2\text{S}_2\text{O}_6$		
Persulphuric acid $\text{H}_2\text{S}_2\text{O}_7$		

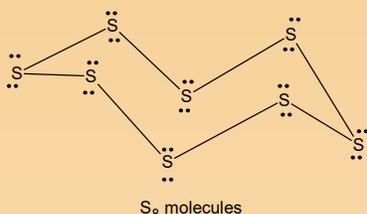
But the oxyacid's of Sulphur are more important.

Allotropes of Sulphur

Main three types of allotropes of Sulphur are discussed here:

(a) Rhombic Sulphur

It is most stable and common form of Sulphur also called as α -Sulphur. It has bright yellow color. It is insoluble in water and carbon desulphated. Its density is 2.07 gm cm^{-3} and exists as S_8 molecules. The 8 Sulphur atoms in S_8 molecule forms a puckered ring as shown below. It is solid in nature.



(b) Monoclinic Sulphur

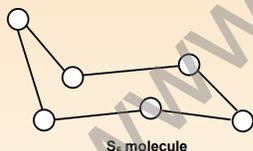
It is another form of Sulphur which is stable only above 369 K. It is dull yellow colored solid, also called β -Sulphur. It is soluble in CS_2 but insoluble in H_2O .

It slowly changes into rhombic Sulphur. It also exists as S_8 molecules which have puckered ring structure. It however, differs from the rhombic Sulphur in the symmetry of the crystals.

(c) Plastic Sulphur

It is obtained by pouring molten Sulphur to cold water. It is amorphous form of Sulphur also called as γ -Sulphur. It is insoluble in water as well as CS_2 .

Several other modifications of Sulphur containing 6- 20 Sulphur atoms per ring have been artificially synthesized. In cyclol S_6 , the ring adopts the chain form dimensions.



Sulphuric acid (H_2SO_4)

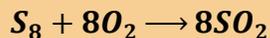
It is the most important oxyacid of Sulphur. It is also called as 'oil of vitriol' because of its large application in industries it is also known as 'king of chemicals'.

Manufacture of sulphuric acid

Sulphuric acid (H_2SO_4) is manufactured by **contact process** which involves following three steps.

(a) Production of Sulphur dioxide

It is carried out by burning Sulphur powder or roasting of Sulphur rich ores.



(b) Oxidation of SO₂ to SO₃



This step is the key step of the whole process so with applying Le – Chatelier's principle we can enhance the forward reaction rate to achieve better yield of SO₃.

(i) Temperature

As the reaction is already exothermic so temperature must be kept low. An optimum temperature is maintained between 673 – 723K.

(ii) Pressure

The catalyst is required due to low temperature, so *platinised asbestos* or *divanadium pentoxide* (V₂O₅) is used.

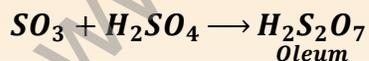
(iv) Purity of gases

To prevent the poisoning of catalyst, the gases must be free from the impurities of As₂O₃, dust particles and moisture.

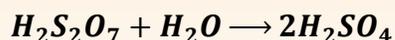
(v) Excess of oxygen

To have a better yield of SO₃, O₂ is used in excess.

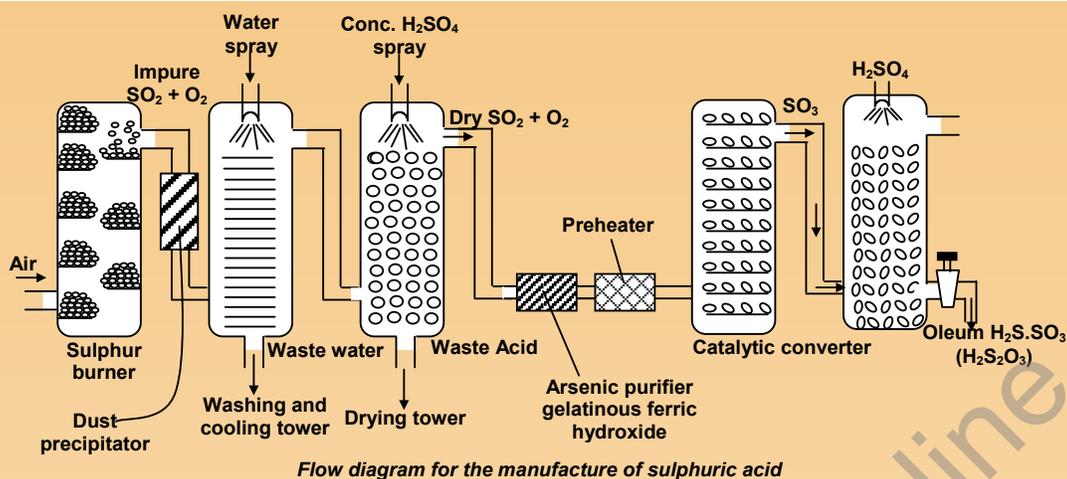
(c) Conversion of SO₃ in H₂SO₄



Oleum is then diluted with calculated amount of water



The sulphuric acid obtained through contact process is generally of 96 – 98% purity.



Physical Properties of H₂SO₄

- (i) Pure H₂SO₄ is colorless but commercial acid is yellow in color due to presence of some impurities.
- (ii) Highly concentrated H₂SO₄ (98%) has a specific gravity of 1.84 and high b.p indicates about the hydrogen bonding as shown below:

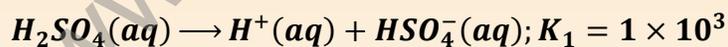
Hydrogen bonds
- (iii) Conc. H₂SO₄ has a great affinity for water. Its dissolution is highly exothermic in water.
- (iv) It can burn the skin while comes in contact with it.

Chemical properties of H₂SO₄

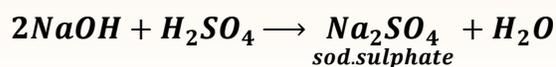
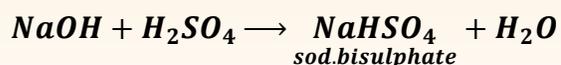
(i) Dissociation

On heating strongly it dissociates into SO₃ and H₂O. $H_2SO_4 \rightleftharpoons H_2O + SO_3$

(ii) Acidic nature



Thus, it forms two series of salts, sulphates and persulphates. e.g.



(iii) As a dehydrating agent

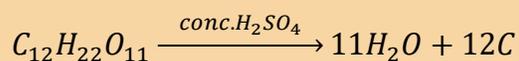
Due to strong affinity for water, H_2SO_4 acts as a powerful dehydrating agent.

(a) Drying of gases

Certain gases like CO_2 , SO_2 , Cl_2 , HCl etc, can be dried by passing through conc. H_2SO_4 .

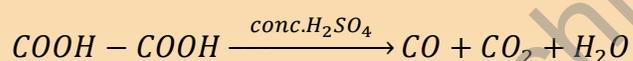
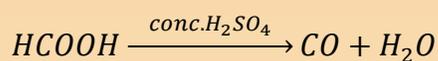
(b) Charring

Concentrated H_2SO_4 reacts with sugar, wood, paper etc to form black mass of carbon. This phenomenon is called *charring*.



(c) Dehydration of acids

Acids like formic and oxalic acid get dehydrated according to the equation,



Uses of sulphuric acid

- As an acid in laboratory and industries.
- In storage batteries and lead accumulators.
- As a dehydrating agent.
- In fertilizers.
- In drying of gases.
- In preparing other acids like HCl , HF etc.
- Detergent industries.
- Manufacture of pigments paints and dyestuff.
- Metallurgical applications.

CHEMICAL PROPERTIES OF GROUP -17 ELEMENTS (HALOGEN FAMILY)

Among all the halogens fluorine is the most reactive and reactivity decreases down the group. The high reactivity of fluorine is due to high electronegativity and low bond dissociation energy among the group.

1. Oxidizing power

The halogens are strong oxidizing agents. This is due to their high electron affinities. The oxidizing power of the halogens decreases on going down the group from fluorine to astatine.



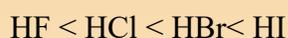
2. Hydrides

Halogens combine with hydrogen to form volatile hydrides of the formula HX. Due to hydrogen bonding in HF it is liquid but all other like HCl, HBr and HI are gases.



Hydrogen bonding in HF

The bonding is covalent in nature in all the halides. All hydrogen halides act as acid in their aqueous solution.



Order in acidity

H – F bond is strongest, while HI is weakest so can easily liberate the H⁺ ion hence more acidic than HF.

Reducing property of hydrogen halide also increases down the group due to decrease in H – X bond strength.

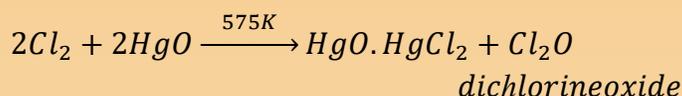
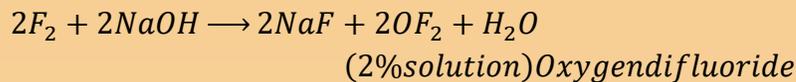
3. Halides

The halogens are very reactive and form compounds with most of the metals and non-metals except He, Ne and Ar. These halides may be simple or complex.

- (i) With the alkali & alkaline metals like Na, Mg, K etc. halogens form ionic halides due to low IP of metals. Their ionic character decreases as the size of halogen atom increases.
- (ii) With metals having high IP like Sn, Pb, Sb halogen forms covalent halides. Halides in higher oxidation state is more covalent ($SnCl_4, PbCl_4, SbCl_5$) than the halides in lower oxidation state ($SnCl_2, PbCl_2, SbCl_3$)
- (iii) With non – metals like P, As, S, the halogens form covalent halides as $PF_5, AlCl_3, AsCl_3, S_2Cl_2$ etc.

4. Oxides

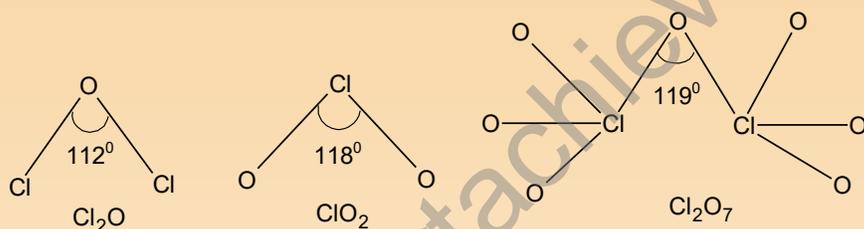
Due to high electron affinity of both halogens and oxygen they do not combine directly with oxygen but their oxides with oxygen can be prepared indirectly.



The compounds of oxygen with fluorine are called as fluorides because fluorine is more electro negative than oxygen. Most of these compounds are endothermic and unstable and are likely to explode resulting in the formation of more stable products.

All the oxides are powerful oxidizing agents and decompose explosively when they are given mechanical shock or heat.

The structures of some molecules is as follows

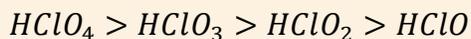


5. oxyacid's

Halogens form oxyacid's in which fluorine forms only hydrolatrous acid (HOF). Cl_2 , Br_2 and I_2 form four series of acids with formulae HOX, HXO_2 , HXO_3 and HXO_4 .

Strength of these acids increases as the oxidation state of halogen atoms increases. And also their conjugate base becomes more stabilized due to resonance.

Acidic strength

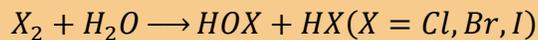


Parhelic acid > Halic acid > Halaus acid > Hypohalous acid

In particular acid the acidity decreases as the size of the halogen atom increases.

$HOCl > HOBr > HOI$

$HOCl$, $HOBr$ and HOI are weak acids, formed due to disproportionations of the halogen water.



Salts of these acids known as hypohalites

e.g., $CaOCl_2$ (bleaching powder)

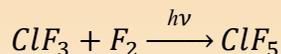
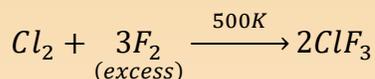
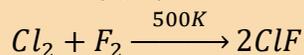
The halic acids $HClO_3$ and $HBrO_3$ are also known in solutions, but iodic acid HIO_3 exists as white solid. Thus we can say that the stability of these acids increase as increasing the size of halogen acid. The salts of these acids are called halite's. e.g. $NaClO_3$ is a powerful weed killer and $KClO_3$ is used in fire works.

Parhelic acids forms phthalates as their salts.

Inter halogen compounds

When halogens combine with themselves form interhalogen compounds. These are divided into four types. i.e.

- i. $AX(ClF, BrF, BrCl, ICl, IBr)$
- ii. $AX_3(ClF_3, BrF_3, ICl_3)$
- iii. $AX_5(BrF_5, IF_5)$
- iv. $AX_7(IF_7)$



Characteristics of interhalogen compounds

- i. They are covalent compounds
- ii. They are more reactive than their parent halogens. It is because A – X bond is relatively weaker than X – X bond.
- iii. They are very good oxidizing property having compounds.
- iv. Their m.p and b. p. increase as the electronegativity difference between them increases.
- v. Chloroform hydrocarbons are known as Freon and are used as refrigerators.
- vi. For example, Freon – 11 is CCl_3F , Freon- 12 is CCl_2F_2 , Freon-13 is $CClF_3$ etc.

THE NOBLE GASES

Group 18 of the periodic table includes the inert gases helium (He), Neon (Ne), argon (Ar), krypton (Kr) and Xenon (Xe).

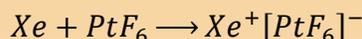
All are present in gaseous form and exists in atomic form.

CHEMICAL PROPERTIES OF GROUP-18 ELEMENTS

The noble gases are inert in nature. They do not participate in the reactions easily. The inertness is due to

- having stable electronic configuration i.e. complete octet.
- having high ionization energies.
- having very low electron affinity.

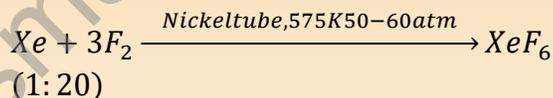
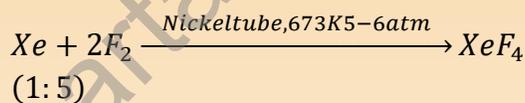
In 1962, N. Bartlett observed that O_2 when reacts with PtF_6 to form the compound $[O_2^+][PtF_6]^-$. In this compound O_2 is oxidised to O_2^+ by PtF_6 . Then tried Xe rather using O_2 by direct interaction and synthesized the first compound of noble gases $Xe^+[PtF_6]^-$ in the form of red crystalline solid.



Compounds of Xenon: Fluorides, oxides & oxyfluorides

Three basic fluorides are known for xenon i.e. XeF_2 , XeF_4 and XeF_6 .

When Xe is heated in nickel tube directly with fluorine under appropriate experimental conditions.



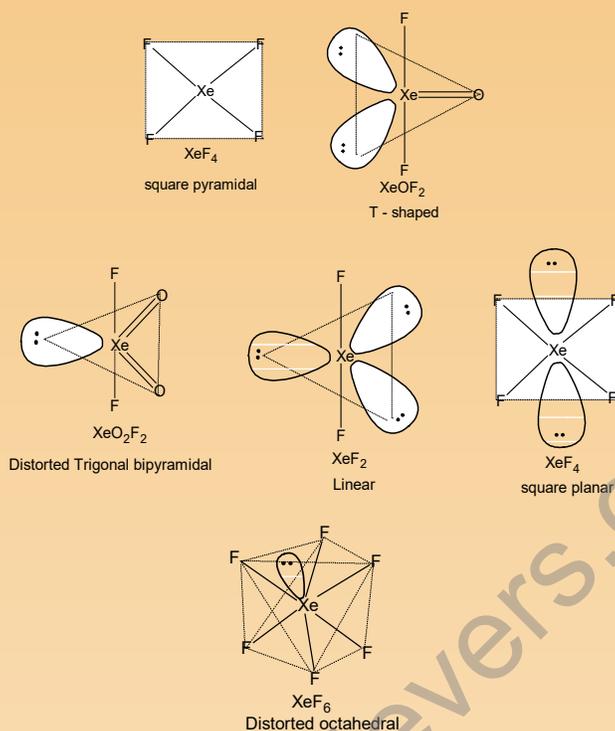
Structure of Xenon compounds

The structure of xenon compounds are explained on the basis of VSEPR theory as well as the concept of hybridization.

Molecule	Total electron pairs (BP + LP)	Hybridization	Shape
XeF_2	5	Sp^3d	Linear
XeF_4	6	Sp^3d^2	Square planar
XeF_6	7	sp^3d^3	Distorted octahedral

The structures of oxyfluorides and oxides of xenon can be best explained by the concept of hybridization.

The structures of compounds are shown below



Uses of Nobles gas

The noble gases are used in following ways:

(A) Helium

- It is used to fill airships and observation balloons.
- In the oxygen mixture of deep sea divers.
- In treatment of asthma.
- used in inflating aero plane tires.
- Used to provide inert atmosphere in melting and welding of easily oxidizable metals.

(B) Neon

- It is used for filling discharge tubes, which have different characteristic colors and are used in advertising purposes.
- Also used in beacon lights for safety of air navigators as the light possesses fog and stream penetrating power.

(C) Argon

Along with nitrogen it is used in gas – filled electric lamps because argon is more inert than nitrogen.

Group 16 Elements

- Electronic configuration : ns^2np^4
- Atomic and ionic radii : Increase down the group
- IE : Decreases down the group
- Electron Gain enthalpy : O has less -ve than S.
- Electro-negativity : Decreases with increase in atomic number
- Physical properties : O and S are non metals, Se and Te metalloids whereas Po is a metal. All exhibit allotropy
- M.P. and B.P. : Increases down the group
- Chemical properties : variable
 - Reactivity with hydrogen : stable hydrides
 - Reactivity with halogens : $F > Cl > Br > I$
- Oxoacids of S :
 - $\text{HO}-\text{O}-\text{SO}_2-\text{OH}$ (H₂SO₄)
 - $\text{HO}-\text{O}-\text{SO}-\text{OH}$ (H₂SO₃)
- Dioxygen (O₂) :
 - Preparation : $2\text{KClO}_3 \xrightarrow{\Delta} 2\text{KCl} + 3\text{O}_2$
 - Properties : Colourless and odourless gas
 - $2\text{Ca} + \text{O}_2 \rightarrow 2\text{CaO}$; $4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$
 - $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_5} 2\text{SO}_3$; $4\text{HCl} + \text{O}_2 \xrightarrow{\text{CuCl}} 2\text{Cl}_2 + 2\text{H}_2\text{O}$

Group 18 Elements

- Electronic configuration : ns^2np^6
- Atomic and ionic radii : Increase down the group
- Electron gain enthalpy : Largely positive
- Physical properties : Monoatomic, colourless, odorless and tasteless. Sparingly soluble in water.
- M.P. and B.P. : Low
- Chemical properties : Least reactive ; Xenon fluoride compounds : $\text{XeF}_2, \text{XeF}_4, \text{XeF}_6$ and XeF_8 .
- Xenon oxygen compounds : $\text{XeO}_3, \text{XeOF}_2, \text{XeOF}_4$

Group 17 Elements

- Occurrence : All except radon occur in atmosphere
- Electronic configuration : $ns^2 np^5$ except He
- IE : High
- Atomic radii : Increases down group
- Electron gain enthalpy : Largely positive
- Physical properties : Monoatomic, colourless, odorless and tasteless. Sparingly soluble in water.
- M.P. and B.P. : Low
- Chemical properties : Least reactive ; Xenon fluoride compounds : $\text{XeF}_2, \text{XeF}_4$ and XeF_6 .
- Xenon oxygen compounds : $\text{XeO}_3, \text{XeOF}_2, \text{XeOF}_4$

Group 15 Elements

- Electronic configuration : ns^2np^3
- Atomic and ionic radii : Increase down the group.
- Electron gain enthalpy : Increases in a zig-zag pattern due to gradual increase in atomic size.
- Electro-negativity : Decreases down the group with increasing atomic size.
- Physical properties : Polyoatomic, metallic character increases down the group. N and P are non-metals, As and Sb metalloids and Bi metal. B.P. increases top to bottom and M.P. increases upto As and then decreases upto Bi. Except Nl all show allotropy.
- Chemical properties : Common O.N. : -3, +3 and +5. Nitrogen shows anomalous behaviour.
- Dinitrogen preparation :
 - In laboratory :** $\text{NH}_4\text{Cl} + \text{NaNO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} + \text{NaCl}$
 - Thermal decomposition :** $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{Heat}} \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$
 - $\text{Ba}(\text{N}_3)_2 \rightarrow \text{Ba} + 3\text{N}_2$
- Oxides of nitrogen : Colourless, odourless, tasteless and non-toxic gas

Group 15 Elements

- Ammonia preparation :
 - $\text{NH}_4\text{CO NH}_2 + 2\text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{CO}_3$
 - $2\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{NH}_4\text{CO NH}_2$ $\Delta H^\circ = -46.1 \text{ kJ mol}^{-1}$
 - Properties : Colourless with pungent odour, soluble in water
 - $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
 - $\text{ZnSO}_4 + 2\text{NH}_4\text{OH} \rightarrow \text{Zn}(\text{OH})_2 + (\text{NH}_4)_2\text{SO}_4$ (white ppt)
 - $\text{FeCl}_3 + \text{NH}_4\text{OH} \rightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O} + \text{NH}_4\text{Cl}$ (Brown ppt)
- Oxides of nitrogen :
 - $\text{N}-\text{N}-\text{O}$ $\text{N}-\text{O}$ $\text{N}-\text{O}$
 - 113pm 119pm 115pm
 - 105° 130° 135° 175pm 119°
 - 186pm 117pm 121pm

Group 17 Elements

- Occurrence : All except radon occur in atmosphere
- Electronic configuration : $ns^2 np^5$ except He
- IE : High
- Atomic radii : Increases down group
- Electron gain enthalpy : Largely positive
- Physical properties : Monoatomic, colourless, odorless and tasteless. Sparingly soluble in water.
- M.P. and B.P. : Low
- Chemical properties : Least reactive ; Xenon fluoride compounds : $\text{XeF}_2, \text{XeF}_4$ and XeF_6 .
- Xenon oxygen compounds : $\text{XeO}_3, \text{XeOF}_2, \text{XeOF}_4$

Group 16 Elements

- Occurrence : All except radon occur in atmosphere
- Electronic configuration : $ns^2 np^6$ except He
- IE : High
- Atomic radii : Increases down group
- Electron gain enthalpy : Largely positive
- Physical properties : Monoatomic, colourless, odorless and tasteless. Sparingly soluble in water.
- M.P. and B.P. : Low
- Chemical properties : Least reactive ; Xenon fluoride compounds : $\text{XeF}_2, \text{XeF}_4$ and XeF_6 .
- Xenon oxygen compounds : $\text{XeO}_3, \text{XeOF}_2, \text{XeOF}_4$

Group 17 Elements

- Occurrence : All except radon occur in atmosphere
- Electronic configuration : $ns^2 np^5$ except He
- IE : High
- Atomic radii : Increases down group
- Electron gain enthalpy : Largely positive
- Physical properties : Monoatomic, colourless, odorless and tasteless. Sparingly soluble in water.
- M.P. and B.P. : Low
- Chemical properties : Least reactive ; Xenon fluoride compounds : $\text{XeF}_2, \text{XeF}_4$ and XeF_6 .
- Xenon oxygen compounds : $\text{XeO}_3, \text{XeOF}_2, \text{XeOF}_4$

Group 17 Elements

- Occurrence : All except radon occur in atmosphere
- Electronic configuration : $ns^2 np^5$ except He
- IE : High
- Atomic radii : Increases down group
- Electron gain enthalpy : Largely positive
- Physical properties : Monoatomic, colourless, odorless and tasteless. Sparingly soluble in water.
- M.P. and B.P. : Low
- Chemical properties : Least reactive ; Xenon fluoride compounds : $\text{XeF}_2, \text{XeF}_4$ and XeF_6 .
- Xenon oxygen compounds : $\text{XeO}_3, \text{XeOF}_2, \text{XeOF}_4$

Inter-halogen compounds : $\text{XX}' - \text{sp}^3$ (linear), $\text{XX}'_2 \text{sp}^2$ (T-shaped), $\text{XX}'_3 \text{sp}^3$ (see-saw), $\text{XX}'_4 \text{sp}^3$ (square planar), $\text{XX}'_5 \text{sp}^3$ (square pyramidal), $\text{XX}'_6 \text{sp}^3$ (octahedral)

PRACTICE QUESTIONS

- Nitrogen does not have d- orbitals in its valence shell, which restricts its ability to
 - exhibit orbital hybridization
 - exhibit the oxidation state of + 5
 - forms oxides with oxidation state greater than +3
 - have covalency greater than three
- When HNO_3 is heated with P_4O_{10} , the resulting oxide of nitrogen is:
 - NO_2
 - N_2O_5
 - N_2O_4
 - N_2O_3
- Red phosphorus exhibits lower reactivity, volatility, and solubility in non-polar solvents compared to white/yellow phosphorus because:
 - it has high molecular energy
 - it has low molecular energy
 - it forms condensation products
 - it possesses highly polymerized structure
- The compound that cannot act as both an oxidizing and reducing agent is:
 - H_2SO_3
 - H_3PO_4
 - HNO_2
 - H_2O_2
- All the hydrides of group 16 elements except one possess reducing properties. The hydride that does not possess reducing properties is:
 - H_2Se
 - H_2O
 - H_2S
 - H_2Te
- The Low volatility of water compared to hydrogen sulfide (H_2S) can be explained by
 - H_2O has a bond angle of nearly 150°
 - hydrogen is loosely bonded with the Sulphur
 - S-atom is less electronegative than O-atom
 - S-atom is more electronegative than O-atom
- What is the hybridization and structure of tetrafluorides of group-16 elements? \ol type="a">- sp^3 and trigonal pyramidal
- sp^3d^3 and tetrahedral
- sp^3d^3 and trigonal bipyramidal
- sp^3d^3 and tetrahedral

40. Nessler's reagent is used for the detection of
- (A) NH_4^+ ions (B) NO_3^- ions
(C) NO_2^- ions (D) CN^- ions
41. Which of the following is the dioxygenyl ion?
- (A) O_2 (B) O_2^+
(C) O_2^- (D) O_2^{2-}
42. Ozone with KI solution produces
- (A) Cl_2 (B) I_2
(C) HI (D) IO_3
43. Which of the following acid possesses oxidising, reducing and complex forming properties?
- (A) H_2SO_4 (B) HNO_3
(C) HCl (D) HNO_2
44. Which of the following hydrogen halides is most volatile?
- (A) HF (B) HCl
(C) HBr (D) HI
45. The acid which forms two series of salts is
- (A) H_3PO_4 (B) H_3PO_3
(C) H_3BO_3 (D) H_3PO_2
46. I_2 reacts with conc. HNO_3 to form an oxo acid
- (A) HIO (B) HIO_3
(C) HIO_4 (D) HIO_2
47. White phosphorus does not have
- (A) six P – P single bonds (B) four P – P single bonds
(C) four lone pairs of electrons (D) P-P-P angle of 60°

48. Which of the following compound is least basic?
- (A) NH_3 (B) PH_3
(C) AsH_3 (D) SbH_3
49. Which of the following has maximum solubility in water?
- (A) NH_3 (B) PH_3
(C) AsH_3 (D) SbH_3
50. The number of P – O – P bonds in cyclic meta phosphoric acid is
- (A) Zero (B) Two
(C) Three (D) Four
51. Which of the following is a cyclic oxo acid?
- (A) $\text{H}_4\text{P}_2\text{O}_7$ (B) $\text{H}_4\text{P}_2\text{O}_6$
(C) $\text{H}_3\text{P}_3\text{O}_9$ (D) $\text{H}_5\text{P}_5\text{O}_{15}$
52. Which of the following on reaction with H_2S does not produce metallic sulphide
- (A) HgCl_2 (B) ZnCl_2
(C) COCl_2 (D) CuCl_2
53. Which of the following does not have S – S bond?
- (A) $\text{S}_2\text{O}_4^{2-}$ (B) SO_3
(C) $\text{S}_2\text{O}_5^{2-}$ (D) $\text{S}_2\text{O}_7^{2-}$
54. Which acid forms two series of salts?
- (A) H_3PO_4 (B) H_3PO_3
(C) H_3BO_3 (D) H_3PO_2
55. Oxygen is more electronegative than sulphur, yet H_2S is slightly acidic. This is because
- (A) Water is highly associated compound
(B) Molecular mass of H_2S > than that of H_2O
(C) H_2S is gas under ordinary conditions while H_2O is liquid
(D) H – S bond is weaker than H – O bond

56. Which colourless gas is evolved by reaction of formic acid and conc. H_2SO_4

- (A) H_2S (B) CO
(C) SO_2 (D) CO_2

57. Which of the following halide is most acidic?

- (A) PCl_3 (B) SbCl_3
(C) BCl_3 (D) CCl_4

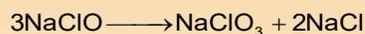
58. KF combines with HF to form KHF_2 . The compound contains the species

- (A) $\text{K}^+, \text{F}^-, \text{H}^+$ (B) $\text{K}^+, \text{F}^-, \text{HF}^-$
(C) K^+ and $(\text{HF}_2)^-$ ions (D) K^+, H^+

59. Which of the following species is not a pseudohalide?

- (A) CNO^- (B) RCOO^-
(C) OCN^- (D) SCN^-

60. What is the correct about the reaction?



- (A) It represents disproportionation
(B) The reaction is used for manufacture of halates
(C) The reaction does not occur
(D) The process involves simply increase in O.N. of chlorine

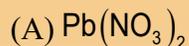
61. When I_2 is passed through KCl , HF , KBr

- (A) Cl_2 and Br_2 are evolved (B) Cl_2 is evolved
(C) Cl_2 , Br_2 F_2 are evolved (D) none of these

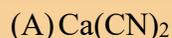
62. The hybridization in atomic orbitals of nitrogen in NO_2^+ , NO_3^- and NH_4^+ are

- (A) sp , sp^3 and sp^2 respectively (B) sp , sp^2 and sp^3 respectively
(C) sp^2 , sp and sp^3 respectively (D) sp^2 , sp^3 and sp respectively

66. Nitrogen dioxide is released by heating



67. The formula of calcium cyanamide is



68. Which of the following molecular species has unpaired electron (s)?



69. Water is oxidized to oxygen by



70. In nitroprusside ion, the iron and NO exist as Fe^{II} and NO^+ rather than Fe^{III} and NO. These forms can be differentiated by

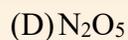
(A) Estimating the concentration of iron

(B) Measuring the concentration of CN^-

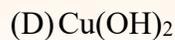
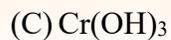
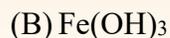
(C) Measuring the solid state magnetic moment

(D) Thermally decomposing the compound

71. Which oxide does not act as a reducing agent?



72. Substance soluble in NH_3 is

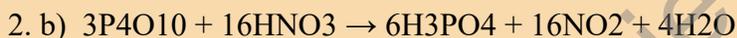


73. The soldiers of Napoleon's army while at the Alps during freezing winter suffered a serious problem as regards the tin buttons of their uniforms. White metallic tin buttons got converted into grey powder. This transformation is related to

- (A) an interaction with nitrogen of the air at very low temperatures
- (B) a change in the crystalline structure of tin
- (C) a change in the partial pressure of oxygen in the air
- (D) an interaction with water vapour contained in the humid air

HINTS AND SOLUTIONS

1. b) In summary, due to the lack of d-orbitals in its valence shell, nitrogen cannot exhibit d-orbital hybridization, show an oxidation state greater than +3, form more than three covalent bonds, or produce higher oxides with oxidation states beyond +4.



3. d) Red phosphorus has a highly polymerized structure and forms condensation products, which make it less reactive and less prone to vaporization or dissolution in non-polar solvents.

4. b) It is neither a strong oxidizing agent nor a strong reducing agent.

5. b) H₂O (water) - Water does not exhibit reducing properties due to its stable molecular structure and high electronegativity of oxygen

6. c) Water has stronger intermolecular hydrogen bonding and is polar, while hydrogen sulfide has weaker intermolecular forces and is nonpolar. These differences result in water having higher boiling points and lower volatility than hydrogen sulfide.

7. c) Tetrafluorides of group-16 elements, like sulfur (SF₄), selenium (SeF₄), and tellurium (TeF₄), exhibit sp³ hybridization and a trigonal bipyramidal molecular structure. In sp³ hybridization, the central atom forms four hybrid orbitals, with one holding a lone pair.

This arrangement allows for strong covalent bonding between the central atom and fluorine atoms in the tetrafluorides.

8. d) The most electronegative elements of the third period refer to the elements found in the third row of the periodic table. In this period, the most electronegative elements are chlorine (Cl) and sulfur (S). Electronegativity is a measure of an atom's ability to attract electrons towards itself in a chemical bond. Chlorine and sulfur have high electronegativities, indicating their strong ability to attract electrons. This property makes them highly reactive and capable of forming various chemical compounds with other elements.

9. c) The correct order of increasing electron affinity for the given elements is (c) $\text{Be} < \text{C} < \text{N} < \text{O} < \text{F}$. Electron affinity increases from beryllium to fluorine due to factors such as atomic size, electronegativity, and effective nuclear charge. Beryllium has the lowest electron affinity, while fluorine has the highest electron affinity among the listed elements.

10. c) Phosphorus can show oxidation states ranging from -3 to +5. In its -3 state, it gains three electrons, forming compounds like phosphides. In its +3 state, it loses three electrons, resulting in compounds like phosphine or phosphorus trichloride. Phosphorus can also exhibit a +5 state by losing all its valence electrons, forming compounds such as phosphorus pentoxide or phosphoric acid. The range of oxidation states in phosphorus allows for the formation of diverse compounds with varying properties and reactivities.

11. d) NO_2 is a colored gas because it absorbs certain wavelengths of visible light, resulting in the perception of color. The absorption of light is due to the electronic transitions that occur within the molecule when it interacts with photons. Specifically, NO_2 absorbs in the blue region of the spectrum, giving it a brownish color. This is why NO_2 is often observed as a brownish gas.

12. a) The ionization energy of nitrogen is greater than that of oxygen due to differences in their electron configurations and atomic structures. Nitrogen has one less electron compared to oxygen, resulting in a smaller atomic radius and stronger attraction between the electrons and the nucleus. As a result, it requires more energy to remove an electron from nitrogen, leading to a higher ionization energy. Additionally, the half-filled p orbital in nitrogen provides greater stability, making it more difficult to remove an electron compared to oxygen.

13. a) Nessler's reagent is used for the detection of ammonium ions (NH_4^+). Nessler's reagent is a chemical solution used for the detection and quantification of ammonium ions (NH_4^+). It contains a mixture of potassium tetraiodomercurate (II) and potassium hydroxide. When ammonia is present, it reacts with Nessler's reagent to form a brown-colored complex. The intensity of the brown color can be used to determine the concentration of ammonia in a solution. This test is commonly used in analytical chemistry and environmental monitoring to detect the presence of ammonia in various samples.

14. b) The ozone oxidizes the iodide ions (I⁻) in the potassium iodide solution to form iodine molecules (I₂), along with the formation of potassium oxide (K₂O) and oxygen gas (O₂) as byproducts. This reaction is commonly used as a test for the presence of ozone, as the production of iodine results in a characteristic color change from colorless to brown or blue.

15. b) The volatility of hydrogen halides is determined by the strength of intermolecular forces. In this case, HCl has the weakest intermolecular forces compared to the other hydrogen halides. This is because chlorine is larger in size compared to fluorine and bromine, resulting in weaker van der Waals forces between HCl molecules. Due to the weaker intermolecular forces, HCl has a lower boiling point and is more volatile compared to HF and HBr. Therefore, the correct answer is (B) HCl.

16. a) BCl₃ is the most acidic halide because boron has a less polar bond with chlorine compared to the other elements in the options. This allows for easier dissociation of H⁺ ions, making it a stronger acid compared to SbCl₃, BiCl₃, and CCl₄. $S_2O_7^{(2-)}$

17. a) The lightning bolts in the atmosphere cause the formation of NO. This is because the high temperatures and energy associated with lightning can cause the nitrogen and oxygen molecules in the air to react and form nitrogen monoxide (NO).

18. a) XePtF₆ was the first noble gas compound discovered, consisting of xenon (Xe) bonded to platinum (Pt) and surrounded by six fluoride (F) ions. Its discovery by Neil Bartlett in 1962 challenged the notion that noble gases are chemically inert, opening up new avenues for studying their chemistry.

19. d) Among XeO₃, XeO₄, and XeF₆, all three molecules have the same number of lone pairs on xenon (Xe). This is because xenon has a valence electron configuration of ns²np⁶, which allows it to accommodate up to six lone pairs. In XeO₃, Xe has three lone pairs, in XeO₄ it has four lone pairs, and in XeF₆ it also has four lone pairs. Therefore, XeO₃, XeO₄, and XeF₆ all have the same number of lone pairs on xenon.

20. d) Fluorine exhibits anomalous behavior due to its small size, high electronegativity, low F-F bond dissociation enthalpy, and the absence of d-orbitals in its valence shell. Its small size leads to strong electron-electron repulsion and high reactivity. The high electronegativity results in a strong attraction for electrons and the ability to form stable compounds. The low F-F bond dissociation enthalpy makes the F-F bond relatively weak and easily broken. Furthermore, the absence of d-orbitals limits fluorine's ability to expand its valence shell and participate in d-orbital-based bonding. Collectively, these factors contribute to the anomalous behavior of fluorine.

22: a) F

Explanation: Electronegativity is the tendency of an atom to attract a shared pair of electrons towards itself. Fluorine (F) is the most electronegative element in the periodic table. It has the highest electron affinity and the smallest atomic size in the third period, leading to the highest electronegativity.

23: c) I^-

Explanation: Among the given species, anions are generally larger than their corresponding neutral atoms due to the addition of extra electrons. Among Br^- , I^- and I^- , I^- has the largest size because it has one more electron than Br^- , leading to increased electron-electron repulsion and a larger atomic radius.

24: b) $PH_3 > NH_3 > AsH_3 > SbH_3$

Explanation: The basicity of a compound depends on the availability of lone pairs of electrons to donate. Phosphorus (P) is less electronegative than nitrogen (N), so it is more willing to donate its lone pair. Also, the larger size of phosphorus atoms compared to nitrogen atoms makes it easier for the lone pair to be donated. Therefore, PH_3 is the strongest base among the given options.

25: b) $SbCl_3$

Explanation: The acidity of a compound is related to its ability to donate a proton (H^+). In $SbCl_3$, the central antimony (Sb) atom can accept an electron pair from the chlorine atom, leading to the formation of a stable $SbCl_4^-$ ion. This ability to accept an electron pair makes $SbCl_3$ the most acidic among the given options.

26: b) $Be < C < O < N < F$

Explanation: Electron affinity is the energy released when an atom gains an electron. Among the given elements, fluorine (F) has the highest electron affinity due to its small atomic size and high effective nuclear charge. As you move from left to right across a period, electron affinity generally increases.

27: b) the 2p orbital of F is relatively more compact than 3p orbital of chlorine

Explanation: The compactness of orbitals influences electron affinity. Fluorine's 2p orbital is smaller and closer to the nucleus than chlorine's 3p orbital, making it easier for an incoming electron to experience stronger electron-electron repulsion in fluorine. This makes it less favorable for fluorine to accept an additional electron, resulting in a lower electron affinity compared to chlorine.

28: b) N_2

Explanation: Ammonium dichromate $(NH_4)_2Cr_2O_7$ decomposes upon heating to produce nitrogen gas (N_2), water (H_2O), and chromium(III) oxide (Cr_2O_3).

29: c) only covalent

Explanation: N_2O_5 consists of covalent bonds between nitrogen and oxygen atoms. It does not contain ionic bonds because there are no metal atoms present.

30: c) 3

Explanation: In $[Fe(H_2O)_5NO]^+SO_4^-$, the complex has a positive charge of +1. Since each water molecule contributes a neutral charge, and nitric oxide (NO) has a neutral charge, the positive charge must come from the iron (Fe) ion. Iron's oxidation state is +3 in this complex.

31: d) NO_2

Explanation: Nitrogen dioxide (NO_2) is a brown-colored gas. It absorbs light in the visible spectrum, leading to its characteristic color.

32: a) NO

Explanation: Lightning bolts cause nitrogen and oxygen molecules in the atmosphere to react, forming nitrogen monoxide (NO).

33: b) HOI

Explanation: Concentrated nitric acid (HNO_3) reacts with iodine (I_2) to form hypoiodous acid (HOI).

34: a) N_2O_5

Explanation: N_2O_5 is the most acidic oxide among the given options. It reacts with water to form nitric acid (HNO_3), which is a strong acid.

35: d) HI

Explanation: HI (hydrogen iodide) is a strong acid and can form salts like KI.

36: c) It forms dimer

Explanation: This statement is incorrect. NO does not form a dimer. Nitrogen monoxide (NO) is a diatomic molecule and does not dimerize.

37: c) N_2O_4

Explanation: At equilibrium, the pale blue liquid obtained from an equimolar mixture of nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4) gases is N_2O_4 . The color arises due to the equilibrium between the brown NO_2 and the colorless N_2O_4 .

38: (B) NaOH.

Explanation: Boric acid is prepared from borax (sodium borate) by the action of sodium hydroxide (NaOH). The reaction involves neutralization, resulting in the formation of boric acid.

39: (D) Two lone pairs of electrons on the O atom.

Explanation: Carbon monoxide (CO) acts as a Lewis base due to the presence of two lone pairs of electrons on the oxygen atom. These lone pairs can be donated to Lewis acids.

40: (B) Ammonium ions (NH_4^+).

Explanation: Nessler's reagent is used for detecting the presence of ammonium ions (NH_4^+) in a solution. It forms a brown precipitate when reacting with ammonium ions.

41: (B) O_2^{2+} .

Explanation: The dioxygenyl ion (O_2^{2+}) is a species consisting of two oxygen atoms with a positive charge on each. It is represented as $O = O^{2+}$.

42: (C) I_2 .

Explanation: When ozone (O_3) reacts with potassium iodide (KI) solution, it produces iodine (I_2) and oxygen gas (O_2).

43: (A) HNO_3 .

Explanation: Nitric acid (HNO_3) possesses oxidizing, reducing, and complex forming properties. It can oxidize various substances, reduce some metal ions, and form complexes with certain ligands.

44: (D) HI (Hydrogen iodide).

Explanation: Among the hydrogen halides, hydrogen iodide (HI) is the most volatile due to its weaker intermolecular forces compared to the other hydrogen halides.

45: (A) H_3PO_4 (Phosphoric acid).

Explanation: Phosphoric acid (H_3PO_4) can form two series of salts: orthophosphates (HPO_4^{2-}) and hydrogen phosphates ($H_2PO_4^-$).

46: (A) HIO.

Explanation: When iodine pentoxide (I_2O_5) reacts with concentrated sulfuric acid (H_2SO_4), it forms iodic acid (HIO₃).

47: (D) P-P-P angle of 90 degrees.

Explanation: White phosphorus (P_4) does not have a P-P-P angle of 90 degrees. It exists as P_4 tetrahedral molecules with a bond angle of around 60 degrees.

48: (A) $C_6H_5NH_2$ (Aniline).

Explanation: Aniline ($C_6H_5NH_2$) is the least basic among the provided compounds due to the electron-withdrawing nature of the phenyl group, which weakens the basicity of the amino group.

49: (D) NaCl.

Explanation: Sodium chloride (NaCl) has maximum solubility in water due to its strong ionic interactions with water molecules.

50. (C) Three.

Explanation: Cyclic metaphosphoric acid $(\text{HPO}_3)_n$ contains three P–O–P bonds within its cyclic structure.

51: (D) None of these.

Explanation: None of the provided options represents a cyclic oxo acid.

52: (A) HgCl_2 .

Explanation: Mercury(II) chloride (HgCl_2) does not produce a metallic sulfide when reacting with hydrogen sulfide. It forms a complex with HgS .

53: (B) SO_3 .

Explanation: Sulfur trioxide (SO_3) does not have an S–S bond. It is composed of sulfur and oxygen atoms bonded by double bonds.

54: (C) H_3BO_3 (Boric acid).

Explanation: Boric acid (H_3BO_3) forms two series of salts: borates and metaborates.

55: (D) H – S bond is weaker than H – O bond.

Explanation: Although oxygen is more electronegative than sulfur, the H–S bond is weaker than the H–O bond. This weaker bond contributes to the slight acidity of hydrogen sulfide (H_2S).

56: (A) CO.

Explanation: The reaction of formic acid (HCOOH) with concentrated sulfuric acid (H_2SO_4) evolves carbon monoxide (CO) gas.

57: (D) AlCl_3 .

Explanation: Aluminum chloride (AlCl_3) is the most acidic among the provided options due to its Lewis acidity.

58: (D) K^+ and SiF_6^{2-} .

Explanation: The compound K_2SiF_6 contains potassium cations (K^+) and hexafluorosilicate anions (SiF_6^{2-}).

59. (C) SCN^- .

Explanation: The thiocyanate ion (SCN^-) is a pseudohalide

60: (A) It represents disproportionation.

Explanation: The given reaction represents a disproportionation reaction where chlorine is both oxidized and reduced simultaneously.

61:(A) Cl_2 is evolved.

Explanation: When iodine (I_2) is passed through KCl , HF , and KBr , chlorine gas (Cl_2) is evolved.

62: (D) sp^2 , and respectively.

Explanation: The hybridization of nitrogen in ammonia (NH_3) is sp^3 , in nitrate ion (NO_3^-) it's sp^2 , and in nitrite ion (NO_2^-) it's sp^2 .

63:(B) Disproportionation of NO .

Explanation: Nitrogen(I) oxide (NO) can be produced by the disproportionation of nitrogen(II) oxide (NO_2).

64: (C) S .

Explanation: Oxygen gas is not evolved when concentrated sulfuric acid (H_2SO_4) reacts with sulfur (S).

65: (B) O_2 and SO_2 .

Explanation: Alkaline pyrogallol absorbs oxygen (O_2), and terpineol oil absorbs sulfur dioxide (SO_2).

66: (C) Lead nitrate ($\text{Pb}(\text{NO}_3)_2$).

Explanation: Nitrogen dioxide (NO_2) can be released by heating lead nitrate ($\text{Pb}(\text{NO}_3)_2$).

67: (C) CaCN_2 .

Explanation: The formula of calcium cyanamide is CaCN_2 .

68: (C) O_2 .

Explanation: Molecular oxygen (O_2) has two unpaired electrons.

69: (C) H_2O_2 .

Explanation: Hydrogen peroxide (H_2O_2) can oxidize water (H_2O) to produce oxygen gas (O_2).

70: (D) Thermally decomposing the compound.

Explanation: The forms of iron and NO in nitroprusside ion can be differentiated by thermally decomposing the compound.

71: (D) N_2O_5 .

Explanation: Nitrogen pentoxide (N_2O_5) is an acidic oxide and does not act as a reducing agent.

72: (C) $\text{Cr}(\text{OH})_3$.

Explanation: Chromium(III) hydroxide ($\text{Cr}(\text{OH})_3$) is soluble in ammonia (NH_3) due to the formation of complex ions.

73: (C) A change in the partial pressure of oxygen in the air.

Explanation: The transformation of white metallic tin to grey powder in cold conditions is related to a change in the partial pressure of oxygen in the air. This transformation is known as "tin pest."

www.smartachievers.online