07

p-Block Elements - II

Elements of group 15, 16, 17 and 18 are included in *p*-block elements-II. These have general electronic configuration ns^2np^{3-6}. The similarity among these elements is that most of them are non-metals. The *p*-block elements II can be described on a group-by-group basis as 15, the pnictogens; 16, the chalcogens; 17, the halogens; and 18, the helium group, composed of the noble gas (excluding helium) and oganesson.

IN THIS CHAPTER ....

VA (15) Group Elements and their Compounds

Group VA contains 5 elements, namely, nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). These elements are collectively called as **pnictogens** (taken from Greek word *'pniomigs'* meaning suffocating) and their compounds are called **pniconides**.

Occurrence

Nitrogen constitutes about 78% (by volume) of atmosphere. In combined state, it is found as nitrates or in proteins and amino acids. Phosphorus is the eleventh most abundant element in the earth's crust. It is usually found in its phosphate. From the rest of the elements occur as sulphides or oxides.

General and Physical Properties

Elements of this group exhibit as a regular trend in general and physical properties, which are discussed below.

(i) **Electronic configuration** It is clear from the electronic configuration (given in table 7.1) that their *p*-orbitals of valence shell are half-filled. This is a stable configuration in accordance with Hund's rule. Thus, these elements are not so reactive (e.g. nitrogen behaves as almost inert element).

(ii) **Atomic volumes and radii** It increases on moving down the group, however arsenic shows exceptionally low value of atomic volume.

(iii) **Physical state** A gradual transition in physical state is seen among the elements under ordinary conditions, i.e. nitrogen is a gas which can be converted into a liquid at very low temperature; phosphorus exist as a solid but can pass readily into vapour state. Arsenic, antimony and bismuth are infact solids of varying boiling and melting points.

(iv) **Ionisation energy** The ionisation enthalpy of these group elements are much higher than the corresponding elements of group 14. The values for succeeding elements decreases symmetrically as seen in *s*-block elements.

(v) **Metallic character** It increases on moving down the group as, nitrogen and phosphorus are distinctly **non-metals,** succeeding two members are **amphoteric** in nature, i.e. As and Sb have metallic as well as non-metallic character while, the last element Bi is a **metal.**

(vi) **Electronegativity** It decreases down the group as we move from N to Bi indicating a gradual change from non-metallic to metallic character.
These elements are more electronegative as compared to the elements of 14 group.

(vii) **Melting and boiling points** These elements do not show a regular trend of melting and boiling points.
In this group, the melting point first increases from N to As and afterwards decreases. While boiling point first increases from N to Sb and then decreases. But Bi has low boiling point as compared to Sb.

We can write these order as;

$$N < P < As > Sb > Bi \text{ (melting point)}$$

$$N < P < As < Sb > Bi \text{ (boiling point)}$$

(viii) **Oxidation state** The normal oxidation states of these elements are +5 and +3. Out of which +3 stabilises on moving down the group due to **inert pair effect**. Nitrogen show all oxidation states from +5 to –3 as +5 in N_2O_5, +4 in N_2O_4, + 3 in N_2O_3, +2 in NO, +1 in

N_2O, 0 in N_2, –1 in NH_2OH, –2 in N_2H_4 and –3 in NH_3.

Nitrogen even shows oxidation state of $-\frac{1}{3}$ in hydrazoic acid, N_3H.
Phosphorus show three different oxidation states +4 and +5 while, rest of the elements show only +5 and +3 oxidation states.

Nitrogen, have least tendency to form compounds in + 5 oxidation state because it does not have vacant *d*-orbitals.

All the elements in their tripositive state (+3 oxidation state) have the tendency to donate one **electron pair.** Nitrogen shows this tendency to maximum extent. All elements (except N) also show the tendency to accept electron pair. Nitrogen does not show such a property due to absence of vacant d-orbital in it.

The above described properties are summarised in the table given below

Physical Properties of Group 15 Elements

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
At. no.	7	15	33	51	83
Electronic. configuration	$[He]2s^2p^3$	$[Ne]3s^2p^3$	$[Ar]3d^{10}$ $4s^2p^3$	$[Kr]\,4d^{10}$ $5s^2p^3$	$[Xe]\,4f^{14}5d^{10}$ $6s^2p^3$
At. mass (amu)	14.007	30.970	74.922	121.750	208.980
Density in solid state (g cm^{-3})	1.03	1.82	5.73	6.62	9.78
Atomic volume (cm^3)	17.3	17.0	13.1	18.4	21.3
Atomic radius (Å)	0.75	1.06	1.19	1.38	1.46
Ionic radius of trivalent ion (Å)	1.71	2.12	2.22	2.45	1.20
IE (kJ mol^{-1})	1402	1012	946	840	703
Oxidation state	–3, –2, –1, 0 +1, +2, +3, +4 , +5	–3, +3, +4, +5	–3, +3, +5	–3, +3, +5	+3, +5
Electronega-tivity	3.0	2.1	2.0	1.8	1.7
MP (°C)	–210	44.1 (white phosphorus)	817 (at 36 atm)	630.5	271.3
BP (°C)	–195.8	280	615 (sublimes)	1587	1564
Heat of fusion (kJ mol^{-1})	0.36	0.63	27.7	19.9	10.9

(ix) **Nature of compounds** From stability point of view, it is not easy to gain three electrons to achieve stable configuration, therefore the formation of trinegative (A^{3-}) ion is rare. Only N has the capability to form such a type of ion due to its **small size**.

However, covalent compounds of nitrogen are more common. The electronegativities of other elements are so lower that they would generally form covalent bonds even with highly electropositive elements. Bi compounds, although covalent, do give ions in polar solvents like water.

(x) **Catenation** All the elements of this group show property of catenation, (i.e. self linkage) to a very smaller extent (in comparison with carbon).

The catenation in stable nitrogen compounds is restricted generally upto two or three nitrogen atoms as, in N_2H_4, N_3^- etc.

The P atom has maximum tendency to catenate amongst group 15th elements**.** This can be explained on the basis of

P—P bond energy (200.8 kJ/mol) which is more closer to C—C bond energy (353.9 kJ/mol) in comparison to N—N or As—As bond energies (163.1 and 146.1 kJ/mol) respectively.

(xi) **Molecular state** Nitrogen have the tendency to form $p\pi$-$p\pi$ bonds with other atoms of similar type (N) or different type, e.g. carbon.

Thus, nitrogen usually exists as discrete diatomic gaseous molecule ($N \equiv N$). Stable nitrogen compounds contain maximum two or three nitrogen atoms. Other members, however, do not have a tendency of $p\pi$-$p\pi$ bonding. However, they **have empty** d-orbitals. Thus, they exist as discrete **tetra atomic** molecules like P_4, As_4, Sb_4 in which, the atoms are linked together by single bonds.

(xii) **Allotropy** All the elements of group 15 (except Bi) show allotropy as,

- N exists in two solid forms namely α**-nitrogen** with cubic crystalline structure and β**-nitrogen** with hexagonal crystalline structure. The transition temperature is –238.5°C. It also has one gaseous allotropic form.
- Phosphorus exists in a number of allotropic forms, e.g. white phosphorus, red phosphorus, scarlet phosphorus, metallic or α-black phosphorus, β-black phosphorus, violet phosphorus etc.
- Arsenic exists as **grey, yellow** and **black** arsenic.
- Similarly, Sb exists as **metallic**, α- or **yellow** and β or **black antimony**.

Chemical Properties

Elements of this group form mainly covalent compounds with other elements.

Chemical properties of these compounds are described below.

1. Reactivity Toward Hydrogen or Formation of Hydrides

- These elements form AH_3 type hydrides, e.g. **ammonia** (NH_3), **phosphine** (PH_3), **arsine** (AsH_3), **stibine** (SbH_3) and **bismuthine** (BiH_3).
- These hydrides are prepared from binary metal compounds, e.g. ($Mg_3N_2, Ca_3P_2, Zn_3As_2, Mg_3Sb_2, Mg_3Bi_2$ etc.) as

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

$$Zn_3As_2 + 6HCl \longrightarrow 3ZnCl_2 + 2AsH_3$$

- These can also be prepared by the reduction of trihalides of these elements with $LiAlH_4$ as,

$$MCl_3 + 3LiAlH_4 \longrightarrow MH_3 + 3LiCl + 3AlH_3$$

- The hydrides have pyramidal structure with sp^3-hybridisation .

Some physical properties of hydrides can be explained as,

(i) **Thermal stability** The decrease in thermal stability can also be explained by increase in size of central atom. Due to such increase, the tendency to form stable covalent bond with comparatively small H atom decreases.

In other words, the strength of M—H bond decreases resulting to decreased thermal stability. Thus, the thermal stability decreases in the order as,

$$NH_3 > PH_3 > ASH_3 > SbH_3 > BiH_3.$$

(ii) **Reducing behaviour** The increase in reducing behaviour can be explained on the basis of decrease in thermal stability.

In other words, we can say that, on moving down the group their tendency to liberate hydrogen increases and hence their reducing character increase. Thus, the order will be, $NH_3 < PH_3 < ASH_3 < SbH_3 < BiH_3$.

(iii) **Bond angles** The variation in bond angles may be explained on the basis of size and electronegativity of central atom.

On moving down the group, the size of central atom increases and electronegativity decreases. So, the location of bond pairs of electrons shifts more and more away from the central atom as we go from NH_3 to SbH_3.

Due to such a shifting, the repulsion between bond pair of electrons decreases owing to which bond angle also decreases.

Thus, the order will be,

$$\underset{107.8^\circ}{NH_3} > \underset{93.6^\circ}{PH_3} > \underset{91.8^\circ}{AsH_3} > \underset{91.3^\circ}{SbH_3}$$

(iv) **Boiling point** The boiling point of these hydrides follows the trend as,

$$PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$$

The abnormally high boiling point of NH_3 is due to the presence of intermolecular H–bonding in NH_3.

(v) **Solubility** NH_3 is soluble in H_2O while PH_3 and other hydrides are insoluble. This is because, NH_3 forms H-bonds with H_2O while PH_3 and other hydrides do not.

(vi) **Basic nature** All these hydride behaves as Lewis bases because the central atom possess a lone pair of electrons.

As the size of central atom increases, the electron density on central atom decreases and consequently its tendency to donate a pair of electrons decreases. Hence, the basis character decreases in order as

$$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$$

The physical properties of these hydrides are summarised in the following table

Comparative Study of the Properties of Hydrides

Property	**NH_3**	**PH_3**	**AsH_3**	**SbH_3**	**BiH_3**
Thermal stability	Highly stable	Not stable, so decomposes at 400°C	Unstable 230°	Unstable at room temperature	Unstable, having half-life of 20 min
Reducing character	Not good	Moderate	Good	Strong	Strong
Basic character	Base	Weak base	Neutral	Neutral	Feebly acidic
Reactions					
(i) with metal salt solutions	Precipitate as hydroxides, e.g. $Fe(OH)_3$	Precipitate as phosphides, e.g. Ag_3P	Precipitate as arsenides, e.g. Ag_3As	Precipitate as antimonides e.g. Ag_3Sb (unstable)	No such reaction occur
(ii) complexes	Stable, complex e.g. $[Cu(NH_3)_4]^{2+}$	Non stable complexes	Non stable complexes	Non stable complexes	Non-stable complexes
Structure	Pyramidal	Pyramidal	Pyramidal	Pyramidal	
Bond angle	107.3°	93.5°	91.8°	91.3°	90°
Melting point	–78°C	–132°C	–119°C	–88°C	—
Boiling point	–34.5°C	–87.5°C	–62.4°C	–18.4°C	+ 16.8°C
Bond length	1.02	1.42	1.52	1.71	—
H-bonding	Present	Not present	Not present	Not present	Not present

2. Reactivity Toward Halogens or Formation of Halides

These are form trihalides of AX_3 type and pentahalides of AX_5 type.

Trihalides

Some important characteristics of these trihalides are as follows

(i) **Ionic character** These trihalides are mostly covalent and their ionic character increases on moving down the group, (i.e. trihalides of Bi are ionic in nature).

(ii) **Structure** These halides have **pyramidal structure** in which central atom is sp^3-hybridisation.

(iii) **Hydrolysis** The halides, particularly the chlorides, are readily hydrolysed. However, the products of hydrolysis differ in different cases. e.g.

If trihalides are **completely hydrolysed**

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HClO$$

$$2AsCl_3 + 3H_2O \longrightarrow As_2O_3 + 6HCl$$

If **partially hydrolysed,**

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$

$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$$

The ease of hydrolysis of trihalides (for same halogens) decreases in the order as

$$NCl_3 > PCl_3 > AsCl_3 > SbCl_3 > BiCl_3$$

Note NF_3 and PF_3 do not undergo hydrolysis.

(iv) **Stability** Trihalides of N are least stable as compared to halide of this group elements. This is because their is a large difference in the size of N and X atoms. This result in the weaking of N—X bond. However, BF_3 is stable because size difference in N and F is small.

(v) **Acidic character** The trihalides of P, As and Sb, especially fluorides and chlorides, are **Lewis acids**. Thus, the order will be

$$NH_3 > PH_3 > AsH_3 > SbH_3$$

$$PF_3 + F_2 \longrightarrow PF_5$$

$$SbF_3 + 2F^- \longrightarrow [SbF_5]^{2-}$$

$$SbCl_3 + 2Cl^- \longrightarrow [SbCl_5]^{2-}$$

(vi) **Basic character** The order of basic character of trihalides of nitrogen is

$$NI_3 > NBr_3 > NCl_3 > NF_3$$

Except NF_3, all other trihalides of nitrogen are unstable. They decompose with explosive violence.

(vii) **Bond angle** The bond angle decreases while acidic strength increases as the electronegativity of central atom increases,

i.e. Bond angle ∝ electronegativity of central atom

$$\propto \frac{1}{\text{acid strength}}$$

Thus, the order will be

$$NH_3 > PH_3 > AsH_3 > SbH_3.$$

Pentahalides

P, As and Sb have the ability to form pentahalides. However, Bi and N (due to the absence of vacant *d*-orbital) do not form such pentahalides. The pentahalides of P (except PCl_5) are not stable due to inert pair effect. Thus, it decomposes to give PCl_3 and Cl_2.

The other properties of pentahalides are as follows

- These pentahalides have sp^3d-hybridisation and **trigonal bipyramidal** structure.
- These are thermally less stable than the trihalides.
- PCl_5 is molecular in gaseous phase but exists as, $[PCl_4]^+[PCl_6]^-$ in crystalline state, Similarly, PBr_5 and PI_5 also exist in ionic forms as, $[PBr_4]^+[Br]^-$ and $[PI_4]^+[I]^-$ respectively in solid state.

Other Halides

Some other halides are also known, e.g. N_2F_4, N_2F_2, N_3F etc. Besides this, several mixed halides of nitrogen are also known, e.g. $NCl_2F, NClF_2$, $NBrF_2$, NF_2H, NF_2H, NCl_2H etc.

However, these are unstable and difficult to isolate. P also forms P_2Br_4 and several mixed halides like PCl_4F, $PClF_4, PCl_2F_3$ etc. As and Sb also form mixed halides like AsF_2Cl, $AsFCl_2, AsClBr_2, AsCl_2Br, SbCl_4F$ etc.

3. Reactivity Toward Oxygen or Formation of Oxides

All elements of this group form oxides of type R_2O_3 and R_2O_5. Some of them also form dioxides of formula RO_2. N show all oxidation states from +1 to +5 in its oxides as shown below

Different Oxides of V Group Elements

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

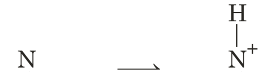
- The trioxides of nitrogen, phosphorus and arsenic are acidic; the trioxide of Sb is **amphoteric** while that of Bi is **basic** in nature. This is because on moving down the group, metallic character increases, and metal oxides are more basic than the non-metal oxides.
- However, the pentoxides are acidic in all the cases. Their acidic nature decreases down the group. All the pentoxides (except P_2O_5) can readily lose oxygen to form lower oxides.
- Thus, they act as **strong oxidising agents**. The stability of pentaoxides follows the order

$$P_2O_5 > As_2O_5 > Sb_2O_5 > N_2O_5 > Bi_2O_5$$

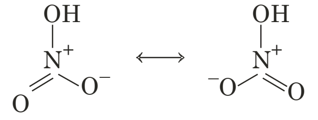
4. Oxyacids

All elements (except Bi) of this group form oxyacids.

- Oxyacids of nitrogen are hyponitrous acid, ($H_2N_2O_2$), nitrous acid (HNO_2), nitric acid (HNO_3), pernitrous acid (HOONO), pernitric acid ($HOONO_2$). Out of these, the most important one is nitric acid. The structure of nitrous acid and nitric acid are given below



(Nitrous acid)



(Nitric acid)

- Phosphorus form many oxyacids that are discussed latter in this chapter.

Anomalous Behaviour of Nitrogen

Nitrogen, shows many properties that are quite different from other members of the group. This is because of its small size, high electronegativity, high ionisation energy, non-availability of *d*-orbital and capacity of $p\pi$- $p\pi$ multiple bond formation.

These properties are as follows

- It is found in a gas while other members are found in solid state.
- It exists in diatomic form while other elements like phosphorus, arsenic and antimony exist as tetra-atomic molecules (P_4, As_4, Sb_4).
- It forms trinegative ion, i.e. N^{3-}, while other members do not form.
- It is chemically inert under ordinary conditions due to high bond dissociation energy. While other members are quite reactive because of the presence of single bond in their molecules.
- It does not show pentacovalency due to non-availability of *d*-orbitals while it is shown by all other elements.
- The hydride of nitrogen (NH_3) is highly basic in nature while the hydrides of other elements are slightly basic. Moreover, only hydrides of nitrogen shows H-bonding while other members do not.
- It forms oxides of five types (i.e. N_2O, NO, N_2O_3, N_2O_4 and N_2O_5) while other members of this family form oxides of only two types (i.e. tri and pentaoxides).
- Except NF_3, other halides of nitrogen i.e. NCl_3, NBr_3 and NI_3 are unstable while the halides of other elements are fairly stable.
- It does not form complexes due to the non- availability of *d*-orbitals while other members have a tendency of complex formation, e.g. $[PCl_6]^-$, $[AsCl_6]^-$ etc.

Nitrogen (N)

N is fairly widely distributed in nature, both are present in free as well as in combined state. In combined state it occurs only as nitrates, e.g. $NaNO_3$ (chile salt petre), KNO_3 (salt petre). Coal containing compounds of nitrogen yield NH_3 on distillation which is an important compound. N is also an essential constituent of all living cells as the protein part which contains about 16% of nitrogen. Some important compounds of nitrogen are discussed below.

1. **Dinitrogen** (N_2)

It is the molecular form of elemental nitrogen and is chemically inert.

Its methods of preparation are given below.

Methods of Preparation

- In laboratory, dinitrogen is obtained by heating ammonium chloride or ammonium dichromate.

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

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

- Pure nitrogen in small amounts can be obtained by heating sodium or barium azides.

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

- On commercial scale, nitrogen is invariably obtained by liquifying air and then carrying out its fractional evaporation. It having a lower boiling point (77.2 K).

Physical Properties

The important physical properties of nitrogen are as follows

- It is a colourless, tasteless, odourless gas. It does not support combustion and non-poisonous in nature. However, animals die in this atmosphere for needs of oxygen.
- It is sparingly soluble in water.
- It boils at 195.8°C.
- On rapid evaporation, it changes into an ice like solid.
- Naturally occurring nitrogen consists of two isotopes N^{14} and N^{15}. N^{15} is often used as an isotopic tracer.

Chemical Properties

The heat of dissociation of N_2 is extremely large (945 kJ). It has very strong $N\equiv N$ bond which is principally responsible for the inactivity of free nitrogen.

Its structure is $\ddot{N}\equiv\ddot{N}$.

However, nitrogen shows the following chemical reaction as,

- N_2 combines readily with **highly electropositive metals** (first group elements) even at room temperature and form ionic nitrides with N^{3-} ion. These nitrides are crystalline compounds with high melting points.
- N_2 combines with less electropositive elements like Mg, Ca, Sr, Ba etc., at red heat with B and Al at bright red heat and with Si at white heat, to form corresponding nitrides as,

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

$$2Al + N_2 \longrightarrow 2AlN$$

$$3Si + 2N_2 \longrightarrow Si_3N_4$$

Out of these nitrides, the group 2nd elements are generally ionic, while those of group 3rd and 4th are covalent in nature.

The nitrides formed with transition metals like Fe, Mn, Mo, W are true interstitial compounds. In these compounds, N_2 atoms occupy the interstices space in the metal structure. These nitrides are extremely hard with high melting point, metallic lustre and metallic conductivity.

- N_2 combines with H_2 to give NH_3 (Haber's process) as,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (\Delta H = -92 \text{ kJ})$$

The reaction is carried out in the presence of finely divided Fe with a little Mo. The pressure and temperature maintained for this process is 100-1000 atm and 400-550°C respectively.

- N_2 combines **with** O_2 to give NO as

$$N_2 + O_2 \rightleftharpoons 2NO \qquad (\Delta H = +180.7 \text{ kJ})$$

The reaction is highly endothermic and takes place at elevated temperatures (about 3000°C). However, even at such a high temperature, the yield is 5% maximum.

- When N_2 combines with $CaCl_2$, the product is calcium cynamide, (CaNCN) as,

$$CaC_2 + N_2 \longrightarrow CaNCN + C$$

(The reaction takes place at 1000°C in the current of N_2.)

2. **Active Nitrogen**

When we pass electric discharge in the atmosphere of nitrogen at low pressure, **active nitrogen** is produced. It is accompanied by a yellow glow which persists for several hours which indicates slow release of energy in the process. This nitrogen gets deactivated on collision with the walls of vessels.

It is highly reactive chemically on reacting with liquid Hg, Na vapours, As, P etc., their nitrides are produced.

Uses

Nitrogen is used

- for filling electric lamps.
- to dilute the action of oxygen in air.
- to provide inert atmosphere in certain metallurgical operations
- in the packets of foodstuffs.
- for the manufacture of certain chemicals like NH_3. HNO_3, calcium cyanamide and other nitrogen compound.

Example 1. *The compound that does not produce nitrogen gas by the thermal decomposition is* ***(JEE Main 2018)***

(a) $Ba(N_3)_2$ (b) $(NH_4)_2Cr_2O_7$ (c) NH_4NO_2 (d) $(NH_4)_2SO_4$

Sol. (*d*) The thermal decomposition of given compounds is shown below

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2\uparrow + 4H_2O + Cr_2O_3$$
$$NH_4NO_2 \xrightarrow{\Delta} N_2\uparrow + 2H_2O$$
$$(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$$
$$Ba(N_3)_2 \longrightarrow Ba + 3N_2\uparrow$$

Thus, only $(NH_4)_2SO_4$ does not gives N_2 on heating (It give NH_3). While rest of the given compounds gives N_2 on their thermal decomposition.

3. Ammonia

It was first isolated by **Priestley (in 1774)**. It is a stable binary and simplest pnictogen hydride.

Methods of Preparation

Some following methods are employed to prepare NH_3 are

- NH_3 is prepared on **industrial scale** by **Haber's process** involves the direct combination of N_2 and H_2 as,

  $$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (\Delta H = -92.0 \text{ kJ})$$

  The reaction is reversible, exothermic and proceeds with a tremendous decrease in volume. Thus, it requires **low temperature** and **high pressure** (according to Le-Chatelier's principle) along with highly porous finely divided iron containing small amount of promotors (Mo or oxides of K and Al).
- It can also be prepared by decomposing ammonium salts with caustic alkalies (NaOH) or slaked lime ($Ca(OH)_2$). In **laboratory**, it is prepared by heating with quick lime (CaO).

  $$2NH_4Cl + CaO \longrightarrow CaCl_2 + H_2O + 2NH_3\uparrow$$

  Ammonia obtained, cannot be dried over concentrated sulphuric acid, calcium chloride or phosphorus pentoxide as the gas reacts with these substances. However, quicklime can be used.
- It is also prepared by the hydrolysis of calcium cyanamide with superheated steam at 450 K.

  $$CaCN_2 + 3H_2O \xrightarrow{450\text{ K}} CaCO_3 + 2NH_3\uparrow$$

Physical Properties

NH_3 is a colourless, pungent smelling gas, lighter than air and highly soluble in water. Because of **hydrogen bonding**, it has a higher boiling point (–33.4°C) than the expected value. Its aqueous solution is basic in nature.

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

Chemical Properties

Some important chemical properties are as follows

- Ammonia burns in oxygen with a greenish-yellow flame as, $4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$
- When electric spark is passed over a mixture of NH_3 and O_2, it gets exploded. But if the temperature is 500°C and Pt guaze is present as catalyst, the reaction occurs as,

  $$4NH_3 + 5O_2 \xrightarrow[\text{electric spark, Pt gauze}]{500^\circ\text{C}} 4NO + 6H_2O$$
- It acts as reducing agent and reduces metallic oxides like CuO and PbO to metals and itself gets oxidised to N_2.
  e.g. $3CuO + 2NH_3 \longrightarrow 3Cu + 3H_2O + N_2\uparrow$
- With calcium, it forms calcium hydride and nitrogen.
- It reacts with conc. HCl and produces white fumes of the ammonium chloride.

  $$NH_3 + HCl \longrightarrow \underset{\text{(White fumes)}}{NH_4Cl}$$
- When heated with alkali metals and barium, amides are obtained.

  $$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2\uparrow$$
- With chlorine, it forms NH_4Cl and nitrogen gas.

  $$\underset{\text{Excess}}{8NH_3} + 3Cl_2 \longrightarrow N_2\uparrow + 6NH_4Cl$$

  However, if chlorine is in excess, the following reaction occurs

  $$NH_3 + \underset{\text{Excess}}{3Cl_2} \longrightarrow \underset{\text{Explosive}}{NCl_3} + 3HCl$$
- Aqueous ammonia contains uncombined ammonia (46.2%), hydrated ammonia ($H_3N\ldots HOH$, 52.4%) and relatively few (1.4%) NH_4^+ and OH^- ions. It precipitate many metallic hydroxides from their salt solutions. In some cases, the precipitated hydroxides dissolve in excess ammonia and form complex amines.

  $$CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2\downarrow + (NH_4)_2SO_4$$
  $$Cu(OH)_2 + 4NH_3 \longrightarrow [Cu(NH_3)_4](OH)_2$$
- It gives yellow-brown colour precipitate with Nessler's reagent (i.e. alkaline K_2HgI_4) as ,

  $$\underbrace{2K_2HgI_4 + 3KOH}_{\text{(Nessler's reagent)}} + NH_3 \longrightarrow \underset{\substack{\text{(Iodide of Millon's base)} \\ \text{(yellow-brown)}}}{H_2NHgOHgI} + 7KI + 2H_2O$$
- It gives yellow precipitate of ammonium chloroplatinate with chloro-platinic acid.

  $$2NH_4Cl + H_2PtCl_6 \rightleftharpoons (NH_4)_2PtCl_6 + 2HCl$$

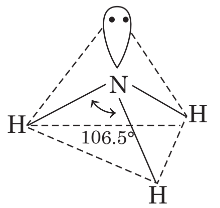
  Liquid ammonia is an excellent ionising solvent. It ionises as,

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

  In this solvent, alkali metals and a lesser extent Ca, Sr and Ba are dissolves and by giving deep blue solutions. These deep blue solutions are excellent reducing agents and are electrical conductor due to the presence of solvated electrons.

Structure of Ammonia

Ammonia is covalent molecule, in which three H-atoms are linked to N by single covalent bonds.



Pyramidal structure of NH_3

Uses

Ammonia is used

- for the manufacture of other reagents like HNO_3 (Ostwald's process), $NaHCO_3$ (Solvay process), $(NH_4)_2SO_4$, etc.
- as a cleansing agent for removing greese.
- as a refrigerant.
- for the synthesis of urea, an excellent fertilizer.

Example 2. *When ammonia reacts with a solution of* Cu^{2+}, *colour of solution becomes* ***(NCERT** Exemplar)*

(a) orange red (b) deep green

(c) deep blue (d) greenish yellow

Sol. (c) When ammonia (in aqueous solution as ammonium hydroxide) reacts with a solution of Cu^{2+}, a deep blue solution is obtained due to the formation of tetraamine copper (II) ion.

$$Cu^{2+}(aq) + 4NH_4OH(aq) \xrightarrow{\Delta} \underset{\substack{\text{Tetraamine copper}\\ \text{(II) ion}\\ \text{(deep blue solution)}}}{[Cu(NH_3)_4]^{2+}} + 4H_2O$$

Nitric Acid (HNO_3)

It is the hydrate form of N_2O_5. It is also known as ***aqua fortis*** and **spirit of niter**. It is a highly corrosive mineral acid.

Methods of Preparation

Some following methods can be employed to prepare nitric acid are

- In the **laboratory,** it is prepared by heating $NaNO_3$ or KNO_3 with conc. H_2SO_4. Reddish brown vapours of HNO_3 so produced and condensed in a water-cooled receiver.

  $$NaNO_3 + H_2SO_4(\text{conc.}) \longrightarrow NaHSO_4 + HNO_3$$

  The acid produced is yellow in colour due to the presence of NO_2 formed by the decomposition of HNO_3.

  $$4HNO_3 \xrightarrow{\Delta} 4NO_2\uparrow + 2H_2O + O_2\uparrow$$

  The acid is purified by redistillation and by passing a current of dry air or CO_2 through the warm acid.

- **On a large scale,** the acid is generally prepared by **Ostwald's process** which consists of the following steps

  ***Step* I** $NH_3 (N = -3)$ obtained by Haber's process is oxidised to NO (N = +2) by atmospheric O_2 (free from dust) in the presence of platinum-guaze catalyst electrically heated at 750 − 900° C

  $$4NH_3 + 5O_2 \xrightarrow[\text{Platinum-guaze}]{750\text{-}900^\circ C} 4NO + 6H_2O;$$

  $$(\Delta H = -\ 90.0 \text{ kJ})$$

  Since, the reaction is exothermic, heat generated in the reaction maintains the temperature for the catalyst.

  ***Step* II** NO produced as above is oxidised by atmospheric O_2 to NO_2 which is cooled to about 50°C and then absorbed in water (in the presence of air) to give HNO_3.

  $$2NO + O_2 \longrightarrow 2NO_2\uparrow$$

  $$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

  The usual concentrated nitric acid contains 98% HNO_3 and its specific gravity = 1.5.

Physical Properties

Some important physical properties of HNO_3 are as follows

- Pure HNO_3 is colourless fuming liquid of specific gravity 1.56 (at 0°C). It boils at 86°C and freezes to a colourless solid having melting point − 41.3° C. It is soluble in water in all proportions.
- It is highly corrosive in nature. It causes painful blisters when it comes in contact with skin.
- It is colourless but often gradually turns yellow. This is because HNO_3, when exposed to light, undergoes decomposition to form NO_2 which gets dissolved in HNO_3 and gives it yellow colour.

  $$4HNO_3 \longrightarrow 4NO_2\uparrow + O_2\uparrow + 2H_2O$$

  The yellow colour of the acid can be removed by warming it to 60-80°C and bubbling dry air through it.

Chemical Properties

HNO_3 is a strong acid and also a very strong oxidising agent. Its important chemical reactions are as follows

- At room temperature, the pure acid undergoes dissociation to give N_2O_4 and O_2.

  $$HNO_3 \longrightarrow N_2O_5 + H_2O$$

  $$N_2O_5 \rightleftharpoons N_2O_4 + \frac{1}{2}O_2\uparrow$$

  On heating, HNO_3 decomposes to give O_2 and brown fumes of NO_2.

  $$4HNO_3 \longrightarrow \underset{\text{(Brown fumes)}}{4NO_2\uparrow} + O_2\uparrow + 2H_2O$$

- HNO_3 being a very strong monobasic acid, reacts with basic oxides, carbonates, bicarbonates, sulphites and hydroxides, forming corresponding nitrates.

e.g. $CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$

$$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$$

- Being a strong acid, it is completely ionised in water as,
$$HNO_3 \longrightarrow H^+ + NO_3^-$$
- HNO_3 is a very strong oxidising agent, since it can easily give nascent oxygen both in the conc. and dil. forms.
$$2HNO_3 \longrightarrow H_2O + 2NO_2\uparrow + [O]$$
In these reactions, HNO_3 is reduced to NO_2, O_2, NH_4NO_3 (or NH_4^+ ions), N_2O, NO, N_2 or NH_2OH. Thus, the product obtained depend on the nature of the substance to be oxidised, concentration of HNO_3 and the temperature employed.

Non-metals and metalloids (e.g. C, Sn, P, As, Pb, S and I) are oxidised to their corresponding highest oxy-acids. But metals like Mg, Mn, Zn, Fe, Sn, Pb, Cu, Ag and Hg are oxidised to their corresponding nitrates.

Some examples of such type of reactions (i.e. the reactions in which HNO_3 acts as an oxidising agent) are given below.

I. **HNO_3 oxidises non-metals and metalloids to their oxyacids as**

(i) P is oxidised to H_3PO_4.

$$P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$$

This reaction takes place through the following steps

$$2P + \underset{(\text{From } HNO_3)}{5O} \longrightarrow P_2O_5$$

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

$$\overline{2P + 5O + 3H_2O \longrightarrow 2H_3PO_4}$$

(ii) Carbon is oxidised to H_2CO_3.

$$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + H_2O$$

(iii) Tin is oxidised to metastannic acid, H_2SnO_3

$$Sn + \text{Conc. } 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

(iv) P, As and Sb are oxidised to H_3PO_4 (phosphoric acid), H_3AsO_4 (arsenic acid) and H_3SbO_4 (antimonic acid) respectively

$$M + 5HNO_3 \longrightarrow H_3MO_4 + 5NO_2 + H_2O \quad (M = \text{P, As, Sb})$$

(v) Sulphur is oxidised to H_2SO_4.

$$S + \underset{(\text{Conc. and hot})}{6HNO_3} \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

(vi) Iodine is oxidised to iodic acid, HIO_3.

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

II. **It converts, into reactive metals** (present above hydrogen in electrochemical series) to **metal nitrates**. Here, HNO_3 is reduced to H_2 (in case of Mg and Mn) or to NH_4NO_3, NO_2 , NO and NO_2 (with other metals). Actually in later case following two steps are involved.

***Step* 1** The metal (M) on being treated with HNO_3 is converted into metallic nitrate and nascent hydrogen is produced as,

$$M + 2HNO_3 \longrightarrow M(NO_3)_2 + 2[H]$$

***Step* 2** Nascent hydrogen, produced as above, reduces HNO_3 to NH_4NO_3 (or NH_4^+ ion), N_2O, NO or NO_2

$$2HNO_3 + 8[H] \longrightarrow NH_4NO_3 + 3H_2O$$

$$2HNO_3 + 8[H] \longrightarrow N_2O + 5H_2O$$

$$HNO_3 + [H] \longrightarrow NO_2 + H_2O$$

$$HNO_3 + 3[H] \longrightarrow NO + 2H_2O$$

Some important examples of such reactions are as follows

(a) Zinc

(i) Zn reacts with very dil. HNO_3 (6%) and is oxidised to $Zn(NO_3)_2$. Here, HNO_3 is reduced to NH_4NO_3 as,

$$4Zn + \underset{(\text{Very dilute})}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

(ii) Zn reacts with cold and dil. HNO_3 (20%) and is oxidised to $Zn(NO_3)_2$. Here, HNO_3 is reduced to N_2O as,

$$4Zn + \underset{\substack{(\text{Cold and} \\ \text{dilute}) (20\ \%)}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

(iii) Zn reacts with cold and conc. HNO_3 (70%) and is oxidised to $Zn(NO_3)_2$. Here, HNO_3 is reduced to NO_2 as ,

$$Zn + \underset{(\text{Cold and conc.})}{4HNO_3} \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

(iv) Zn reacts with cold and moderately conc. HNO_3 (50%) and is oxidised to $Zn(NO_3)_2$. Here, HNO_3 is reduced to NO_2 as,

$$3Zn + \underset{[50\ \%]}{8HNO_3} \longrightarrow 3Zn(NO_3)_2 + 4H_2O + 2NO$$

(b) Iron

(i) Fe reacts with very dil. HNO_3 and is oxidised to $Fe(NO_3)_2$. Here, HNO_3 is reduced to NH_4NO_3 as

$$4Fe + \underset{(\text{Very dilute})}{10HNO_3} \longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

(ii) Fe is oxidised to $Fe(NO_3)_2$ by dil. HNO_3 and HNO_3 is reduced to N_2O as

$$4Fe + \underset{(\text{Dilute})}{10HNO_3} \longrightarrow 4Fe(NO_3)_2 + N_2O + 5H_2O$$

(iii) Fe reacts with cold and conc. HNO_3 and is oxidised to $Fe(NO_3)_3$. Here, HNO_3 is reduced to NO_2 as

$$Fe + \underset{(\text{Cold and conc.})}{6HNO_3} \longrightarrow Fe(NO_3)_3 + 3NO_2 + 3H_2O$$

(iv) With hot and conc. HNO_3, Fe is oxidised to $Fe(NO_3)_3$ and HNO_3 is reduced to NO as

$$Fe + \underset{(\text{Hot and conc.})}{4HNO_3} \longrightarrow Fe(NO_3)_3 + 2H_2O + NO$$

III. **HNO_3 also oxidises less reactive metals** (present below hydrogen in the electrochemical series) Examples of such metals are Cu, Ag and Hg. These metals when treated with HNO_3 are oxidised to their corresponding nitrates.

Here, HNO_3 is reduced to NO_2, NO, NO_2 or N_2 depending on the nature of the metal, concentration of the acid and temperature employed. e.g.

$$M + 2HNO_3 \longrightarrow M(NO_3)_2 + N_2O,\ NO,\ NO_2 \text{ or } N_2 + H_2O$$

$(M = \text{Cu, Ag, Hg})$

These reactions, are involve in the following two steps

(i) Since, Cu, Ag and Hg lie below hydrogen in the electrochemical series, they are not able to liberate hydrogen from HNO_3 as Zn, Fe, Sn and Pb can do. In case of these metals HNO_3 acts as an oxidising agent, i.e. HNO_3 gives nascent oxygen and is itself reduced to N_2O, NO, NO_2 or N_2.

$$2HNO_3 \longrightarrow N_2O + H_2O + 4[O]$$
$$2HNO_3 \longrightarrow 2NO + H_2O + 3[O]$$
$$2HNO_3 \longrightarrow 2NO_2 + H_2O + [O]$$
$$2HNO_3 \longrightarrow N_2 + H_2O + 5[O]$$

(ii) Nascent oxygen obtained as above, oxidises the metal to its oxide which on reaction with HNO_3, gives metallic nitrate.

$$M + [O] \longrightarrow MO \text{ (metallic oxide)}$$
$$MO + 2HNO_3 \longrightarrow M(NO_3)_2 + H_2O$$

Some important examples of such reactions are

(a) Reaction with Copper

(i) With cold and dil. HNO_3 evolves N_2O as,

$$\underset{(\text{Cold and dil.})}{10HNO_3} + 4Cu \longrightarrow N_2O\uparrow + 5H_2O + \underset{(\text{Copper nitrate})}{4Cu(NO_3)_2}$$

(ii) With cold and moderately conc. HNO_3 evolves NO as,

$$3Cu + \underset{\substack{(\text{Cold and}\\ \text{moderately conc.})}}{8HNO_3} \longrightarrow \underset{(\text{Copper nitrate})}{3Cu(NO_3)_2\uparrow} + 2NO\uparrow + 4H_2O$$

(iii) With cold and conc. HNO_3 evolves NO_2 as,

$$Cu + \underset{(\text{Cold and conc.})}{4HNO_3} \longrightarrow Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

(iv) With hot and conc. HNO_3 evolves N_2 as,

$$\underset{(\text{Cold and conc.})}{12HNO_3} + 5Cu \longrightarrow N_2\uparrow + 6H_2O + 5Cu(NO_3)_2$$

(b) Reaction with Silver

(i) With dil HNO_3, $AgNO_3$ is obtained and NO is evolved as,

$$3Ag + \underset{(\text{Dilute})}{4HNO_3} \longrightarrow \underset{\text{Silver nitrate}}{3AgNO_3} + NO\uparrow + 2H_2O$$

(ii) With conc. HNO_3, NO_2 is evolved as,

$$Ag + \underset{(\text{Conc.})}{2HNO_3} \longrightarrow AgNO_3 + NO_2\uparrow + H_2O$$

(c) Reaction with Mercury

(i) With dil HNO_3, $Hg_2(NO_3)_2$ is formed and NO is evolved as,

$$6Hg + \underset{(\text{Dilute})}{8HNO_3} \longrightarrow \underset{\text{Mercurous nitrate}}{3Hg_2(NO_3)_2} + 2NO\uparrow + 4H_2O$$

(ii) With conc. HNO_3, mercuric nitrate, $Hg(NO_3)_2$ is obtained and NO_2 is evolved as,

$$Hg + \underset{(\text{Conc.})}{4HNO_3} \longrightarrow Hg(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

IV. **HNO_3** (both dil. and conc.), It can also oxidise many compounds). In these reactions, dil. HNO_3 reduced to NO while conc. HNO_3 is reduced to NO_2. When HNO_3 oxidises $SnCl_2$ in presence of HCl, it is reduced to NH_2OH.

Some important examples of such reactions with HNO_3 are as follows

(i) **I_2 is liberated from KI solution** $(I^- \longrightarrow I_2^0)$

$$\text{e.g. } \underset{(\text{Dil.})}{8HNO_3} + 6KI \longrightarrow 2NO\uparrow + 4H_2O + 6KNO_3 + 3I_2$$

(ii) **CuS is oxidised to sulphur** $(S^{2-} \longrightarrow S)$

$$\text{e.g. } \underset{(\text{Dil.})}{8HNO_3} + 3CuS \longrightarrow 2NO\uparrow + 4H_2O + 3S + 3Cu(NO_3)_2$$

(iii) **H_2S is oxidised to sulphur** (by both dil. and conc. HNO_3 $(S^{2-} \longrightarrow S)$

$$\underset{(\text{Dil.})}{2HNO_3} + 3H_2S \longrightarrow 2NO\uparrow + 4H_2O + 3S$$

$$\underset{(\text{Conc.})}{2HNO_3} + H_2S \longrightarrow 2NO_2\uparrow + S + 2H_2O$$

(iv) **FeS is oxidised to $FeSO_4$** $(S^{2-} \longrightarrow SO_4^{2-})$

$$FeS + \underset{(\text{Conc.})}{8HNO_3} \longrightarrow FeSO_4 + 8NO_2\uparrow + 4H_2O$$

(v) **SO_2 is oxidised to H_2SO_4** (by both dil. and conc. HNO_3) $(SO_2 \longrightarrow SO_4^{2-})$

$$SO_2 + \underset{(\text{Conc.})}{2HNO_3} \longrightarrow H_2SO_4 + 2NO_2\uparrow$$

$$\underset{(\text{Dil.})}{2HNO_3} + 2H_2O + 3SO_2 \longrightarrow 2NO\uparrow + 3H_2SO_4$$

(vi) **Solution of $FeSO_4$ is oxidised to $Fe_2(SO_4)_3$** (by both dil. and conc. HNO_3) in the presence of H_2SO_4 $(Fe^{2+} \longrightarrow Fe^{3+})$

$$\underset{\substack{\text{Green}\\ \text{solution}}}{6FeSO_4} + 3H_2SO_4 + \underset{\text{Dil.}}{2HNO_3} \longrightarrow \underset{\substack{\text{Yellow}\\ \text{solution}}}{3Fe_2(SO_4)_3} + 2NO\uparrow + 4H_2O$$

$$2FeSO_4 + \underset{\text{Conc.}}{2HNO_3} + H_2SO_4 \longrightarrow Fe_2(SO_4)_3\uparrow + 2NO_2 + 2H_2O$$

(vii) **HBr and HI are oxidised to Br_2 and I_2 respectively**

$$(Br^- \longrightarrow Br_2,\ I^- \longrightarrow I_2)$$

$$\underset{\text{(Dil.)}}{2HNO_3} + 6HX \longrightarrow 2NO\uparrow + 4H_2O + 3X_2$$

$$\underset{\text{(Conc.)}}{2HNO_3} + 2HX \longrightarrow X_2 + 2NO_2 + 2H_2O$$

(viii) **As_2O_3 is oxidised to H_3AsO_4** ($As^{3+} \longrightarrow AsO_4^{3-}$)

$$2HNO_3 + As_2O_3 + H_2O \longrightarrow 4NO_2\uparrow + 2H_3AsO_4$$

(ix) **Cane sugar** (sucrose), $C_{12}H_{22}O_{11}$ is oxidised to oxalic acid, $H_2C_2O_4$ by conc. HNO_3

$$\underset{\text{(Conc.)}}{36HNO_3} + C_{12}H_{22}O_{11} \longrightarrow 23H_2O + 36NO_2 + 6H_2C_2O_4$$

(x) **Toluene** ($C_6H_5CH_3$) is oxidised to benzoic acid (C_6H_5COOH) by dil. HNO_3

$$\underset{\text{(Dil)}}{2HNO_3} + C_6H_5CH_3 \longrightarrow 2NO\uparrow + 2H_2O + C_6H_5COOH$$

(xi) **$SnCl_2$ is oxidised to $SnCl_4$ in presence of HCl**

$$(Sn^{2+} \longrightarrow Sn^{4+})$$

$$3SnCl_2 + 6HCl + HNO_3 \longrightarrow 2H_2O + 3SnCl_4 + NH_2OH$$

V. **Metals like Cr, Ni, Al, Fe become *passive*** (*inert*) When treated with conc HNO_3. For example, Fe displaces Cu from $CuSO_4$ solution but this property of Fe is lost when it is dipped in slightly conc HNO_3. This is because, a thin oxide (iron oxide) layer is deposited over the metal surface, when it is treated with conc HNO_3. This layer makes the iron passive or inert.

VI. **When 1st part of conc.** HNO_3 It is mixed with 3rd parts of conc. HCl, we get ***aqua-regia***. *Aqua-regia* produces nascent chlorine (Cl) along with nitrosyl chloride (NOCl) as,

$$HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2[Cl]$$

Due to production of nascent chlorine, *aqua-regia* is very active. Noble metals like Au and Pt, which are not acted upon by HNO_3 get dissolved in aqua-regia due to the formation of soluble complexes namely $H[AuCl_4]$ and $H_2[PtCl_6]$ respectively. e.g.

$$2Au + 3HNO_3 + 11HCl \longrightarrow H[AuCl_4] + 2NOCl + 6H_2O$$

VII. **Conc. HNO_3** It attacks on many aromatic organic compounds (e.g. C_6H_6, $C_6H_5CH_3$, C_6H_5OH etc.) in the presence of conc. H_2SO_4. In these reactions it substitutes one or more H-atoms by nitro group, producing nitro compounds (nitration). Here, H_2SO_4 absorbs water, liberated in the reaction and also produces nitronium ion (NO_2^+) by reacting with HNO_3. This NO_2^+ ion makes the nitration of aromatic compounds.

e.g. $$HNO_3 + \underset{\text{Benzene}}{C_6H_6} \xrightarrow{H_2SO_4} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$

VIII. With protein, HNO_3 gives yellow coloured xanthoprotein. That's why it produces yellow stain on skin and wood.

Uses

Nitric acid is used

- as a laboratory reagent and making aqua-regia.
- as strong oxidising agent.
- to clean noble metals such as Au, Ag, Pt.
- to make explosive materials such as TNT, picric acid, gun cotton etc.
- in making of colour, perfume, artificial fibre etc.
- for the manufacture of fertilizers.

Example 3. *Iodine reacts with concentrated* HNO_3 *to yield Y along with other products. The oxidation state of iodine in Y, is* ***(JEE Main 2019)***

(a) 1 (b) 3 (c) 7 (d) 5

Sol. (*d*) Iodine reacts with concentrated HNO_3 to yield HIO_3 along with NO_2 and H_2O. The reaction involved in as follows

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

The oxidation state of 'I' in HIO_3 is + 5 as calculated below

$$1 + x + 3(-2) = 0\ ,\ \ x - 5 = 0\ ,\ x = +5$$

Oxides of Nitrogen

Nitrogen forms several oxides. The preparation and properties of these oxides can be summarised as,

Preparation and Properties of Various Oxides of Nitrogen

Formula	Name	Preparation	Properties
N_2O	Nitrous oxide or laughing gas	$NH_4NO_3 \rightarrow N_2O + 2H_2O$	Colourless gas, rather unreactive.
NO	Nitrogen monoxide (Nitric oxide)	$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$	Colourless gas, reactive, paramagnetic.
NO_2	Nitrogen dioxide	$Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$	Brown gas, reactive, paramagnetic.
N_2O_3	Dinitrogen trioxide or nitrous anhydride	$NO + NO_2 \rightarrow N_2O_3$	Dark blue in the liquid or solid state, unstable in the gas phase.
N_2O_4	Dinitrogen tetroxide (mixed anhydride of N_2O and NO)	$2NO_2 \rightleftharpoons N_2O_4$	Colourless, exists in equilibrium with NO_2 both in the gaseous and liquid state.
N_2O_5	Dinitrogen pentoxide	$2HNO_3 + P_2O_5 \rightarrow 2HPO_3 + N_2O_5$	Unstable as gas; in the solid state exists as $[NO_2]^+[NO_3]^-$.

Some other Properties of Oxides of Nitrogen

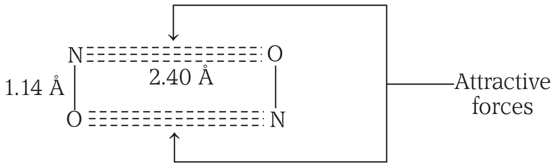
(i) **N_2O** (nitrous oxide) is a colourless gas, fairly soluble in cold water but practically insoluble in hot water. It is easily liquifiable at room temperature by applying pressure (critical temperature 35°C). It has a faint odour. When inhaled in moderate quantities, it produces hysterical laughter (that's why called

laughing gas). Its higher quantity doses may make a person unconcious.

Chemically, it is relatively inert and does not reacts with halogens, alkali metals and even ozone at room temperature. However, it decomposes to N_2 and O_2 at 600°C and form metal azides with molten alkali metals as,

$$NaNH_2 + N_2O \xrightarrow{200^\circ C} NaN_3 + H_2O$$

(ii) **NO** (nitric oxide) is an odd electron molecule, due to the presence of an unpaired electron. It undergoes partial dimerisation in liquid state and exists as a dimer in solid state as,



It readily reacts with oxygen to give brown fumes of NO_2 as,

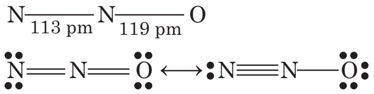
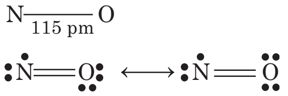
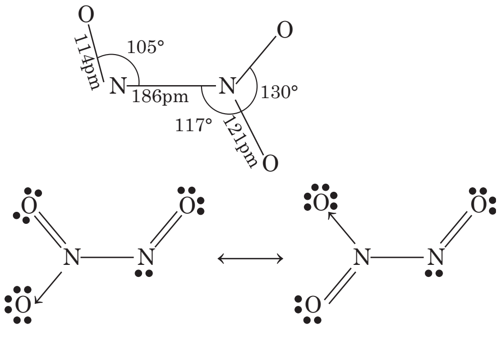
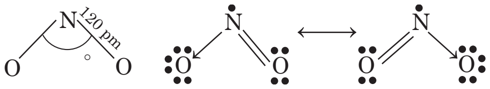
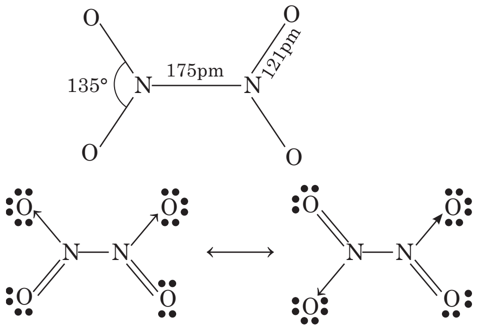
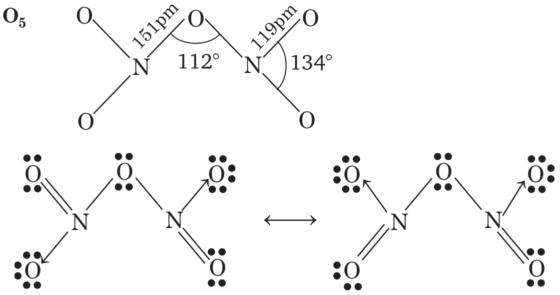
$$2NO(g) + O_2(g) \longrightarrow \underset{\text{Brown fumes}}{2NO_2(g)}$$

(iii) **NO_2** (nitrogen dioxide) is also an odd electron molecule. In gaseous phase, exists in equilibrium with dimer N_2O_4 which is colourless. e.g.

$$\underset{\substack{\text{Brown}\\\text{(paramagnetic)}}}{2NO_2(g)} \rightleftharpoons \underset{\substack{\text{Colourless}\\\text{(diamagnetic)}}}{N_2O_4(g)}$$

(iv) **N_2O_5** (dinitrogen pentaoxides) is the strongest acid among all the pentoxides and a very strong oxidising agent.

Structure of Different Oxide of Nitrogen

(i)	**N_2O**	
(ii)	**NO**	
(iii)	**N_2O_3**	
(iv)	**NO_2**	
(v)	**N_2O_4**	
(vi)	**N_2O_5**	

Example 4. The correct order of the oxidation states of nitrogen in NO, NO_2, N_2O and N_2O_3 is ***(JEE Main 2019)***

(a) $NO_2 < NO < N_2O_3 < N_2O$
(b) $N_2O < NO < N_2O_3 < NO_2$
(c) $O_2 < N_2O_3 < NO < N_2O$
(d) $N_2O < N_2O_3 < NO < NO_2$

Sol. (*b*) Oxidation state of N in N_2O is $2(x) - 2 = 0; \ x = +\frac{2}{2} = +1$

Oxidation state of N in NO is $x - 2 = 0; \ x = +2$

Oxidation state of N in N_2O_3 is $2x + 3(-2) = 0; \ x = \frac{6}{2} = 3$

Oxidation state of N in NO_2 is
$x + 2(-2) = 0; \ x - 4 = 0; \ x = +4$

The correct increasing order of oxidation state of nitrogen for nitrogen oxides is

$$\overset{+1}{N_2}O < \overset{+2}{N}O < \overset{+3}{N_2}O_3 < \overset{+4}{N}O_2$$

Phosphorus

It is the most reactive element in this group and found in the combined state as phosphates in the rocks and in the soil. It is an essential constituent of teeth, bones, blood and nervous tissues. Its important minerals are phosphorite $[Ca_3(PO_4)_2]$, chlorapatite $[3Ca_3(PO_4)_2.CaCl_2]$, fluorapatite or apatite $[3Ca_3(PO_4)_2.CaF_2]$. Its yellow form is always stored in water.

Methods of Preparation

Some following methods are employed to prepare phosphorus are

(i) It is prepared by using phosphorite (as main material). The reactions are involved

$$\underset{\text{Phosphorite}}{Ca_3(PO_4)_2} + 3H_2SO_4 \longrightarrow \underset{\text{Orthophosphoric acid}}{2H_3PO_4} + 3CaSO_4$$

$$H_3PO_4 \longrightarrow \underset{\text{Metaphosphoric acid}}{HPO_3} + H_2O$$

$$4HPO_3 + 10C \longrightarrow P_4 + 10CO + 2H_2O$$

(ii) Phosphorus is obtained from direct reduction of mineral phosphorite by carbon in presence of silica.

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \xrightarrow{1400\text{-}1500^\circ C} 6CaSiO_3 + P_4 + 10\ CO$$

(iii) It is manufactured by heating bone ash or phosphorite with sand (SiO_2) and coke (C) in an electric furnance as

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow 6CaSiO_3 + 10CO + P_4$$

Allotropes of Phosphorus

Phosphorus exists in following allotropic forms, which are inter convertible process.

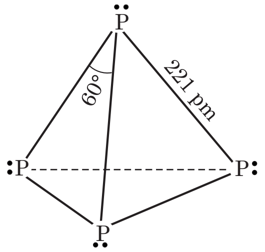
1. **White Phosphorus**

$$2Ca_3(PO_4)_2 + 6\ SiO_2 \xrightarrow{1773\ K} 6CaSiO_3 + P_4O_{10}$$

$$P_4O_{10} + 10\ C \xrightarrow{1773\ K} P_4 + 10CO$$

Structure It exist in tetrahedra tetraatomic discrete P_4 unit in which each P-atom is sp^3-hybridised and linked to each of three atoms by covalent bond.

Its P—P—P angle is 60° and show high angular strain. That's why it is highly reactive.



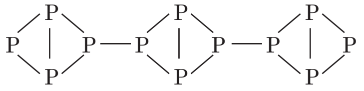
Tetrahedral phosphorus molecule

Properties

- It is a waxy transluscent solid, readily soluble in CS_2.
- Below 800° C, it exists as P_4 while above 800° C, it dissociates to P_2.
- It melts at 44.1° C and boils at 280° C.
- Its ignition temperature is very low.
- When exposed to air, it undergoes oxidation which gradually raises its temperature. When temperature exceeds 30° C, it catches fire That's why, **it is always kept in water.**
- Being extremely poisonous, it proves fatal if taken internally.
- P glows in dark on account of its slow oxidation (phosphorescence).
- It is readily soluble in turpentine oil and ether.

2. **Red Phosphorus**

- **Preparation** It is obtained by heating white P_4 at 573 K in an inert atmospher for many days.
- **Structure** Its structure consist of chains of P_4 tetrahedra linked together through covalent bond as shown below



P_4 chain structure

Properties

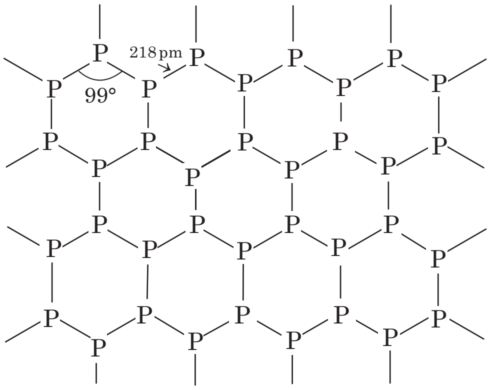
- It is non-poisonous, hard crystalline, odourless solid with grey lustre.
- It is stable at room temperature.
- Its ignition temperature is 543 K which is greater than that of white phosphorus.
- It is converted into red phosphorus by sublimation method.
- Its density is higher than white phosphorus.
- Due to presence of polymeric chain it is less reative than white phosphorus. However, reacts with halogen, sulphur alkali metals only when heated.
- It can be separated from red phosphorus (if mixed) with the help of caustic alkalies as it does not react with it.

3. **Metallic or α-black P** It is a very stable allotrope of P and does not oxidise in air unless heated very strongly. It does not conduct electricity.

Preparation White phosphorus $\xrightarrow[4000\text{-}12000\ \text{atm pressure}]{473\ K}$ β-black phosphorus

Structure It is the only form of phosphorus whose structure is definitely known. It is crystalline in nature and consists of corrugated sheets.

Here, each P-atom is covalently bonded to other three neighbouring atoms as shown in figure below



Layered structure of β-black phosphorus

The atoms within a layer are more strongly bound than the atoms in adjacent layers. This gives rise to flaky crystals which resemble to graphite.

Properties

- Its melting point is 587° C and specific gravity is 2.69.
- It does not burn in air even up to 400° C.
- It is good conductor of electricity just like graphite.
- It is stable allotrope and does not oxidise in air until heated very strongly.

Chemical Properties of Phosphorus

White phosphorus is more reactive than other varieties and exhibits the following reactions

- It burns in air forming its trioxide and pentoxide.
- White phosphorus combines with hot solutions of KOH or NaOH giving phosphene.

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$$

  However, red phosphorus does not react with dilute alkalies. Thus, this property is helpful in separating red phosphorus form white phosphorus.
- Phosphorus forms trihalides and pentahalides with halogens. White phosphorus reacts more vigorously than red phosphorus.
- Phosphorus combines to S with explosive violence forming a number of sulphides, e.g. P_2S_3, P_2S_5, P_4S_3 and P_4S_7 etc.
- Phosphorus combines with metals to form phosphides as

$$6Mg + P_4 \longrightarrow 2Mg_3P_2$$
$$6Ca + P_4 \longrightarrow 2Ca_3P_2$$

- Since, white phosphorus can be easily oxidised, it acts as strong reducing agent. It reduces HNO_3 to nitrogen dioxide and H_2SO_4 to SO_2. It also reduces solutions of Cu, Ag and Au salts to the corresponding metals, e.g.

$$P_4 + 8CuSO_4 + 14H_2O \longrightarrow 8Cu + 8H_2SO_4 + 2H_3PO_4 + 2H_3PO_3$$

Uses

Uses of phosphorus are

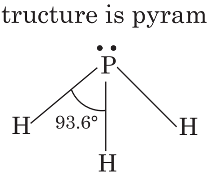
- Red phosphorus is used in match box industry.
- Radioactive phosphorus is used in the treatment of leukemia and other blood disorders.
- Yellow phosphhorus and zinc phosphide are used as a rat poison.

Some compounds of phosphorus are

Phosphine (PH_3)

It is discovered by **Gembre** in 1783.

In phosphine, three H-atoms are attached with P-atom through covalent bonds and P has one lone pair of electrons, thus, its structure is pyramidal like NH_3.



Structure of PH_3

Methods of Preparation

Some following methods are used to prepare PH_3 (phosphine) are

- It is generally prepared by boiling the white phosphorus with a concentrated solution of NaOH in inert atmosphere of CO_2, oil gas or hydrogen as

$$\underset{\text{White}}{P_4} + \underset{\text{Conc.}}{3NaOH} + 3H_2O \xrightarrow[\text{of } CO_2]{\text{Inert atmosphere}} 3NaH_2PO_2 + PH_3\uparrow$$

  It is necessary to exclude air from the apparatus because, although pure PH_3 will not burn unless ignited, it is often accompanied with P_2H_4 and H_2 which are spontaneously flammable.

$$2P + 2NaOH + 2H_2O \longrightarrow 2NaH_2PO_2 + H_2\uparrow$$
$$6P + NaOH + 4H_2O \longrightarrow 4NaH_2PO_2 + P_2H_4$$

  Because of this reaction, phosphine is used in making **Holme's signals.**

  (Pure phosphine is obtained by using alcoholic KOH in place of aqueous NaOH solution).
- It can also be obtained by heating phosphorus acid.

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

- Treatment of phosphonium iodide with 30% KOH solution also gives phosphine.

$$PH_4I + KOH \longrightarrow KI + H_2O + PH_3$$

  The evolved gas is passed through HCl (which decomposes P_2H_4) and then through NaOH (where HI is absorbed).
- It is also obtained by the hydrolysis of Ca_3P_2 with water or dilute HCl.

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

Physical Properties

It is colourless, highly reactive and extremely toxic gas with a slight smell of garlic or rotten fish. It liquefies at –89°C and solidifies at –134°C.

Chemical Properties

Some important chemical properties exhibited by phosphine are as follows

- PH_3, unlike NH_3, is not very soluble in water. Its aqueous solution is neutral. It is more soluble in non-polar solvent like CS_2 and other organic solvents.
- When heated in contact of air to 440°C or when electric sparks are passed, phosphine decompose to gives red phosphorus and hydrogen gas as,

$$4PH_3 \longrightarrow P_4 + 6H_2\uparrow$$

  A pure sample of phosphine is not spontaneously inflammmable. It burns in air or oxygen when heated at 150°C. To give white smoke (vortex rings). This is because of the formation of vortex ring of P_2O_5 due to impurity of P_2H_4 (diphosphine).

$$2PH_3 + 4O_2 \xrightarrow{\Delta} P_2O_5 + 3H_2O$$

- In contact with nitric acid, phosphine begins to burn.

$$2PH_3 + 16HNO_3 \longrightarrow P_2O_5 + 16NO_2 + 11H_2O$$

- It forms addition compounds with anhydrous $AlCl_3$ and $SnCl_4$.

$$AlCl_3 + 2PH_3 \longrightarrow AlCl_3 \cdot 2PH_3$$

$$SnCl_4 + 2PH_3 \longrightarrow SnCl_4 \cdot 2PH_3$$

- Phosphine gives a black precipitate of cupric phosphide, when passed through $CuSO_4$ solution.

$$3CuSO_4 + 2PH_3 \longrightarrow \underset{\text{(Black)}}{Cu_3P_2} + 3H_2SO_4$$

- It also gives a similar reaction with silver nitrate solution.

$$3AgNO_3 + PH_3 \longrightarrow Ag_3P + 3HNO_3$$

- The mixture of PH_3 and N_2O or PH_3 and NO explodes in the presence of electric spark.

$$PH_3 + 4N_2O \xrightarrow{\text{electric spark}} H_3PO_4 + 4N_2\uparrow$$

- PH_3 is a better reducing agent than NH_3. It reduces
  (i) Ag^+ to Ag metal as,

$$6Ag^+ + PH_3 + 3H_2O \longrightarrow H_3PO_3 + 6Ag\downarrow + 6H^+$$

(ii) Cu^{2+} to Cu metal as,

$$4Cu^{2+} + PH_3 + 4H_2O \longrightarrow H_3PO_4 + 4Cu\downarrow + 8H^+$$

- In liquid NH_3, phosphine dissolves to give $NH_4^+PH_2^-$.

$$\underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{PH_3} \longrightarrow NH_4^+PH_2^-$$

Uses

PH_3 is used

- for making smoke screens.
- for making metallic phosphides.
- for making **Holme's signals**.

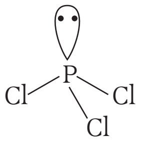
Working of Holme's Signals

For Holme's signals a mixture of calcium carbide, CaC_2 and calcium phosphide, Ca_3P_2 is placed in metallic containers. Two holes are made and the container is thrown into the sea. Water enters in the container and produces acetylene and phosphine.

The gaseous mixture catches fire spontaneously because of the presence of P_2H_4. The acetylene gives a bright luminous flame which serves as a signal to the approaching ship.

2. Phosphorus Trichloride, PCl_3

Its structure is similar to ammonia, i.e. it has pyramidal geometry.



PCl_3 pyramidal geometry

Method of Preparation

It is obtained when dry Cl_2 is passed over red or white phosphorus heated gently in a retort over a water bath.

$$P_4 + \underset{\text{(Dry)}}{6Cl_2} \xrightarrow{\text{Heated-water bath}} 4PCl_3$$

Physical and Chemical Properties

Some important properties of PCl_3 are as follows

- It is a low boiling liquid (b.p. 74°C) with a pungent odour and fumes in moist air.
- It violently hydrolysed by water as,

$$PCl_3 + 3H_2O \longrightarrow 3HCl + H_3PO_3$$

- It reacts with chlorine and sulphur chloride as,

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

$$3PCl_3 + SCl_2 \longrightarrow PCl_5 + 2PSCl_3$$

- It reacts with oxygen and SO_3 as,

$$2PCl_3 + O_2 \longrightarrow 2POCl_3$$

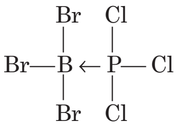
$$3PCl_3 + SO_3 \longrightarrow POCl_3 + SO_2$$

- It gives many substitution reactions as,

$$PCl_3 + 3AgCN \longrightarrow P(CN)_3 + 3AgCl$$

$$PCl_3 \xrightarrow{PF_3} PCl_2F + PClF_3$$

- It forms adduct with BBr_3 as,



$$PCl_3 + BBr_3 \longrightarrow Br{-}\overset{Br}{\underset{Br}{B}} \leftarrow \overset{Cl}{\underset{Cl}{P}}{-}Cl$$

- It acts as reducing agent and reduces SO_2Cl_2 and SO_3 to SO_2 and itself gets oxidised to PCl_5 or $POCl_3$. It also reduces $SOCl_2$ and SO_2Cl_2 as :

$$PCl_3 + SO_2Cl_2 \longrightarrow PCl_5 + SO_2\uparrow$$

$$3PCl_3 + SOCl_2 \longrightarrow POCl_3 + PSCl_3 + PCl_5$$

- It reacts with finely divided metals when hot as

$$12Ag + 4PCl_3 \longrightarrow 12AgCl + P_4$$

- It reacts with concentrated H_2SO_4 forming chloro-sulphonic acid as,

$$\underset{\text{Conc.}}{4H_2SO_4} + 2PCl_3 \longrightarrow \underset{\substack{\text{Chloro-sulphonic}\\ \text{acid}}}{2HSO_3Cl} + P_2O_5 + 2SO_2 + 4HCl + H_2O$$

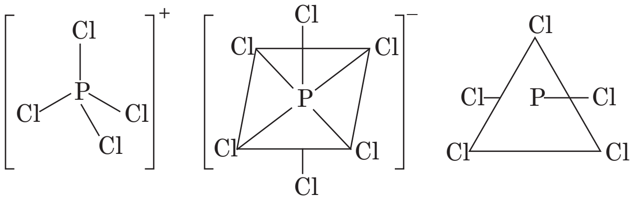
- It reacts with organic compounds containing hydroxyl group to give H_3PO_3.

$$\underset{\text{Ethyl alcohol}}{3C_2H_5OH} + PCl_3 \longrightarrow \underset{\text{Ethyl chloride}}{3C_2H_5Cl} + H_3PO_3$$

$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 \longrightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + H_3PO_3$$

3. Phosphorus Pentachloride, PCl_5

X-ray studies have revealed that solid PCl_5 consists of ionic lattices, i.e. tetrahedral $[PCl_4]^+$ cations and octahedral $[PCl_6]^-$ anions. In vapour state, it has trigonal bipyramidal shape in which P has sp^3d-hybridisation.



(a) $[PCl_4]^+$ (b) $[PCl_6]^-$ (c) PCl_5 in vapour state

Structure of PCl_5 in solid and vapour phase

Method of Preparation

It is prepared either by passing dry Cl_2 gas (in excess) over PCl_3 or by the action of SO_2Cl_2 on P_4 or PCl_3.

$$PCl_3 + \underset{\text{(Dry)}}{Cl_2} \longrightarrow PCl_5$$

$$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$$

Physical and Chemical Properties

Some important properties of PCl_5 are as follows

- It is yellowish white crystalline compound with a sharp odour. Its m.p. is – 45°C (under pressure) and sublimation temperature is 160°C.
- It have the ability to dissociate as

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2\uparrow$$

- It is violently hydrolysed by water as

$$PCl_5 + H_2O \xrightarrow{\text{Insufficient water}} POCl_3 + 2HCl$$

$$PCl_5 + 4H_2O \xrightarrow{\text{Excess of water}} H_3PO_4 + 5HCl$$

- It reacts with compounds containing —OH group as

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

$$H_2SO_4 + PCl_5 \longrightarrow \underset{\substack{\text{Sulphuryl}\\\text{chloride}}}{SO_2Cl_2} + 2POCl_3 + HCl$$

- It reacts with P_4O_{10} as

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

- It reacts with ammonium chloride as

$$nPCl_5 + nNH_4Cl \xrightarrow{150°C} (NPCl_2)_n + 4nHCl$$

- It reacts with Cl^- acceptors as

$$PCl_5 + BCl_3 \longrightarrow [PCl_4]^+[BCl_4]^-$$

- With hydrogen it forms PCl_3 as

$$PCl_5 + H_2 \longrightarrow PCl_3 + 2HCl$$

- It reacts with KF as

$$PCl_5 + 6KF \longrightarrow KPF_6 + 5KCl$$

Uses

PCl_5 is used

- as chlorinating agent in organic chemistry.
- in parmaceutical industry for manufacturing penicillin.
- to produce acid chloride.
- as catalyst in many reactions.

Oxides of Phosphorus

Phosphorus trioxide exists as a dimer and is formulated as P_4O_6.

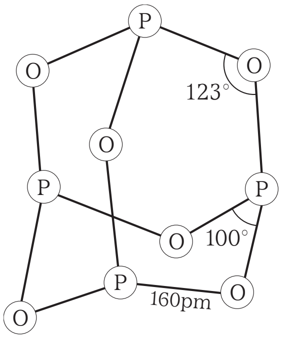
When white phosphorus is burnt in the limited supply of air both P_4O_6. and P_4O_{10} are formed. The vapour of the mixture of oxides are passed through a condensor in which water at 50-60°C is circulated, P_4O_{10} being solid at 60°C separates out easily.

P_4O_{10} is obtained by burning phosphorus in a free supply of air or oxygen. The pentoxide formed is purified further by sublimation at 360°C.

Properties and Uses

Among the various pentoxides, P_2O_5 has the strongest affinity for water. It can extract water from several inorganic and organic compounds, hence it acts as a strong **dehydrating agent**. It dehydrates H_2SO_4 to SO_3, HNO_3 to N_2O_5, **cellulose** to **carbon** and **amides** to **nitriles.**

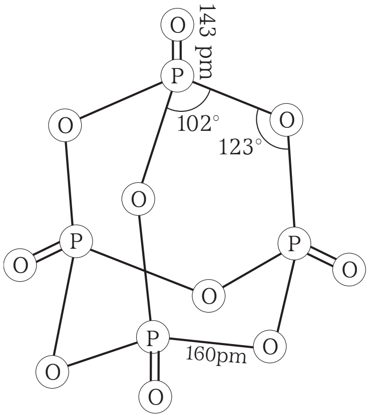
The tetrahedral structure of P_4O_6 is



Structure of P_4O_6

This structure has been confirmed by X-ray diffraction data. The oxides As_4O_6, Sb_4O_6 also have tetrahedral structures.

The structure assigned to P_4O_{10} molecule is



Structure of P_4O_{10}

Oxyacids of Phosphorus

The oxyacids of phosphorus can be grouped into following series are given below

- Phosphorous acid series which contains following acids
  - (i) Hypophosphorus acid, H_3PO_2
  - (ii) Phosphorus acid, or orthophosphorus acid, H_3PO_3
  - (iii) Pyrophosphorus acid, $H_4P_2O_2$
  - (iv) Metaphosphorus acid, HPO_2
- Phosphoric acid series, which contains following acids
  - (i) Hypophosphoric acid, $H_4P_2O_6$
  - (ii) Pyrophosphoric acid, $H_4P_2O_5$
- Polyphosphoric acid series with general formula $H_{n-2}\,P_nO_{3n+1}$
  - (i) Diphosphoric acid or pyrophosphoric acid, $H_4P_2O_7$
  - (ii) Triphosphoric acid, $H_5P_3O_{10}$
  - (iii) Tetraphosphoric acid, $H_6P_4O_{13}$
  - (iv) Metaphosphoric acid, HPO_3
  - (v) Orthophosphoric acid, H_3PO_4
- Peroxyphosphoric acid series, which contains following acids
  - (i) Peroxymonophosphoric acid, H_3PO_5
  - (ii) Peroxydiphosphoric acid, $H_4P_2O_8$

The strength and solubility of the oxyacids follow the order,

$$HNO_3 > H_3PO_4 > H_3AsO_4 > H_3SbO_4$$

Some important facts related to oxyacids of phosphorus are

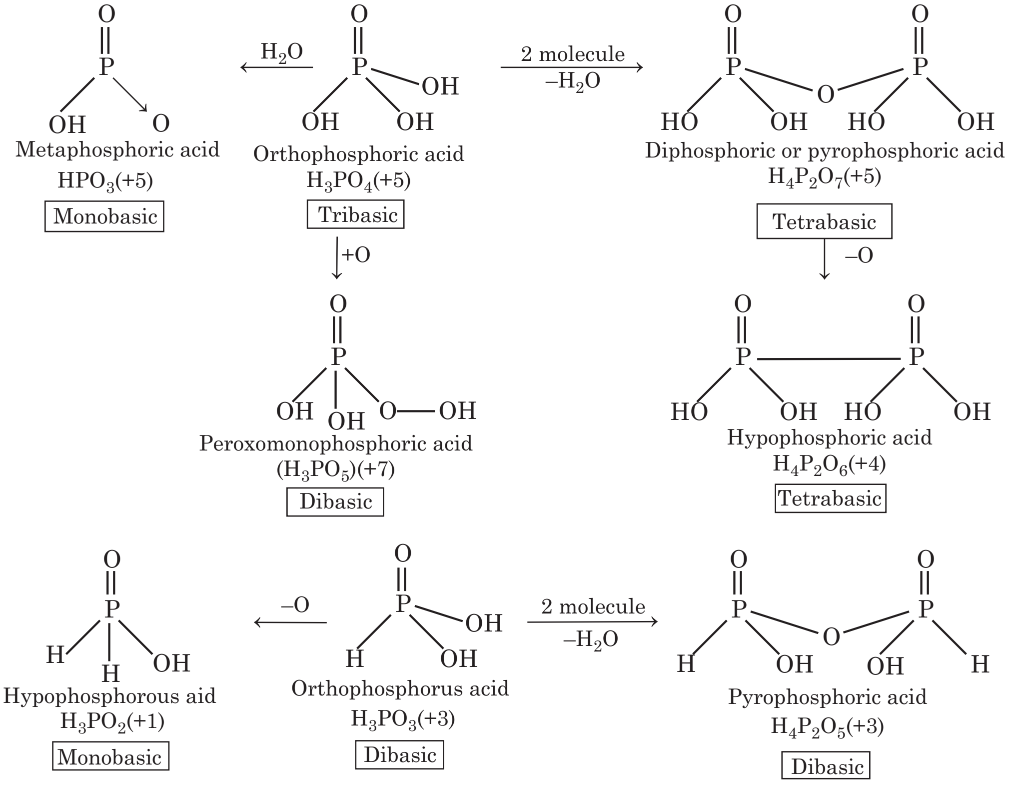
(i) H_3PO_3 is a strong reducing agent but weaker as compared to H_3PO_2.

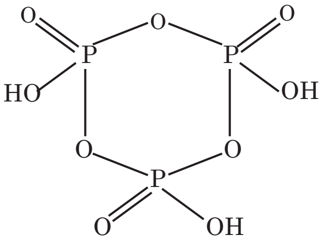
(ii) $4H_3PO_3 \xrightarrow[-PH_3]{475\text{ K}} 3H_3PO_4 \xrightarrow{520\text{ K}} H_4P_2O_7 \xrightarrow{>520\text{ K}} HPO_3$

(iii) Aqueous solutions of both pyrophosphoric acid, $H_4P_2O_7$ as well as metaphosphoric acid (HPO_3) on heating give orthophosphoric acid.

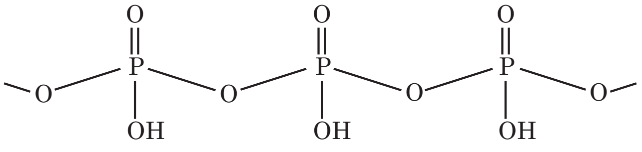
Structures

The structures of some oxyacids of phosphorus are given below





Cyclometaphosphoric acid $(HPO_3)_3$



Polymeta phosphoric acid (HPO_3)

Example 5. *White phosphorus on reaction withu concentrated NaOH solution in an inert atmosphere of* CO_2 *gives phosphine and compound (X). (X) on acidification with* HCl *gives compound (Y). The basicity of compound (Y) is* ***(JEE Main 2020)***

(a) 4 (b) 3 (c) 2 (d) 1

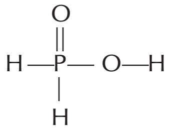
Sol. (*d*)

$$\underset{\substack{\text{White}\\\text{phosphorus}}}{P_4} + \underset{\text{Conc.}}{3NaOH} + 3H_2O \xrightarrow{\text{Inert atm. of } CO_2} \underset{\text{Phosphours}}{PH_3} + \underset{(X)}{3NaH_2PO_2}$$

$$\downarrow +3HCl$$

$$\underset{(Y)}{3H_3PO_2} + 3NaCl$$

H_3PO_2 (Y) is a monobasic acid. Here, the H-atom of OH group is ionisable and cause the basicity.



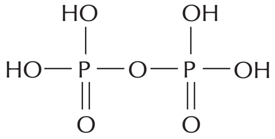
Only one such atom are present. Thus, basicity of compound (*Y*) is 1.

Example 6. *In a molecule of pyrophosphoric acid, the number of* P—OH, P$=$O *and* P—O—P *bonds/moiety(ies) respectively are* ***(JEE Main 2020)***

(a) 2, 4 and 1 (b) 3, 3, and 3

(c) 4, 2, and 0 (d) 4, 2, and 1

Sol. (*d*) The structure of pyrophosphoric acid ($H_4P_2O_7$) molecule is



Number of P—OH moieties = 4, P $=$ O bonds = 2 and P—O—P bond = 1.

Example 7. *On reaction with* Cl_2*, phosphorus forms two types of halides 'A' and 'B'. Halide 'A' is yellowish white powder but halide 'B' is colourless oily liquid. Which of the following is/are their hydrolysis products?* ***(NCERT Exemplar)***

(I) H_3PO_2 (II) H_3PO_3

(III) H_3PO_4 (IV) H_3PO_4

(a) I and II (b) II and III

(c) III and IV (d) I and IV

Sol. (a) '*A*' is PCl_5 and '*B*' is PCl_3.

$$P_4 + 10Cl_2 \longrightarrow \underset{\substack{\text{Yellowish}\\\text{white powder}\\(A)}}{4PCl_5}$$

$$P_4 + 6Cl_2 \longrightarrow \underset{\substack{\text{Coloureless}\\\text{oily liquid}\\(B)}}{4PCl_3}$$

When '*A*' and '*B*' are hydrolysed as,

(a) $\underset{\substack{[A]\\\text{Phosphorus}\\\text{pentachloride}}}{PCl_5} + 4H_2O \longrightarrow \underset{\substack{\text{Phosphoric}\\\text{acid}}}{H_3PO_4} + 5HCl$

(b) $\underset{\substack{[B]\\\text{Phosphorus}\\\text{trichloride}}}{PCl_5} + 3H_2O \longrightarrow \underset{\substack{\text{Phosphrous}\\\text{acid}}}{H_3PO_3} + 3HCl$

VIA (16) Group Elements and Their Compounds

This group contains 5 elements, i.e. **oxygen, sulphur**, **selenium, tellurium** and **polonium**. These are collectively called as **oxygen family**. The first four members are non-metals and collectively known as **chalcogens** (meaning ore forming) as metal ores normally occur in the form of oxides, sulphides etc.

Occurrence

Oxygen is most abundant element on earth. It constitutes contains 50% by weight of earth crust and about 23.2% by weight of atmosphere. There are three naturally occurring isotopes of oxygen, i.e. ${}_8O^{16}$ (99.762%), ${}_8O^{17}$ (0.038%) and ${}_8O^{18}$ (0.200%). Water contains 88.8% oxygen by weight.

Sulphur occurs in the earth crust to the extent of 0.05% mostly as metal sulphides and sulphates. It also occur (in elemental form) in large underground beds. Se and Te are less abundant than S. Polonium is radioactive and occurs in nature in radium minerals such as pitch blend to the extent of 5×10^{-9} %.

General and Physical Properties

Elements of group 16 shows following trends in their general and physical properties.

(i) **Electronic configuration** General electronic configuration for the elements of this group is ns^2np^4. According to Hund's rule; the four p-electrons are arranged in p-orbitals as $p_x^2\ p_y^1\ p_z^1$. (where, n = 2, 3, 4, 5,...)

(ii) **Atomic volume and atomic radii** Both atomic volume and atomic radii increase on moving down the group.

(iii) **Physical state** Oxygen is a gas while, all other elements exists in solid state.

(iv) **Ionisation energy** On moving down the group, the ionisation energy decreases. These elements, have unexpectedly lower first ionisation energy than the corresponding elements of group 15.
This is because of the stable electronic configuration of the elements of this group is as compared to group 16 elements. But their second ionisation enthalpy is higher than those of group 15 elements because after removal of one electron, the electronic configuration become more stable. So it is difficult to remove second electron from this stable configuration.

(v) **Electronegativity** These elements are more electronegative as compared to the corresponding elements of group 15. There is seen a steep drop in electronegativity as the atomic size increases. Oxygen is the second most electronegative element of the periodic table. Hence, its all compounds (except with fluorine) are called **oxides**.

(vi) **Electron affinity** These elements also decreases as the atomic size increases. However, electron affinity of O is lesser as compared to S. This is because of the small size and high charge density of O-atom.

Along the period these element have large electron affinity next only to the halogens.

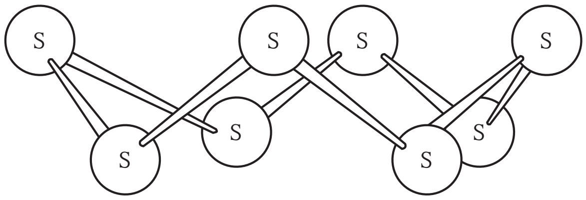
(vii) **Nature of bonding** Oxygen can form ionic as well as covalent compounds but other elements, because of their low electronegativity, form mainly covalent compounds. Compounds of oxygen with highly electropositive metals like Li, Mg etc., are ionic while with less electropositive metals and non-metals are covalent.

(viii) **Oxidation state** Oxygen, being highly electronegative, exhibit +2, –2 and –1 oxidation states while other elements show +2, +4 and +6 oxidation states.
On moving down the group, the stability of +4 oxidation state increases while that of +6 state decreases due to **inert pair effect**.

(ix) **Metallic character** The first four elements are non-metals. This non-metallic character is stronger in oxygen and sulphur. Po is distinctly a metal but it is radioactive and only short lived.

(x) **Melting and boiling points** On moving down the group, as the atomic size increases the magnitude of van der Waals' interatomic forces increases. Thus, the melting and boiling point increase regularly in the same way.

(xi) **Molecular state** Oxygen exists as O_2 (diatomic gaseous molecule). S and Se occur as S_8 and Se_8 with Puckered ring structure as seen below



Puckered ring structure of S_8 molecule

The reason for such a difference is the tendency of O-atom to form multiple bonds ($p\pi$- $p\pi$ bonds) which is missing in the case of sulphur and selenium.

(xii) **Catenation** Sulphur has a high while oxygen has some tendency to catenate.
e.g. H—O—O—H (H_2O_2) H— S—S—S—S—H (H_2S_4).

(xiii) **Allotropy** Oxygen exist in two allotropic forms, i.e. O_2 and O_3. Sulphur exists as–**rhombic** or **α-form, monoclinic** or **β-form, plastic** or **γ-form, colloidal** or **δ-form, λ-sulphur** and **μ-sulphur**.

- Selenium exists in two forms, i.e. **red form** and **grey form**.
- Tellurium exists in two forms, one of which is metallic and other is non-metallic.
- Polonium exists in two forms namely α and **β-forms**. Both of them are metallic.

The above physical properties can be summarised in the following table below

Physical Properties of 16 Group Elements

Property	Oxygen	Sulphur	Selenium	Tellurium	Polonium
Atomic number	8	16	34	52	84
Electronic configuration	[He]$2s^2 2p^4$	[Ne]$3s^2 3p^4$	[Ar]$3d^{10} 4s^2 4p^4$	[Kr]$4d^{10} 5s^2 5p^4$	[Xe]$4f^{14} 5d^{10} 6s^2 6p^4$
Atomic mass (amu)	15.999	32.064	78.96	127.60	210
Density in solid state (g cm^{-3})	1.14	2.07	4.79	6.23	9.2
Atomic radius (Å)	0.73	1.09	1.16	1.35	—
Ionic radius (Å) of divalent ion	1.40	1.84	1.98	2.21	—
Atomic volume (cc)	14.0	15.5	16.5	20.5	22.7
Ionisation energy (kJ mol^{-1})	1313.7	999.4	940.9	869.5	813.5
Oxidation states	–2, –1, +2	–2, +2, +4, +6	–2, +2, +4, +6	–2, +2, +4, +6	+2, +4
Electronegat - ivity	3.5	2.5	2.4	2.1	2.0
Melting point (°C)	–218.8	114.0	217.0	449.5	254.0
Boiling point (°C)	–183.0	444.6	685.0	989.8	962
Heat of fusion (kJ mol^{-1})	0.22	1.42	5.3	17.7	11.0
Heat of atomisation (kJ mol^{-1})	250	280	207	197	145

Chemical Properties

Some of the important chemical properties of element of group 16 are discussed below

1. Reactivity Towards Oxygen or Formation of Oxides

- Among the compounds of group 16 elements the most important ones are **oxides**.
- In general, the oxides of metals are basic, that of non-metals are acidic and that of semi-metals are amphoteric in nature.
- The acidic character of oxides increases across a period from left to right and basic character of oxides increases down a group.
- The oxides are mainly **monoxides** (*A*O type**),** **dioxides** (AO_2) type and trioxides (AO_3 type). However, sulphur forms heptoxide also with formula S_2O_7. Out of these the oxides of sulphur are most important commercially.
- The oxides formed by S, Se, Te and Po are tabulated below.

Different Oxides of 16 Group Elements

Type of oxide	S	Se	Te	Po
Monoxide	SO	—	TeO	PoO
Dioxide	SO_2	SeO_2	TeO_2	PoO_2
Trioxide	SO_3	SeO_3	TeO_3	PoO_3
Heptoxide	S_2O_7	—	—	—

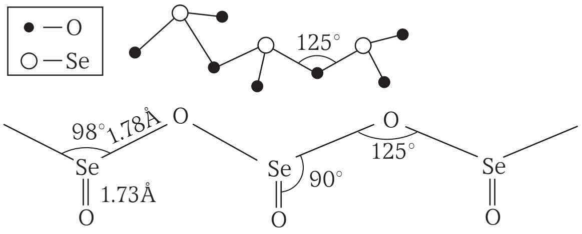
Some important facts related to the oxides are given below

(i) Monoxides

All elements of this group (except Se) forms **monoxides** but all them are not so stable. Out of these, SO is formed by passing electric discharge through SO_2 while TeO and PoO are formed by heating corresponding trioxides.

(ii) Dioxides

- Dioxides (MO_2) are formed by all the members of this group by burning them in air (except oxygen of course). These dioxides differ from each other considerably. For example SO_2 and SeO_2 are acidic oxides with good solubility in water while TeO_2 and PoO_2 are amphoteric in nature and have poor solubility in water.
- SO_2 has angular structure. It exists as discrete molecule even in solid state. It is held together by weak van der Waals' forces of attraction. (It exist as gas at room temperature). SeO_2 in gaseous phase has angular structure but in solid state (white volatile solid) it has polymeric structure comprising of infinite chains as



Polymeric structure of SeO_2 in solid state

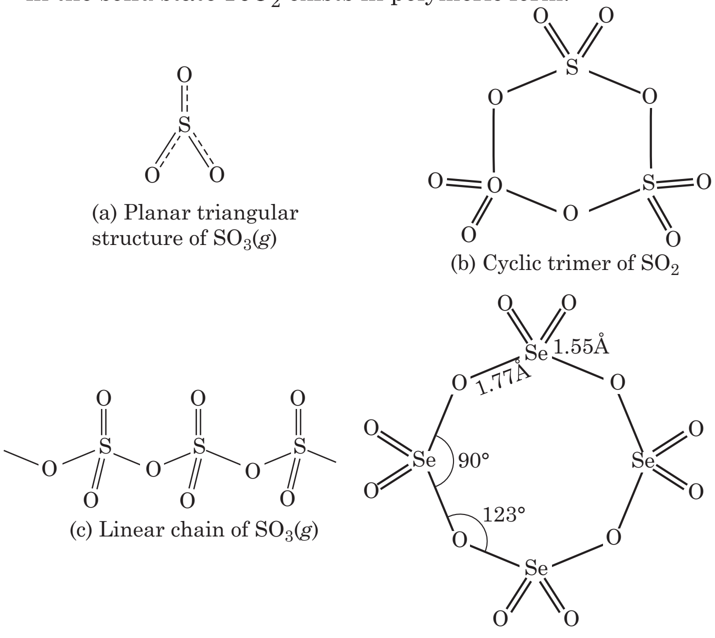
Dioxides of Te and Po are also non-volatile crystalline ionic solids, out of which TeO_2 has a layer structure consisting of TeO_4 units.

Dioxides show differences in their reaction with water as

- SO_2 dissolves in water giving H_2SO_3 (known in solution only).
- SeO_2 gives selenious acid with water which can be isolated in crystalline state.
- TeO_2 is almost insoluble in water. It however dissolves in alkalies (to form tellurites) and in acids (to form basic salts) showing its amphoteric nature.
- PoO_2 shows similar behaviour.

(iii) Trioxides (MO_3)

- Generally, these oxides are acidic in nature, i.e. form acids with water. This acidic nature decreases on moving down the group.
- Among trioxides, SO_3 is the most important
- In gaseous phase, it exists as planar triangular geometry while in solid state, has linear cyclic trimer or a polymeric chain structure.
- SeO_3 on the other hand, exists as a cyclic tetramer (Se_4O_{12}) in the solid state TeO_2 exists in polymeric form.



(a) Planar triangular structure of $SO_3(g)$

(b) Cyclic trimer of SO_2

(c) Linear chain of $SO_3(g)$

(d) The cycle structure of tetrameric Se_4O_{12}

Structure of (a) gaseous SO_3, (b) Cyclic of solid SO_3,
(c) Linear chain form of solid SO_3,
(d) Cyclic tepramer of solid SeO_3.

2. Reactivity Towards Hydrogen or Formation of Hydrides

- Group 16 elements form binary hydrides of type M_2A (where, A = O, S, Se, Te or Po). Unlike H_2O, other hydrides are unpleasant foul smelling poisonous gases. The unique behaviour of H_2O is due to extensive intermolecular H-bonding.
- Hydrides of S, Se and Te are prepared by the action of acids on metal sulphides, selenides and tellurides respectively. H_2S, H_2Se and H_2Te are weak diprotic acids in aqueous solutions.

Structure

Hydrides of these group have angular shape involving sp^3 hybridisation of central atom.

Their bond angle decreases in order as,

$$\underset{104.5^\circ}{H_2O} > \underset{92.1^\circ}{H_2S} > \underset{91^\circ}{H_2Se} > \underset{90^\circ}{H_2Te}$$

On moving down the group, the size of the central atom increases and electronegativity decreases. Due to this the position of the two bond pair shift away from the central atom. As a result of this repulsion between the bond pairs decreases as we move down the group. Therefore, bond angle decrease in this order.

Volatility and Boiling Point

The volatility first increases from H_2O to H_2S and then decreases from H_2S to H_2Te, i.e boiling point first decreases and then increases.

- Due to strong intermolecular H-bonding H_2O has very high boiling point. The electronegativity of other element, (i.e. S, Se, Te) is much lower therefore, they do not show H-bonding. Thus, their boiling point is less.
- Now on moving down the group, size of central atom increases, therefore van der Waals' forces of attraction increases hence boiling point increases gradually from H_2S to H_2Se.

  Thus, the order of voltality will be $H_2S > H_2Se > H_2Te > H_2O$ and the order as boiling point will be

$$H_2O > H_2Fe > H_2Se > H_2S.$$

Acidic Strength

The acidity increases in the series as $H_2S < H_2Se < H_2Te$. H_2O is neutral in nature. Increase in acidic strength of hydrides can be easily explained on the basis of increase in the size of central atom from oxygen to Te.

As the result of such an increase, the length of R—H bond also increases gradually which is always inversely proportional to bond strength. Thus, bond strength decreases.

Thermal Stability and Reducing Power

As the size of central atom increases, the M—H (M = O to Po) bond becomes weaker and longer. Consequently, the thermal stability decreases. Since, reducing power varies inversely with bond strength, it increases as the bond strength decreases or bond length increases.

$$H_2O\ \ H_2S\ \ H_2Se\ \ H_2Te$$
$$\xrightarrow{\text{Thermal stability decreases}}$$
$$\xrightarrow{\text{Reducing character increases}}$$

The properties of these hydrides are summarised given below

Properties of Hydrides of Group 16 Elements

Property	H_2O	H_2S	H_2Se	H_2Te
Melting point (°C)	0	– 85.5	– 65.7	–51.1
Boiling point (°C)	100.0	– 60.75	– 41.5	–1.8
Bond angle H—X—H	104.5°	92.5°	90°	89°
Bond length H—X (Å)	0.95	1.30	1.45	1.72
Dissociation constant as an acid at 25°C	1.0×10^{-14}	1.0×10^{-7}	1.7×10^{-4}	2.3×10^{-3}

First two members of the family also form hydrides of the formula H_2R_2 (i.e. H_2O_2 and H_2S_2). However, these two hydrides differ considerably from each other.

e.g. H_2O_2 is fairly stable but H_2S_2 is unstable. It decomposes readily to give S and H_2S as,

$$H_2S_2 \xrightarrow{OH^-} H_2S + S$$

Similarly, H_2O_2 on account of hydrogen bonding is highly associated while, H_2S_2 forms discrete molecules.

3. Reactivity Towards Halogens or Formation of Halides

Oxygen forms halides only with fluorine (OF_2 or F_2O-oxygen difluoride) and its compounds with rest of the halogens are called **oxides** (not halides) as its electronegativity is more than any other halogen. S and other chalcogens form a number of halides.

The general preparation routes for chalcogen halides involve the direct reaction of chalcogens with respective halogen, i.e.

$$\frac{1}{8}S_8(s) + 3F_2(g) \longrightarrow SF_6(g)$$
$$Te\ (s) + 2Cl_2(g) \longrightarrow TeCl_4(s)$$

Direct fluorination of elemental sulphur yields mainly SF_6 along with traces of $SF_4 \cdot SF_4$ is also prepared by the fluorination of SCl_2 with NaF in acetonitrile at 350 K as,

$$3SCl_2 + 4NaF \xrightarrow{\text{MeCOCN, 350 K}} S_2Cl_2 + SF_4 + 4NaCl$$

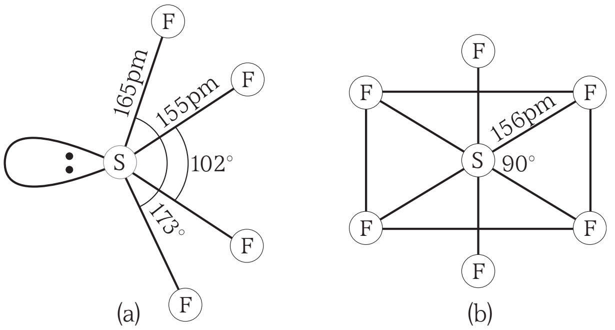
All the halides of these elements can be tabulated as,

Halides of Oxygen Family

Elements	F	Cl	Br	I
O	OF_2, F_2O_2	Cl_2O_6, Cl_2O_7, Cl_2O, ClO_2 etc	Br_2O, BrO_2, BrO_3	I_2O, I_2O_4, I_2O_5
S	S_2F_2, SF_4, SF_6, S_2F_{10}	S_2Cl_2, SCl_2, SCl_4	S_2Br_2	
Se	SeF_2, SeF_4 SeF_6	Se_2Cl_2, $SeCl_4$	Se_2Br_2, $SeBr_4$	
Te	TeF_4, Te_2F_{10}, TeF_6	$TeCl_2$, $TeCl_4$	$TeBr_2$, $TeBr_4$	TeI_4
Po	—	$PoCl_2$, $PoCl_4$	$PoBr_2$, $PoBr_4$	PoI_4

Some important facts related to halides of 16 group elements are as follows

- The stability of halides decreases in the order F > Cl > Br > I. The highest oxidation state is found only with fluorides.
- SF_6 is an inert non-toxic gas at room temperature. It is inert due to sterically protected atom. In contrast, less sterically hindered SeF_6 and SF_4 undergo hydrolysis readily.



Trigonal bipyramidal (*see-saw* geometry)
The structure of (a) SF_4 (b) SF_6

- Compared to sulphur halides, the halides of Se and especially Te adopt oligomeric or polymeric structures. In +4 oxidation state, $SeCl_4$, $SeBr_4$, $TeCl_4$, $TeBr_4$ and TeI_4 exist as tetramer while, TeF_4 has polymeric structure.
- All hexafluorides have a high degree of covalency and low boiling points.
- The tetrahalides act as Lewis bases (electron donor) due to the presence of lone pair and also as Lewis acids (electron acceptors) due to the ability to extend their coordination number.
- All the member of this group form dihalides. They show sp^3 hybridisation with bent structure.
- Known monohalides are dimer in nature which disproportionate.

e.g. $$2\overset{+1}{Se_2}Cl_2 \longrightarrow \overset{+4}{SeCl_4} + \overset{0}{Se}$$

4. Oxyacids

Among the group, only **oxy acids** of S, Se and Te are known. S forms many **oxy acids** while Se and Te forms two oxy acids each.

Some of these oxyacids are given in the following table below.

Oxyacids of S, Se and Te

S	Se	Te
H_2SO_3 (sulphurous acids)	H_2SeO_3 (selenous acid)	H_2TeO_3 (tellurous acid)
H_2SO_4 (sulphuric acid or oil of vitriol)	H_2SeO_4 (selenic acid)	H_6TeO_6 (telluric acid)
H_2SO_5 (peroxomono sulphuric acid or Caro's acid)		
$H_2S_2O_8$ (peroxodisulphuric acid or Marshall's acid)		

Anomalous Behaviour of Oxygen

Owing to its small size, high charge density and non-availability to *d*-orbitals, oxygen differs from rest of the members in following respects.

- Oxygen is a diatomic gas while all other members are solid.
- Most of the compounds of oxygen are ionic and polar covalent due to its high electronegativity.
- Maximum covalency that can be exhibited by oxygen in its compounds is two while rest of the members can show a maximum covalency is six.
- Oxygen forms $p\pi$- $p\pi$ multiple bond with elements of similar size while, S form $d\pi$- $p\pi$ bonds.
- Only the hydride of oxygen, i.e. H_2O is non-poisonous and is a liquid while, the hydrides of other members are poisonous gases.
- Oxygen is paramagnetic while, rest are not.
- Molecule of oxygen is diatomic (O_2) while the molecules of the other elements are more complex, e.g. sulphur (S_8) and selenium have octa-atomic molecules with puckered ring structure.
- Oxygen show oxidation state of – 2 while other member show additional oxidation states of +4 and +6 due to the presence of vacant *d*-orbital

- H_2O shows hydrogen bonding due to the presence of electronegative oxygen atom. Other hydride does not show hydrogen bonding.

Ozone (O_3)

It is formed in the upper layer of atmosphere by the action of UV rays from sun on oxygen. It prevents the UV rays from entering the earth's atmosphere. CFCs, common refrigerants deplete the ozone layer.

Method of Preparation

It is prepared in ozoniser by subjecting dry and cold dioxygen to the action of silent electric discharge.

$$3O_2(g) \xrightleftharpoons{\text{Silent electric discharge}} 2O_3(g)$$

Physical Properties

- It is a pale blue gas with a characteristic pungent odour.
- It condenses to a deep blue liquid (b.p. 161.2 K) and to a violet black solid (m.p. 80.6 K).
- It is diamagnetic in nature. It acts as a powerful oxidising agent due to liberation of O_2. The colour of O_3 is due to intense absorption of red light.

Chemical Properties

Chemical properties of O_3 involves

- It is thermodynamically unstable and decomposes to O_2.

$$2O_3 \longrightarrow 3O_2; \qquad \Delta G = -\ 163 \text{ kJ mol}^{-1}$$

- It is an extremely powerful oxidising agent.

$$O_3 + 2H^+ + 2e^- \rightleftharpoons O_2 + H_2O$$

$$O_3 + H_2O + 2e^- \rightleftharpoons O_2 + 2OH^-$$

It oxidises as,

(i) $3PbS + 4O_3 \longrightarrow 3PbSO_4$

(ii) $6NO_2 + O_3 \longrightarrow 3N_2O_5$

(iii) $S + H_2O + O_3 \longrightarrow H_2SO_4$

(iv) $2KOH + 5O_3 \longrightarrow 2KO_3 + 5O_2 + H_2O$

(Potassium ozonide KO_3 is an orange coloured solid and contains the paramagentic O_3^- ion)

(v) $O_3 + 2KI + H_2O \longrightarrow I_2 + 2KOH + O_2$

The amount of O_3 in a gas mixture can be determined by passing the gas into a KI solution (at a constant pH 9.2 using borate buffer).

By calculating iodine that is liberated is titrated with sodium thiosulphate solution.

$$O_3 + 2I^- + H_2O \longrightarrow I_2 + 2OH^- + O_2\uparrow$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

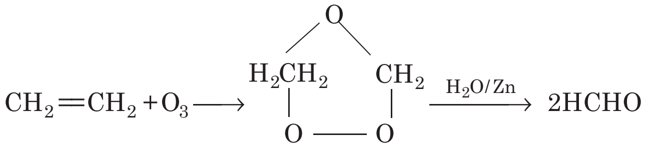
(vi) $3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$

(vii) $2[Fe(CN)_6]^{4-} + H_2O + O_3 \longrightarrow 2[Fe(CN)_6]^{3-} + O_2\uparrow + 2OH^-$

- O_3 can also be decomposed catalytically and change in volume measured

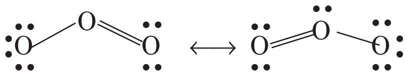
$$\underset{\text{(2 volume)}}{2O_3} \longrightarrow \underset{\text{(3 volume)}}{3O_2}$$

- O_3 also adds to unsaturated organic compounds at room temperature forming ozonides which can be cleaved as aldehydes and ketones in solution.



Structure

Structure of O_3 is best described as a resonance hybrid of following canonical forms



Both the O—O bond here are of equal length, i.e. 128 pm.

Uses

Some important uses of ozone are as follows

- It is used as a disinfectant.
- It is used to purify drinking water, since it can destroy bacteria and viruses.
- It is better than Cl_2 since it avoids the unpleasant smell and taste of Cl_2 and any excess O_3 soon decomposes to O_2.
- It also absorbs UV light. This is particularly important since, there is a layer of O_3 in the upper atmosphere which absorbs harmful UV radiation from the sun, thus, protecting people on the earth. The use of chlorofluorocarbons (CFC_5) in aerosols and refrigerators, and their subsequent escape into the atmosphere, is blamed for making **holes in the ozone layer** over the Antarctic and Arctic. It is feared that this will allow an excessive amount of UV light to reach the earth. This UV light will cause melanoma (skin cancer) in humans. Oxides of nitrogen (from car exhausts) and the halogens can also damage the O_3 layer.

Ozone destroying reactions are as follows

(a) Based on oxides of nitrogen.

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$O_3 + h\nu \longrightarrow O_2 + [O]$$

$$NO_2 + O \longrightarrow NO + O_2$$

$$\text{Net reaction ; } 2O_3 + h\nu \longrightarrow 3O_2$$

(b) Based on reactive chlorine species from CFC.

$$Cl + O_3 \longrightarrow ClO + O_2\uparrow$$
$$O_3 + h\nu \longrightarrow O + O_2\uparrow$$
$$ClO + O \longrightarrow Cl + O_2\uparrow$$
$$\text{Net reaction ; } 2O_3 + h\nu \longrightarrow 3O_2$$

Sulphur

It is found in free as well as in combined state. In combined state, it occurs as sulphides and sulphates in the form of galena (PbS), iron pyrites (FeS_2), gypsum ($CaSO_4 \cdot 2H_2O$) barytes ($BaSO_4$) etc.

Allotropes of sulphur

Sulphur exists in several allotropic forms. The properties of these forms are as follows

1. **Rhombic or octahedral or α-sulphur** is the most common form of sulphur.
   - **Preparation** It is prepared when a solution in CS_2 is evaporated in a china dish.
   - **Properties** It is stable at temperatures below 95.6°C. Its specific gravity is 2.06. It melts at 114°C. It is soluble in carbon disulphide.
   - **Structure** Its crystal structure contains cyclic S_8 rings, packed in a manner which leads to the formation of rhombic crystals.
2. **Monoclinic or prismatic** or **β-sulphur** is stable above 95.6°C.
   - **Preparation** It is prepared by melting rhombic sulphur in a dish and allowing it to cool until a crust is formed at the surface. On removing the crust, small needle-like crystals of monoclinic sulphur become visible.
   - **Properties** Its specific gravity is 1.96. It is dull yellow and soluble in carbon disulphide.

   $$\text{Rhombic sulphur} \xrightarrow[< 369\text{ K}]{> 369\text{ K}} \text{Monoclinic sulphur}$$

   - **Structure** Like α-sulphur, its crystal structure also contains cyclic S_8 rings but the mode of packing is different than that in α-sulphur. The packing in this case is such that it leads to the formation of monoclinic crystals.
3. **γ-sulphur** is a tough elastic substance. It is also known as plastic sulphur.
   - **Preparation** It is best obtained by decomposing ethylene xanthate of copper (I) in pyridine or by chilling hot solution of sulphur in carbon disulphide.
   - **Properties** Its specific gravity is 2.18. γ-sulphur slowly changes into α and β-forms of sulphur.
   - **Structure** Its crystal structure also consists of cyclic S_8 rings which are packed in lattice in a more compact manner than in the crystals of α or β-sulphur.
4. **Colloidal or δ-sulphur Preparation** It is obtained, when hydrogen sulphide is passed through an oxidising solution such as nitric acid, potassium permanganate, etc.

   $$2HNO_3 + H_2S \longrightarrow \underset{\substack{\text{Colloidal}\\\text{sulphur}}}{S} + 2NO_2 + 2H_2O$$

   It is also obtained by passing hydrogen sulphide through water containing dissolved sulphur dioxide.

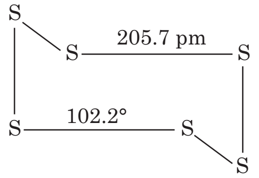
   $$2H_2S + \underset{\substack{\text{Dissolved}\\\text{form}}}{SO_2} \longrightarrow 2H_2O + 3S$$

5. **Plastic** or **χ-sulphur**
   - **Preparation** It is obtained, when molten sulphur heated to about 350°C is poured into cold water.
   - **Properties** It is a soft rubber-like mass. It hardens on standing and changes gradually into rhombic sulphur.
     - (i) It is soluble in carbon disulphide and has no sharp melting point.
     - (ii) This form is a mixture of allotropes of sulphur containing cyclic S_8 rings and long helical chains of a large number of S-atoms.
     - (iii) It can be converted into fibres when it is heated in an atmosphere of nitrogen at 300°C for a few minutes and then quenched in water. Their structure contains open polymeric helical chains of S-atoms.
     - (iv) It is also considered as **supercooled liquid,** i.e. the liquid which due to rapid cooling below its freezing point had no time to settle into a crystalline form.
6. **Cyclohexasulphur** Sulphur allotropes containing cyclic S_6, S_7, S_{10}, S_{12}, S_{18} and S_{20} rings are also found. These cyclosulphurs are quite unstable with the exception of S_{18} and S_{20}.

   Cyclohexasulphur (Engel's sulphur) containing cyclic S_6 rings and can be prepared by the following reaction as,

   $$S_2Cl_2 + H_2S_4 \longrightarrow S_6 + 2HCl$$

   The structure of cyclohexasulphur consists of closely packed cyclic S_6 rings in chair form. As a result of this close packing the specific gravity (2.2 at –110°C) of this form is higher than specific gravities of all the other forms. This form of sulphur is highly reactive. It structure is given below



Properties and Uses

- Sulphur is a yellow solid which is tasteless and odourless.
- It is freely soluble in CS_2, sparingly soluble in alcohol and ether and totally insoluble in water.
- Its vapours are poisonous for bacteria and fungi but not for other animals or human beings.

Sulphuric Acid (Oil of Vitriol, H_2SO_4)

In ancient days, it was called **oil of vitriol,** since it was prepared by distilling green vitriol (ferrous sulphate) $FeSO_4 \cdot 7H_2O$.

$$\underset{\text{Green vitriol}}{2[FeSO_4 \cdot 7H_2O]} \xrightarrow{\text{Distillation}} Fe_2O_3 + SO_2 + 13H_2O + \underset{\text{Oil of vitriol}}{H_2SO_4}$$

Methods of Preparation

Sulphur is burnt in air so that it is oxidised to SO_2. SO_2 thus, obtained is oxidised to SO_3 which, when dissolved in H_2O, gives H_2SO_4. The whole process can be summarised as :

$$S \xrightarrow{+O_2} SO_2 \xrightarrow{+\frac{1}{2}O_2} SO_3 \xrightarrow{+H_2O} H_2SO_4$$

Industrial Preparation of H_2SO_4

Sulphuric acid is manufactured these days by the following two processes are,

1. **Lead chamber process** In this process, a mixture containing SO_2, air and NO is treated with steam (H_2O). Here, NO acts as a catalyst.

$$2SO_2 + \underset{\text{(From air)}}{O_2} + \underset{\text{(Steam)}}{2H_2O} + \underset{\text{Catalyst}}{[NO]} \longrightarrow 2H_2SO_4 + \underset{\text{Catalyst}}{[NO]}$$

The steps involved during this process are as follows

***Step* I Preparation of SO_2** By heating sulphur or iron pyrites (FeS_2) in the excess of air.

$$S + O_2 \longrightarrow SO_2 \uparrow$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2 \uparrow$$

***Step* II Oxidation of SO_2 to SO_3 by HNO_3 or by NO_2**

$$2HNO_3 + 2SO_2 \longrightarrow H_2 + NO \uparrow + NO_2 \uparrow + 2SO_3$$

$$SO_2 + NO_2 \longrightarrow SO_3 + NO \uparrow$$

***Step* III Preparation of** H_2SO_4 from SO_3 By allowing SO_3 obtained in step (II) to react with steam (H_2O).

$$O_3 + H_2O \text{ (steam)} \longrightarrow H_2SO_4$$

2. **Contact process** It is the current process of producing sulphuric acid. This process involves the following steps

***Step* I Preparation of SO_2** By burning sulphur or iron pyrites (FeS_2) in the excess of air.

$$S + O_2 \xrightarrow{\Delta} SO_2 \uparrow$$

$$4FeS_2 + 11O_2 \xrightarrow{\Delta} 2Fe_2O_3 + 8SO_2 \uparrow$$

***Step* II Oxidation of SO_2 to SO_3** By the atmospheric O_2 in presence of a catalyst which may be **Pt-asbestos,** V_2O_5 or a mixture of ferric and cupric oxide.

$$2SO_2 + O_2 \underset{}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_3 ; \Delta H = -196.6 \text{ kJ}$$

The gases (i.e. SO_2 and O_2) must be purified before allowing them to combine to form SO_3. If they are not purified, the impurities will poison the catalyst used in the reaction. These days V_2O_5 is used as catalyst, as it is cheaper and not poisoned by impurities.

The oxidation of SO_2 to SO_3 by atmospheric O_2 as shown at step (II) is a reversible and exothermic process. According to Le Chatelier's principle, the favourable conditions for the maximum yield of SO_3 are

(i) **Low temperature,** since the forward reaction is exothermic, but a minimum temperature of 450°C, in needed called as optimum temperature and a suitable catalyst, is needed to get the maximum yield of SO_3.

(ii) **Optimum pressure** favour the forward reaction since the volume of the gaseous product (i.e. SO_3) is less than that of the gaseous reactants (i.e. SO_2 and O_2). But a very high pressure is likely to cause the corrosion of the vessel in which oxidation is carried out. Thus, a optimum pressure of 2-3 atmospheres is sufficient for oxidation.

(iii) **Excess of atmospheric** O_2-Maximum yield of SO_3 is obtained when SO_2 and atmospheric O_2 are taken in 2 : 3 ratio.

***Step* III Dissolution of SO_3 in 98% H_2SO_4,** to get **oleum,** $H_2S_2O_7$ (fuming sulphuric acid).

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

- Fuming sulphuric acid is that acid which contains dissolved SO_3 in it.
- It may be noted that SO_3 cannot be dissolved in water because it produces a dense fog which does not easily condense.

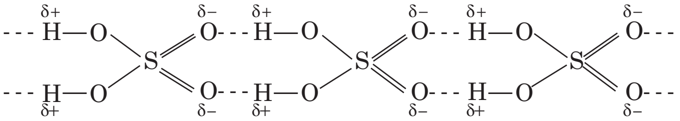
***Step* IV Dilution of oleum by water** to get the H_2SO_4 of any desired concentration.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

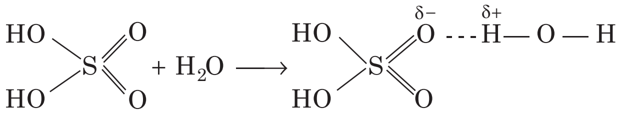
Physical Properties

(i) Pure H_2SO_4 is a colourless, viscous, heavy and syrupy oily liquid of density 1.84 (at 15°C) which does not fume.

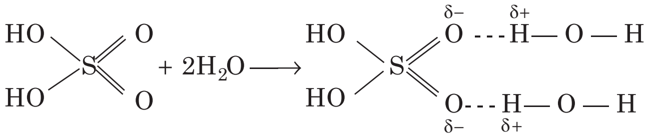
High boiling point and high viscosity of H_2SO_4 is due to the fact that H_2SO_4 molecules are associated together by H-bonding as shown below



(ii) It is highly soluble in water. When water is added to the acid, a large amount of heat is produced and the temperature rises as high as 120°C. The heat produced is so large that the acid spirit out of the container. Therefore, *if the acid is to be diluted, the acid should* be added to water slowly with constant stirring and *not water to the acid*. The production of heat is due to the formation of hydrates like $H_2SO_4 \cdot H_2O$ (m.p. = 8.5°C) and $H_2SO_4 \cdot 2H_2O$ (m.p. = 38°C).



Monohydrate, $H_2SO_4 \cdot H_2O$



Dihydrate, $H_2SO_4 \cdot 2\,H_2O$

(iii) It is a good conductor of heat and electricity.

Chemical Properties

H_2SO_4 exhibits the following chemical reactions are

I. (i) **H_2SO_4, when heated undergoes dissociation to give steam (H_2O) and SO_3 as,**

$$H_2SO_4 \overset{\Delta}{\rightleftharpoons} H_2O \text{ (steam)} + SO_3$$

The dissociation is almost complete at 444°C.

(ii) When the acid vapours are passed through a strongly heated Pt or quartz tube, it gets decomposed into SO_2, steam (H_2O) and O_2.

$$2H_2SO_4 \xrightarrow{\text{Heated Pt or quartz tube}} 2SO_2 + H_2O \text{ (steam)} + O_2$$

II. **The aqueous solution of the acid behaves as a strong dibasic acid,** since it ionises in two stages and gives two H^+ ions.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \text{ (bisulphate ion)}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \text{ (sulphate ion)}$$

Thus, H_2SO_4 forms two types of salts which are called **bisulphates** (e.g. $NaHSO_4$) and sulphates (e.g. Na_2SO_4). The acidic nature of H_2SO_4 is confirmed by the following reactions or properties, shown by H_2SO_4

(i) H_2SO_4 is sour in taste and turns blue litmus red.

(ii) It neutralises alkalies and forms bisulphates (HSO_4^-) and sulphates (SO_4^{2-}).

$$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O\uparrow$$

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O\uparrow$$

(iii) It decomposes carbonates and bicarbonates into CO_2.

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2\uparrow$$

$$2NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O + 2CO_2\uparrow$$

(iv) Dilute H_2SO_4 usually reacts with all metals (except Pb) such as Al, Sn, Mn, Zn, Fe, Mg etc., evolve H_2 gas.

$$M + H_2SO_4 \longrightarrow MSO_4 + H_2\uparrow$$

(M = Zn, Fe, Mg etc.)

Less reactive metals like Cu, Ag, Hg, Pb etc, are not attacked by dil H_2SO_4. However, these metals react with hot conc. H_2SO_4 (oxidising properties).

III. H_2SO_4 is a strong acid and it decomposes the salts of more volatile acids (e.g. chlorides, nitrates, sulphides, sulphites, carbonates etc.) to form their sulphate salt and more volatile acid.

Some examples are as follows

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

$$2KNO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_3$$

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2H\underset{\substack{\downarrow \\ NO + NO_2 + H_2O}}{NO_2}$$

IV. Hot concentrated H_2SO_4 acts as a **powerful oxidising agent,** since it can lose nascent oxygen quite readily. When H_2SO_4 oxidises any of the substance, it itself reduced to SO_2.

$$\underset{\substack{\text{(Hot and} \\ \text{concentrated)}}}{H_2SO_4} \longrightarrow H_2O + SO_2\uparrow + [O]$$

Occasionally, H_2SO_4 is also reduced to sulphur, sulphide or H_2S.

$$SO_4^{2-} + 8H^+ + 6e^- \longrightarrow S + 4H_2O$$

$$SO_4^{2-} + 8H^+ + 8e^- \longrightarrow S^{2-} + 4H_2O$$

$$SO_4^{2-} + 10H^+ + 8e^- \longrightarrow H_2S + 4H_2O$$

(i) H_2SO_4 oxidises non-metals like carbon and sulphur to their corresponding oxides *viz.,* CO_2 and SO_2.

$$2H_2SO_4 + C \longrightarrow 2H_2O + 2SO_2\uparrow + CO_2\uparrow$$

$$2H_2SO_4 + S \longrightarrow 2H_2O + 3SO_2\uparrow$$

It oxidises phosphorus to H_3PO_4,

$$2P + 5H_2SO_4 \longrightarrow 2H_3PO_4 + 5SO_2\uparrow$$

(ii) Metals like Cu, Ag, Hg, Pb etc., react with hot conc. H_2SO_4 and are oxidised to their oxides which get convert into sulphate. Here, H_2SO_4 is reduced to SO_2.

e.g. $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

Some other examples are given below

$$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + 2H_2O + SO_2\uparrow$$
$$Hg + 2H_2SO_4 \longrightarrow HgSO_4 + SO_2\uparrow + 2H_2O$$
$$Pb + 2H_2SO_4 \longrightarrow PbSO_4 + 2H_2O + SO_2\uparrow$$

Dil. H_2SO_4 reacts with commercial Zn, evolving H_2. Hot and conc H_2SO_4 attacks Zn, giving off SO_2.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + SO_2\uparrow + H_2O$$

Moderately conc acid (20%) when heated with Zn metal gives H_2S and precipitates a little sulphur.

$$4Zn + 5H_2SO_4 \longrightarrow 4ZnSO_4 + H_2S + 4H_2O$$
$$3Zn + 4H_2SO_4 \longrightarrow 3ZnSO_4 + S + 4H_2O$$

(iii) H_2SO_4 cannot oxidise HF (or CaF_2) and HCl (or NaCl, KCl etc.) but it can oxidise HBr (or NaBr, KBr) and HI (or NaI, KI) to Br_2 and I_2 respectively. When H_2SO_4 oxidises HBr (or NaBr or KBr), itself it is reduced to SO_2.
However, when it oxidises HI (or NaI or KI), it is reduced to SO_2 or S or H_2S depending on the amount of HI used in the reaction.

$$H_2SO_4 + 2HBr \longrightarrow SO_2\uparrow + 2H_2O + Br_2$$

Similarly, $H_2SO_4 + 2HI \longrightarrow SO_2\uparrow + 2H_2O + I_2$

$$H_2SO_4 + 6HI \longrightarrow S + 4H_2O + 3I_2$$
$$H_2SO_4 + 8HI \longrightarrow H_2S + 4H_2O + 4I_2$$

(iv) In presence of catalyst (Hg), naphthalene ($C_{10}H_8$) is oxidised to phthalic acid ($C_8H_6O_4$).

$$9H_2SO_4 + C_{10}H_8 \xrightarrow{\text{Hg (catalyst)}} 10H_2O + 9SO_2\uparrow + C_8H_6O_4 + 2CO_2\uparrow$$

(v) H_2SO_4 oxidises H_2S to S

$$H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2\uparrow + S$$

(vi) H_2SO_4 oxidises H_2 (H = 0) to H_2O (H = +1).

$$H_2SO_4 + H_2 \longrightarrow 2H_2O + SO_2\uparrow$$

V. **Conc. sulphuric acid is a strong dehydrating agent**. It dissolves in water and forms sulphuric acid hydrates, $H_2SO_4\cdot nH_2O$. Thus, it absorbs water from many organic compounds and dehydrates them. Absorption of water is highly exothermic.

Some of its reaction in which it act as a strong dehydrating agent are as follows.

(i) Cane sugar, glucose and starch are dehydrated to carbon.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2SO_4 \longrightarrow \underset{\text{Sugar charcoal}}{12C} + \underset{\text{Hydrate}}{[H_2SO_4\cdot 11H_2O]}$$

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + H_2SO_4 \longrightarrow 6C + [H_2SO_4\cdot 5nH_2O]$$

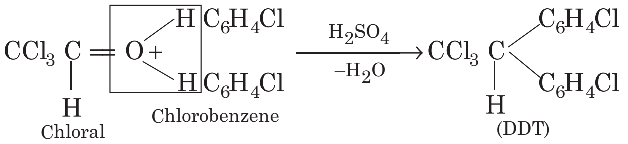
(ii) Oxalic acid, $(COOH)_2$ is dehydrated to CO and CO_2 and formic acid (HCOOH) gets dehydrated to CO only.

$$(COOH)_2 + H_2SO_4 \longrightarrow CO + CO_2 + [H_2SO_4\cdot H_2O]$$
$$HCOOH + H_2SO_4 \longrightarrow CO + [H_2SO_4\cdot H_2O]$$

(iii) Ethyl alcohol (C_2H_5OH) is dehydrated to diethyl ether.

$$2C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5OC_2H_5 + [H_2SO_4\cdot H_2O]$$

(iv) Dehydration of a mixture of chlorobenzene (C_6H_5Cl) and trichloroacetaldehyde (CCl_3CHO), also called **chloral**, gives DDT.



It is due to the dehydrating property of conc H_2SO_4 that cloth, wood, starch paper etc [which are largely cellulose $(C_6H_{10}O_5)_x$ materials] get charged in this acid, i.e. conc H_2SO_4 removes water from these substances and charge them. The dehydrating property of conc, H_2SO_4 is used

(i) in drying the gases which do not react with the acid (e.g. Cl_2, SO_2, HCl etc.)

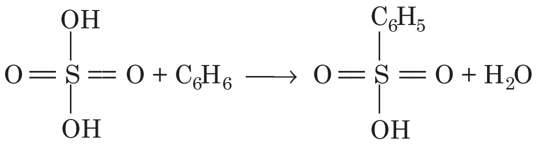
(ii) in many reactions like esterification etc.

(iii) in the manufacture of dyes and explosives.

H_2SO_4 has very corrosive action on skin because it acts as dehydrating agent and absorption of water is accompanied by the release of heat.

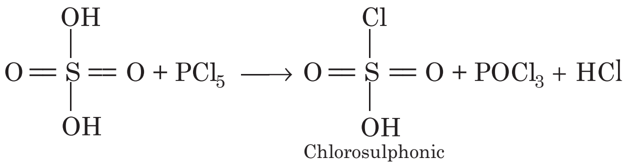
VI. **The molecule of** H_2SO_4 contains two OH groups. One or both these groups can be replaced by other groups or atoms by treating H_2SO_4 with the appropriate compound. e.g.

(i) When conc. H_2SO_4 is heated with C_6H_6, one OH group of H_2SO_4 is replaced by phenyl group (C_6H_5) and benzene sulphonic acid, $C_6H_5(OH)SO_2$ (also called benzene sulphuric acid) is obtained.



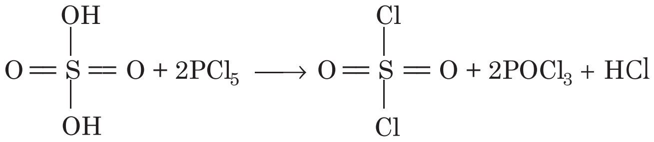
$$O = \overset{\overset{\large OH}{|}}{\underset{\underset{\large OH}{|}}{S}} = O + C_6H_6 \longrightarrow O = \overset{\overset{\large C_6H_5}{|}}{\underset{\underset{\large OH}{|}}{S}} = O + H_2O$$

(ii) One or both the —OH groups of H_2SO_4 can be replaced by Cl-atom when H_2SO_4 is treated with PCl_5.



$$O = \overset{\overset{\large OH}{|}}{\underset{\underset{\large OH}{|}}{S}} = O + PCl_5 \longrightarrow O = \overset{\overset{\large Cl}{|}}{\underset{\underset{\large OH}{|}}{S}} = O + POCl_3 + HCl$$

Chlorosulphonic acid



$$O=S(OH)_2=O + 2PCl_5 \longrightarrow O=SCl_2=O + 2POCl_3 + HCl$$

Sulphuryl chloride

(iii) One Cl-atom can also be replaced by the action of $POCl_3$ on it by giving chlorosulphonic acid as formed

$$2O_2S(OH)_2 + POCl_3 \longrightarrow 2Cl \cdot SO_2 \cdot OH + HCl + HPO_3$$

VII. **On heating** $KClO_3$ with conc. H_2SO_4, ClO_2 is evolved with explosion.

$$3KClO_3 + 3H_2SO_4 \xrightarrow{\Delta} 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$$

VIII. H_2SO_4 when treated with P_2O_5, loses water which combines with $\mathbf{P_2O_5}$ **and forms** HPO_3.

$$H_2SO_4 + P_2O_5 \longrightarrow SO_3 + 2HPO_3$$

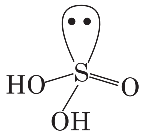
Uses

Sulphuric acid is used

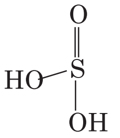
- as a laboratory reagent.
- for preparation of important acids such as HCl, HNO_3, H_3PO_4.
- for making of fertilizers.
- for sulphonation of organic compounds.
- for making of lead storage batteries.
- in the purification of petroleum.

These are many oxoacids formed by the sulphur. Among the acids, H_2SO_3 (sulphurous acid) and oil of vitriol, i.e. H_2SO_4 are of commercial importance.

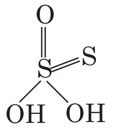
The structure of some of oxyacids of sulphur with their name and oxidation states are given below



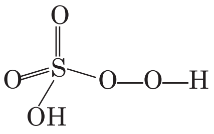
$H_2SO_3(+4)$
(strong reducing agent)
Sulphurous acid



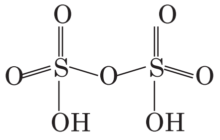
$H_2SO_4(+6)$
(strong dehydrating agent)
Sulphuric acid oil of vitriol



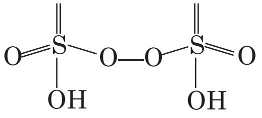
$H_2S_2O_3(+2)$
(reducing agent)
Thiosulphuric acid



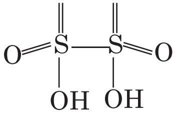
$H_2SO_5(+6)$
(strong oxidising agent)
Peroxomono sulphuric acid
or Caro's acid



$H_2S_2O_7(+6)$
(strong oxidising agent)
Pyrosulphuric acid or
oleumor disulphuric acid



$H_2S_2O_8(+6)$
(strong oxidising agent)
Peroxomono sulphuric acid or
Marshall's acid



$H_2S_2O_6(+5)$
(oxidising agent)
Dithionic acid

VIIA(17) Group Elements and their Compounds

This group consists of five elements namely **fluorine** (F), **chlorine** (Cl), **bromine** (Br), **iodine** (I) and **astatine** (At). These elements are also called **halogen** (means sea salts), i.e. their salts are abundantly present in sea water.

Occurrence

They do not occur free in nature but occur in combined state abundantly. Astatine is radioactive and occur in very infrequent way. These are mainly found as metal halides although iodine also occurs as iodate (IO_3^-).

Chlorine is most abundant among halogen and its commercial source is NaCl (common salt).

Sources of Halogens

Halogen	Main sources
Fluorine	Fluorspar (CaF_2), Fluorapatite [$Ca_5(PO_4)_3F$], Cryolite (Na_3AlF_6) etc.
Chlorine	Sea water, salt wells, salt beds (NaCl, KCl, $MgCl_2$, $CaCl_2$) etc.
Bromine	Sea water, salt lakes (NaBr, KBr, $MgBr_2$) etc.
Iodine	Brine wells, sea weeds (I^-), chile salt petre ($NaIO_3$ present as impurity) etc.

General and Physical Properties

Trends of general and physical properties exhibited by these elements are as follows

(i) **Electronic configuration** The general electronic configuration of halogens is ns^2np^5 (where, $n = 2, 3, 4, \ldots$). Due to the presence of 7 electrons in their valence shell, these elements have a high tendency to gain one electron and achieve nearest noble gas configuration.

(ii) **Atomic and Ionic radii** Halogens have small atomic radii than the elements of group 16 due to high effective nuclear charge. On moving down the group, it increases as the number of shells increases by one.

(iii) **Physical state** On moving down the group, the tendency to form condensed molecules increases. Thus, fluorine and chlorine are gases at ordinary temperature, bromine is a highly fuming liquid while iodine is a volatile solid.

(iv) **Melting and boiling points** On moving down the group from F to At, there is an increase in melting and boiling points. This is because van der Waals' forces increase as the size increases.

(v) **Ionisation energy** These all have high ionisation energy, i.e. have a little tendency to lose electrons. On moving down the group this tendency of ionisation energy decreases. Iodine because of the lowest IE, has some tendency to form I^+ ion as it forms compounds like ICl, ICN, etc, which in molten state conduct electricity showing the existence of I^+ cation.

(vi) **Electronegativity** Halogens have the high values of electronegativities and it decreases on moving downward from F to I. Thus, fluorine has the maximum value of electronegativity. As a result of the decrease of electronegativity, the non-metallic character increases from F to I. Hence, somewhat metallic character is observed in iodine.
e.g. In a few cases it forms a positive ion and has a metallic lustre.

(vii) **Electron gain enthalpy** These elements have maximum electron gain enthalpies in their respective periods because they have only one electron less than noble gas configuration, i.e. ns^2np^6. On moving down the group the magnitude of electron gain enthalpy (i.e., electron affinity) usually decreases. But electron affinity of fluorine is unexpectedly lower than Cl. This is because of the smaller size of F.
As a result of which the incoming electron does not feel much attraction but feels some repulsion. Chlorine has the highest electron affinity in the periodic table. Thus, the correct order will be
Cl > F > Br > I.

(viii) **Molecular state** Halogens exist as diatomic covalent molecules. In between their atoms weak van der Waals' forces exist. On account of which, the halogens are volatile in nature. With the increase in size, these forces increase and hence, change in physical state occurs from gas (F_2 and Cl_2) to solid (I_2).

(ix) **Oxidation state** When a halogen atom combines with an element of lesser electronegativity, it shows –1 oxidation state. On the other hand, when it combines with an element having higher electronegativity, it exhibits +1 oxidation state. However, F being most electronegative atom which always shows –1 oxidation state.
Other elements of this group also show +3, +5 and +7 oxidation states due to the presence of vacant *d*-orbitals in their valence shell.

(x) **Solubility** Halogens, being non-polar molecules, do not dissolve to a considerable extent in a polar solvent like water. However, fluorine reacts with water readily and forms mixture of oxygen and ozone as,

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

$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

Cl_2, Br_2 and I_2 are more soluble in non-polar solvents like $CHCl_3$, paraffins etc. In non-polar solvents, halogens exist as free molecules while in nucleophilic solvents like alcohols, liquid SO_2 etc halogens produce brown solution due to the formation of complex.
I_2 is more soluble in KI solution due to the formation of KI_3 (I_3^- ion), which also increases its solubility in water.

(xi) **Oxidising power** Standard reduction potentials of halogens are positive and decrease on going down the group. Thus, halogens act as **strong oxidising agents** and their oxidising power decreases from fluorine to iodine. The strength of an oxidising agent depends on several energy terms as

$$\boxed{E = \frac{1}{2}H_f + \frac{1}{2}H_{ev} + \frac{1}{2}H_d - EA - H_{hyd}}$$

where, H_f = enthalpy of fusion
H_{ev} = enthalpy of evaporation
H_{diss} = enthalpy of dissociation
H_{hyd} = enthalpy of hydration
EA = electron affinity

The value of E decreases from fluorine to iodine. Hence, fluorine is the **strongest oxidising agent**.

(xii) **Nature of bonds** Halogens due to the presence of seven electrons in their valence shell, are highly reactive. They form ionic compounds with highly electropositive metals readily. However, with weakly electropositive metals and non-metals, they form covalent bonds.

(xiii) **Bond dissociation energy** With the increase of size, the bond length increases from fluorine to iodine. Since, the bond length of fluorine is minimum, its bond dissociation energy should be highest. However, the bond dissociaition energy of fluorine is less than Cl—Cl and Br—Br.
It is due to the high interelectronic repulsions between non-bonding electrons in the 2*p*-orbitals of fluorine. Consequently, F—F bond becomes weaker in comparison to Cl—Cl and Br—Br bonds.

(xiv) **Colour** All the halogens are coloured and as the atomic number increases, the colour get deepens.

F	Cl	Br	I
Light yellow	Yellow green	Reddish brown	Deep violet

The colour is due to absorption of energy from visible light by the halogen molecules for excitation of outer electrons to higher energy levels. Fluorine absorbs violet portion of the light and thus, appears yellow. Iodine absorbs yellow and green portions of the light and thus, appears violet.
Thus, it is clear that on moving down the group the colour changes. This is called **blue shift** or **bathchromic shift.**

The physical properties described above can be summarised as

Physical Properties of Halogens

Property	Fluorine	Chlorine	Bromine	Iodine
Atomic number	9	17	35	53
Electronic configuration	[He] $2s^22p^5$	[Ne] $3s^23p^5$	[Ar] $3d^{10}4s^24p^5$	[Kr] $4d^{10}5s^25p^5$
Atomic mass (u)	18.998	35.453	79.909	126.904
Physical state	Gas	Gas	Liquid	Solid
M.P. (°C)	–218.6	–101.0	–7.2	113.9
B.P. (°C)	–188.1	–34.6	59.5	185.2
Density in liquid state (g cm^{-3})	1.108	1.1557	2.948	3.76 (in solid state)

Property	Fluorine	Chlorine	Bromine	Iodine
Colour of vapour	Pale yellow	Greenish yellow	Orange red	Violet
Colour of liquid	Clear yellow	Amber yellow	Reddish brown	Shining dark solid
Atomic radius (Å)	0.72	0.99	1.14	1.33
Ionic radius of X^- ion (Å)	1.33	1.84	1.96	2.20
Atomic volume (cc)	17.1	18.7	23.5	25.7
Electronegativity	4.0	3.0	2.8	2.5
Electron affinity (kJ mol^{-1})	332.6	348.6	324.5	295.5
Ionisation energy (kJ mol^{-1})	1680.8	1255.5	1142.8	1008.3
Oxidation states	–1	–1, +1, +3, +4, +5, +6, +7	–1, +1, +3, +4, +5, +6	–1, +1, +3, +4, +5, +6, +7
Bond energy (kJ mol^{-1})	158.8	242.6	192.8	151.1
Standard electrode potential (volt)	+2.8	+1.36	+1.08	+0.54

Chemical Properties

Halogens are most reactive non-metals and their reactivity decreases on moving down the group. The important factors that are responsible for the low reactivity of fluorine are

(i) the small size and

(ii) the highest electronegativity.

1. Reaction with Water

Fluorine decomposes water very readily even at low temperaure and in dark forming mixture of O_2 and O_3. Cl_2 decomposes water in the presence of sunlight while bromine decomposes water very slowly in presence of sunlight. Iodine, however, does not decompose water.

2. Reaction with Hydrogen or Formation of Halogen Acids

All the halogens react with hydrogen to form volatile covalent hydrides, of formula H*X*. Since, H-atom has less electronegativity than each of the halogens therefore the oxidation state of H in these compounds is +1 and that of halogen is –1. It is the positive oxidation state of H and negative oxidation state of halogens due to which these compounds are called **hydrogen halides** (H^+X^-).

Since, these compounds ionise in aqueous solution to produce H^+ (or H_3O^+) these are also called **'halogen acids'.**

$$HX + H_2O \longrightarrow H_3O^+ + X^-$$

These compounds are also known by other names like **hydroacids** or **hydrohalic acid** etc. The reactivity of halogens towards hydrogen decreases from fluorine to iodine. These are colourless, irritating gases at room temperature.

As we move down the group, *boiling point* increases with increase in size of halogen. However, boiling point of HF is abnormally high due to H-bonding.

Acidic character and reducing character of these hydrides increase on moving from F to I.

3. Reaction with Metals and Non-metals

Halogens combine with metals and non-metals to form halides such as $MgBr_2$, XeF_6, PCl_3, PCl_5, SF_6 etc. The ionic character of *M*—*X* bond decreases as the size of halogen atom increases.

$$M\text{—F} > M\text{—Cl} > M\text{—Br} > M\text{—I}$$

4. Reaction with Oxygen

Halogens form binary compounds with oxygen but most of them are unstable. Fluorine forms only two binary compounds, i.e. OF_2 and O_2F_2 (called **oxygen fluorides).** Chlorine, bromine and iodine form oxides in which the oxidation state of halogen varies from +1 to +7.

e.g. $Cl_2O(+1)$, $ClO_2(+4)$, $Cl_2O_6(+6)$, $ClO_3(+6)$, $Cl_2O_7(+7)$; $Br_2O(+1)$, $BoO_2(+4)$; $I_2O_4(+4)$, $I_2O_5(+5)$ etc.

Anomalous Behaviour of Fluorine

Fluorine, because of its small size, high charge density, non-availability of *d*-orbitals and low bond dissociation energy differs from the rest of the halogens in following ways

- Fluorine shows only –1 oxidation state due to its maximum electronegativity, whereas the other halogens can show negative as well as positive oxidation state, i.e. between –1 and +7.
- Maximum covalency of fluorine is one as there is no *d*-orbital in its valence shell. Other members can have maximum covalency of 7 because of vacant *d* orbitals.
- Fluorine because of its low bond dissociation energy is very reactive. However, in Cl_2 and Br_2, *X*—*X* bond is stronger.
- HF has a high tendency to form H-bond, thus, it is a liquid (b.p. 19°C) while HCl, HBr and HI due to lack of such a tendency, are gases under ordinary conditions.
- Hydrofluoric acid being a dibasic acid (H_2F_2), forms two series of salt such as $NaHF_2$ and Na_2F_2 while HCl, HBr and HI are monobasic in nature.
- Mostly fluorides are ionic and contain F^- ion while other halides have frequently molecular lattices.
- Fluorine when combines with sulphur, forms SF_6 while no other halogen forms the hexahalide with sulphur.

- Fluorine does not form any **oxo acid** but other halogens form a number of oxyacids specially Cl.
- Fluorides are more stable than corresponding chlorine compounds.
- Fluorine does not form polyhalides like F_3^- but other halogens do so, e.g. I_3^-, Br_3^- etc.

Compounds of Group 17 Elements

Being highly reactive, halogens form several compounds but we will study some of them which are important from exam point of view.

Some important compounds of group17 are given below

Halogen Acids

Now, we study their methods of preparation physical and chemical properties in detail.

Methods of Preparation

Halogen acids are prepared by the following methods are

I. **By the direct combination of H_2 and** X_2 (X = Cl, Br, I) **under different conditions,**

(i) HCl is produced by burning Cl_2 in the excess of H_2 or by the action of H_2 on Cl_2 in presence of sunlight.

$$Cl_2 + \underset{\text{(excess)}}{H_2} \xrightarrow{\text{Burn}} 2HCl$$

$$Cl_2 + H_2 \xrightarrow{\text{Sunlight}} 2HCl + \text{heat}$$

(ii) HBr can be prepared by passing a mixture of H_2 and Br_2 over a platinum spiral heated to redness by an electric current.

$$H_2 + Br_2 \xrightarrow[\text{Pt spiral}]{\text{Heat}} 2HBr$$

(iii) HI can be prepared in small quantities by passing H_2 and I_2 vapours over red hot fine platinum.

$$H_2 + I_2 \underset{\text{Pt}}{\overset{\text{Heat (450°C)}}{\rightleftharpoons}} 2HI$$

II. **By heating an appropriate halide with conc. H_2SO_4 or conc. H_3PO_4.**

(i) HF and HCl can be prepared by heating CaF_2 and NaCl respectively with conc H_2SO_4.

$$CaF_2 + H_2SO_4 \xrightarrow{\Delta} CaSO_4 + 2HF$$

$$2NaCl + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2HCl$$

(ii) When NaBr (or KBr) and NaI (or KI) are heated with conc. H_2SO_4, HBr and HI are produced respectively.

$$2MBr(M = \text{Na, K}) + H_2SO_4 \xrightarrow{\Delta} M_2SO_4 + 2HBr$$

$$2MI(M = \text{Na, K}) + H_2SO_4 \xrightarrow{\Delta} M_2SO_4 + 2HI$$

The HBr and HI are formed react with conc. H_2SO_4 and are oxidised to Br_2 and I_2 respectively.

$$2HBr + H_2SO_4 \longrightarrow SO_2 + 2H_2O + Br_2$$

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

$$6HI + H_2SO_4 \longrightarrow S + 4H_2O + 3I_2$$

$$8HI + H_2SO_4 \longrightarrow H_2S + 4H_2O + 4I_2$$

Now as, HBr and HI are not able to reduce conc H_3PO_4, these acids are obtained by heating NaBr and NaI respectively with conc. H_3PO_4.

$$3NaBr + H_3PO_4 \xrightarrow{\Delta} Na_3PO_4 + 3HBr$$

$$3NaI + H_3PO_4 \xrightarrow{\Delta} Na_3PO_4 + 3HI$$

III. **By the action of water on a mixture of red phosphorus and Br_2 or I_2** (for HBr and HI), e.g. HBr and HI can be prepared in the laboratory by slowly pouring a mixture of red phosphorus (1 part) and Br_2 or I_2 (20 parts) from a dropping funnel, fitted to a flask.

$$8H_2O + \underset{\text{(Red)}}{2P} + 5Br_2 \longrightarrow 10HBr + 2H_3PO_4$$

$$8H_2O + \underset{\text{(Red)}}{2P} + 5I_2 \longrightarrow 10HI + 2H_3PO_4$$

Methods of preparation of only HCl

- HCl can be prepared in the laboratory by heating NaCl with conc. H_2SO_4.

$$2NaCl + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2HCl$$

The gas HCl obtained as above cannot be dried over P_2O_5 or quick lime (CaO), since HCl reacts with both of these substances.

$$2P_2O_5 + 3HCl \longrightarrow POCl_3 + 3HPO_3$$

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

- Pure HCl is obtained by the action of water on $SiCl_4$. (hydrolysis $SiCl_4$).

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

- Considerable quantities of HCl are obtained as a by-product in the manufacture of Na_2CO_3 from NaCl by **Le-Blanc process.**

Physical Properties

(i) **Hydrofluoric acid** exists as a dimeric molecule, (H_2F_2) even in the gaseous state because of intermolecular H-bonding.

Due to its dimeric nature, H_2F_2 gives two types of salts which contain HF_2^- and F_2^{2-} ions.

$$2HF \rightleftharpoons HF_2^- + H^+$$

$$HF_2^- \rightleftharpoons F_2^{2-} + H^+$$

$$HX \rightleftharpoons H^+ + X^- \qquad (X = \text{Cl, Br, I})$$

(ii) **Physical state** Anhydrous HF is a liquid at ordinary temperature and fumes strongly in air, while the remaining hydrogen halides, are colourless gas, with pungent smell and acidic taste.

(iii) **Thermal stability** In HX molecule, as the size of the halogen atom increases from F to I, H—X bond length increases (i.e. H—F < H—Cl < HBr < HI) due to which bond strength decreases (H—F > HCl > HBr > HI). By successive decreases in the bond strength the thermal stability of HX decreases, i.e. in H—F > HCl > HBr > HI.

Maximum thermal stability of HF is the reason because of which it is not oxidised even by strong oxidising agents.

(iv) **Boiling point** As we move down the group from HF to HI, the magnitude of van der Waals' forces increases and hence, the boiling point of the hydrides should increase as,

$$\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$$

But, this order is not correct. Actually boiling point first decreases from HF to HCl and then increases until we reach HI. The anomaly is due to the presence of H-bonding in HF. Thus, the actual order will be

$$\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$$

(v) **Volatility** HF is the least volatile and HCl is the most volatile. The least volatility of HF molecule is due to much stronger H—F bond and association of HF molecules to form dimer, H_2F_2, through H-bonding.

The maximum volatility of HCl is due to its monomeric nature and less strength of H—Cl bond in HCl molecule.

(vi) **Solubility** All the hydrogen halides are highly soluble in water and give a constant boiling mixture, which is called azeotropic mixture. The azeotropic mixture of each acid contains a particular weight-percentage of the acid and boils at a fixed temperature.

The dilute solution of the acid cannot be concentrated by boiling it beyond the weight-percentage of the acid.

For example dilute solution of HCl cannot be concentrated by boiling beyond 20.2%.

(vii) **Combustible** All the halogen acids are neither combustible nor supporter of combustion.

(viii) **Ionic character** H—X bond in gaseous state HX molecules is largely covalent and has very small amount of ionic character.

The covalent character of H—X bond is also confirmed by the fact that melting and boiling points of hydrogen halides are low and pure liquid halides are poor conductors of electricity. The ionic character of H—X bond in gaseous HX molecules is in the order

$$\text{H—F} > \text{H—Cl} > \text{H—Br} > \text{H—I}$$

The above order of the ionic character of H—X bond in gaseous HX molecules has been explained on the basis of

- electronegativity difference value, $(\chi_X - \chi_H)$.
- dipole moment values of HX molecules.
- polarisation in between cations and anions (see chemical bonding).

(ix) **Acidic nature** HX molecules in the gaseous state are essentially covalent and hence, are not able to ionise to yield proton (H^+) but in aqueous solution, they give hydrated proton, $H^+(aq)$ and hence, act as Bronsted acids.

$$HX(g) + H_2O \longrightarrow H_3O^+ + X^-(aq)$$

The acidic strength (i.e. proton releasing power) of halogen acids in aqueous solution is in the order as,

$$\text{HF}\,(aq) < \text{HI}(aq) < \text{HCl}(aq) < \text{HBr}(aq)$$

However, the relative order of the acidic strength of HX molecules, in methanol solvent, has been found as

$$\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$$

- The important properties of halogen acids are summarised below in tabulated form.

Properties of Halogen Acids

Property	HF	HCl	HBr	HI
Monomeric or dimeric	Dimeric (H_2F_2)	Monomeric (HCl)	Monomeric (HBr)	Monomeric (HI)
Physical state at 15°C	Liquid	Gas	Gas	Gas
H—X bond length (Å)	0.92	1.27	1.41	1.61
		Increases ⟶		
Strength of H—X bond or thermal stability of HX molecule	Maximum	High	Not so high	Very little
		Decreases ⟶		
H—X bond dissociation energy or heat of dissociation (kJ mol^{-1})	+ 574.0	+ 428.1	+ 362.5	+ 294.6
		Decreases ⟶		
Dissociation temperature (°C)	Does not dissociate	1500	800	180
		Decreases ⟶		
Melting point (°C)	–83	–111	–86	–50.8
Boiling point (°C)	+ 19.4 (Maximum)	– 85 (Minimum)	– 67	–35.0
Hydrogen bonding	Maximum	Little	Very little	Very little
Solubility in water at 0°C (g/L)	85.3	42.0	49.0	57.1
Dipole moment values when HX molecules are assumed to be completely ionic [calculated values (C.m.)]	1.47×10^{-29}	2.03×10^{-29}	2.25×10^{-29}	2.57×10^{-29}
		Increases ⟶		
% of ionic character in the gaseous HX molecules				
(a) as calculated from their moment values	43.5	16.8	11.6	4.9
(b) as calculated from Hanny-Smith's equation	40.14	19.5	15.04	8.87
Heat evolved (kJ mol^{-1}) in the reaction, $HX(g) + aq \longrightarrow HX(aq) \longrightarrow H^+(aq) + X^-(aq)$ or $HX(g) + H_2O \longrightarrow H_3O^+ + X^-(aq)$ (called heat of ionisation)	–9.0 Weakest acid	– 60.8 Very strong acid	– 64.6 Strongest acid	– 58.4 Strong acid
		Decreases ⟶		
Reducing property	Not a reducing agent	Mild reducing agent	Strong reducing agent	Strongest reducing agent
		Increases ⟶		
Heat of formation (kJ mol^{-1}) [$\frac{1}{2} X_2 (s, l, g) + \frac{1}{2} H_2(g) \rightarrow HX(g)$ ΔH = heat required (+) or released (–)]	–271.1 (g)	– 92.3 (g)	–36.4 (g)	+25.4 (g)
		Increases ⟶		
Heat of dehydration (kJ mol^{-1}) [$HX(aq) + \text{heat} \longrightarrow HX(g)$]	+48.0	+18.0	+21.0	+23.0
Heat of neutralisation with NaOH (kJ mol^{-1})	+ 68.2	+57.3	+57.9	+57.6
Apparent degree of dissociation in 0.1 N solution at room temperature	0.08	0.93	0.94	0.95
Solubility of silver salt (g /100 g)	172	0.00154	0.000084	0.000028
		Increases ⟶		
Solubility of calcium salt (g /100 g)	0.0016	42.7	58.8	67.6
		Increases ⟶		

Chemical Properties

Some following reactions are common to halogen acids are

- Anhydrous hydrofluoric acid does not show acidic property and hence, does not attack metals except potassium. However, its concentrated solution shows acidic character because it reacts with metals (e.g. Zn), their hydroxides, carbonates, oxides etc to form metallic fluorides.

$$Zn + H_2F_2 \longrightarrow ZnF_2 + H_2$$
$$2NaOH + H_2F_2 \longrightarrow Na_2F_2 + 2H_2O$$
$$B_2O_3 + 3H_2F_2 \longrightarrow 2BF_3 + 3H_2O$$

The aqueous solution of HCl, HBr and HI show acidic nature and hence, turn blue litmus red. Each of them reacts with metals, their hydroxides, carbonates, oxides etc to form metallic halides as

$$Zn + 2HX(X = Cl, Br, I) \longrightarrow ZnX_2 + H_2\uparrow$$
$$NaOH + HX \longrightarrow NaX + H_2O$$
$$Na_2CO_3 + 2HX \longrightarrow 2NaX + CO_2\uparrow + H_2O$$

- HCl, HBr and HI do not react with SiO_2 and glass. HF attacks on SiO_2 and gives hydro fluosilicic acid (H_2SiF_6)

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

The white fumes of SiF_4 form a gelatinous mass of H_2SiO_3 or H_4SiO_4 and hydro-fluorosilicic acid (H_2SiF_6) with a drop of water held in these fumes.

$$3SiF_4 + 3H_2O \longrightarrow H_2SiO_3 + 2H_2SiF_6$$
$$\text{or } 3SiF_4 + 4H_2O \to H_2SiO_3 \cdot H_2O \text{ or } H_4SiO_4 + 2H_2SiF_6$$

Now, we know that glass is composed of Na_2SiO_3 and $CaSiO_3$. HF reacts with these silicates and form sodium and calcium fluosilicate (Na_2SiF_6 and $CaSiF_6$) respectively.

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$$
$$CaSiO_3 + 6HF \longrightarrow CaSiF_6 + 3H_2O$$

Since, HF reacts with glass as shown above, it should not be kept in glass vessels; it should be stored in waxed glass vessels because wax prevents the action of HF on glass. The property of HF to act on glass has been utilised in the etching of glass and in making scales on the glass instruments. For etching glass, commercial H_2F_2 (40-60%) is used.

- HCl decomposes the salts of weaker acids like carbonates, bicarbonates, sulphides, sulphites, thiosulphates and nitrites as

$$2Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2\uparrow$$
$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2\uparrow$$
$$Na_2S + 2HCl \longrightarrow 2NaCl + H_2S\uparrow$$
$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2\uparrow$$
$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + S + H_2O + SO_2\uparrow$$
$$2NaNO_2 + 2HCl \longrightarrow 2NaCl + H_2O + NO + NO_2\uparrow$$

With metal oxides and hydroxides, HCl forms salt and water.

- With $AgNO_3$ solution, HF forms AgF which becomes soluble in water. On the other hand, HCl, HBr and HI give the precipitate of AgCl (white), AgBr (pale yellow) and AgI (yellow) respectively.

$$AgNO_3 + HF \longrightarrow \underset{\text{Soluble}}{AgF} + HNO_3$$
$$AgNO_3 + \underset{(X = Cl, Br, I)}{HX} \longrightarrow \underset{\text{Ppt.}}{AgX} + HNO_3$$

- HF does not give any precipitate with the solution of Pb (II) salts like $Pb(NO_3)_2$, $(CH_3COO)_2Pb$ etc, while HCl, HBr and HI give the precipitate of $PbCl_2$ (white) $PbBr_2$ (white) and PbI_2 (yellow) respectively.

$$Pb(NO_3)_2 + \underset{(X = Cl, Br, I)}{2HX} \longrightarrow PbX_2 + 2HNO_3$$
$$(CH_3COO)_2Pb + 2HX \longrightarrow PbX_2 + 2CH_3COOH$$

[All the three precipitates (i.e. $PbCl_2$, $PbBr_2$ and PbI_2) are soluble in hot water.]

- HF does not give any precipitate with mercurous and mercuric salts. HCl forms a white precipitate of Hg_2Cl_2 with $Hg_2(NO_3)_2$ solution.

$$2HCl + Hg_2(NO_3)_2 \longrightarrow \underset{\text{White}}{Hg_2Cl_2} + 2HNO_3$$

Hg_2Cl_2 is soluble in *aqua-regia*. HI forms scarlet precipitate of HgI_2 with $HgCl_2$ solution.

$$2HI + HgCl_2 \longrightarrow \underset{\text{Scarlet}}{HgI_2} + 2HCl$$

- HF, HCl and HBr do not react with $CuSO_4$ solution, but HI gives CuI_2 which, being unstable, decomposes into CuI and I_2 as,

$$2HI + CuSO_4 \longrightarrow CuI_2 + H_2SO_4$$
$$2CuI_2 \longrightarrow 2CuI + I_2$$

- With the solution of $BaCl_2$, $SrCl_2$ and $CaCl_2$ salts, H_2F_2 forms white precipitate of BaF_2, SrF_2 and CaF_2 respectively. Other acids do not give any precipitate since MX_2 (M = Ba, Sr, Ca; X = Br, I) are soluble.

$$MCl_2 + H_2F_2 \longrightarrow \underset{\text{Ppt.}}{MF_2} + 2HCl$$
$$MCl_2 + 2HX \longrightarrow \underset{\text{Soluble}}{MX_2} + 2HCl$$

- Anhydrous HF does not attack any metal under ordinary conditions except potassium while acid reacts with many metals to form their fluorides with the evolution of H_2.

$$\text{e.g.} \quad Zn + 2HF \longrightarrow ZnF_2 + H_2\uparrow$$
$$Mg + 2HF \longrightarrow MgF_2 + H_2\uparrow$$

In these reactions, the metal is oxidised and HF is reduced to H_2.

Gaseous HCl reacts with hot metals while aqueous HCl reacts with cold metals. The reaction between aqueous HCl and Pt, Au, Ag and Hg is not unreadable. Some examples of the reaction between metal and HCl are as,

(i) Aqueous HCl reacts with Ag in presence of air.

$$4Ag + 4HCl + O_2 \longrightarrow 4AgCl + 2H_2O$$

(ii) Cu dissolves in conc HCl. Fe reacts with HCl and gives lower chloride *viz*., $FeCl_2$ (not $FeCl_3$).

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2\uparrow$$

HBr dissolves Fe, Zn, Sn, Cu, Ag, Pb etc., with the liberation of H_2 and formation of bromides. HBr attacks Hg very slowly, forming H_2 and $HgBr_2$.

- When HX molecule or X^- ion reacts with an oxidising agent, it reduces the oxidising agent and is itself oxidised to X_2 molecule.

$$2HX + O_2 \longrightarrow 2H_2O + 2X_2 \text{ (molecular equation)}$$

It has been found that the tendency of X^- ions to lose electrons increases from F^- to I^- ion. Accordingly, the order of reducing power of X^- ions or HX molecules is as follow.

$$F^- < Cl^- < Br^- < I^- \quad \text{or} \quad HF < HCl < HBr < HI$$

As a matter of fact, HF or F^- does not show reducing properties at all (even with very strong oxidising agent).

The increasing order of the reducing power of HX molecules or X^- ion can be explained on the basis of decrease in electronegative character from F to I.

I. As reducing agent, HCl molecule or Cl^- ion is weaker than HBr and HI both and hence, reduces only strong oxidising agents and is itself oxidised to Cl_2 which is evolved as a yellowish green gas. Thus, HCl reduces

(i) **MnO_2** (acidified with conc. H_2SO_4) **to** $MnSO_4$

$$MnO_2 + H_2SO_4 + 2HCl \longrightarrow MnSO_4 + 2H_2O + Cl_2\uparrow$$

(ii) **MnO_2 to $MnCl_2$**

$$MnO_2 + \underset{\text{(Conc.)}}{4HCl} \longrightarrow MnCl_2 + 2H_2O + Cl_2\uparrow$$

(iii) **$KMnO_4$ to $MnCl_2$**

$$2KMnO_4 + \underset{\text{(Conc.)}}{16HCl} \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2\uparrow$$

(iv) **$K_2Cr_2O_7$ to $CrCl_3$**

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2\uparrow$$

(v) **PbO_2 to $PbCl_2$**

$$PbO_2 + \underset{\text{(Hot and conc.)}}{4HCl} \longrightarrow PbCl_2 + 2H_2O + Cl_2\uparrow$$

(vi) **Pb_3O_4 (red lead) to $PbCl_2$**

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2\uparrow$$

(vii) **O_2 to H_2O in presence of Cu-salts** (catalyst)

$$O_2 + 4HCl \longrightarrow 2H_2O + 2Cl_2\uparrow$$

(viii) **Bleaching powder ($CaOCl_2$) to $CaCl_2$**

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2\uparrow$$

(ix) **F_2 to HF but neither Br_2 to HBr nor I_2 to HI**

$$2HCl + F_2 \longrightarrow 2HF + Cl_2] \text{ possible}$$

$$\left.\begin{array}{l} 2HCl + Br_2 \longrightarrow 2HBr + Cl_2 \\ 2HCl + I_2 \longrightarrow 2HI + Cl_2 \end{array}\right] \text{not possible}$$

II. Since, HBr or Br^- is a weaker reducing agent than HI or I^-, it reduces some oxidising agents and is itself oxidised to Br_2 which is evolved as reddish brown vapour. Thus, HBr reduces as,

(i) **H_2SO_4 to SO_2**

$$2HBr + H_2SO_4 \longrightarrow SO_2 + 2H_2O + Br_2$$

(ii) **Atmospheric O_2 to H_2O**

$$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$

(iii) **Acidified solution of $KMnO_4$ to $MnSO_4$**

$$2KMnO_4 + 3H_2SO_4 + 10HBr \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5Br_2$$

(iv) **Acidified solution of $K_2Cr_2O_7$ to $Cr_2(SO_4)_3$**

$$K_2Cr_2O_7 + 4H_2SO_4 + 6HBr \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Br_2$$

(v) **H_2O_2 to H_2O**

$$2HBr + H_2O_2 \longrightarrow 2H_2O + Br_2$$

(vi) **$FeCl_3$ to $FeCl_2$**

$$FeCl_3 + 2HBr \longrightarrow 2FeCl_2 + 2HCl + Br_2$$

(vii) **F_2 to HF and Cl_2 to HCl but not I_2 to HI**

$$\left.\begin{array}{l} 2HBr + F_2 \longrightarrow 2HF + Br_2 \\ 2HBr + Cl_2 \longrightarrow 2HCl + Br_2 \end{array}\right] \text{possible}$$

$$2HBr + I_2 \longrightarrow 2HI + Br_2] \text{ not possible}$$

(viii) **Acidified MnO_2 to $MnSO_4$**

$$MnO_2 + H_2SO_4 + 2HBr \longrightarrow MnSO_4 + 2H_2O + Br_2$$

III. Being the strongest reducing agent, HI or I^- reduces even very strong oxidising agents and is itself oxidised to I_2 which is evolved as violet vapour. Thus, HI or I^- reduces

(i) **H_2SO_4 to SO_2, S or H_2S** (or S^{2-})

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

$$6HI + H_2SO_4 \longrightarrow S + 4H_2O + 3I_2$$

$$8HI + H_2SO_4 \longrightarrow H_2S + 4H_2O + 4I_2$$

(ii) **HNO_3 to NO or NO_2**

$$2HNO_3 + 6HI \longrightarrow 2NO + 4H_2O + 3I_2$$

$$2HNO_3 + 2HI \longrightarrow 2NO_2 + 2H_2O + I_2$$

(iii) **HNO_2 to NO**

$$2HNO_2 + 2HI \longrightarrow 2NO + 2H_2O + I_2$$

(iv) **$FeCl_3$ to $FeCl_2$**

$$2FeCl_3 + 2HI \longrightarrow 2FeCl_2 + 2HCl + I_2$$

(v) **$CuSO_4$ to CuI**

$$2CuSO_4 + 4HI \longrightarrow 2CuI + 2H_2SO_4 + I_2$$

(vi) **Atmospheric O_2 to H_2O**

$$4HI + O_2 \longrightarrow 2H_2O + 2I_2$$

(due to the liberation of free I_2, the solution of HI turns brown, when kept in air).

(vii) **Acdified MnO_2 to $MnSO_4$**

$$MnO_2 + H_2SO_4 + 2HI \longrightarrow MnSO_4 + 2H_2O + I_2$$

(viii) **Iodic acid (HIO_3) to I_2**

$$5HI + HIO_3 \longrightarrow 3H_2O + 3I_2$$

(ix) **Arsenate** (AsO_4^{3-}) **to arsenite** (AsO_3^{3-})

$$2I^- + AsO_4^{3-} + 2H^+ \longrightarrow AsO_3^{3-} + H_2O + I_2$$

(x) **Acidified solution of $KMnO_4$ to $MnSO_4$**

$$10HI + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

2. Interhalogen Compounds

Halogens react with each other to produce a number of interhalogen compounds (XX_n' where, $n = 1, 3, 5$ or 7). An interhalogen compound, infact, is regarded as the halide of more electropositive halogen, with a halogen with less electropositive character (electropositive character increases down the group).

Thus, as far as this trend is concerned, F cannot form any interhalogen compound as central atom, while I has the maximum tendency to form interhalogen compounds.

Categories

Interhalogens can be grouped into four categories namely XX' (e.g. ClF, BrF etc.) XX'_3 (e.g. ClF_3 BrF_3 etc.) XX'_5 (e.g. ClF_5, IF_5 etc.) and XX'_7 (e.g. IF_7). The oxidation states of X atom in these are +1, +3, +5 and +7 respectively.

Some important examples of interhalogen compound are

Examples of Interhalogens Compounds

XX'	XX_3'	XX_5'	XX_7'
ClF	ClF_3	ClF_5	IF_7
BrF	BrF_3	BrF_5	
BrCl	IF_3	IF_5	
ICl	$ICl_3(I_2Cl_6)$		
IBr			
IF			

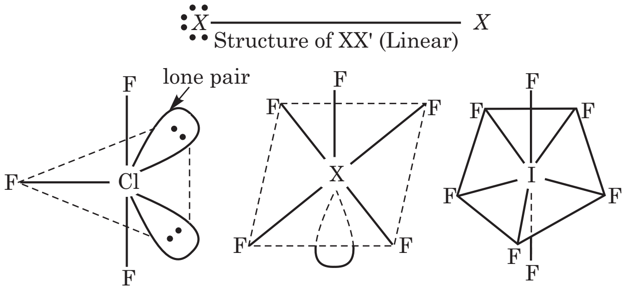
Stability

The stability of interhalogen compounds increases as the size of central atom increases.

Out of two halogens the one with smaller size and higher electronegativity assigned negative oxidation state.

Structure

XX' interhalogen compounds have linear structure, XX_3' compounds have bent T structure, XX_5' compounds have square pyramidal structure and IF_7 have pentagonal bipyramidal structure.



Structure of XX_3' type (*T*-shape)

Structure of XX_5' type (Square pyramidal)

Structure of XX_7' type (Pentagonal bipyramidal)

Structure of interhalogen compounds

Example 8. *The correct statement about* ICl_5 *and* ICl_4^- *is* ***(JEE Main 2019)***

(a) ICl_5 is square pyramidal and ICl_4^- is tetrahedral

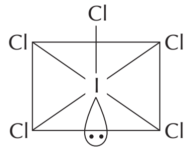
(b) ICl_5 is square pyramidal and ICl_4^- is square planar

(c) Both are isostructural

(d) ICl_5 is trigonal bipyramidal and ICl_4^- is tetrahedral

Sol. (b) For $\ddot{I}Cl_5$,

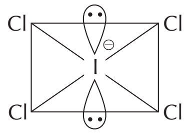
$$H = \frac{1}{2}(7 + 5 - 0 + 0) = 6\ (sp^3d^2)$$



sp^3d^2-hybridised
Geometry : Octahedral
Shape / Structure : Square pyramidal

For $\ddot{I}Cl_4^-$,

$$H = \frac{1}{2}(7 + 4 - 0 + 1) = 6\ (sp^3d^2)$$



sp^3d^2-hybridised
Geometry : Octahedral
Shape/Structure : Square planar

So, ICl_5 and ICl_4^- are isolobal but not isostructural.

Pseudohalides

There are several uni-negative groups which show characteristics of halide ions. These are called **pseudohalides** or **pseudohalide ions.**

As the halides of halide ions are called **halogens**, the covalent dimers of pseudohalide ions are called **pseudohalogens.** Some of them are as follows

Some Pseudohalides and their Formulae

Pseudohalide ions	Formulae	Pseudohalogens	Formulae
Cyanide	CN^-	Cyanogen	$(CN)_2$
Cyanate	OCN^-	Oxocyanogen	$(OCN)_2$
Thiocyanate	SCN^-	Thiocyanogen	$(SCN)_2$
Selenocyanate	$SeCN^-$	Selenocyanogen	$(SeCN)_2$
Azidothiocarbonate	$SCSN_3^-$	Azidocarbon disulphide	$(SCSN_3)_2$
Isocyanate	ONC^-		

I. Some important similarities between halide and pseudohalide ions are

- Both can form ionic compounds, such as AgCl (AgCN), $PbCl_2$ $[Pb(NCS)_2]$, covalent compounds, e.g. ICl(ICN), $SiCl_4$ $[Si(NCS)_4]$, complex ions with transition metal ions, e.g. $[FeF_6]^{3-}$, $Fe(CN)_6^{3-}$; $[CoCl_4]^{2-}$, $[Co(SCN)_4]^{2-}$ etc.
- As halide ions combine together to form *interhalogen* compounds, pseudohalide ions also combine together to form *inter pseudohalogen* compounds like $CN \cdot N_3$, $CN \cdot SCN$ etc.
- Both of them combine with H_2 to form monobasic hydracids, e.g. HCl, HCN etc.
- Both give *insoluble* salts with Ag^+, Pb^{2+} and Hg^+ ions.
  e.g.
  $$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$$
  $$Ag^+ + CN^- \longrightarrow AgCN\downarrow$$
- Both of them can coordinate with two metal ions simultaneously, i.e. can acts as bridging ligands, e.g. CN^- in $R_2Au(CN)_4$, similarly Cl^- in R_2AuCl_2.

II. However, halide and pseudohalide ions differ in following respects

- Pseudohalide ions are stronger ligands than halide ions due to the ability of former to form the σ as well as π-bond.
- Pseudohalide ions, being made up of two hetero atoms can function as **ambidentate ligands** (see coordination compounds for detail). However, halide ions do not show this behaviour.

III. Similarities between halogens and pseudohalogens are

- Both are dimeric and fairly volatile (with the exception of polymeric thiocyanogen) in the free state.
- Pseudohalogens are **isomorphous** to halogens when in the free or solid state. e.g. Cl_2 is isomorphous to $(CN)_2$; Br_2 is isomorphous to $(SCN)_2$.
- Both can be added to ethylenic double bond linkage as
  $$CH_2 = CH_2 + Cl_2 \longrightarrow CH_2Cl—CH_2Cl$$
  $$CH_2 = CH_2 + (SCN)_2 \longrightarrow CH_2SCN—CH_2SCN$$
- Both react with alkalies as
  $$(SCN)_2 + \underset{\text{(Cold and dilute)}}{2KOH} \longrightarrow KSCN + KOSCN + H_2O$$
  $$Cl_2 + \underset{\text{(Cold and dilute)}}{2KOH} \longrightarrow KCl + KOCl + H_2O$$

IV. Halogen and pseudohalogens differ from each other in the fact that pseudohalogens have the ability to undergo polymerisation as,

$$n(CN)_2 \xrightarrow{500^\circ C} 2(CN)_n$$

Similarly, $$n(SCN)_2 \xrightarrow[\text{temp.}]{\text{Room}} 2(SCN)_n$$

On the other hand halogens do not have such a tendency.

4. Oxides of Halogens

In these oxides, bonds are mainly covalent, since there is a very small difference between the electronegativity of oxygen and the halogens.

Oxides of chlorine are acidic. This the acidic nature increases as the percentage of oxygen increases. Moreover, these are powerful oxidising agents and decompose explosively when exposed to mechanical shock or on heating.

All the three monoxides *viz.,* OF_2, Cl_2O and Br_2O have **tetrahedral structure** involving sp^3 hybridisation of oxygen. The bond angle increases as the size of halogen atom increases. Thus, the bond angle varies in the order **FOF < ClOCl < BrOBr.** This is because electrons in the case of OF_2 are nearer to fluorine due to high electronegativity of F compared to Cl to Br.

The bonded electron pairs in Cl_2O and Br_2O are closer to oxygen making the repulsion between them more. Due to this the lone pair-lone pair repulsion on oxygen to some extent decreases. Also due to the bulkiness of Cl and Br, the angles of ClOCl and BrOBr increase to such an extent that $109^\circ 28'$, (the tetrahedral angle), is approached.

Halogens form following oxides are

Oxides of Halogens

Oxides of chlorine	Oxides of bromine	Oxides of iodine
Cl_2O	Br_2O	I_2O_5
ClO_2	BrO_2	
Cl_2O_6	BrO_3	
Cl_2O_7		

5. Oxoacids of Halogens

Because of the high electronegativity and small size, fluorine forms only one oxoacid, i.e. HOF (known as **fluoric acid** or **hypofluorous acid).** Other halogens form many oxoacids. These are stable in aqueous solution or in the form of their salts.

Examples of the oxoacids of halogens are given below

Oxoacids of Halogens

Halogen	Hypohalous acids, HXO (X = +1)	Halous acids, HXO$_2$ (X = + 3)	Halic acids, HXO$_3$ (X = +5)	Perhalic acids, HXO$_4$ (X = +7)
Chlorine	HClO	$HClO_2$	$HClO_3$	$HClO_4$
Bromine	HBrO	—	$HBrO_3$	—
Iodine	HIO	—	HIO_3	HIO_4, $HIO_4 \cdot 2H_2O$, $HIO_4 \cdot 2H_2O$, $2HIO_4 \cdot H_2O$

Some of the general properties of oxoacids are as follows

(i) **Thermal stability** These oxoacids depends on the oxidation number and electronegativity of the central halogen atom.

Greater is the oxidation number or electronegativity of central halogen atom, greater will be the thermal stability of the acid and *vice-versa.*

Thus, the following two cases may be studied

(a) **In case of oxoacids of a same halogen atom** since the electronegativity of the central halogen atom (*viz.,* Cl-atom) in this case remains the same, the thermal stability depends only upon the oxidation number of the central atom. As the oxidation number of the central atom increases, X—O bond in the acids becomes more and more covalent. Hence, thermal stability of the acids increases. For example, thermal stability of the chlorine acids is in the order : $HClO < HClO_2 < HClO_3 < HClO_4$.

(b) **In case of oxoacids, having the same formula and different central halogen atom** In this case since, the oxidation number of the halogen atoms remains the same, the thermal stability depends only upon the electronegativity of the halogen atom. Thermal stability decreases with the decrease in electronegativity of halogen atom. Thus, thermal stability of the given acids is in the order

$$HClO > HBrO > HIO.$$

Reaction with alkalies Fluorine reacts with cold dilute alkalies to give OF_2 (oxygen difluoride) while with concentration alkalies, it evolves oxygen.

$$\underset{\text{(Cold and dilute)}}{2NaOH} + 2F_2 \longrightarrow 2NaF + OF_2 + H_2O$$

$$\underset{\text{(Conc.)}}{4NaOH} + 2F_2 \longrightarrow 4NaF + O_2\uparrow + 2H_2O$$

Fluorine show diffrent behaviour than Cl_2, Br_2 and I_2. They form a mixture of halide and hypohalites with cold dilute alkalies while a mixture of halides and halate with concentrated hot alkalies.

$$\underset{\text{Cold and dilute}}{2NaOH} + X_2 \longrightarrow \underset{\text{Halide}}{NaX} + \underset{\text{Hypohalite}}{NaXO} + H_2O$$

$$\underset{\text{Hot and conc.}}{6NaOH} + 3X_2 \longrightarrow 5NaX + \underset{\text{Halate}}{NaXO_3} + 3H_2O$$

(where, X = Cl, Br, I)

(ii) **Acidity** (or acid strength) of oxoacids also follows the same trend as thermal stability.

(iii) **Oxidising power** Here, also following two cases may be possible

(a) **Oxidising power of oxoacids of a same halogen atom** (e.g. HClO, $HClO_2$, $HClO_3$, $HClO_4$) decreases with the increase in the oxidation number of the central halogen atom. This is because the X—O bond becomes more and more covalent as the oxidation number of the central atom increases. Thus, the oxidising power of the given acids is in the order

$$HClO > HClO_2 > HClO_3 > HClO_4$$

(b) **In case of oxoacids, having the same formula and different halogen atom** (e.g. $HClO_3$, $HBrO_3$ and HIO_3), oxidising power decreases with the decrease in the electronegativity of the halogen atom. Thus, oxidising power of the given acids is in the order

$$HClO_3 > HBrO_3 > HIO_3$$

(iv) **Stability and basicity of the oxo-anions of a given halogen atom** (e.g. ClO^-, ClO_2^-, ClO_3^- and ClO_4^-) have been found to be in the following order

Stability $ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$

Basicity $ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$

Some important oxyacids of halogens as discussed below

1. Hypochlorous Acid, HClO

Hypochlorous acid, HClO is known only in solution. Therefore, it cannot be isolated from them.

Methods of Preparation

It is prepared by following methods are

- By passing Cl_2 into H_2O or into a suspension of $CaCO_3$ in water or into an aqueous solution of potassium hypochlorite (KClO) or bleaching powder ($CaOCl_2$).

$$Cl_2 + H_2O \longrightarrow HCl + HClO$$

In this reaction, Cl_2 undergoes disproportionation into HCl and HClO.

- By the action of atmospheric CO_2 on sodium hypochlorite, NaOCl.

$$NaOCl + CO_2 + H_2O \longrightarrow NaHCO_3 + HOCl$$

- By distilling the aqueous solution of bleaching powder ($CaOCl_2$) with a calculated quantity of 5% HNO_3 or by passing CO_2 into aqueous solution of $CaOCl_2$ and then distilling.

$$2CaOCl_2 + \underset{(5\%)}{2HNO_3} \longrightarrow CaCl_2 + Ca(NO_3)_2 + 2HClO$$

$$CaOCl_2 + H_2O + CO_2 \longrightarrow CaCO_3 + 2HClO$$

- By shaking Cl_2 water with freshly precipitated HgO (General method for the preparation of hypohalous acids).

$$2Cl_2 + 2HgO + H_2O \longrightarrow HgCl_2 \cdot HgO\downarrow + 2HClO$$

The insoluble $HgCl_2 \cdot HgO$ is removed by filtration. The filtrate is distilled when dilute HClO passes over.

Physical Properties

The concentrated solution of HClO is yellow in colour, while the dilute solution is colourless. It is a weak acid, even weaker than H_2CO_3. Its dissociation constant is 3×10^{-8} at 20°C.

Chemical Properties

(i) The dilute solution of the acid is fairly stable in the dark, but when concentrated solution is exposed to light, it becomes unstable and hence, undergoes **disproportionation** into Cl_2 (Cl = 0) and $HClO_3$(Cl =+5).

$$\underset{\substack{(Cl\,=\,+1)\\(Conc.)}}{5HClO} \xrightarrow{\text{In presence of light}} \underset{(Cl\,=\,0)}{2Cl_2} + \underset{(Cl\,=\,+5)}{HClO_3} + 2H_2O$$

The decomposition is accelerated by Pt-black, MnO and CoO.

(ii) When aqueous solution of HClO is heated, it undergoes disproportionation into HCl and $HClO_3$.

$$3HClO \xrightarrow{\Delta} 2HCl + HClO_3$$

- On distillation, HClO decomposes into H_2O and Cl_2O.

$$2HClO \longrightarrow Cl_2O + H_2O$$

- It reacts with metals, e.g. it dissolves in Mg, with the evolution of H_2, in Fe and Al, with the evolution of H_2 and Cl_2, while with Co, Ni and Cu, Cl_2 and O_2 are evolved.

$$Mg + 2HClO \longrightarrow Mg(OCl)_2 + H_2\uparrow$$

When HClO is shaken with Hg, a light brown precipitate of basic mercuric chloride, [HgCl(OH)], which is soluble in HCl, is obtained

$$2Hg + 2HClO \longrightarrow \underset{\text{(Light brown ppt.)}}{2HgCl(OH)}$$

- The aqueous solution of HClO and its salts (e.g. NaOCl) are **oxidising** and **bleaching agents.** This property is due to the fact that HClO or NaOCl decomposes to give nascent oxygen.

$$HClO \xrightarrow{\text{Reduction}} HCl + [O]$$
$$NaClO \xrightarrow{\text{Reduction}} NaCl + [O]$$

- HClO is a **monobasic acid,** since its aqueous solution gives only one H^+ ion on ionisation.

$$HClO\ (aq) \rightleftharpoons H^+(aq) + ClO^-(aq)$$

ClO^- ion is called **hypochlorite ion.** Its monobasic nature shows that HClO molecule has one OH group attached directly with the central Cl-atom.

Being an acid, HClO reacts with alkalies to form the salts which are called hypochlorites.

e.g. $NaOH + HClO \longrightarrow NaOCl + H_2O$

- HClO reacts with $AgNO_3$ and gives silver hypochlorite (AgClO). This compound is unstable and hence, undergoes disproportionation into AgCl and $AgClO_3$.

$$HOCl + AgNO_3 \longrightarrow AgOCl + HNO_3$$
$$3AgOCl \longrightarrow AgCl + AgClO_3$$

2. Chloric Acid ($HClO_3$)

This acid is known only in solution. It is an oxoacid of chlorine. It is the formal precursor of chlorate salts. Its preparation, physical and chemical properties are as follow.

Methods of Preparation

$HClO_3$ is prepared by following methods.

- By the action of dil H_2SO_4 on $Ba(ClO_3)_2$.

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4\ (ppt.) + 2HClO_3$$

The precipitate of $BaSO_4$ is obtained by filtration. The unused H_2SO_4 is precipitated with baryta water. The filtrate is evaporated in a vacuum desicator over concentrated H_2SO_4 until a 4% solution of $HClO_3$ is obtained.

If the solution containing $HClO_3$ is evaporated further more, it gets decomposed into perchloric acid, $HClO_4$.

$$3HClO_3 \xrightarrow{\Delta} HClO_4 + Cl_2 + 2O_2 + H_2O$$

- By the action of hydrofluorosilicic acid (H_2SiF_6) on $KClO_3$.

$$2KClO_3 + H_2SiF_6 \longrightarrow K_2SiF_6(ppt.) + 2HClO_3$$

Physical and Chemical Properties

- Concentrated solution of the acid is colourless and is a pungent smelling liquid.
- It is fairly stable in dark. In light it decomposes and becomes yellow. On heating, $HClO_3$ decomposes to give $HClO_4$.

$$3HClO_3 \xrightarrow{\Delta} HClO_4 + Cl_2\uparrow + 2O_2\uparrow + H_2O$$

- When organic substances like cotton, wool, paper etc, come in contact with the acid, they catch fire.
- The acid is a powerful oxidising and bleaching agent.
- When iodine is evaporated with 25% $HClO_3$, iodic acid (HIO_3) is obtained.

$$2HClO_2 + I_2 \longrightarrow 2HIO_3 + Cl_2\uparrow$$

This reaction has been used for the preparation of HIO_3.

- $HClO_3$ is a monobasic acid.

$$HClO_3 \rightleftharpoons H^+ + ClO_3^-$$

3. Perchloric Acid, $HClO_4$

It is a mineral acid, usually found as an aqueous solution. Its preparation and properties are as follow

Methods of Preparation

$HClO_4$ is prepared as,

- by heating $HClO_3$

$$3HClO_3 \xrightarrow{\Delta} HClO_4 + Cl_2\uparrow + 2O_2\uparrow + H_2O$$

- by treating $Ba(ClO_4)_2$ with calculated quantity of dil. H_2SO_4 and then removing the insoluble $BaSO_4$ by filtration.

$$Ba(ClO_4)_2 + H_2SO_4 \longrightarrow 2HClO_4 + BaSO_4\downarrow$$

- by adding NH_4ClO_4 dissolved in conc. HCl to warm conc. HNO_3 and then evaporating.

$$NH_4ClO_4 + \underset{\text{(Conc.)}}{8HCl} + \underset{\text{(Conc.)}}{3HNO_3} \longrightarrow HClO_4 + 2N_2O + 4Cl_2 + 7H_2O$$

- anhydrous acid is obtained by distilling a mixture of potassium perchlorate ($KClO_4$) with conc. H_2SO_4 under reduced pressure.

$$KClO_4 + H_2SO_4 \longrightarrow HClO_4 + KHSO_4$$

Physical and Chemical Properties

- Anhydrous $HClO_4$ is a colourless, hygroscopic and oily liquid. It fumes strongly in moist air and dissolves in water with hissing sound due to the liberation of much heat.
- It forms hydrates with 1, 2, 2.5, 3 and 3.5 molecules of water of crystallisation.
- It is unstable and decomposes with explosion on heating and sometimes mainly on standing for a few days even in the dark. Aqueous solution of the acid is quite stable and does not decompose and hence, can be kept indefinitely.
- It is highly dangerous acid and produces severe wounds on the skin.
- It is powerful oxidising agent and in flames paper and wood.
- On dehydration with P_2O_5 at $-10°C$, it gives Cl_2O_7 which is the anhydride of perchloric acid.

$$2HClO_4 + P_2O_5 \xrightarrow{-10°C} Cl_2O_7 + 2HPO_3$$

This reaction has been used for the preparation of Cl_2O_7.

- $HClO_4$ is the strongest acid of all the acids.
- The metals like Zn, Fe etc., dissolve in the aqueous solution of the acid and form the soluble perchlorates.

$$Zn + 2HClO_4(aq) \longrightarrow Zn(ClO_4)_2(aq) + H_2\downarrow$$

- The acid is not reduced by nascent hydrogen but gets reduced to chloride by strong reducing agents like $SnCl_2$, $CrCl_2$ etc.
- When a suspension of iodine is heated with $HClO_4$, *para* periodic acid (H_5IO_6) is obtained.

$$2HClO_4 + I_2 + 4H_2O \xrightarrow{\Delta} 2H_5IO_6 + Cl_2$$

Uses

The aqueous solution of this acid is used for the estimation of potassium gravimetrically.

4. Metaperiodic Acid, HIO_4

It is the oxoacid of iodine in which the iodine exists in +7 oxidation state.

Methods of Preparation

It is obtained by heating paraperiodic acid, H_5IO_6.

$$H_5IO_6 \xrightarrow{100°C} HIO_4 + 2H_2O$$

Properties

- It is a weak acid and dissociates as

$$HIO_4 \rightleftharpoons H^+ + IO_4^-$$

- When dissolved in water, it changes back to H_5IO_6.

$$HIO_4 + 2H_2O \longrightarrow H_5IO_6$$

- HIO_4 and its salts are strong oxidising agents in acidic medium.

$$2IO_4^- + 16H^+ + 14e^- \longrightarrow I_2 + 8H_2O$$

VIIIA (18) Group Elements and their Compounds

This group of periodic table contains 6 elements, i.e. He, Ne, Ar, Kr, Xe and Rn. These were called as **inert gases** due to their inert nature. However, these are now as called **noble gases** because some of these elements form compounds under specific conditions.

Occurrence

All these gases except radon (Rn) are present in atmosphere. Rn results from disintegration of radium (is itself radioactive). The total abundance of these elements in dry air (except Rn) is ~1% by volume, out of which Ar is the major component.

General and Physical Properties

(i) **Electronic configuration** These gases have highly stable $ns^2\ np^6$ configuration thus, have very little tendency to form chemical compounds with other elements (inert gases).

(ii) **Atomic and ionic radii** The atomic radii of 18th group elements correspond to the van der Waals' radii and increases on moving down the group.

(iii) **Boiling points** They have low boiling points in comparison to other elements and which increases with increases in atomic sizes, i.e. increases down the group.

(iv) **Ionisation energy and electron affinity** Noble gases have stable ns^2np^6 (fully-filled) electronic configuration, thus, have no tendency to add or lose electron. Therefore, their ionisation energy is very high. On the other hand, their electron affinity is zero.

(v) **Heat of vaporisation and polarisability** They possess very low values of heat of vaporisation. This is due to the presence of very weak van der Waals' forces of attraction between their monoatomic molecules. However, this value increases with atomic number. This shows that there is an increase in polarisability of the larger electronic clouds of the elements with higher atomic number. In other words, the polarisability increases down the group as,

$$He < Ne < Ar < Kr < Xe.$$

(vi) **Solubility** They are slightly soluble in water and their solubility generally increases on moving down the group.

(vii) **Adsorption** Except He, all the noble gases are adsorbed by coconut charcoal. This ease of adsorption increases an moving down the group.

(viii) **Conductivity** They have high electrical conductivity at low pressures.

(ix) **Spectra** All of them give characteristic spectra, by which they can be identified.

(x) **Liquification** Due to the presence of weak van der Waals' forces of attraction, it is difficult to liquify noble gases. Ease of liquification increases down the group from He to Rn due to increase in intermolecular forces.

The above mentioned physical properties can be summarised as,

Physical Properties of Noble Gases

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
Atomic number	2	10	18	36	54	86
Electronic configuration	$1s^2$	$[He] 2s^2 2p^6$	$[Ne] 2s^2 3p^6$	$[Ar] 3d^{10} 4s^2 4p^6$	$[Kr] 4d^{10} 5s^2 5p^6$	$[Xe] 4f^{14} 5d^{10} 6s^2 6p^6$
Molar mass (amu)	4.003	20.183	39.948	83.30	131.30	222
Boiling point (°C)	–268.93	–246.06	–185.86	–153.35	–108.1	–62
Melting point (°C)	–272.1	–246.61	–189.37	–157.2	–111.8	–71
Ionisation energy (kJ mol^{-1})	2372.1	2080.4	1520.6	1350.6	1170.2	1037.0
Heat of vaporisation (kJ mol^{-1})	0.08	1.74	6.52	9.05	12.65	18.1
Atomic radius (Å)	1.4	1.54	1.88	2.02	2.16	—
Critical temperature (°C)	–267.9	–228.7	–122.4	–62.5	+16.6	+14.5
Critical pressure (atm)	2.26	26.9	50.0	54.3	58.3	62.4
$\gamma = C_p / C_V$	1.652	1.642	1.60	1.689	1.60	—
Absorption coefficient in water at 25°C	0.0097	0.0114	0.0053	0.1105	0.2420	0.5100

Chemistry of Noble Gases

The real chemistry of noble gases began in **1962** when **Neil Bartlett** isolated an orange yellow solid from the reaction of Xe and PtF_6.

The possibility of this reaction arise due to similarity in ionisation enthalpies of O_2 and Xe. After this discovery many compounds of Xe were prepared (with oxygen and F only).

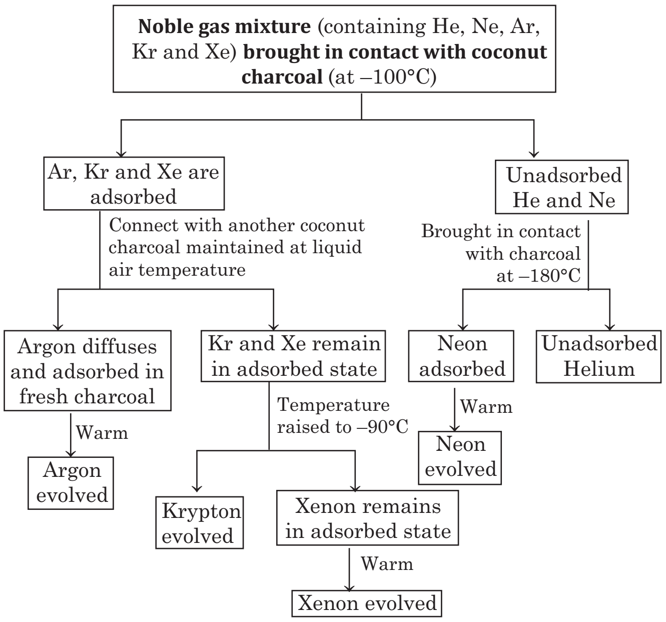
Kr forms comparatively fewer compounds (only KrF_2 have been studied in detail). Compounds of Rn have not been isolated but are identified with radiotracer techniques.

Extraction of Noble Gas

Helium, argon, neon, krypton and xenon are prepared by the fractional distillation of liquid air. Fractional distillation of air gives O_2, N_2 and mixture of noble gases.

The individual gases may be obtained by adsorption of air on coconut charcoal. The charcoal adsorbs different gases at different temperatures and thus, these gases can be collected.

Steps involve in the extraction of noble gas are shown below in a flow chart.



However, radon is obtained by radioactive disintegration of radium (226) as,

$${}_{88}Ra^{226} \longrightarrow {}_{86}Rn^{222} + {}_{2}\alpha^{4}$$

Properties and Uses of Noble gases

Some important properties along with the uses and discoverer of noble gases can be summarised below in tabulated form.

Discovery and Uses of Noble Gases

Noble gas	Discoverer	Uses	Reasons
He	Lockyer and Janssen (1868)	(i) He/O_2 mixture for deep-sea breathing, instead of N_2/O_2 mixture. (ii) Diluent for gaseous anaesthetics	Low solubility in blood; prevents nitrogen narcosis and "bends". Non-flammable, non-reactive.
		(iii) Filling of observation balloons and other lighter air craft	Non-flammable; 93% lifting power as compared to flammable H_2.
		(iv) Liquid He to maintain very low temperature in research (cryogenics)	Extremely low boiling point.
		(v) He/O_2 mixtures for respiratory patients	Low density flows easily through restricted assages.
		(vi) Heat transfer agent in gas cooled nuclear reactors.	Transfers heat readily; does not becomes radioactive; chemically inert.
Ne	Ramsay and Travers	Neon signs.	Even at low pressure Ne, moderate electric current causes bright orange-red glow; can be modified by coloured glass or mixing with Ar or Hg vapour.
Ar	L. Rayleigh and Ramsay	(i) Inert atmosphere for welding (ii) Filling incandescent light bulbs.	Chemically inert. Inert; prevents vaporisation of tungsten and blackening of bulbs.
Kr	Ramsay and Travers (1898)	Airport runway and approach lights	Gives longer life to incandescent lights than Ar, but more expensive.
Rn	Dorn (1900)	For the treatment of cancer (radiotherapy).	Because of radioactive nature.

Compounds of Group 18 Elements

Xenon due to its low ionisation energy forms several compounds. However no true compounds of He, Ne and Ar are known. Most of the compounds of Xe are with F and O.

Some xenon compound are as follows.

Xenon Fluorides

Xenon forms three binary fluorides, i.e. XeF_2, XeF_4 and XeF_6 by the direct union of elements under appropriate experimental conditions. In these fluorides, Xe is in +2, +4 and +6 oxidation states respectively.

1. Xenon Difluorine

XeF_2 is prepared by the following method as

- $\underbrace{Xe + F_2}_{2:1 \text{ ratio}} \xrightarrow[\text{tube (400°C)}]{\text{Sealed Ni}} XeF_2$
- $\underbrace{Xe + F_2}_{2:1 \text{ ratio}} \xrightarrow[\text{discharge}]{\text{Electric}} XeF_2$
- $Xe + F_2 \xrightarrow[\text{(Hg vapours)}]{\text{Photochemical combination}} XeF_2$

Some important properties exhibited by XeF_2 are as follows

- It is a colourless crystalline solid with m.p. is 140°C.
- It is reduced by H_2O to Xe and H_2O is oxidised to O_2.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2\uparrow$$

However, it is rapidly hydrolysed by an aqueous solution of a base.

$$2XeF_2 + 4OH^- \longrightarrow 2Xe + 4F^- + 2H_2O + O_2\uparrow$$

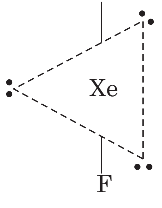
- XeF_2 is a mild fluorinating agent. Thus, it reacts with C_6H_6 to give C_6H_5F.
- It can oxidise many substances and itself gets reduced to xenon. e.g.

$$XeF_2 + H_2 \longrightarrow Xe + 2HF$$
$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2\uparrow$$
$$XeF_2 + I_2 \xrightarrow{BF_3} Xe + 2IF$$

- In BrF_3 solution, XeF_2 forms adducts with MF_5 molecules (M = P, A, Sb etc).

$$XeF_2 + MF_5 \longrightarrow XeF_2 \cdot MF_5$$
$$XeF_2 + 2MF_5 \longrightarrow XeF_2 \cdot 2MF_5$$
$$2XeF_2 + MF_5 \longrightarrow 2XeF_2 \cdot MF_5$$

XeF_2 has sp^3d-hybridisation and linear geometry (due to the presence of 3 lone pairs) which is represented as,



Linear geometry of XeF_2

2. Xenon Tetrafluoride, XeF_4

XeF_4 can be prepared as

$$\underbrace{Xe + 2F_2}_{1:5\ \text{ratio}} \xrightarrow[400^\circ C,\ 5-6\ \text{atm}]{\text{Ni tube}} XeF_4$$

$$\underbrace{Xe + 2F_2}_{1:2\ \text{ratio}} \xrightarrow[-80^\circ C]{\text{Electric discharge}} XeF_4$$

Some important properties are as follows

- It is also a colourless crystalline solid. Its m.p. is 117.1°C. It sublimes readily.
- XeF_4 undergoes disproportionation in water, giving XeO_3 which is a highly explosive solid.

  $$2XeF_4 + 3H_2O \longrightarrow Xe(g) + XeO_3(s) + 6HF(aq) + F_2(g)$$

  If the reaction is carried out at –80°C, $XeOF_2$ is formed. In this reaction, slow and partial hydrolysis of XeF_4 takes place as,

  $$XeF_4 + H_2O \xrightarrow{-80^\circ C} XeOF_2 + 2HF$$
- XeF_4 is a stronger fluorinating agent than XeF_2. Some of its reactions are

  $$2Hg + XeF_4 \longrightarrow Xe + 2HgF_2$$
  $$Pt + XeF_4 \longrightarrow Xe + PtF_4$$
  $$2SF_4 + XeF_4 \longrightarrow Xe + 2SF_6$$
- It also acts as an oxidising agent and itself get reduced to Xe.

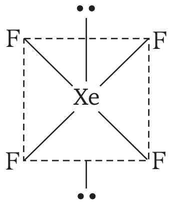
  $$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$
  $$3XeF_4 + 4BCl_3 \longrightarrow 3Xe + 4BF_3 + 6Cl_2$$
  $$XeF_4 + 4I^- \longrightarrow Xe + 4F^- + 2I_2$$
- **XeF_4 dissolves in molten SbF_5 and gives the addition ionic compound, $XeF_4 \cdot SbF_5$** which is represented as $[XeF_3]^+ [SbF_6]^-$.

  $$XeF_4 + SbF_5 \longrightarrow XeF_4 \cdot SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$$

  It also dissolves in molten TaF_5, giving a compound, $Xe(TaF_6)_2$, which is described as an addition compound, $XeF_2 \cdot 2TaF_5$.

  $$XeF_4 + 2TaF_5 \longrightarrow Xe(TaF_6)_2 \text{ or } XeF_2 \cdot 2TaF_5 + F_2$$

XeF_4 has sp^3d^2-hybridisation but square planar geometry because of the presence of two lone pairs of electrons.



Square planar geometry of XeF_4

3. Xenon Hexafluoride, XeF_6

XeF_6 can be prepared as,

$$\underbrace{Xe + 3F_2}_{1:20\ \text{ratio}} \xrightarrow[250\text{-}300^\circ C,\ 50\text{-}60\ \text{atm}]{\text{Ni vessel}} XeF_6$$

$$\underbrace{Xe + 3F_2}_{1:3\ \text{ratio}} \xrightarrow[\text{low temp.}]{\text{Electric discharge}} XeF_6$$

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$
$$XeF_4 + F_2 \longrightarrow XeF_6$$

Its properties include

- It is colourless crystalline solid with melting point 49.5°C.
- It undergoes hydrolysis in water. The final product obtained is XeO_3 (an explosive solid).

  $$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$
  $$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$
  $$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$
- In strongly basic solution, the reaction proceeds as

  $$XeF_6 + 7OH^- \longrightarrow 6F^- + 4H_2O + \underset{\substack{\text{(Xenate ion)}\\(Xe = +6)}}{HXeO_4^-}$$

  $$HXeO_4^- \xrightarrow{+2OH^-} \frac{6}{4} H_2O + \frac{1}{4} Xe + \underset{\substack{\text{(Perxenate ion)}\\(Xe = +8)}}{\frac{3}{4} XeO_6^{4-}}$$

  In acidic solution, main species is $XeOF_4$ (Xe = + 6) and H_6XeO_6 (Xe = + 6). H_6XeO_6 is called **xenic acid.**
- It also acts as an oxidising agent as

  $$XeF_6 + 3H_2 \longrightarrow Xe + 6HF$$
  $$XeF_6 + 8NH_3 \longrightarrow Xe + 6NH_4F + N_2\uparrow$$
  $$XeF_6 + 6HCl \longrightarrow Xe + 6HF + 3Cl_2$$
- It dissolves in HF, giving a solution containing XeF_5^+ and HF_2^+ ions. Due to the presence of these ions solution is a good conductor of electricity.

  $$XeF_6 + HF \longrightarrow XeF_5^+ + HF_2^+$$
- It gives addition compound with AsF_5 and SbF_5 molecules.

  $$\underset{(M = As,\ Sb)}{XeF_6 + MF_5} \longrightarrow XeF_6 \cdot MF_5 \longrightarrow [XeF_5]^+[MF_6]^-$$

  In these reactions, XeF_6 molecule acts as F^- ion donor while MF_5 molecule behaves as F^- ion acceptor.
- It also reacts with alkali metal fluorides (except LiF) and gives species containing XeF_7^- and XeF_8^{2-} ions. In these reactions XeF_6 molecule acts as F^- ion acceptor and MF molecule (M = Na, K, Rb) behaves as F^- ion donor.

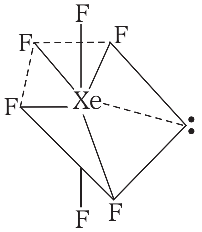
  $$\underset{(M = Na,\ K)}{XeF_6 + 2MF} \longrightarrow \underset{\text{(Octafluoroxenate)}}{M_2XeF_8}$$

  $$XeF_6 + \underset{\text{Molten}}{2RbF} \xrightarrow{200^\circ C} \underset{\text{(Heptafluoroxenate)}}{2RbXeF_7} \xrightarrow{50^\circ C} \underset{\text{(Octafluoroxenate)}}{Rb_2XeF_8} + XeF_6$$
- It is the most volatile among all of the fluorides. Its vapours have a greenish yellow colour.

- It is extremely reactive. Thus, cannot be stored in glass or quartz vessels, since it readily reacts with SiO_2 present in glass as one of its constituents. With SiO_2, XeF_6 gives dangerously explosive XeO_3 as a final product.

$$2XeF_6 + 3SiO_2 \longrightarrow 2XeO_3 + 3SiF_4$$

XeF_6 has sp^3d^3 hybridisation and distorted octahedral geometry because of the presence of one lone pair of electrons.



Distorted octahedral XeF_6

B. Xenon Oxides

Two of its oxides are given below.

1. Xenon Trioxide, XeO_3

XeO_3 can be prepared by complete hydrolysis of XeF_4 and XeF_6 as,

$$6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 3O_2\uparrow + 24HF$$
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

It is a colourless solid, highly explosive and powerful oxidising agent. XeO_3 has sp^3-hybridisation trigonal pyramidal geometry because of the presence of one lone pair of electrons over Xe. The molecule has three $Xe{=}O$ double bonds containing $p\pi$-$d\pi$ overlapping.

2. Xenon Tetraoxide, XeO_4

XeO_4 can be prepared by the action of conc H_2SO_4 on sodium or barium xenate (Na_4XeO_6; Ba_2XeO_6) at room temperature.

$$Na_4XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2Na_2SO_4 + 2H_2O$$
$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$

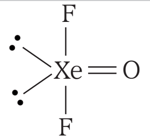
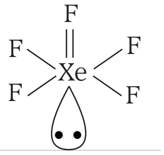
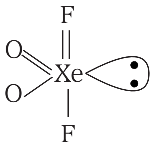
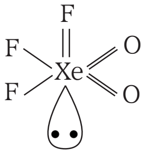
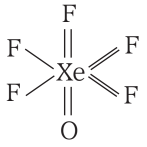
XeO_4 is purified by vacuum sublimation at 195 K. It is quite unstable gas and decomposes to xenon and oxygen,

$$XeO_4 \longrightarrow Xe + 2O_2\uparrow$$

XeO_4 has tetrahedral structure due to sp^3-hybridisation of Xe. There are four Xe—O double bonds containing $p\pi$ - $d\pi$ overlapping.

C. Xenon Oxyfluorides

Xenon forms number of oxyfluorides that are given below in the tabular form.

Molecule	Hybridisation	Geometry	Shape	Structure
$XeOF_2$	sp^3d	Trigonal bipyramidal	T - shaped	
$XeOF_4$	sp^3d^2	Square pyramidal	Square pyramidal	
XeO_2F_2	sp^3d	Trigonal bipyramidal	Distorted trigonal	
XeO_3F_2	sp^3d	Trigonal bipyramid	Trigonal bipyramidal	
XeO_2F_4	sp^3d^2	Octahedral	Octahedral	

- **Preparation**

$$XeF_4 + H_2O \longrightarrow XeOF_2 + 2HF$$
$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$
$$XeF_6 + 2\,H_2O \longrightarrow XeO_2F_2 + 4HF$$

Clathrates

Noble gases form a number of compounds in which these are trapped into the cavities of crystal lattices of certain organic and inorganic compounds. These are called **cage compounds** or **clathrates,** e.g. $Xe \cdot 6H_2O$, quinol clathrate. He and Ne do not form clathrate compounds as the size of the cavity is more than the size of the He or Ne-atom.

Uses of Clathrates

Some important uses of clathrates include

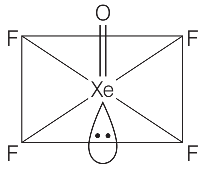
- Separation of noble gases. Ne can be separated from other gases (Ar and Kr) as it does not form clathrate with quinol.
- The clathrates are convenient form of handling, processing and transporting of isotopes of noble gases.

Example 9. *The type of hybridisation and number of lone pair(s) of electrons of Xe in $XeOF_4$, respectively, are*

(JEE Main 2019)

(a) sp^3d^2 and 1
(b) sp^3d and 2
(c) sp^3d and 1
(d) sp^3d^2 and 2

Sol. (a) In $XeOF_4$, Xe is sp^3d^2-hybridised. Geometry of the molecule is octahedral, but shape of the molecule is square pyramidal. According to VSEPR, theory it has one π bond. Remaining six electron pairs form an octahedron with one position occupied by a lone pair.



$$\begin{bmatrix}\text{Number of } bp = 5 \\ \text{Number of } lp = 1\end{bmatrix}$$

Here, Xe contains one lone pair of electrons.

Practice Exercise

ROUND I Topically Divided Problems

Physical and Chemical Properties of Group 15 Elements

1. The element which catches fire in air at 30°C and is stored under water is

(a) sodium (b) phosphorus
(c) magnesium (d) zinc

2. Elements of group 15 form compounds in +5 oxidation state. However, bismuth forms only one well characterised compound in +5 oxidation state. The compound is *(NCERT Exemplar)*

(a) Bi_2O_5 (b) BiF_5 (c) $BiCl_5$ (d) Bi_2S_5

3. Which of the following is not hydrolysed?

(a) PF_3 (b) $SbCl_3$
(c) $AsCl_3$ (d) NF_3

4. The molecule having smaller bond angle is

(a) NCl_3 (b) $AsCl_3$ (c) $SbCl_3$ (d) PCl_3

5. Which of the following oxide is alkaline?

(a) P_2O_3 (b) B_2O_3 (c) Bi_2O_3 (d) As_2O_3

6. Pure nitrogen can be prepared from

(a) NH_4OH (b) NH_4NO_2
(c) $Ba(NO_3)_2$ (d) Ca_3N_2

7. The correct statement with respect to dinitrogen is *(JEE Main 2020)*

(a) N_2 is paramagnetic in nature.
(b) it can combine with dioxygen at 25°C.
(c) liquid dinitrogen is not used in cryosurgery.
(d) it can be used as an inert diluent for reactive chemicals.

8. A group 15 element, which is a metal and forms a hydride with strongest reducing power among group 15 hydrides. The element is *(JEE Main 2021)*

(a) Sb (b) P (c) As (d) Bi

9. On heating ammonium dichromate and barium azide separately we get *(NCERT Exemplar)*

(a) N_2 in both cases
(b) N_2 with ammonium dichromate and NO with barium azide
(c) N_2O with ammonium dichromate and N_2 with barium azide
(d) NO_2 with ammonium dichromate and NO_2 with barium azide

10. Liquid ammonia is used for refrigeration because

(a) it is basic
(b) it is a stable compound
(c) it has a high dipole moment
(d) it has high heat of vaporisation

11. Ammonia on reaction with hypochlorite anion, can form

(a) NO (b) N_2H_4 (c) NH_4Cl (d) HNO_2

12. NH_3 gas is dried over

(a) CaO (b) HNO_3
(c) P_2O_5 (d) $CuSO_4$

13. Which oxide do not act as a reducing agent?

(a) N_2O_5 (b) N_2O
(c) NO (d) NO_2

14. Reaction of ammonia with excess Cl_2 gives *(JEE Main 2020)*

(a) NH_4Cl and N_2 (b) NH_4Cl and HCl
(c) NCl_3 and NH_4Cl (d) NCl_3 and HCl

15. Which of the following products will be obtained when copper metal is reacted with dil and conc. HNO_3 respectively ?

(a) NO and N_2O_5 (b) NO_2 and N_2O_5
(c) NO and NO_2 (d) HNO_2 and N_2

16. The set that represents the pair of neutral oxides of nitrogen is *(JEE Main 2021)*

(a) NO and N_2O (b) N_2O and N_2O_3
(c) N_2O and NO_2 (d) NO and NO_2

17. Nitrogen dioxide

(a) does not dissolve in water
(b) dissolves in water forming nitric acid
(c) dissolves in water to form a mixture of nitrous and nitric acid
(d) dissolves in water to form nitrous acid and gives off oxygen

18. In the reaction, $HNO_3 + P_4O_{10} \longrightarrow HPO_3 + x$, the product x is
(a) NO_2 (b) N_2O_5 (c) N_2O_3 (d) H_2O

19. The reaction of NO with N_2O_4 at 250 K gives *(JEE Main 2020)*
(a) N_2O (b) NO_2 (c) N_2O_3 (d) N_2O_5

20. The species in which the N-atom is in a state of *sp*-hybridisation is *(JEE Main 2016)*
(a) NO_2^- (b) NO_3^- (c) NO_2 (d) NO_2^+

21. Which one of the following properties is not shown by NO ? *([JEE Main 2014)*
(a) It is diamagnetic in gaseous state
(b) It is a neutral oxide
(c) It combines with oxygen to form nitrogen dioxide
(d) Its bond order is 2.5

22. The oxidation states of nitrogen in NO, NO_2, N_2O and NO_3^- are in the order of *(JEE Main 2021)*
(a) $NO_3^- > NO_2 > NO > N_2O$ (b) $NO_2 > NO_3^- > NO > N_2O$
(c) $N_2O > NO_2 > NO > NO_3^-$ (d) $NO > NO_2 > N_2O > NO_3^-$

23. On heating with concentrated NaOH solution in an inert atmosphere of CO_2, white phosphorus gives a gas. Which of the following statement is incorrect about the gas? *(NCERT Exemplar)*
(a) It is highly poisonous and has smell like rotten fish.
(b) Its solution in water decomposes in the presence of light.
(c) It is more basic than NH_3.
(d) It is less basic than NH_3, .

24. Phosphine is produced by adding water to
(a) CaC_2 (b) HPO_3 (c) Ca_3P_2 (d) P_4O_{10}

25. What may be expected to happen when phosphine gas is mixed with chlorine gas?
(a) PCl_5 and HCl are formed and the mixture cools down
(b) PH_3 Cl_2 is formed with warming up
(c) PCl_3 and HCl are formed and the mixture warms up
(d) The mixture only cools down

26. The substance used in Holme's signals of the ship is a mixture of
(a) $CaC_2 + Ca_3P_2$ (b) $Ca_3(PO_4)_2 + Pb_3O_4$
(c) $H_3PO_4 + CaCl_2$ (d) $NH_3 + HOCl$

27. In solid state PCl_5 is a *(NCERT Exemplar)*
(a) covalent solid
(b) octahedral structure
(c) ionic solid with $[PCl_6]^+$ octahedral and $[PCl_4]^-$ tetrahedral
(d) ionic solid with $[PCl_4]^+$ tetrahedral and $[PCl_6]^-$ octahedral

28. Hydrolytic reaction of PCl_5 in heavy water produces.
(a) D_3PO_4 (b) $POCl_3$
(c) Both (a) and (b) (d) None of these

29. Good reducing nature of H_3PO_2 is attributed to the presence of *(JEE Main 2019)*
(a) two P— H bonds (b) one P— H bond
(c) two P— OH bonds (d) one P — OH bond

30. The pair that contains two P—H bonds in each of the oxoacids is *(JEE Main 2019)*
(a) $H_4P_2O_5$ and $H_4P_2O_6$
(b) H_3PO_3 and H_3PO_2
(c) $H_4P_2O_5$ and H_3PO_3
(d) H_3PO_2 and $H_4P_2O_5$

31. The pair in which phosphorus atoms have a formal oxidation state of +3 is *(JEE Main 2016)*
(a) pyrophosphorous and hypophosphoric acids
(b) orthophosphorous and hypophosphoric acids
(c) pyrophosphorous and pyrophosphoric acids
(d) orthophosphorous and pyrophosphorous acids

Physical and Chemical Properties of Group 16 Elements

32. Sulphur in +3 oxidation state is present in
(a) dithionous acid (b) sulphurous acid
(c) thionous acid (d) pyrosulphuric acid

33. When the first electron gain enthalpy $(\Delta_{eg}H)$ of oxygen is -141 kJ / mol, its second electron gain enthalpy is *(JEE Main 2019)*
(a) a positive value
(b) a more negative value than the first
(c) almost the same as that of the first
(d) negative, but less negative than the first

34. $SO_2 + H_2S \longrightarrow x + y$, the final products are
(a) H_2SO_3 (b) H_2SO_4
(c) $H_2S_2O_3$ (d) $H_2O + S$

35. If the boiling point of H_2O is 373 K, the boiling point of H_2S will be *(JEE Main 2020)*
(a) less than 300 K
(b) equal to 373 K
(c) more than 373 K
(d) greater than 300 K but less than 373 K

36. The correct order of thermal stability of the hydrides of group 16 elements is
(a) $H_2Po > H_2Te > H_2Se > H_2S > H_2O$
(b) $H_2O < H_2S > H_2Se > H_2Te > H_2Po$
(c) $H_2O > H_2S > H_2Se > H_2Te > H_2Po$
(d) $H_2O > H_2S > H_2Se > H_2Te > H_2Po$

37. Ozone with KI solution produces

(a) IO_3 (b) I_2 (c) Cl_2 (d) HI

38. Sulphur on boiling with NaOH solution gives

(a) $Na_2SO_3 + H_2S$ (b) $Na_2S_2O_3 + Na_2S$
(c) $Na_2S_2O_3 + NaHSO_3$ (d) $Na_2SO_3 + SO_2$

Compounds of Group 18 Elements

39. S—S bond is present in

(a) α-$(SO_3)_n$ (b) γ-(S_3O_9)
(c) $H_2S_2O_3$ (d) $H_2S_2O_8$

40. In the reaction, $HCOOH \xrightarrow{H_2SO_4} CO + H_2O$;

H_2SO_4 acts as

(a) reducing agent (b) oxidising agent
(c) dehydrating agent (d) All of these

41. Concentrated sulphuric acid can be reduced by

(a) NaCl (b) NaF (c) NaOH (d) NaBr

42. Copper turnings when heated with concentrated sulphuric acid will give

(a) H_2S (b) SO_2 (c) SO_3 (d) O_2

43. Sulphuric acid has great affinity for water because

(a) acid decomposes water
(b) it hydrolyses the acid
(c) it decomposes the acid
(d) acid forms hydrates with water

44. The oxoacid of sulphur that does not contain bond between sulphur atoms is *(JEE Main 2019)*

(a) $H_2S_2O_3$ (b) $H_2S_2O_4$ (c) $H_2S_2O_7$ (d) $H_2S_4O_6$

45. Which of the following are peroxoacids of sulphur?

(a) H_2SO_5 and $H_2S_2O_8$
(b) H_2SO_5 and $H_2S_2O_7$
(c) $H_2S_2O_7$ and $H_2S_2O_8$
(d) $H_2S_2O_6$ and $H_2S_2O_5$

Physical and Chemical Properties of Group 17 Elements

46. The chief source of iodine in which it is present as sodium iodate is

(a) carnallite
(b) sea weeds
(c) caliche
(d) iodine never exists as sodium iodate

47. Which of the following is strongest oxidising agent?

(a) I_2 (b) Br_2 (c) Cl_2 (d) F_2

48. Fluorine reacts with water to give

(a) HF, O_2 and O_3 (b) HF and F_2
(c) HF and O_2 (d) HF and O_3

49. The solubility of iodine in water increases in presence of

(a) chloroform (b) alcohol
(c) potassium iodide (d) sodium hydroxide

50. Metal halide which is insoluble in water is

(a) AgF (b) AgI (c) KBr (d) $CaCl_2$

51. Iodine is formed when potassium iodide reacts with a solution of

(a) $ZnSO_4$ (b) $CuSO_4$
(c) $(NH_4)_2SO_4$ (d) Na_2SO_4

52. Among the give compounds, the strongest acid is

(a) HI (b) HBr (c) HCl (d) HF

Compounds of Group 17 Elements

53. The acid employed for etching of glass is

(a) HCl (b) $HClO_4$
(c) HF (d) aqua regia

54. HF has highest boiling point among hydrogen halides, because it has *(JEE Main 2019)*

(a) lowest ionic character
(b) strongest van der Waals' interactions
(c) strongest hydrogen bonding
(d) lowest dissociation enthalpy

55. Which of the following is the most volatile compound?

(a) HCl (b) HI (c) HBr (d) HF

56. Afinity for hydrogen decreases in the group from fluorine to iodine. Which of the halogen acids should have highest bond dissociation enthalpy?

(a) HF (b) HCl
(c) HBr (d) HI

57. Euchlorine is a mixture of

(a) $Cl_2 + ClO_2$ (b) $Cl_2 + Cl_2O$
(c) $Cl_2O_3 + ClO_2$ (d) $Cl_2O + Cl_2O_3$

58. Total number of lone pair of electron in I_3^- ion is *(JEE Main 2018)*

(a) 3 (b) 6 (c) 9 (d) 12

59. Which among the following is the most reactive? *(JEE Main 2015)*

(a) Cl_2 (b) Br_2 (c) I_2 (d) ICl

60. Which one of the following given below is a pseudohalide?

(a) I_3^- (b) IF^- (c) ICl (d) CN^-

61. Concentrated HNO_3 reacts with I_2 to gives

(a) HI (b) HOI
(c) HIO_3 (d) $HOIO_2$

62. Reduction potentials of some ions are given below. Arrange them in decreasing order of oxidising power.

Ion ClO_4^- IO_4^- BrO_4^-

Reduction $E^V = 1.19\,V$ $E^V = 1.65$ V

$E^V = 1.74$ V

potential (E^V/V) *(NCERT Exemplar)*

(a) $ClO_4^- > IO_4^- > BrO_4^-$ (b) $IO_4^- > BrO_4^- > ClO_4^-$

(c) $BrO_4^- > IO_4^- > ClO_4^-$ (d) $BrO_4^- > ClO_4^- > IO_4^-$

63. Which one of the following is the anhydride of $HClO_4$?

(a) ClO_2 (b) Cl_2O_7

(c) Cl_2O (d) Cl_2O_6

64. Among the following oxoacids, the correct decreasing order of acid strength is *(JEE Main 2014)*

(a) $HOCl > HClO_2 > HClO_3 > HClO_4$

(b) $HClO_4 > HOCl > HClO_2 > HClO_3$

(c) $HClO_4 > HClO_3 > HClO_2 > HOCl$

(d) $HClO_2 > HClO_4 > HClO_3 > HOCl$

65. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are *(JEE Main 2017)*

(a) ClO^- and ClO_3^- (b) ClO_2^- and ClO_3^-

(c) Cl^- and ClO^- (d) Cl^- and ClO_2^-

66. $HClO_4 + P_2O_5 \longrightarrow (A)$ and (B)

A and B are

(a) $HClO_3, H_3PO_4$ (b) Cl_2O_6, HPO_3

(c) ClO_2, H_2PO_4 (d) Cl_2O_7, HPO_3

67. What products are expected from the disproportionation reaction of hypochlorous acid?

(a) $HClO_3$ and Cl_2O (b) $HClO_2$ and $HClO_4$

(c) HCl and Cl_2O (d) HCl and $HClO_3$

68. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order

HOCl(I) HOBr(II) HOI(III)

(a) I > II > III (b) II > I > III

(c) III > II > I (d) I > III > II

Physical and Chemical Properties of Group 18 Elements

69. Which one has the highest boiling point? *(JEE Main 2015)*

(a) He (b) Ne

(c) Kr (d) Xe

70. Welding of magnesium can be done in an atmosphere of

(a) Xe (b) He (c) Kr (d) Ne

71. Noble gases are sparingly soluble in water due to

(a) dipole-dipole interaction

(b) dipole-induced dipole interaction

(c) induced dipole-induced dipole interaction

(d) hydrogen bonding

72. The noble gas which can diffuse through rubber and glass easily is

(a) Xe (b) Ne (c) Ar (d) He

73. The correct order of solubility in water for He, Ne, Ar, Kr, Xe is

(a) Xe > Kr > Ar > Ne > He

(b) Ar > Ne > He > Kr > Xe

(c) He > Ne > Ar > Kr > Xe

(d) Ne > Ar > Kr > He > Xe

74. When the mineral clevite is heated, it give off the inert gas

(a) helium (b) xenon (c) radon (d) argon

75. The noble gas which shows abnormal behaviour in liquid state and behave as super fluid is

(a) Ne (b) He (c) Ar (d) Xe

76. Which of the following is the life saving mixture for an asthma patient?

(a) Mixture of helium and oxygen

(b) Mixture of neon and oxygen

(c) Mixture of xenon and nitrogen

(d) Mixture of argon and oxygen

77. The noble gas which forms maximum number of compounds is

(a) Ar (b) He

(c) Ne (d) Xe

Compounds of Group 18 Elements

78. XeF_2 on hydrolysis gives

(a) XeO_3 (b) XeO

(c) Xe (d) XeO_2

79. Which of the following is not obtained by direct reaction of constituent elements?

(a) XeO_3 (b) XeF_2

(c) XeF_6 (d) XeF_4

80. Among the following molecule

(i) XeO_3 (ii) $XeOF_4$

(iii) XeF_6

those having same number of lone pairs on Xe are

(a) (i) and (iii) only (b) (i) and (ii) only

(c) (ii) and (iii) only (d) (i), (ii) and (iii)

81. The geometry of $XeOF_4$ molecule is

(a) tetrahedral (b) square pyramidal

(c) square planar (d) octahedral

82. The pair of species having identical shape for molecules of both species is

(a) XeF_2, IF_2^- (b) BF_3, NH_3
(c) CF_4, SF_4 (d) PCl_5, ICl_5

83. Number of $p\pi$ - $d\pi$ bonds present in XeO_4 are

(a) four (b) two
(c) three (d) zero

84. XeO_2F_2 is obtained by partial hydrolysis of

(a) $XeOF_4$ (b) XeF_6
(c) Both (a) and (b) (d) None of these

85. Which of the following compounds can not be stored in glass vessels ?

(a) XeF_4 (b) XeF_6 (c) XeO_3 (d) XeF_2

86. Xenon hexafluoride reacts with silica to form a xenon compound X. The oxidation state of xenon in X is

(a) +2 (b) +4 (c) +6 (d) 0

87. Clathrates are

(a) non-stoichiometric compounds
(b) complex compounds
(c) interstitial compounds
(d) ionic compounds

ROUND II Mixed Bag

1. The number of P—O—P bridges in the structure of phosphorus pentoxide and phosphorus trioxide are respectively

(a) 5, 5 (b) 6, 5 (c) 5, 6 (d) 6, 6

2. Bleaching powder is disinfectant for purification of water, when water born germs are killed, but disinfectant activity is destroyed. It is due to its disproportionation into

(a) $CaCl_2$ and Cl_2
(b) $CaCl_2$ and $Ca(ClO_3)_2$
(c) CaO and Cl_2
(d) CaO, Cl_2 and $CaCl_2$

3. A substance which gives a yellow precipitate when boiled with an excess of nitric acid and ammonium molybdate and red precipitate with $AgNO_3$ is

(a) orthophosphate
(b) pyrophosphate
(c) metaphosphate
(d) hypophosphate

4. In compounds of type ECl_3, where E = N, P, As or Bi the angles Cl—E—Cl for different E are in the order

(a) N > P > As > Bi (b) N > P = As = Bi
(c) N < P = As = Bi (d) N < P < As < Bi

5. The electron affinity values (in kJ mol^{-1}) of three halogens X, Y and Z are respectively – 349, – 333 and – 325. Then X, Y and Z respectively, are

(a) F_2, Cl_2 and Br_2 (b) Cl_2, F_2 and Br_2
(c) Cl_2, Br_2 and F_2 (d) Br_2, Cl_2 and F_2

6. The stability of interhalogen compounds follows the order

(a) $IF_3 > BrF_3 > ClF_3$ (b) $BrF_3 > IF_3 > ClF_3$
(c) $ClF_3 > BrF_3 > IF_3$ (d) $ClF_3 > IF_3 > BrF_3$

7. Which of the following statements is true?

(a) H_3PO_3 is a stronger acid than H_2SO_3
(b) In aqueous medium HF is a stroonger acid than HCl
(c) $HClO_4$ is weaker acid than $HClO_3$
(d) HNO_3 is a stronger acid than HNO_2

8. The acidic, basic and amphoteric oxides, respectively, are

(JEE Main 2020)

(a) Cl_2O, CaO, P_4O_{10} (b) N_2O_3, Li_2O, Al_2O_3
(c) Na_2O, SO_3, Al_2O_3 (d) MgO, Cl_2O, Al_2O_3

9. Which of the following dissolves in water but does not give any oxyacid solution?

(a) SO_2 (b) OF_2 (c) SCl_4 (d) SO_3

10. Which one of the following statements is a correct statement?

(a) Basicity of H_3PO_4 and H_3PO_3 is 3 and 3 respectively
(b) Acidity of H_3PO_4 and H_3PO_3 is 3 and 3 respectively
(c) Acidity of H_3PO_4 and H_3PO_3 is 3 and 2 respectively
(d) Basicity of H_3PO_4 and H_3PO_3 is 3 and 2 respectively

11. Correct order of decreasing thermal stability is as

(a) $NH_3 > PH_3 > AsH_3 > SbH_3$
(b) $PH_3 > NH_3 > AsH_3 > SbH_3$
(c) $AsH_3 > PH_3 > NH_3 > SbH_3$
(d) $SbH_3 > AsH_3 > PH_3 > NH_3$

12. The reaction in which the hybridisation of the underlined atom is affected is *(JEE Main 2020)*

(a) $\underline{Xe}F_4 + SbF_5 \longrightarrow$
(b) $H_2\underline{S}O_4 + NaCl \xrightarrow{420\text{ K}}$
(c) $H_3\underline{P}O_2 \xrightarrow{\text{Disproportionation}}$
(d) $\underline{N}H_3 \xrightarrow{H^+}$

13. A green yellow gas reacts with an alkali metal hydroxide to form a halate which can be used in fireworks and safety matches. The gas and halate respectively are

(a) Br_2, $KBrO_3$
(b) Cl_2, $KClO_3$
(c) I_2, $NaIO_3$
(d) Cl_2, $NaClO_3$

14. Which one of the following reaction is not feasible?

(a) $2KI + Br_2 \longrightarrow 2KBr + I_2$
(b) $2KBr + I_2 \longrightarrow 2KI + Br_2$
(c) $2KBr + Cl_2 \longrightarrow 2KCl + Br_2$
(d) $2H_2O + 2F_2 \longrightarrow 4HF + O_2$

15. The following two reactions of HNO_3 with Zn are given as (equations are not balanced)

$$Zn + \text{conc. } HNO_3 \longrightarrow Zn(NO_3)_2 + X + H_2O \ (A)$$
$$Zn + \text{dil. } HNO_3 \longrightarrow Zn(NO_3)_2 + Y + H_2O \ (B)$$

In reactions A and B, the compounds X and Y respectively, are

(a) NO_2 and NO
(b) NO_2 and NO_2
(c) NO and NO_2
(d) NO_2 and NH_4NO_3

16. Which one of the following statements regarding helium is incorrect?

(a) It is used to produce and sustain powerful super conducting magnets
(b) It is used in gas-cooled nuclear reactors
(c) It is used to fill gas balloons instead of hydrogen because it is lighter and non-inflammable
(d) It is used as a cryogenic agent for carrying out experiments at low temperature

17. The formation of $O_2^+[PtF_6]^-$ is the basis for the formation of xenon fluorides. This is because

(a) O_2 and Xe have comparable sizes
(b) both O_2 and Xe are gases
(c) O_2 and Xe have comparable ionisation energies
(d) Both (a) and (b)

18. Which of the following statements are correct for SO_2 gas? *[NCERT Exemplar]*

(a) It acts as bleaching agent in moist conditions
(b) Its dilute solution is used as disinfectant
(c) It can be prepared by the reaction of dilute H_2SO_4 with metal sulphide
(d) (a) and (b) both are correct

19. A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct?

(a) MCl_2 is more volatile than MCl_4
(b) MCl_2 is more soluble in anhydrous ethanol than MCl_4
(c) MCl_2 is more ionic than MCl_4
(d) MCl_2 is more easily hydrolysed than MCl_4

20. Which of the following statements is/are incorrect ?

(a) He_{II} has much lower entropy
(b) Transition of He to He_{II} takes place, across the line $\lambda - \lambda' = 2.2$ K
(c) It has very high viscosity
(d) He_{II} is unique liquid that exhibits superconductivity

21. Which of the following statement is wrong ?

(a) The stability of hydrides increases from NH_3 to BiH_3 in group 15 of the periodic table
(b) Nitrogen can't from $d\pi$-$p\pi$ bond
(c) Singe N—N bond is weaker than the single P—P bond.
(d) N_2O_4 has two resonance structure

22. Which one of the following reaction of xenon compounds is not feasible?

(a) $XeO_3 + 6HF \longrightarrow XeF_6 + 3H_2O$
(b) $3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + 1.5\ O_2$
(c) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$
(d) $XeF_6 + RbF \longrightarrow Rb[XeF_7]$

23. A liquid X is treated with Na_2CO_3 solution. A mixture of two salts Y and Z are produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid X again. Identify X.

(a) Cl_2
(b) Br_2
(c) Hg
(d) I_2

24. On heating, compound (A) gives a gas (B) which is a constituent of air. This gas when treated with 3 moles of hydrogen (H_2) in the presence of a catalyst gives another gas (C) which is basic in nature. Gas C on further oxidation in moist condition gives a compound (D) which is a part of acid rain. Identify compound (D). *[NCERT Exemplar]*

(a) HNO_2
(b) HNO_3
(c) H_2SO_4
(d) HCl

25. On heating lead (II) nitrate gives a brown gas "A". The gas "A" on cooling changes to colourless solid "B". Solid "B" on heating with NO changes to a blue solid "C". Identify "C". *(NCERT Exemplar)*

(a) NO_2
(b) N_2O_4
(c) N_2O_5
(d) N_2O_3

26. PCl_3 and PCl_5 both exist; NCl_3 exist but NCl_5 does not exist. It is due to *(AIEEE 2002)*

(a) lower electronegativity of P and N
(b) lower tendency of N to form covalent bond
(c) availability of vacant d-orbital in P but not in N
(d) statement is itslelf incorrect

27. A dark brown solid (X) reacts with NH_3 to form a mild explosive which decomposes to give a violet coloured gas. (X) also reacts with H_2 to give an acid (Y). (Y) can also be prepared by heating its salt with H_3PO_4. X and Y are

(a) Cl_2, HCl (b) SO_2, H_2SO_4
(c) Br_2, HBr (d) I_2, HI

28. Reaction of an inorganic sulphite X with dilute H_2SO_4 generates compound Y. Reaction of Y with NaOH gives X. Further, the reaction of X with Y and water affords compound Z. Y and Z respectively, are *(JEE Main 2020)*

(a) SO_2 and Na_2SO_3 (b) SO_3 and $NaHSO_3$
(c) SO_2 and $NaHSO_3$ (d) S and Na_2SO_3

29. A black compound of manganese reacts with a halogen acid to give greenish yellow gas. When excess of this gas reacts with NH_3 an unstable trihalide is formed. In this process the oxidation state of nitrogen changes from *(NCERT Exemplar)*

(a) –3 to +3 (b) –3 to 0 (c) –3 to +5 (d) 0 to –3

30. The correct statement among the following is *(JEE Main 2019)*

(a) $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$.
(b) $(SiH_3)_3N$ is pyramidal and more basic than $(CH_3)_3N$.
(c) $(SiH_3)_3N$ is pyramidal and less basic than $(CH_3)_3N$.
(d) $(SiH_3)_3N$ is planar and more basic than $(CH_3)_3N$.

31. Which of the following option are not in accordance with the property mentioned against them ?

(a) $F_2 > Cl_2 > Br_2 > I_2$ (Oxidising power)
(b) $MI > MBr > MCl > MF$ (Ionic character of metal halide)
(c) $Cl_2 > Br_2 > F_2 > I_2$ (Bond dissociation energy)
(d) HI < HBr < HCl < HF (H—X bond shrength)

32. Copper metal on treatment with dilute HNO_3 produces a gas (X). (X) when passed through acidic solution of stannous chloride, a nitrogen containing compound (Y) is obtained. (Y) on reaction with nitrous acid produces a gas (Z). Gas (Z) is

(a) NO (b) N_2
(c) NO_2 (d) N_2O

33. White phosphorus on reaction with lime water gives calcium salt of an acid (A) along with a gas (X). Which of the following statement is correct with respect to above?

(a) (A) on heating gives (X) and O_2
(b) The bond angle in (X) is less than that in case of ammonia
(c) (A) is a dibasic acid
(d) (X) is more basic than ammonia

34. An oxide of a non-metal has the following properties

(i) It acts both as a proton donor as well as proton acceptor
(ii) It reacts readily with basic and acidic oxides
(iii) It oxidises Fe at its boiling point.

The oxide is

(a) P_2O_5 (b) SiO_2
(c) H_2O (d) CO_2

35. Which of the following statements regarding sulphur is incorrect?

(a) S_2 molecule is paramagnetic
(b) The vapour at 200°C consists mostly of S_8 rings
(c) At 600°C the gas mainly consists of S_2 molecules
(d) The oxidation state of sulphur is never less than +4 in its compounds

36. Identify the incorrect statement among the following.

(a) Ozone reacts with SO_2 to give SO_3
(b) Silicon reacts with NaOH (*aq*) in the presence of air to give Na_2SiO_3 and H_2O
(c) Cl_2 reacts with excess of NH_3 to give N_2 and HCl
(d) Br_2 reacts with hot and strong NaOH solution to give NaBr, $NaBrO_4$ and H_2O

37. Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. The explanation for it is that

(a) concentrated hydrochloric acid emits strongly smelling HCl gas all the time
(b) oxygen in air reacts with the emitted HCl gas to form a cloud of chlorine gas
(c) strong affinity of HCl gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke
(d) due to strong affinity for water, concentrated hydrochloric acid pulls moisture of air towards itself. This moisture forms droplets of water and hence, the cloud

Numeric Value Questions

38. The number of S—O—S bonds in suphur trioxidetrimer (S_3O_9) is ……… .

39. In NO_3^- ion, the number of bond pair of electrons on nitrogen atom are ………

40. The basicity of orthophosphoric acid is ……… .

41. The number of hydrogen atom(s) directly phosphorus atom in hypophosphorus acid is ………

42. In H_3PO_3 acid, if x is the number of lone pairs, y is the number of σ bonds and z is the number of π bonds then the value of $x + y + z$ is ………

43. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives X and Y with evolution of Z gas. The sum of total number of X, Y, Z molecule formed in the balanced chemical equation is ………

44. In the preparation of HNO_3, we get NO gas by catalytic oxidation of ammonia. The moles of NO produced by the oxidation of two moles of NH_3 will be ……… .

45. Among the given oxoacids of phosphorous $H_4P_2O_7$, $H_2P_2O_8$, $H_4P_2O_6$, $H_2P_2O_5$ and H_3PO_2, the total number of tetrabasic compounds is/are ………

46. If X is the number of moles of phosphine formed on thermal decomposition of hypophosphorus acid, then the value of $(x^2 - 0`5)$ is ………

47. Nitric acid forms an oxide of nitrogn on reaction with P_4O_{10}. The resonating structures of the oxide of nitrogen formed will be *(NCERT Exemplar)*

48. White phosphorus reacts with chlorine and the product hydrolyses in the presence of water.
The mass of HCl obtained by the hydrolysis of the product formed by the reaction of 62 g of white phosphorus with chlorine in the presence of water will be …… (g).

Answers

Round I

1. (b)	**2.** (b)	**3.** (d)	**4.** (c)	**5.** (c)	**6.** (b)	**7.** (d)	**8.** (d)	**9.** (a)	**10.** (d)
11. (b)	**12.** (a)	**13.** (a)	**14.** (d)	**15.** (c)	**16.** (a)	**17.** (c)	**18.** (b)	**19.** (c)	**20.** (d)
21. (a)	**22.** (a)	**23.** (c)	**24.** (c)	**25.** (a)	**26.** (a)	**27.** (d)	**28.** (a)	**29.** (a)	**30.** (d)
31. (d)	**32.** (a)	**33.** (a)	**34.** (d)	**35.** (a)	**36.** (c)	**37.** (b)	**38.** (b)	**39.** (c)	**40.** (c)
41. (d)	**42.** (b)	**43.** (d)	**44.** (c)	**45.** (a)	**46.** (c)	**47.** (d)	**48.** (a)	**49.** (c)	**50.** (b)
51. (b)	**52.** (a)	**53.** (c)	**54.** (c)	**55.** (a)	**56.** (a)	**57.** (a)	**58.** (c)	**59.** (d)	**60.** (d)
61. (c)	**62.** (c)	**63.** (b)	**64.** (c)	**65.** (c)	**66.** (d)	**67.** (d)	**68.** (a)	**69.** (d)	**70.** (b)
71. (b)	**72.** (d)	**73.** (a)	**74.** (a)	**75.** (b)	**76.** (a)	**77.** (d)	**78.** (c)	**79.** (a)	**80.** (d)
81. (b)	**82.** (a)	**83.** (a)	**84.** (c)	**85.** (b)	**86.** (c)	**87.** (a)			

Round II

1. (d)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (b)	**6.** (a)	**7.** (d)	**8.** (b)	**9.** (b)	**10.** (d)
11. (a)	**12.** (a)	**13.** (b)	**14.** (b)	**15.** (d)	**16.** (c)	**17.** (c)	**18.** (d)	**19.** (c)	**20.** (c)
21. (a)	**22.** (a)	**23.** (b)	**24.** (b)	**25.** (d)	**26.** (c)	**27.** (d)	**28.** (c)	**29.** (a)	**30.** (a)
31. (b)	**32.** (d)	**33.** (b)	**34.** (c)	**35.** (d)	**36.** (d)	**37.** (b)	**38.** (3)	**39.** (4)	**40.** (3)
41. (2)	**42.** (13)	**43.** (9)	**44.** (2)	**45.** (3)	**46.** (0.5)	**47.** (2)	**48.** (219)		

Solutions

Round I

1. Due to very low ignition temperature (303 K) of phosphorus, it is always kept under water.

2. Bismuth forms BiF_5 only in which its oxidation state is +5.

3. Due to absence of *d*-orbitals in N-atom, it cannot accept electrons from H_2O for hydrolysis of NF_3.

4. MCl_3 [where, $M =$ has sp^3-hybridised M-element N, P, As, Sb] with one lone pair.

Lone pair and bond pair repulsion decreases bond angle. However, the bond pairs of electrons are much farther away from the central atom in NCl_3 than they are in PCl_3, $AsCl_3$ and $SbCl_3$.

Thus, bond angle decreases from NCl_3 (maximum) to $SbCl_3$ (minimum).

5. $\underbrace{P_2O_3 \quad A_2O_3 \quad B_2O_3}_{\text{Acidic oxides}} \qquad \underbrace{Bi_2O_3}_{\text{Alkaline}}\}$ as Bi is most metallic among the group.

7. (a) All electrons in N_2 are paired, thus it is diamagnetic, not paramagnetic.

(b) $N_2 + O_2 \xrightleftharpoons{\text{Above } 2000°C} 2NO(g)$,

(c) Liquid N_2 gas is used to create extremely cold temperature to destroy diseased tissues located outside the body.

(d) N_2 gas used as a diluent due to it's inert nature.

Hence, the correct option is (d).

8. In group 15, N and P = Non metal;

As and Sb = Metalloid; Bi = Metal

In NH_3, hydrogen atom gets partial positive charge due to less electronegativity.

But in BiH_3, hydrogen atom gets partial negative charge because hydrogen is more electronegative than bismuth. i.e. BiH_3 is a strong reducing agent than others because we know that H^- is a strong reducing agent.

9. $$\underset{\substack{\text{Ammonium}\\\text{dichromate}}}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} Cr_2O_3 \downarrow + N_2 \uparrow + 4H_2O$$

$$\underset{\text{Barium azide}}{Ba(N_3)_2} \xrightarrow{\Delta} Ba + 3N_2$$

10. Liquid ammonia is used in refrigeration because it has high heat of vaporisation.

11. $3NH_3 + OCl^- \longrightarrow NH_2 - NH_2 + NH_4Cl + OH^-$

12. NH_3 reacts with P_2O_5, therefore, it cannot be dried over either of them.

$CuSO_4$ and HNO_3 are not drying agent. NH_3 can be dried over CaO only because it is a drying agent with which it does not react.

13. In N_2O_5, the oxidation state of N is +5. Further, increase in oxidation state is not possible. That's why, its does not behave as reducing agent.

14. (*d*) A yellow explosive liquid nitrogen trichloride is formed as,

$$NH_3 + \underset{\text{(Excess)}}{3Cl_2} \longrightarrow 3HCl + \underset{\substack{\text{Nitrogen}\\\text{trichloride}}}{NCl_3}$$

Here, ammonia is taken in excess then ammonium chloride is formed.

$$\underset{\text{(Excess)}}{7NH_3} + 3Cl_2 \longrightarrow NH_4Cl + N_2 \uparrow$$

15. (*c*) The products of the reaction of copper with HNO_3 depends upon the concentration of HNO_3 used.

Copper metal reacts with dilute HNO_3 to form nitrogen (II) oxide (NO).

$$3Cu + 8HNO_3 \text{(dilute)} \longrightarrow 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$$

Copper metal reacts with conc. HNO_3 to form nitrogen (IV) oxide or nitrogen dioxide (NO_2).

$$Cu + 4HNO_3 \text{(conc.)} \longrightarrow Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

16. Neutral oxides show neither basic nor acidic properties and hence do not form salts when reacted with acids or bases. e.g. carbon monoxide (CO); nitrous oxide (N_2O); nitric oxide (NO), etc., are neutral oxides.

N_2O and NO are neutral oxides of nitrogen NO_2 and N_2O_3 are acidic oxides.

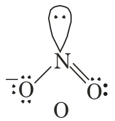
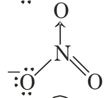
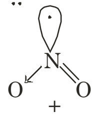
18. $4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$

19. Nitrogen monoxide react with dinitrogen tetraoxide at 250 K temperature forms blue solid of N_2O_3.

$$2NO + N_2O_4 \xrightarrow{250\text{ K}} 2N_2O_3$$

N_2O_3 is acidic in nature. In N_2O_3, N has $+3$ oxidation state. Generally, oxides with higher oxidation states are more acidic than oxides having lower oxidation state. It is a blue solid because it strongly absorbs in the visible region to appear bright blue in colour.

20.

Species	**Hybridisation**
	sp^2
	sp^2
	sp^2
$O=\overset{+}{N}=O$	sp

Thus, the correct option is (d).

21. The electronic configuration of NO $[15\ e^-]$ is given by $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_z^1$

Thus, NO possess one unpaired electron, hence, it is paramagnetic in nature.

However, it dimerises at low temperature to become diamagnetic.

$$2NO \rightleftharpoons N_2O_2$$

Bond order of NO $= \frac{1}{2}[10-5] = 2.5$

Thus, bond order of NO is 2.5 and it combines with O_2 to give NO_2.

Hence, the correct option is (a).

22. The oxidation states of nitrogen in following molecules are as follows

$$NO_3^- \rightarrow +5$$
$$NO_2 \rightarrow +4$$
$$NO \rightarrow +2$$
$$N_2O \rightarrow +1$$

Hence, correct order is

$$NO_3^- > NO_2 > NO > N_2O.$$

23. (*c*) White phosphorus combines with a concentrated solution of NaOH in inert atmosphere of CO_2, to yield a highly poisonous gas, phosphine. It has rotten fish like smell.

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3 \uparrow$$

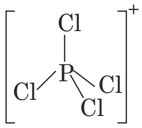
Its aqueous solution is neutral, so it is not more basic than NH_3.

24. $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

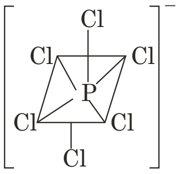
25. $PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$

26. In Holmes signals of the ship, mixutre of CaC_2 and Ca_3P_2 is used.

27. Solid PCl_5 shows ionic lattices. It has tetrahedral cations $[PCl_4]^+$ and octahedral anions $[PCl_6]^-$.



$[PCl_4]^+$



$[PCl_6]^-$

28. Here, reactions are same as those with water (H_2O).

PCl_5 shows following hydrolytic reactions with heavy water (D_2O).

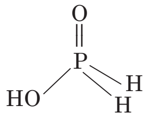
***Step* I** $PCl_5 + D_2O \longrightarrow POCl_3 + 2DCl$

***Step* II** $POCl_3 + 3D_2O \longrightarrow D_3PO_4 + 3DCl$

Overall reaction

$$PCl_5 + 4D_2O \longrightarrow \underset{\text{Deuterio phosphoric acid}}{D_3PO_4} + \underset{\text{Deuterium chloride}}{5DCl}$$

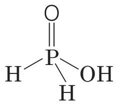
29. The structure of H_3PO_2 (hypophosphorous) acid is



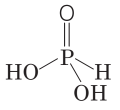
Due to the presence of two P—H bonds, H_3PO_2 acts a strong reducing agent. e.g.

$$4\overset{+1}{Ag}NO_3 + H_3\overset{+1}{P}O_2 + 2H_2O \longrightarrow 4\overset{0}{Ag}\downarrow + H_3\overset{+5}{P}O_4 + 4HNO_3$$

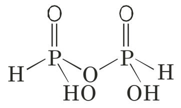
30. Let us consider the structure of the phosphorus oxyacids,



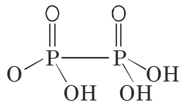
H_3PO_2
Hypophosphorus acid
(P — H bonds = 2)



H_3PO_3
Orthophosphorus acid
(P — H bond = 1)

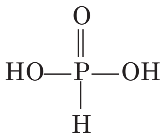


$H_4P_2O_5$
Pyrophosphorus acid
(P — H bonds = 2)



$H_4P_2O_6$
Hypophosphoric acid
(P — H bond = 0)

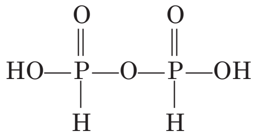
31. Orthophosphorous acid, H_3PO_3 :



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

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

Pyrophosphorous acid, $H_4P_2O_5$



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

$$\mathrm{H_4\overset{x}{P_2}O_5} = 4 + 2x + 5(-2) = 0$$

$$4 + 2x - 10 = 0 \quad \Rightarrow x = +3$$

32. Dithionous acid ($H_2S_2O_4$) has sulphur in +3 oxidation state.

33. As given, the first electron gain enthalpy of oxygen can be shown as,

$$O(g) + e^- \longrightarrow O^-(g),\ \Delta_{e_g}H_1 = -141\ \text{kJ/mol}$$

The expression of second electron gain enthalpy of oxygen will be,

$$O^-(g) + e^- \longrightarrow O^{2-}(g),\quad \Delta_{e_g}H_2 = +\ \text{ve}$$

$\Delta_{e_g}H_2$ of oxygen is positive, i.e. endothermic, because a strong electrostatic repulsion will be observed between highly negative O^- and the incoming electron (e^-).

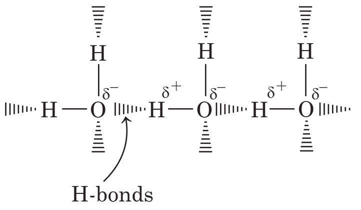
A very high amount of energy will be consumed (endothermic) by the system to overcome the electrostatic repulsion.

34. SO_2 acts as an oxidising agent particularly when treated with stronger reducing agents. SO_2 oxidises H_2S into S.

$$SO_2 + 2H_2S \longrightarrow 2H_2O + S$$

35. Two O—H bonds of a H_2O molecule make stronger and extensive intermolecular hydrogen bonds which lead two association of H_2O molecules into water or $H_2O(l)$. One H_2O molecule can make four H–bonds.

$$nH_2O \xrightarrow[\text{intermolecular H—bonds}]{\text{Association through}} \underbrace{(H_2O)_n \text{ or } H_2O(l)}_{\text{Water}}$$



But S—H bonds of H_2S cannot make H–bonds. So, boiling point of H_2O is more 373 K than H_2S, because :

Boiling point ∝ molecular association.

36. Thermal stability ∝ bond dissociation energy,

$$\Delta_{\text{diss}}H(H-E)/\text{kJ mol}^{-1} \propto \frac{1}{\text{Size of central atom}}$$

(where, $E = 16$ group elements)

On moving down the group, bond dissociation energy decreases because bond length increases.

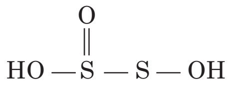
Thus, the order of bond dissociation energy is

$$H_2O > H_2S > H_2Se > H_2Te > H_2Po$$

This is also the order of thermal stability.

38. $3S + 4NaOH \xrightarrow{\text{Boiling}} Na_2S_2O_3 + Na_2S$

39. $H_2S_2O_3$,



$$\mathrm{HO-\overset{\overset{O}{\|}}{S}-S-OH}$$

40. H_2SO_4 acts as dehydrating agent in the following reaction.

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

41. Concentrated sulphuric acid, being a strong acid, oxidises bromides and iodides but not chlorides and fluorides.

Since, the later are more electronegative. Hence, it can be reduced only by NaBr among the given options.

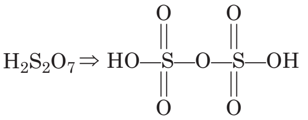
$$H_2\overset{+6}{S}O_4 + 2Na\overset{-1}{Br} \longrightarrow NaH\overset{+6}{S}O_4 + H\overset{-1}{Br}$$

$$2H\overset{-1}{Br} + H_2\overset{+6}{S}O_4 \longrightarrow 2H_2O + \overset{0}{Br_2} + \overset{+4}{S}O_2$$

Reduction

43. The great affinity of H_2SO_4 for water is because it forms hydrates with water.

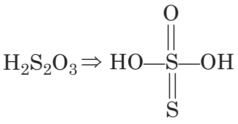
44. S — S bond is not present in $H_2S_2O_7$ (pyrosulphuric acid or oleum).



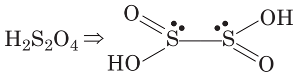
$$H_2S_2O_7 \Rightarrow \mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$$

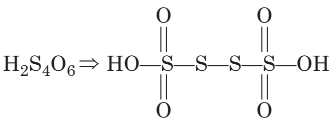
While the other given oxoacids of sulphur, i.e.

$H_2S_2O_3$ (thiosulphuric acid), $H_2S_2O_4$ (hyposulphurous or dithionous acid) and $H_2S_4O_6$ (tetrathionic acid) contains S—S bonds.



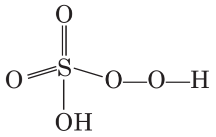
$$H_2S_2O_3 \Rightarrow \mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{S}{\|}}{S}}-OH}$$



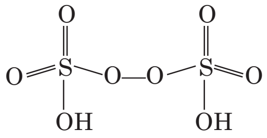


$$H_2S_4O_6 \Rightarrow \mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$$

45. In peroxoacids, —O—O— linkage is present H_2SO_5 and $H_2S_2O_8$ are peroxoacids of sulphur.



H_2SO_5
Peroxomonosulphuric acid or Caro's acid



$H_2S_2O_8$
Peroxodisulphuric acid or Marshall's acid

46. Caliche is crude chile salt petre which contains about 0.02% iodine as sodium iodate ($NaIO_3$), from which iodine is extracted.

47. Fluorine is the strongest oxidising agent. It will oxidise other halide ions to halogens in solution or even in dry.

$$F_2 + 2X^- \longrightarrow 2F^- + X_2$$

48. $2F_2 + 2H_2O \longrightarrow 4HF + O_2$

$3F_2 + 3H_2O \longrightarrow O_3 + 6HF$

49. Iodine has the least affinity for water and is only slightly soluble in it. However, it dissolves in 10% aqueous solution of KI due to the formation of a complex ion, i.e. I_3^-.

$$I_2 + KI \rightleftharpoons KI_3$$

or $$I_2 + I^- \rightleftharpoons \underset{\text{(Complex ion)}}{I_3^-}$$

50. AgI is a covalent compound so, it is insoluble in water.

51. $CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4$

$$2CuI_2 \longrightarrow \underset{\text{Cuprous iodide}}{2CuI} + I_2$$

52. HI is the strongest acid because H—I bond is weakest bond.

54. HF has highest boiling point among hydrogen halides because it has strongest hydrogen bonding.

Here, the hydrogen bond exists between hydrogen of one molecule and fluorine atom of another molecule as shown below.

$$\ldots\overset{\delta+}{H}—\overset{\delta-}{F}\ldots\overset{\delta+}{H}—\overset{\delta-}{F}\ldots\overset{\delta+}{H}—\overset{\delta-}{F}$$

In this molecule, hydrogen bond behaves like a bridge between two atoms that holds one atom by covalent bond and the other by hydrogen bond.

55.

Hydride	HF	HCl	HBr	HI
B. pt. (in K)	293	189	206	238

Because of having low boiling point HCl is more volatile.

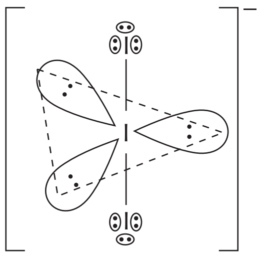
56. As the size of the halogen atom increases from F to I, H—*X* bond length in H*X* molecules also increases from H—F to HI

$$HF < HCl < HBr < HI$$

The increase in H*X* bond length decreases the strength of H*X* bond from HF to HI (HF > HCl > HBr > HI). Due to decrease in the strength of H*X* bonds, their bond dissociation enthalpy decreases from HF to HI.

H*X*	HF	>	HCl	>	HBr	>	HI
Bond dissociation enthalpy (kJ/mol)	574.0		428.1		362.5		294.6

58. The structure of I_3^- ion is



Hence, 9 is the correct answer.

59. Cl_2, Br_2 and I_2 are homonuclear diatomic molecule in which electronegativity of the combining atoms is same, so they are more stable and less reactive. Whereas, I and Cl have different electronegativities and bond between them are polarised and hence, reactive. Therefore, interhalogen compounds are more reactive.

Time Saving Technique In this type of question of halogen, only go through the polarity of the molecule.

As we know, diatomic molecule does not have polarity but molecules with dissimilar sizes have polarity resulting in more reactivity.

61. $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

62. Oxidising power of species is directly proportional to reduction potentials.

Therefore, order of oxidising power of given ions is as follows

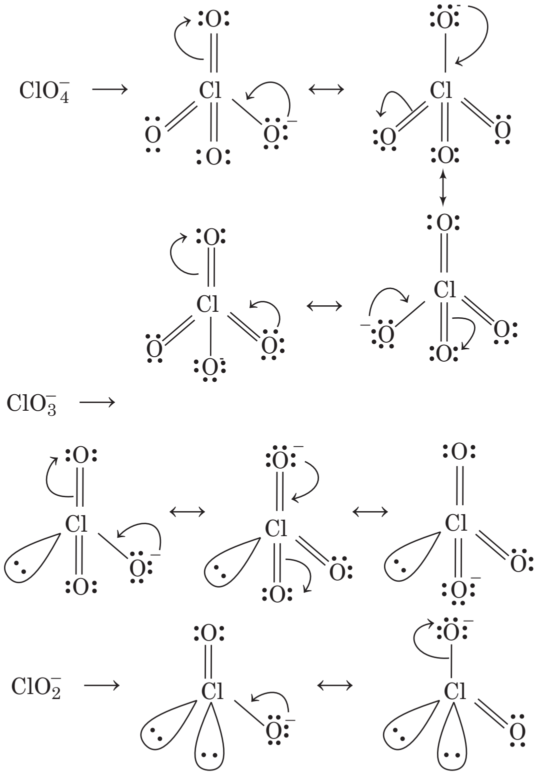
Ion	BrO_4^- >	IO_4^- >	ClO_4^-
E_c(V)	1.74	1.65	1.19

63. $2HClO_4 \longrightarrow H_2O + Cl_2O_7$

64. Acidic strength of oxoacids depends upon the stability of conjugate base. More stable the conjugate base of an acid, stronger is the acid.

$$HClO_4 \rightleftharpoons ClO_4^- + H^+$$
$$HClO_3 \rightleftharpoons ClO_3^- + H^+$$
$$HClO_2 \rightleftharpoons ClO_2^- + H^+$$
$$HOCl \rightleftharpoons ClO^- + H^+$$

Conjugate bases stabilises by resonance.



ClO^- does not show resonance. Thus, the stability order of conjugate base due to resonance is

$$ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$$

Hence, the acidic strength of given oxoacids is as follows

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

65. Cl_2, Br_2 and I_2 form a mixture of halide and hypohalites when react with cold dilute alkalies while a mixture of halides and haloate when react with concentrated cold alkalies.

$$\underset{\text{(Cold and dilute)}}{Cl_2 + 2NaOH} \longrightarrow NaCl + NaClO + H_2O$$

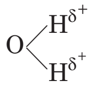
$\therefore$ Cl^- and ClO^- are obtained as products when chlorine gas reacts with cold and dilute aqueous NaOH.

67. $3HOCl \longrightarrow 2HCl + HClO_3$

68. Acid strength decreases from HClO to HIO as the electronegativity of halogen decrease.

69. As we move down the group of noble gases, molecular mass increases by which dipole produced for a moment and hence, London forces increases from He to Xe. Therefore more amount of energy is required to break these forces. Thus, boiling point also increases from He to Xe.

70. Welding of Mg is done in the atmosphere of He due to its inert and non-inflammable nature.

71. Dipole of water  induces dipole in noble gases which interact and causes solubility in water.

72. He, because of its small size can diffuse through rubber, glass PVC etc. easily.

73. Solubility increases on moving down the group.

Xe > Kr > Ar > Ne > He

74. Clevite is uranium mineral, on heating it gives He.

78. $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2 \uparrow$

79. XeF_2, XeF_4 and XeF_6 can be directly prepared by

$Xe + F_2 \xrightarrow[673\text{ K}]{\text{Ni tube}} XeF_2$;

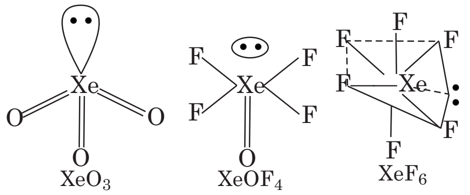
$Xe + 2F_2 \xrightarrow[6\text{ atm}]{673\text{ K}} XeF_4$

$Xe + 3F_2 \xrightarrow[50\text{-}60\text{ atm}]{523\text{-}573\text{ K}} XeF_6$

XeO_3 is obtained by the hydrolysis of XeF_6.

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

81.



82. Both XeF_2 and IF_2^- are linear species but the central atoms Xe and I undergo sp^3d hybridisation with all the three equatorial positions occupied by the lone pairs of electrons.

83. XeO_4 is formed by promoting one 5*s* and three 5*p*-electrons of Xe to higher energy. 5*d* orbitals giving eight unpaired orbitals hybridize to give sp^3 hybridisation which form sigma bonds with four O atoms. The four unhybridised singly occupied 5*d* orbitals form four $p\pi$ - $d\pi$ bonds with oxygen atoms.

84. $XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$

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

85. XeF_6 cannot be stored in glass vessels because it reacts with SiO_2 of the glass to give highly explosive XeO_3.

$2XeF_6 + 3SiO_2 \longrightarrow 2XeO_3 + 3SiF_4$

86. Xenon hexafluoride reacts with silica to form $XeOF_4$ as

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

The oxidation state of xenon in $XeOF_4$ is calculated as

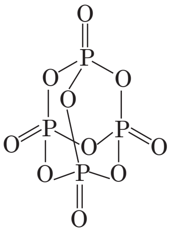
$$\overset{x}{Xe}\,\overset{-2}{O}\overset{-1}{F_4}$$

$$x + (-2) + 4 \times (-1) = 0$$
$$x - 2 - 4 = 0$$
$$x = +6$$

87. Clathrates are non-stoichiometric compounds where the ratio of guest and host molecules does not correspond to ideal chemical formula.

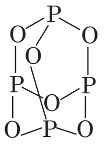
Round II

1. P_2O_5, i.e. P_4O_{10}



$\Rightarrow$ Six P—O—P bridges

P_2O_3, i.e. P_4O_6



$\Rightarrow$ Six P—O—P bridges

2. $CaCl(OCl) \longrightarrow Ca(ClO_3)_2 + CaCl_2$

3. Orthophosphate + Ammonium molybdate

$$\xrightarrow[\Delta]{HNO_3} \text{Yellow ppt.}$$
$$\downarrow + AgNO_3$$
$$\text{Red ppt.}$$

4. As we go down the group, bond angle decreases, since the repulsion between the bonded pairs of electrons decreases. So, N > P > As > Bi.

5. The electron affinity (in kJ/mol)

Fluorine = 332.6	Chlorine = 348.5
Bromine = 324.7	Iodine = 295.5

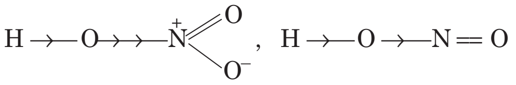
Chlorine has highest electron affinity value.

So, according to question the correct order of electron affinity will be $Cl_2 > F_2 > Br_2$.

6. Due to electronegativity difference, the stability of interhalogen compounds follows following the order

$$IF_3 > BrF_3 > ClF_3$$

7.



Polarity along O—H in HNO_3 is more in comparison to —O—H in HNO_2.

Thus, H^+ ion can easily be removed due to which acidity is increased in HNO_3.

8. The normal oxides of the elements present on extreme left of periodic table are most acidic (Li_2O) as they form strong base when dissolved in water and oxides of the elements present in extreme right are acidic (N_2O_3). The amphoteric oxides show both the acidic and basic character (Al_2O_3).

The acidic, basic and amphoteric oxides, respectively are N_2O_3, Li_2O and Al_2O_3.

9. OF_2 dissolves in water but does not give any oxyacid solution while SO_2, SCl_4 and SO_3 give oxyacid solution in water.

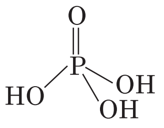
$$SO_2 + H_2O \longrightarrow \underset{\text{Sulphurous acid}}{H_2SO_3}$$

$$SCl_4 + 3H_2O \longrightarrow \underset{\text{Sulphurous acid}}{H_2SO_3} + 4HCl$$

$$SO_3 + H_2O \longrightarrow \underset{\text{Sulphuric acid}}{H_2SO_4}$$

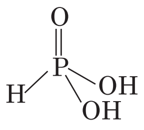
10. Orthophosphoric acid (H_3PO_4) is a tribasic acid because it has three replaceable hydrogen atoms. Hence, the basicity of H_3PO_4 is 3.

Its structure is shown below as,



H_3PO_4 (Tribasic acid)

While phosphorous acid (H_3PO_3) is a dibasic acid because it has two replaceable hydrogen atom. Hence, the basicity of H_3PO_3 is 2. Its structure is shown below as



H_3PO_3 (Dibasic acid)

11. The thermal stability of the hydrides of nitrogen family or group 15 elements decreases on moving downwards in the group.

Therefore, NH_3 is the most stable and SbH_3 is the least stable. The stability of the hydrides of group 15 elements decreases in the order as,

$$NH_3 > PH_3 > AsH_3 > SbH_3$$

12. Complete reaction with change in hybridisation is as follows

(a) $$\underset{sp^3d^2}{\underline{X}eF_4} + SbF_5 \longrightarrow \underset{sp^3d}{[XeF_3]^+}[SbF_6]^-$$
Change in hybridisation

(b) $$\underset{sp^3}{H_2\underline{S}O_4} + 2NaCl \longrightarrow \underset{sp^3}{Na_2SO_4} + 2HCl$$
No change in hybridisation

(c) $$\underset{sp^3}{H_3\underline{P}O_2} \xrightarrow[\Delta]{\text{Disproportionation}} H_3\underline{P}O_4 + \underset{sp^3}{P\underline{H}_3}$$
No change in hybridisation

(d) $$\underset{sp^3}{\ddot{\underline{N}}H_3} \xrightarrow{N^+} \underset{sp^3}{\overset{+}{\underline{N}}H_4}$$
No change in hybridisation

In the reaction (a), hybridisation of Xe in XeF_4 is sp^3d^2 converted into $[XeF_3]^+$ and hybridisation of Xe in $[XeF_3]^+$ is sp^3d.

In this reaction, sp^3d^2 hybridisation change into sp^3d.

13. A halate will be formed from halogen and the greenish yellow gas is Cl_2. The halate which is used in fireworks and safety matches is $KClO_3$.

$$\underset{\text{(Greenish yellow gas)}}{3Cl_2} + 6KOH \longrightarrow KClO_3 + 5HCl + 3H_2O$$

15. $$Zn + \text{conc. } 4HNO_3 \longrightarrow Zn(NO_3)_2 + \underset{(X)}{2NO_2} + 2H_2O$$

$$4Zn + \text{dil. } 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + \underset{(Y)}{NH_4NO_3} + 3H_2O$$

17. The first ionisation energy of xenon is quite close to that of oxygen and the molecular diameter of xenon and oxygen are almost identical.

Based on the above facts, it is suggested that as oxygen combines with PtF_6, so xenon should also form similar compound with PtF_6.

18. (a) In the presence of moisture, SO_2 liberates nascent hydrogen. Due to which it can bleach delicate articles like silk and straw.

$$SO_2 + H_2O \longrightarrow H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{2-}$$

(b) Its dilute solution is used as disinfectant.

(c) SO_2 is prepared by the reaction of conc. H_2SO_4 with metals.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

19. MCl_2; oxidation state of $M = +2$

MCl_4; oxidation state of $M = +4$

Higher the oxidation state, smaller the size.

Greater is the polarizing power, greater is the covalent characteristics. Hence, MCl_4 is more covalent and MCl_2 is more ionic.

20. He_{II} has extremely low viscosity and readily form films only a few hundred atom thick, which flow without friction.

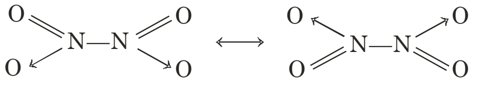
21. (a) Thermal stability of the hydrides decreases as we move down the group in Periodic Table for group 15 (N-family).

	BiH_3 <	SbH_3 <	AsH_3 <	PH_3 <	NH_3
Least stable					
M-H Bond energy (kJ mol^{-1})	–	255	247	322	391

(b) Due to absence of d-orbital, nitrogen can't form $d\pi$-$d\pi$ bond, thus it is correct.

(c) The N—N bond (BE 160 kJ mol^{-1}) is weaker than P—P bond (BE 209 kJ mol^{-1}). Thus, it is correct.

(d) N_2O_4 can form two resonance structures.



Thus, it is correct.

23. The liquid X is bromine which on treatment with sodium carbonate forms a mixture of NaBr and $NaBrO_3$ (sodium bromate). The mixture with conc. H_2SO_4 on distillation, gives the liquid bromine again.

$$\underset{(X)}{3Br_2} + 3Na_2CO_3 \longrightarrow \underset{(Y)}{5NaBr} + \underset{(Z)}{NaBrO_3} + 3CO_2$$

$$5NaBr + NaBrO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 3Br_2 + 3H_2O$$

24. The main constituent of air are nitrogen (78%) and oxygen (21%). Only N_2 reacts with three moles of H_2 in the presence of a catalyst to give NH_3 (ammonia) which is a gas having basic nature. On oxidation NH_3 gives NO_2 which is a part of acid rain. So, the compounds A to D are as

$A = NH_4NO_2$; $B = N_2$; $C = NH_3$; $D = HNO_3$.

25. $$\underset{\text{Lead nitrate}}{Pb(NO_3)_2} \xrightarrow[673\text{ K}]{\Delta} 2PbO + \underset{\substack{\text{Brown}\\ [A]}}{4NO_2(g)}$$

$$2NO_2(g) \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} \underset{\substack{\text{Colourless}\\ [B]}}{N_2O_4(g)}$$

$$2NO + N_2O_4 \xrightarrow{250\text{ K}} \underset{\substack{\text{Blue}\\ [C]}}{2N_2O_3(s)}$$

26. Phosphorus (3rd period element) can raise covalency facilitating vacant d-orbitals

P (ground) = [Ne] $3s^2\ 3p^3\ 3d^0$

P (excited) = [Ne] $3s^1\ 3p^3\ 3d^1$

27. $X = I_2$, $Y = HI$

$$\underset{(X)}{3I_2} + 2NH_3 \longrightarrow \underset{\text{(Explosive)}}{NH_3 \cdot NI_3}$$

$$8NI_3 \cdot NH_3 \longrightarrow 5N_2 + I_2 + 6NH_4I$$

$$I_2 + H_2 \longrightarrow \underset{(Y)}{2HI}$$

$$3NaI + H_3PO_4 \xrightarrow{\Delta} Na_3PO_4 + 3HI$$

28. $$\underset{(X)}{Na_2SO_3} \xrightarrow{\text{Dil. } H_2SO_4} \underset{(Y)}{SO_2} \xrightarrow{NaOH} \underset{(X)}{Na_2SO_3} \xrightarrow{SO_2+H_2O} \underset{(Z)}{NaHSO_3}$$

Here, X, Y, Z are

$X = Na_2SO_3$, $Y = SO_2$, $Z = NaHSO_3$

Na_2SO_3 react with dil. H_2SO_4 form sulphur dioxide (SO_2) gas. SO_2 on reaction with NaOH again form Na_2SO_3. By the reaction of SO_2 and H_2O with Na_2SO_3 form $NaHSO_3$.

29. $$\underset{\substack{\text{Manganese oxide}\\ \text{(black)}}}{MnO_2} + H_2SO_4 + 2HCl \longrightarrow MnSO_4 + 2H_2O + \underset{\substack{\text{Chlorine gas}\\ \text{(greenish yellow)}}}{Cl_2\uparrow}$$

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Excess}}{3Cl_2} \longrightarrow \underset{\substack{\text{Nitrogen trichloride}\\ \text{(Unstable and explosive)}}}{NCl_3} + 3HCl$$

In NH_3, let the oxidation state of N = x

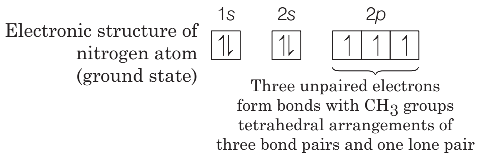
$$x + 3(+1) = 0$$
$$x = -3$$

NCl_3, Let the oxidation state of N = y

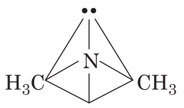
$$y + 3(-1) = 0$$
$$y = +3$$

30. The correct statement is that $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$. The compounds trimethylamine $(CH_3)_3N$ and trisilylamine $(SiH_3)_3N$ have similar formulae, but have totally different structures.

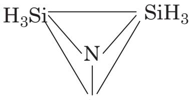
In trimethylamine, the arrangement of electrons is as follows



In trisilylamine, three sp^2 orbitals are used for σ-bonding, giving a plane triangular structure.



$N(CH_3)_3$ molecule



$N(SiH_3)_3$ molecule

In $(SiH_3)_3N$ the lone pair of electrons on nitrogen are used up in $p\pi$ - $d\pi$ back bonding while in $(CH_3)_3N$ such $p\pi$ - $d\pi$ bonding is not possible due to absence of vacant d-orbitals in carbon atom.

Therefore, $(CH_3)_3N$ is more basic than $(SiH_3)_3N$.

31. The ionic character of M—X bond decrease as the size of halogen atom increases $MF > MCl > MBr > MI$.

32. Cu produces NO gas when treated with dil. HNO_3. This gas is reduced by $SnCl_2$ / HCl and then oxidised by HNO_2 to give N_2O.

The reactions are as follows

$$Cu + \text{dil. } HNO_3 \longrightarrow \underset{(X)}{NO} \xrightarrow{SnCl_2/HCl} \underset{(Y)}{NH_2OH\cdot HCl} \xrightarrow{HNO_2} \underset{(Z)}{N_2O}$$

$$\underset{(X)}{NO} \xrightarrow{SnCl_2/HCl} \underset{(Y)}{NH_2OH\cdot HCl}$$

$$\underset{(Y)}{NH_2OH\cdot HCl} \xrightarrow{HNO_2} \underset{(Z)}{N_2O}$$

33. $$\underset{\text{White}}{8P} + \underset{\text{Lime water}}{3Ca(OH)_2} + 6H_2O \longrightarrow \underset{(A)}{3Ca(H_2PO_2)_2} + \underset{(X)}{2PH_3\uparrow}$$

(A) is H_3PO_2 (hypophosphorous acid), a monobasic acid. PH_3 is less basic than NH_3. The bond angle in (X) is less than that present in NH_3.

H_3PO_2 on heating gives orthophosphoric acid and phosphine (X).

34. H_2O is a amphoteric oxide. It can accept protons and also can donate them.

Thus, it readily reacts with basic as well as acidic oxides. Only water vapour react with Fe.

35. (a) S_2 molecule is paramagnetic due to unpaired electrons in its M.O configuration and is blue-coloured compound, thus true.

(b) The vapour at 200°C consists mostly of S_8 rings, thus correct.

(c) At 600°C, the gas mainly consists of S_2 molecules, thus, correct.

(d) Oxidation states of sulphur are

–2	in	H_2S
0	in	S_8
+2	in	$S_2O_3^{2-}$
+4	in	SO_2
+6	in	SO_3

Thus, option (d) is incorrect.

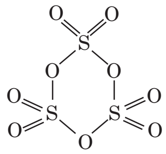
36. $3SO_2 + O_3 \longrightarrow 3SO_3$ (correct)

$2Si + 2NaOH + 4H_2O \longrightarrow 2NaSiO_3 + 5H_2$ (correct)

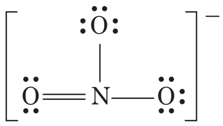
$3Br_2 + 6NaOH \longrightarrow NaBrO_3 + 5NaBr + 3H_2$ (correct)

Hence, option (d) is incorrect.

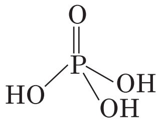
38.



Trioxide trimer (3S—O—S bond)

39.  Number of bond pair = 4.

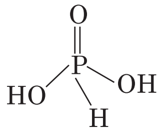
40. H_3PO_4



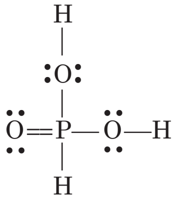
(Orthophosphoric acid)

The basicity is 3.

41. Structure of hypophosphorus acid H_3PO_2 is



Thus, the number of hydrogen atoms directly attached to phosphorus atom is 2.

42. 

$x = 6,\ y = 6,\ z = 1$

Total $= 6 + 6 + 1 = 13$

43. $3Br_2 + 3Na_2CO_3 \longrightarrow \underset{(X)}{5NaBr} + \underset{(Y)}{NaBrO_3} + \underset{(Z)}{3CO_2}\uparrow$

Total sum $= X + Y + Z = 9$

45. $H_4P_2O_7$, $H_4P_2O_8$ and $H_4P_2O_6$ are tetrabasic compound hence answer is 3.

46. $2H_3PO_2 \xrightarrow{\Delta} H_3PO_4 + PH_3$; Here, $x = 1$

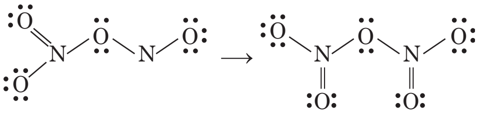
$(x^2 - 0.5) = (1)^2 - 0.5 = 1 - 0.5 = 0.5$

47. P_4O_{10} being a dehydrating agent, removes a molecule of water and forms anhydride of HNO_3.

$$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$$

N_2O_5 have two resonating structure.

e.g.



48. Equations for the reactions

$$\begin{array}{l} P_4 + 6Cl_2 \longrightarrow 4PCl_3 \\ PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl \times 4 \\ \hline \underset{1\text{ mol}}{P_4} + 6Cl_2 + 12H_2O \longrightarrow 4H_3PO_3 + \underset{12\text{ mol}}{12HCl} \\ \hline 31 \times 4 = 124\text{ g} \qquad 12 \times 36.5 = 438.0\text{ g} \end{array}$$

$\because$ 124 g of white phosphorus produces HCl = 438 g

$\therefore$ 62 g of white phosphorus will produces

$$HCl = \frac{438}{124} \times 62 = 219.0\text{ g HCl}$$