p-Block Elements (Part-2)

Group 15(Nitrogen Family)

15^{th} group or VA group of the extended form of the periodic table consists of 5 elements. $^{14}_{7}$N -nitrogen, $^{31}_{15}$P -Phosphorus, $^{75}_{33}$As -arsenic, $^{122}_{51}$Sb -antimony and $^{209}_{83}$Bi -bismuth. This group of five elements constitutes a family. Collectively these are known as **pnicogens** and their compounds as **pnictides**. (Greek, pniomigs meaning suffocation).

Period	Group 14 (IV A)	Group 15 (V A)	Group 16 (VI A)
2	C (6)	N (7)	O (8)
3	Si (14)	P (15)	S (16)
4	Ge (32)	As (33)	Se (34)
5	Sn (50)	Sb (51)	Te (52)
6	Pb (82)	Bi (83)	Po (84)

Occurrence

1. Nitrogen is most abundant in nature both in free and in the combined state.
2. Air is the most abundant source of free nitrogen.
3. It forms 75% by mass and 78% by volume of the air.
4. In combined state, it is found as nitrates such as chile salt petre ($NaNO_3$), Indian salt petre (KNO_3) and ammonium compounds.

Concept Ladder

Nitrogen is much less reactive than phosphorous, thats why it has greater tendency for catenation than Nitrogen.

Rack your Brain

Which element shows anomalous behaviour among group 15 and why?

Previous Year's Questions

Nitrogen is relatively inactive element because

[AIPMT]

(1) its atom has a stable electronic configuration
(2) it has low atomic radius
(3) its electronegativity is fairly high
(4) Bond dissociation energy of its molecule is fairly high.

5. Nitrogen is found in the form of proteins and amino acids in living organisms.
6. Phosphorus occurs in minerals e.g. flourapatite $Ca_9.[PO_4]_6.CaF_2$ which is the main constituent of phosphate rocks.
7. Ar, Sb and Bi are commonly associated with sulphide minerals, ores are Bi_2O_3 bismuth oxide and bismuth sulphide Bi_2S_3.

Rack your Brain

What is the percentage of Nitrogen in air?

Electronic configuration :

Element	At. Nu.		Electronic Configuration	Brief represention of electronic configuration
Nitrogen (N)	7	2, 5	$1s^2\ 2s^2\ 2p^3$	$[He]\ 2s^2\ 2p^3$
Phosphorus (P)	15	2,8,5	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	$[Ne]\ 3s^2\ 3p^3$
Arsenic (As)	33	2, 8, 18, 5	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$	$[Ar]\ 3d^{10}\ 4s^2\ 4p^3$
Antimony (Sb)	51	2, 8, 18, 18, 5	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^3$	$[Kr]\ 4d^{10}\ 5s^2\ 5p^3$
Bismuth (Bi)	83	2, 8, 18, 32, 18, 5	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^3$	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$

Trends in physical and chemical properties :

Physical property

1. **Electronic configuration :** Valence shell electronic configuration of 15th group elements is $ns^2\ np^3$, where n = 2 to 6.
2. **Atomic radii :** It increases as we move down the group. However, there is small increase in covalent radii from As to Bi, this is because of poor shielding of the valence electrons by the d- and f-electrons present in the inner shell.
3. **Ionization enthalpy :** Ionization enthalpy of these elements is much higher than the corresponding elements of group 14 due to increased nuclear charge and stable exactly half-filled electronic configuration.

Previous Year's Questions

Number of electrons shared in the formation of nitrogen molecule is **[AIPMT]**

(1) 6	(2) 10
(3) 2	(4) 8

4. **Electronegativity :** It decreases due to a gradual increase in the atomic radii of the elements.
5. **Melting and boiling points :** M.P and B.P. of group 15 elements first increases from N to As due to increase in their atomic size and then decreases from Sb and Bi due to their tendency to form three covalent bonds instead of five due to inert pair effect.
6. **Oxidation state :** These elements can show negative as well as positive oxidation states. Going down the group, the stability of +3 oxidation state increases while that of +5 oxidation state decreases due to inert pair effect.
7. **Non-metallic and metallic character :** Down the group, metallic character increases.

Concept Ladder

Nitrogen have higher ionisation enthalpy as compare to oxygen and carbon because of its half filled stable configuration.

Some properties of group 15 elements :

Sr.	Property	N	P	As	Sb	Bi
1	Atomic number	7	15	33	51	83
2	Valence shell configuration	$[He]^2\ 2s^2\ 2p^3$	$[Ne]^{10}\ 3s^2\ 3p^3$	$[Ar]^{18}\ 4s^2\ 4p^3$	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^3$	$[Xe]^{54}\ 4F^{14}\ 5d^{10}\ 6s^2\ 6p^3$
3	Atomic mass g/mol^{-1}	14.01	30.97	74.92	121.75	209.00
4	Covalent radius (Pm)	70	110	120	140	150
5	Ionic radius (Pm)	171 (N^{-3})	212 (P^{-3})	222 (As^{-3})	76 (Sb^{-3})	108 (Bi^{-3})
6	Electronegativity	3.00	2.10	2.20	1.82	1.67
7	Ionisation enthalpy ΔH / kJ mol^{-1} I II III	1402 2856 4577	1012 1903 2910	947 1798 2736	834 1595 2443	703 1610 2466
8	Density (g/cm^3)	0.879 at 63 K	1.823	5.778 (Grey form)	6.580	9.808
9	Melting point (°C)	– 210	44 (White P)	614 Sublime	631	631
10	Boiling point (°C)	– 196	280	610	1587	1564

Allotropy:

All the elements except bismuth show allotropy. Phosphorus exists in three allotropic forms such as white or yellow, red or violet and black phosphorus.

Rack your Brain

How Phosphorus is categorised into its white, red and black allotropic form?

Property	White phosphorus	Red phosphorus	Black phosphorus
Colour	White, but turns yellow on exposure	Dark red	Black
State	Waxy solid, can be cut with knife	Brittle powder	Crystalline with greasy touch
Smell	Garlic smell	Odourless	—
Density	1.849 cm^{-3}	2.19 cm^{-3}	2.69 g cm^{-3}
Ignition Temperature	307 K	543 K	673 K

Chemical properties :

1. **Action of air :**

$N_2 + O_2 \longrightarrow 2NO$

2. **Action of oxidising acids :**

$P_4 + 20\ HNO_3 \xrightarrow{hot} 4H_3PO_4 + 20\ NO_2 + 4H_2O$

phosphoric acid

$As_4 + 20\ HNO_3 \longrightarrow 4H_3ASO_4 + 20\ NO_2 + 4H_2O$

Arsenic acid

$Sb_4 + 20\ HNO_3 \longrightarrow Sb_4O_{10} + 20NO_2 + 10H_2O$

Antimony oxide

$Bi + 6HNO_3 \longrightarrow Bi\ (NO_3)_3 + 3H_2O + 3NO_2$

Bismuth nitrate

3. Hot concentrated nitric acid and sulphuric acid has no reaction with nitrogen.

$P_4 + 10\ H_2SO_4 \longrightarrow 4H_3PO_4 + 10\ SO_2 + 4H_2O$

$As_4 + 10\ H_2SO_4 \longrightarrow 4H_3ASO_4 + 10SO_2 + 4H_2O$

$2Sb + 6H_2SO_4 \longrightarrow Sb_2\ (SO_4)_3 + 3SO_2 + 6H_2O$

$2Bi + 6H_2SO_4 \longrightarrow Bi_2\ (SO_4)_3 + 3SO_2 + 6H_2O$

Concept Ladder

- Dinitrogen combines with dioxygen only at very high temperature (2000 K) to form nitric oxide.
- Dinitrogen is a colourless, odourless, tastless and non-toxic gas.

4. Action of alkalies :

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

$AS_4 + 12\ NaOH \longrightarrow \underset{\text{Salt}}{4Na_3AsO_3} + 6H_2$

$2Sb + 6NaOH \longrightarrow \underset{\text{Salt}}{2Na_3SbO_3} + 3H_2$

Alkalies have no reaction with nitrogen.

5. Action of metals :

$6\ Li + N_2 \longrightarrow 2Li_3N$

$3\ Mg + N_2 \longrightarrow Mg_3N_2$

$6\ Mg + P_4 \longrightarrow 2Mg_3P_2$

$6\ Ca + P_4 \longrightarrow 2Ca_3P_2$

Fulfillment of Octet

The elements of group 15 have $ns^2\ np^3$ as their valence shell electronic configuration.

They can complete their octets in two different ways:

(a) Electron Transfer:

The atoms of the elements of this group may accept three electrons from more metallic elements to form triply charged negative ions such as nitride, N^{3-} ion and phosphide, P^{3-} ion and thereby attain noble gas configuration. Only small atoms can form highly charged negative ions because of their greater electronegativities. The other members of nitrogen family show little tendency to form triply charged negative ions and this tendency decreases down the group because of increase in size and decrease in electronegativity. These group elements also exhibit oxidation states ranging from -3 to +5.

Concept Ladder

Oxides of nitrogen have open chain structure, while those of phosphorous have closed chain or cage structures.

Rack your Brain

Why NO_2 diamerises to form N_2O_4?

Previous Year's Questions

Which of the following oxides is most acidic?

[AIPMT]

(1) As_2O_5 (2) P_2O_5

(3) N_2O_5 (4) Sb_2O_5

(b) Electron Sharing:

Since the atoms of these elements contain three unpaired p-electrons so these can pair with unpaired p-electrons in another atom or atoms to form three covalent bonds, e.g., NH_3, PH_3, AsH_3, SbH_3, BiH_3.

Concept Ladder

Tendency to form pentahalides decreases down in group 15 elements.

Compounds formed by Group 15 Elements

Hydrides :

Stability order : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Basicity : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

H-E-H bond angle : $NH_3 > PH_3 > AsH_3 > SbH_3$

Boiling point : $SbH_3 > NH_3 > AsH_3 > PH_3$

Reducing character : $BiH_3 > SbH_3 > AsH_3 > PH_3 > NH_3$

The bond angle in PH_3, AsH_3 and SbH_3 is close to 92° which suggests that orbitals used for bonding are close to pure p-orbitals.

Rack your Brain

Nitrogen does not form pentahalides, why phosphorus does so?

Oxides :

Oxides with higher oxidation state are more acidic :

$$\underbrace{\overset{I}{N_2O} < \overset{II}{NO}}_{\text{neutral}} < \underbrace{\overset{III}{N_2O_3} < \overset{IV}{NO_2} < \overset{V}{N_2O_5}}_{\text{acidic}}$$

Moreover, acidity decreases down the group :

$$\underbrace{N_2O_3 > P_4O_6}_{\text{acidic}} > \underbrace{As_4O_6 > Sb_4O_6}_{\text{Amphoteric}} > \underbrace{Bi_2O_3}_{\text{basic}}$$

Q.1 What is fuming nitric acid? What colour is it have?

A.1 Concentrated nitric acid in which oxides of nitrogen (i.e., NO, NO_2, N_2O_3 etc.) are dissolved is called fuming nitric acid. Its colour is yellow.

Halides :

Ammonia forms NCl_3, $NBr_3.6NH_3$ and $NI_3.6NH_3$ (used as explosives) with Cl_2, Br_2 and I_2 respectively. NCl_3 was formerly used to bleach flour to make white bread .It can react with the amino acid methionine in proteins to form toxic methionine sulphoximine, and is no longer used.

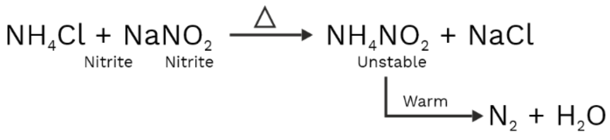
Penta halides are more covalent than trihalides because higher oxidation state leads to high polarising power.

Nitrogen and its Compounds :

Nitrogen is present in air to the extent of 78.06 % by volume. N_2 is colourless, tasteless, odorless and diamagnetic. It is lighter than air, sparingly soluble in water and a non-supporter of combustion.

Preparation:

1. In laboratory, nitrogen samples are obtained by warming ammonium nitrite or by oxidising ammonia by bromine water, sodium hypochlorite (NaOCl) or CuO.



$$\underset{\text{Nitrite}}{NH_4Cl} + \underset{\text{Nitrite}}{NaNO_2} \xrightarrow{\Delta} \underset{\text{Unstable}}{NH_4NO_2} + NaCl$$

$$NH_4NO_2 \xrightarrow{\text{Warm}} N_2 + H_2O$$

$$2NH_3 + 3CuO \longrightarrow N_2 + 3Cu + 3H_2O$$

$$8NH_3 + 3Br_2 \longrightarrow N_2 + 6NH_4Br$$

2. Small quantities of very pure N_2 is obtained by carefully warming sodium azide.

$$NaN_3 \xrightarrow{300°C} N_2 + Na$$

3. Heating ammonium salts with more oxidizing anion ($Cr_2O_7^{2-}$, NO_2^-, NO_3^-, ClO_4^-)

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4N_2O$$

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

Concept Ladder

The molecules NH_3 & NF_3 have same dipole moments in opposite direction.

Rack your Brain

Why all NX_3 compounds unstable except NF_3?

Previous Year's Questions

Identify the incorrect statements related to PCl_5 from the following :

[NEET-2019]

(1) PCl_5 molecule is non-reactive.

(2) Three equatorial P—Cl bonds make an angle of 120° with each other.

(3) Two axial P—Cl bonds make an angle of 180° with each other.

(4) Axial P—Cl bonds are longer than equatorial P—Cl bonds.

Chemical Properties

(a) Ammonia (NH_3)

Ammonia is a colorless gas having characteristic pungent smell. It is quite poisonous and brings tears in eyes. NH_3 is highly soluble in water due to extensive hydrogen bonding.

Concept Ladder

Haber process also known as artificial nitrogen fixation, is the main industrial procedure for the production of ammonia.

Preparation:

1. **In laboratory:**

NH_3 produced is dried with quick lime CaO. Note that it cannot be dried with H_2SO_4, $CaCl_2$ or P_4O_{10} as they react with the gas instead of drying it.

2. **Haber - Bosch Process :**

$$N_2 + H_2 \underset{\substack{\text{High pressure (200 atm)} \\ \text{low temp. (500°C)}}}{\overset{\text{Finely divided Fe + Mo}}{\rightleftharpoons}} NH_3\uparrow ;$$

$$\Delta H^{\ominus} = -46.1 kJ / mol$$

3. **NH_3 is prepared by the Cynamide process :**

$$\begin{tikzcd} CaO + C \arrow[r, "1000°C"] & CaC_2 + CO\uparrow \arrow[d, "+N_2"] \\ Na_3\downarrow + CaCO_3 & \underset{\substack{\text{Calcium} \\ \text{cynamide}}}{CaNCN} + C \arrow[l, "+H_2O"'] \end{tikzcd}$$

4. **Serpeck's Process(metallurgy of aluminium) :**

$$Al_2O_2 + 3C + N_2 \longrightarrow 2\,AlN + 3CO$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3 \uparrow$$

Previous Year's Questions

Pure nitrogen is prepared in the laboratory by heating a mixture of **[AIPMT]**

(1) $NH_4OH + NaCl$
(2) $NH_4NO_3 + NaCl$
(3) $NH_4Cl + NaOH$
(4) $NH_4Cl + NaNO_2$

Chemical Properties:

1. Ammonia is a non-supporter of combustion but burns in oxygen with a pale-yellow flame if continuous heat is supplied.

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 3H_2O$$

Q.2 What happens when a mixture of ammonium sulphate and sodium nitrate is heated. Write the equation.

A.2 Double displacement reaction first occurs to form ammonium nitrate which then decomposes to yield laughing gas (N_2O).

$$(NH_4)_2SO_4 + 2NaNO_3 \longrightarrow \underset{\substack{\text{Ammonium} \\ \text{nitrate}}}{2NH_4NO_3} + Na_2SO_4$$

$$\underset{\substack{\text{Ammonium} \\ \text{nitrate}}}{2NH_4NO_3} \longrightarrow 2\,N_2O + 4\,H_2O$$

2. Formation of complex ions used in qualitative analysis:

$$\underset{\text{excess}}{2NH_4OH} + \underset{\text{white}}{AgCl} \rightarrow \underset{\text{colourless}}{[Ag(NH_3)_2]Cl} + H_2O$$

$$2NH_4OH + CuSO_4 \rightarrow \underset{\text{Blue}}{Cu(OH)_2} \downarrow + (NH_4)_2SO_4;$$

$$2NH_4OH + ZnSO_4 \rightarrow \underset{\text{white}}{Zn(OH)_2} \downarrow + (NH_4)_2SO_4$$

$$4NH_3 + CuSO_4 \rightarrow \underset{\text{Deep Blue}}{\left[Cu(NH_3)_4\right]SO_4}$$

3. Reaction with Nessler's Reagent is used as a test to detect ammonia:

$$HgCl_2 + 2KI \longrightarrow 2KCl + \underset{\substack{\text{Red}\\\text{colour}}}{HgI_2} \xrightarrow{+2KI} \underset{\substack{\text{Nessler's}\\\text{reagent}}}{K_2HgI_4}$$

$$2K_2HgI_4 + 3KOH + NH_3 \longrightarrow 2H_2O + 7KI + \underset{\substack{\text{Red-Brown}\\\text{Precipitate}\\\text{[Iodide of Million's base]}}}{NH_2 - Hg - O - Hg - I}$$

4. Reaction with chlorine:

$$NH_3(\text{excess}) + Cl_2 \rightarrow \underset{\text{white fumes}}{NH_4Cl} + N_2$$

$$NH_3 + Cl_2(\text{excess}) \rightarrow NCl_3 + HCl$$

(b) Ammonium Salt

All ammonium salts are very soluble in water. They are usually slightly acidic and decompose readily on heating producing NH_3, N_2 or N_2O.

- If the anion (B^{x-}) is not particularly oxidising (eg. Cl^-, CO_3^{2-} or SO_4^{2-}) the ammonia is evolved.

$$NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$$

$$(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$$

Concept Ladder

Due to H-bonding NH_3 exists in both solid and liquid states and has higher melting and boiling points than expected on the basis of its molecular mass.

Previous Year's Questions

Which one has the lowest boiling point?

[AIPMT]

(1) NH_3 (2) PH_3
(3) AsH_3 (4) SbH_3

- If the anion is more oxidising (e.g. $NO_2^-, NO_3^-, ClO_4^-, Cr_2O_7^{2-}$) than NH_4^+ is oxidized to N_2 or N_2O.

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

$$\underset{\text{Orange}}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$$

Concept Ladder

The bond angle (O—N—O) are not of the same value in NO_2^- and NO_2^+.

(c) Oxides of Nitrogen:

1. Nitrous oxides N_2O [Laughing gas]:

It is colourless, non-combustible gas with a sweetish odour and taste. It is a neutral oxide and is diamagnetic.

$$:\overset{-}{\underset{\cdot\cdot}{N}} = \overset{+}{N} = \ddot{O}: \longleftrightarrow N \equiv \overset{+}{N} - O^{-}$$

Preparation:

(i) It is prepared by careful thermal decomposition of molten ammonium nitrate at about 280°C

$$NH_4Cl + NaNO_3 \xrightarrow{-NaCl} NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$$

(ii) $\underset{\text{dil.}}{10HNO_3} + 4Zn \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

$$\underset{\text{sulphamicacid}}{HSO_3NH_2} + \underset{\text{conc.}}{HNO_3} \rightarrow N_2O + H_2SO_4 + H_2O$$

(iii) $2NO + \underset{\text{moist}}{SO_2} + H_2O \rightarrow H_2SO_4 + N_2O$

Rack your Brain

Write the name and formula of neutral oxides of nitrogen.

Chemical Properties:

(a) $2N_2O \xrightarrow{900°C} 2N_2 + O_2$

(b) Reduction of N_2O to N_2:

$$N_2O + \underset{\text{hot}}{Cu} \rightarrow CuO + N_2$$

$$N_2O + Mg \rightarrow MgO + N_2$$

Previous Year's Questions

Which of the following oxides of nitrogen is paramagnetic?

[AIPMT]

(1) NO_2	(2) N_2O_3
(3) N_2O	(4) N_2O_5

$$2N_2O + C \rightarrow CO_2 + 2N_2$$

$$10N_2O + P_4 \rightarrow P_4O_{10} + 5N_2$$

(c) Oxidation:

$$5N_2O + 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 10NO$$

Uses:

It is used as an anaesthetic by dentists and a propellant for whipped ice-cream.

2. Nitric Oxide (NO):

It is a colourless, neutral gas which is paramagnetic due to the presence of odd electrons. It is sparingly soluble in water.

$$:N \overset{\cdots}{=} O: \; ;:\ddot{N} = \ddot{O}:$$

Concept Ladder

NO is paramagnetic in its gaseous state but diamagnetic in its liquid or solid state.

Preparation

(a) NO is prepared in the laboratory by the reduction of dilute HNO_3 with Cu.

$$8HNO_3 + 3Cu \rightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$$

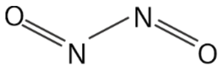
(b) Commercial Method

$N_2 + O_2 \xrightarrow{\text{electric arc}} 2NO$ (In Birkeland and Eyde Process)

Or $4NH_3 + 5O_2 \overset{\text{Ptgauze}}{\rightarrow} 4NO + 6H_2O$ (Catalytic Oxidation of Ammonia)

Chemical Properties:

(i) It is sparingly soluble in water and its solid-state forms diamagnetic dimer



(ii) NO + 1/2O_2 → NO_2 (brown fumes), thus it is not possible to detect its smell.

[This reaction is also used to detect O_2]

Rack your Brain

Why in the structure of HNO_3 molecule, the N—O bond (121 pm) is shorter than N—OH (140 pm).

(iii) Action of heat:

$$2NO \xrightarrow{900^\circ C} N_2 + O_2$$

(iv) Reduction (to N_2):

$$2NO + S \rightarrow SO_2 + N_2$$

$$NO + Cu \rightarrow CuO + \frac{1}{2}N_2$$

(v) Oxidation/Reduction properties

$$10NO + 6KMnO_4 + 9H_2SO_4 \rightarrow 3K_2SO_4 + 6MnSO_4 + 6H_2O + 10HNO_3$$

$$2NO + Cl_2 \rightarrow 2NOCl$$

$$NO + 2HNO_3 \rightarrow 3NO_2 + H_2O$$

Concept Ladder

N_2O_3 i.e. Nitrogen trioxide, is a highly toxic compound and can be partially dissociated into NO & NO_2.

3. Dinitrogen Trioxide N_2O_3:

It exists only in solid state at low temperature which is pale blue in colour. N_2O_3 is an acidic anhydride of nitrous acid (HNO_2). It is diamagnetic.

Rack your Brain

Why N_2O is diamagnetic in nature?

Preparation:

(a) It can be made by condensing equimolar amounts of NO and NO_2 together at 253 K.

$$NO + NO_2 \rightarrow N_2O_3$$

(b) $$\underset{(5N)}{2Cu + 6HNO_3} \rightarrow 2Cu(NO_3)_2 + NO + NO_2 + 3H_2O$$

(c) $$As_2O_3 + \underset{(50\%)}{2HNO_3} + 2H_2O \rightarrow NO + NO_2 + 2H_3AsO_4$$

Previous Year's Questions

Which of the following is a nitric acid anhydride?

[AIPMT]

(1) NO
(2) NO_2
(3) N_2O_5
(4) N_2O_3

Chemical Properties:

(i) $$N_2O_3(s) \xrightarrow{\Delta} NO_2 + \underset{\text{(liquid)}}{NO}$$

(ii) It being the anhydride of nitrous acid forms nitrites with alkalies.

$$(NO + NO_2) + 2KOH \rightarrow \underset{\text{nitrites}}{2KNO_2} + H_2O$$

(iii) It forms brown coloured $FeSO_4.NO$ with $FeSO_4$. This is used as a test for nitrates called Brown Ring Test.

4. Nitrogen Dioxide NO_2:

It's a reddish-brown gas and exists at the room temperature. Being an odd electron molecule, it is paramagnetic and dimerises into N_2O_4 at low temperature. It is acidic in nature.

Concept Ladder

NO_2 is coloured but its dimer form N_2O_4 is colourless in nature.

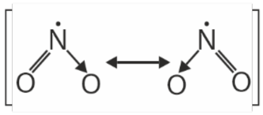
Rack your Brain

Why NO_2 is called as mixed anhydride of nitrous acid?

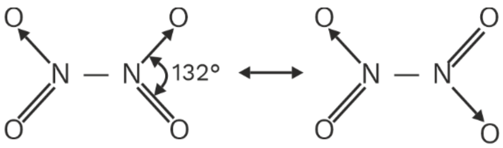
$$\underset{\substack{\text{solid}\\\text{colourless}}}{N_2O_4} \xrightarrow{10°C} \underset{\substack{\text{solid}\\\text{yellow}}}{N_2O_4} \xrightarrow{20°C} \underset{\substack{\text{vapour}\\\text{Reddish}\\\text{Brown}}}{N_2O_4} \xrightarrow{140°C} \underset{\substack{\text{Dark}\\\text{Brown}}}{2NO_2} \xrightarrow{620°C} \underset{\substack{\text{Colour}\\\text{less}}}{2NO} + O_2$$

Structure:

NO_2:



N_2O_4:



Q.3 Why does NO_2 dimerize?

A.3 NO_2 is an odd electron (7 + 2 × 8 = 23) molecule. In the valence shell, N has seven electrons and hence is less stable. To become more stable by acquiring inert gas configuration having 8 electrons in the valence shell, it underoges dimerization to form N_2O_4.

Separation:

(a) In the laboratory it is prepared by heating dried lead nitrate:

$$2\,Pb(NO_3)_2 \longrightarrow 2\,Pb + \underbrace{4\,NO_2 + 2O_2}_{\substack{\text{Passed through U-tube}\\ \text{cooled in ice to separate}\\ \text{the condensed } NO_2}}$$

(b) It is produced on a large scale by oxidizing NO in the Ostwald's Process for the manufacture of nitric acid.

$$2NO + O_2 \rightarrow 2NO_2$$

Concept Ladder

NO_2 is an intermediate in the industrial synthesis of nitric acid, it is paramagnetic, bent in shape and used in fertilizers.

Chemical Properties:

(i) $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

Thus, NO_2 is called as mixed anhydride of nitrous acid and nitric acid. The reaction of NO_2 with aqueous alkalies is similar to that of a mixture of HNO_2 and HNO_3.

$$2NO_2 + 2NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O$$

(ii) Oxidation:

$$10NO_2 + 3H_2SO_4 + 2KMnO_4 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 10HNO_3$$

$$2NO_2 + H_2SO_4 \rightarrow HNO_3 + \underset{\text{nitrosulphuricacid}}{NO_2.SO_2(OH)}$$

(iii) Reduction:

$$NO_2 + SO_2 + H_2O \rightarrow \underset{(\text{here } NO_2 \text{ behaves like } HNO_3)}{H_2SO_4 + NO}$$

$$NO_2 + H_2S \rightarrow H_2O + NO + S$$

Previous Year's Questions

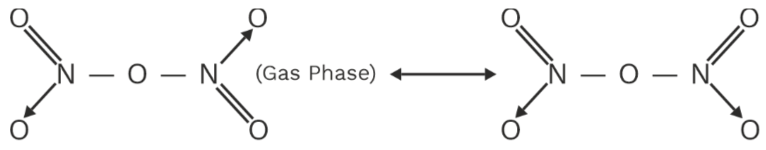
When copper is heated with conc. HNO_3 it produces

[NEET-2016]

(1) $Cu(NO_3)_2$, NO and NO_2
(2) $Cu(NO_3)_2$ and N_2O
(3) $Cu(NO_3)_2$ and NO_2
(4) $Cu(NO_3)_2$ and NO

5. Dinitrogen Pentoxide N_2O_5:

N_2O_5 is a colourless crystalline solid which sublimes readily and is acidic.



The solid form consists of ($NO_2^+ + NO_3^-$) which is ionic and called as nitronium nitrate while in solution it is covalent.

Preparation:

(a) $2HNO_3 \xrightarrow[1000°C]{P_2O_5} N_2O_5 + H_2O\,(\text{Dehydration})$.

Thus N_2O_5 is the anhydride nitric acid.

(b) $AgNO_3 + Cl_2 \xrightarrow{60-90°C} AgCl + N_2O_5 + O_2$

(c) $4NO_2 + O_2 \rightarrow 2N_2O_5$

Chemical Properties

(i) N_2O_5 dissolves in H_2O with a hissing sound.

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

Thus it is called as nitric anhydride and neutralisation reactions similar to HNO_3

$$N_2O_5 + 2NaOH \rightarrow 2NaNO_3 + H_2O$$

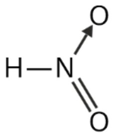
(ii) Since $N_2O_5 \xrightarrow{\Delta} NO_2 + NO + O_2$ it is a very powerful oxidising agent. It destroys all organic substances.

$$5N_2O_5 + I_2 \rightarrow 10NO_2 + I_2O_5$$

(d) Oxoacids of Nitrogen:

1. Nitrous acid HNO_2:

It is unstable except in dil. aq. solution. It is a tautomeric mixture of two forms:

$H-O-N=O$ and 

Concept Ladder

N_2O_5 i.e. Nitric anhydride is an ore of binary nitrogen oxides, a family of compounds that only contain nitrogen and oxygen.

Rack your Brain

Find the covalency of N in N_2O_5?

Previous Year's Questions

Urea reacts with water to form A which will decompose to form B. B when passed through $Cu^{2+}_{(aq)}$, deep blue colour solution C is formed. What is the formula of C from the following?

[NEET-2020]

(1) $CuSO_4$
(2) $[Cu(NH_3)_4]^{2+}$
(3) $Cu(OH)_2$
(4) $CuCO_3.Cu(OH)_2$

Preparation:

(a) It is made by acidifying a solution of a nitrite

$$Ba(NO_2)_2 + H_2SO_4 \rightarrow 2HNO_2 + \underset{\text{filtered off}}{BaSO_4 \downarrow}$$

(b) Dissolving nitrous anhydride (N_2O_3) in H_2O of course forms HNO_2:

$$N_2O_3 + H_2O \rightarrow 2HNO_2$$

Concept Ladder

The N—O bond in NO_2^- is shorter than N—O bond in NO_3^-.

Oxidising Properties:

NO_2^- ion is a weak oxidising agent and gets reduced to NO which forms a red complex with haemoglobin and improves the look of meat.

$$NO_2^- + Fe^{2+} + 2H^+ \rightarrow Fe^{3+}NO + H_2O$$

$$2NO_2^- + 2I^- + 4H^+ \rightarrow I_2 + 2NO + 2H_2O$$

However, it is oxidised by $KMnO_4$, Cl_2 forming NO_3^- (but to NO_2 by H_2SO_4):

$$HNO_2 + Cl_2 + H_2O \rightarrow HNO_3 + 2HCl$$

$$2HNO_2 + H_2SO_4 \rightarrow SO_2 + 2NO_2 + H_2O$$

Rack your Brain

Draw the structure of $N_2O_5^-$.

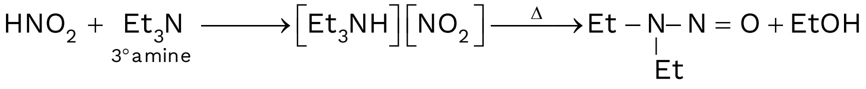
Reaction with Amines :

$$HNO_2 + \underset{\text{ammonia}}{NH_3} \longrightarrow \underset{\text{unstable}}{[NH_4NO_2]} \longrightarrow N_2 + 2H_2O$$

$$HNO_2 + \underset{1^\circ\text{amine}}{EtNH_2} \longrightarrow EtOH + N_2 + H_2O$$

Secondary and tertiary aliphatic amines form nitrosamines with nitrites:

$$HNO_2 + \underset{2^\circ\text{amine}}{Et_2NH} \longrightarrow Et_2NO + H_2O$$



$$HNO_2 + \underset{3^\circ\text{amine}}{Et_3N} \longrightarrow [Et_3NH][NO_2] \xrightarrow{\Delta} Et-\underset{\underset{Et}{|}}{N}-N=O + EtOH$$

Nitrites are used to make diazo compounds used in azo dyes:

$$\underset{\text{aniline}}{PhNH_2} + HNO_2 + HCl \rightarrow Ph-N=\overset{+}{N}Cl^- + 2H_2O$$

Other Reactions:

On standing HNO_2 decomposes into NO and NO_2 :

$$2HNO_2 \rightarrow NO + NO_2 + H_2O$$

While on boiling it disproportionate:

$$3\overset{III}{HNO_2} \xrightarrow{\Delta} \overset{V}{HNO_3} + 2\overset{II}{NO}\uparrow + H_2O$$

2. Nitric acid HNO_3:

Also called as Aqua fortis, it is colourless fuming liquid with a pungent smell. Yellow colour occurs on standing due to decomposition into NO_2.

$$2HNO_3 \xrightarrow{\text{Light}} 2NO_2 + 1/2O_2 + H_2O$$

Concept Ladder

N_2O_5 is a rare example of a compound that adopts two structures depending on the conditions. The solid form is a salt in which nitronium nitrate, consisting of seperate nitronium cations $[NO_2]^+$ and nitrate anions $[NO_3]^-$.

Preparation:

1. In laboratory

$$\underset{\text{nitrates}}{2NaNO_3} + \underset{\text{conc.}}{H_2SO_4} \xrightarrow{\text{distilling in glass retort}} Na_2SO_4 + 2HNO_3\uparrow$$

HNO_3 vapours are then condensed in a water-cooled receiver.

2. Birkeland and Eyde Process

$$\underset{\substack{\text{Dry air free from}\\ CO_2,H_2}}{N_2 + O_2} \xrightarrow{\text{Electric arc } 3000°C} 2NO \xrightarrow{+O_2} 2NO_2 \xrightarrow{+H_2O} HNO_3 + HNO_2 \xrightarrow{\Delta} NO_2 + 2H_2O$$

Q.4 How is nitrogen prepared from ammonia?

A.4 Nitrogen is prepared by ammonia according to the following equations :

$$NH_3(g) + HCl(aq) \longrightarrow NH_4Cl(aq)$$
$$NH_4Cl(g) + NaNO_2(aq) \longrightarrow NH_4NO_2(aq) + NaCl(aq)$$
$$NH_4NO_2(aq) \xrightarrow{\Delta} N_2(g) + 2H_2O(l)$$

3. Ostwald Process

Step (a): $4NH_3(g) + 5O_2 \xrightarrow{\text{Pt gauze 300°C}} 4NO + 6H_2O$ (Catalytic Oxidation)

Step (b): $4NO \underset{50°C}{\overset{2O_2}{\rightleftharpoons}} 4NO_2 \xrightarrow{+2H_2O+O_2} \underset{(60\%)}{4HNO_3} \xrightarrow{\text{distillation}} \underset{\substack{(68\%)\\ \text{azeotrope}}}{4HNO_3}$

Due to the formation of azeotrope, HNO_3 cannot be further concentrated by distillation and other methods are used like dehydrating using sulphuric acid vapours.

$$\underset{68\%}{HNO_3} \xrightarrow{\text{dehydration with } H_2SO_4} \underset{98\%}{HNO_3}(\text{conc.})$$

Oxidising Properties:

NO_3^- is a very powerful oxidising agent in acidic solution. Cu, Ag which are insoluble in HCl dissolve in HNO_3. Concentrated HNO_3 forms NO_2 with a reducing agent although. Fe, CO, Al, Ni, Cr and B are rendered passive by concentrated HNO_3 due to the formation of a protective oxide layer (like Fe_3O_4 with iron). Dilute HNO_3 forms NO with a poor reducing agent (Cu, Hg); N_2O with a good reducing agent in hot conditions and NH_4NO_3 with a good reducing agent in cold conditions.

$$\left.\begin{array}{l}
\underset{\text{conc.}}{HNO_3} \longrightarrow Fe_3O_4 + NO_2 \,(\text{Rendered passive}) \\
\underset{\text{dil}}{HNO_3} + Fe \xrightarrow{\text{Hot}} \overset{III}{Fe}(NO_3)_3 + N_2O \\
\underset{\text{dil}}{HNO_3} + Fe \xrightarrow{\text{Cold}} \overset{II}{Fe}(NO_3)_2 + NH_4NO_3
\end{array}\right]\text{With Fe}$$

$$\left.\begin{array}{l}
\underset{\text{conc.}}{HNO_3} + Hg \longrightarrow \overset{II}{Hg}(NO_3)_2 + NO_2 \\
\underset{\text{dil}}{HNO_3} + Hg \longrightarrow \overset{I}{Hg}(NO_3)_2 + NO
\end{array}\right]\text{With Hg}$$

$$\left.\begin{array}{l}
\underset{\text{conc.}}{HNO_3} + Sn \longrightarrow H_2SnO_3 + NO_2 \\
\underset{\text{dil. hot}}{HNO_3} + Sn \xrightarrow{\text{Hot}} H_2SnO_3 + N_2O \\
\underset{\text{dil. cold}}{HNO_3} + Sn \xrightarrow{\text{Cold}} Sn(NO_3)_2 + NH_4NO_3
\end{array}\right]\text{With Sn}$$

Previous Year's Questions

Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because **[AIPMT]**

(1) Zn act as oxidisinng agent when react with HNO_3

(2) HNO_3 is weaker acid than H_2SO_4 and HCl

(3) in electrochemical series Zn is above hydrogen

(4) NO_3^- is reduced in preference to hydronium ion.

Rack your Brain

How conc. HNO_3 turns yellow on expossure to sunlight.

Some reactions with non-metals are:

$$\underset{\text{dil. or conc.}}{HNO_3} + N_2 \rightarrow \text{no reaction}$$

$$\left.\begin{aligned}
&\underset{\text{conc.}}{HNO_3} + P_4 \longrightarrow H_3PO_4 + NO_2\\
&\underset{\text{dil. hot}}{HNO_3} + P_4 \xrightarrow{\text{Hot}} H_3PO_4 + NO\\
&\underset{\text{dil. cold}}{HNO_3} + P_4 \xrightarrow{\text{Cold}} H_3PO_3 + NO
\end{aligned}\right] \text{With } P_4$$

$$\left.\begin{aligned}
&\underset{\text{conc.}}{HNO_3} + As \longrightarrow H_3AsO_4 + NO_2\\
&\underset{\text{dil. hot}}{HNO_3} + As \xrightarrow{\text{Hot}} H_3AsO_4 + NO\\
&\underset{\text{dil. cold}}{HNO_3} + As \xrightarrow{\text{Cold}} H_3AsO_3 + NO
\end{aligned}\right] \text{With As}$$

- Only Mg and Mn react with 2% dil. HNO_3
  HNO_3 (dil.2%) + Mg (or Mn) $\longrightarrow Mg(NO_3)_2 + H_2\uparrow$
- Solution of 75% HCl and 25% HNO_3 is called Aqua Regia which contains NO^+ Cl^- ions. Aqua Regia is capable of dissolving Gold and Platinum by forming soluble H_3AuCl_4 and H_2PtCl_6 respectively.

Other Oxoacids:

Other Oxoacids	
HOONO	Pernitrous acid
H_2NO_2	Hydronitrous acid
HNO_4	Pernitric acid
$H_2N_2O_2$	Hyponitrous acid

Concept Ladder

Aqueous HNO_3 can be concentrated by distillation upto 68% by mass. Further concentration to 98% can be achieved by dehydration with conc. H_2SO_4.

Rack your Brain

Draw structure of compounds H_2NO_2 and $H_2N_2O_2$. Is there any possibility of having double bond between N and O?

Q.5 What is the product formed by the following reaction?

$$HNO_3 \xrightarrow{P_4O_{10},\ \Delta}$$

A.5 P_4O_{10} being a strong dehyderating agent, eliminates a molecule of H_2O from two molecules of HNO_3 giving dinitrogen pentoxide (N_2O_5).

$$4\,HNO_3 + P_4O_{10} \xrightarrow{\Delta} 2N_2O_5 + 4HPO_3$$

Phosphorous and its Compounds :

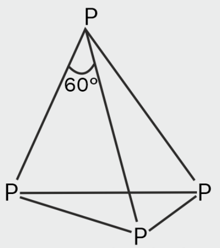
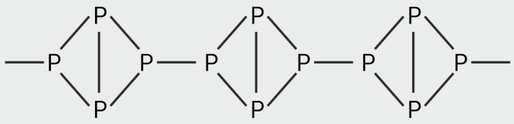
Allotropy :

It exists in many allotropic forms, the important ones being white, red and black phosphorous.

$$\text{White P} \xrightarrow[\text{inert atmosphere for several days}]{300^\circ\text{C}} \text{Red P} \xrightarrow{\Delta} \underset{\text{Thermodynamically most stable allotrope}}{\text{Black P}}$$

Rack your Brain

Why Phosphorous only exist in cage or close chain structure?

White phosphorus	Red phosphorus
It is a white, waxy and highly toxic solid. It glows in dark (Chemiluminescence/Phosphoresence)	It is non poisonous and does not show phosphorescence
It is unstable due to angular strain and spontaneously reacts with O_2 and catches fire. $P_4 + 5O_2 \longrightarrow P_4O_{10}$ Thus it is stored in water in which it is insoluble (white phosphorous is soluble in CS_2)	It is stable in air and not stored in water. It is insoluble in organic solvents.
 Tetrahedral	

Only white phosphorous reacts with caustic alkalies to undergoes a disproportion reaction.

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{sodiumhyposphite}}{3NaH_2PO_4} + \underset{\text{Phosphine}}{PH_3} \uparrow$$

Uses :

Red phosphorus is used in Match - Industry and white phosphorus as a rat poison.

Preparation:

Phosphorous is obtained by the reduction of calcium phosphate with C in an electric furnace. Sand (SiO_2) is added to remove the calcium as a fluid slag.

$$2Ca_3(PO_4)_2 + 6SiO_2 \rightarrow \underset{slag}{6\,CaSiO_3} + P_4O_{10}$$

$$2P_2O_5 + 10C \rightarrow P_4 + 10CO\uparrow$$

Overall reaction :

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

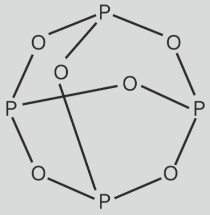
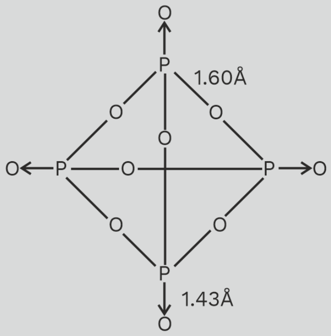
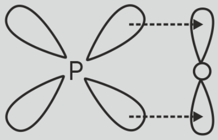
Previous Year's Questions

Which of the following phosphorus is the most reactive?

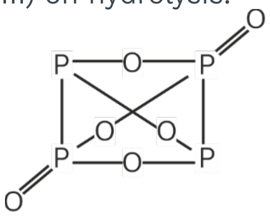
[AIPMT]

(1) Scarlet phosphorus
(2) White phosphorus
(3) Red phosphorus
(4) Violet phosphorus

Oxides of Phosphorous

Phosphorous Trioxide [P_2O_3/P_4O_6]	Phosphorous Pentoxide [P_2O_5/P_4O_{10}]
It is also called Phosphorus oxide or phosphorous anhydride. It is a soft white sold.	It is called phosphoric oxide or Phosphoric anhydride.
Phosphorous trioxide is dimeric and written as P_4O_6  Structure of phosphorus trioxide P_4O_6	 The shorter P→O coordinate bond is in fact a 'double bond' different from the usual double bond. A full p orbital on O overlap side ways with an empty d orbital on p atom forming pπ–dπ back bonding or a dative bond. 

Other oxides like P_4O_8 and P_4O_9 are intermediate between P_4O_6 and P_4O_{10} and form a mixture of phosphoric acid P(+V) and phosphorous acid P(+III) on hydrolysis.



Oxo Acids of Phosphorous

All oxo acids of phosphorous can be categorized into two main acid series namely, phosphorus acid series and phosphoric acid series.

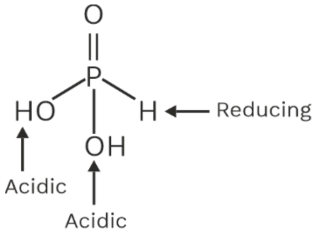
The Phosphorus acid series:

The series contain P(+3) and are generally reducing agents due to the presence of P – H bonds which are reducing (as they break down easily to loose H^+).

(I) Ortho phosphorous acid H_3PO_3:

It is a dibasic acid formed by hydrolysis of P_4O_6.

$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$



It forms phosphites on hydrolysis which are very strong reducing agents in basic solutions.

$$H_3PO_3 \rightleftarrows H^+ + H_2PO_3^- ; K_{a_1} = 1.6\times10^{-2}$$

$$H_2PO_3^- \rightleftarrows H^+ + HPO_3^{2-} ; K_{a_2} = 7\times10^{-7}$$

On heating orthophosphorous acid disproportionates :

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

Concept Ladder

Phosphinic acid behaves as a mono protic acid where as Ortho Phosphorus acid is diprotic acid.

Rack your Brain

Find the product formed when PCl_5 reacts with heavy water.

Previous Year's Questions

Which is the correct statement for the given acids?

[NEET-2016]

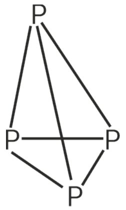
(1) Phosphinic acid is a mono protic acid while phosphonic acid is a diprotic acid.
(2) Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid.
(3) Both are diprotic acids
(4) Both are triprotic acids.

(II) Hypophosphorous Acid H_3PO_2 :

Hypophosphorous acid is prepared by alkaline hydrolysis of (white) phosphorous.

$$P_4 + 3OH^- + 3H_2O \rightarrow PH_3\uparrow + \underset{\text{Hypophosphiteion}}{3H_2PO_2^-}$$

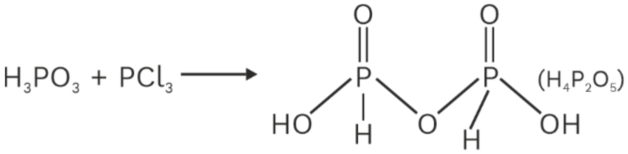
Structure of P_4



H_3PO_2 is a monobasic acid and a very strong reducing agent.

$$4Ag^+ + H_3PO_2 + 2H_2O \rightarrow 4Ag + H_3PO_4 + 4H^+$$

(III) Pyrophosphorous Acid $H_4P_2O_5$:



While reaction with PCl_5 is

$$H_3PO_3 + 3PCl_5 \rightarrow \underset{\text{Trichloride}}{PCl_3} + \underset{\text{Oxychloride}}{3POCl_3} + 3HCl$$

Concept Ladder

$H_4P_2O_5$ is dibasic as metals can replace the hydrogen in the pair of attached hydroxide ions.

Q.6 H_3PO_3 undergoes disproportionation reaction but H_3PO_4 does not?

A.6 The maximum and minimum oxidation states of P are –3 and +5. But the oxidation state of P in H_3PO_3 is +3. therefore, it can increase its oxidation to +5 in H_3PO_3 and decrease its oxidation state to –3 in PH_3.

Thus, H_3PO_3 shows disporportionation reaction : $4\,H_3\overset{+3}{P}O_3 \longrightarrow 3H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$

In contrast, the oxidation state of P in H_3PO_4 is +5, therefore, it cannot increase its oxidation state beyond +5 and hence it does not show disproportionation reaction.

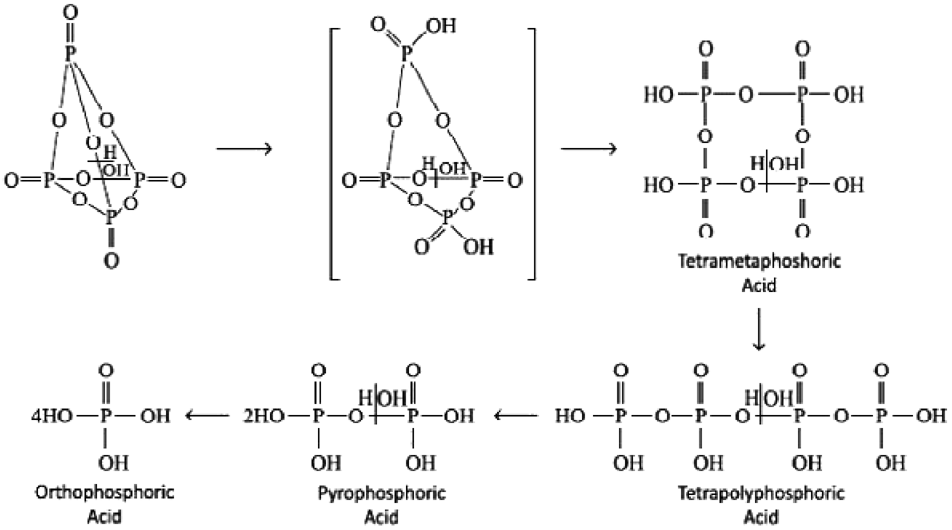
The Phosphoric Acid Series:

They usually contain P(+V) and have oxidising properties. The simplest phosphoric acid is orthophosphoric acid.

(I) Orthophosphoric acid H_3PO_4:

Preparation:

It is formed by hydrolysis of phosphorous pentoxide (P_2O_5 or P_4O_{10}). The scheme for its hydrolysis is :



In laboratory

$$\underset{\text{conc.}}{P_4 + 20HNO_3} \xrightarrow{I_2\ \text{Catalyst}} 4H_3PO_4 + 20NO_2 + 4H_2O$$

Impure H_3PO_4 is prepared in large amounts by 'Wet Process'.

$$\underset{\text{Phosphate Rock}}{Ca_3(PO_4)_2} + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4$$

$CaSO_4$ is hydrated to gypsum $CaSO_4.2H_2O$ and filtered off. H_3PO_4 thus produced is used to make fertilizers.

Properties:

1. H_3PO_4 is hydrogen bonded in aqueous solution and thus the 'concentrated acid' is syrupy and viscous.

Rack your Brain

How many P—O—P bonds are there in $H_4P_2O_7$?

Previous Year's Questions

P_2O_5 is heated with water to give **[AIPMT]**

(1) hypophosphorous acid
(2) phosphorous acid
(3) hypophosphoric acid
(4) orthophosphoric acid

2. It forms meta phosphates on heating:

$$\underset{}{H_3PO_4} \xrightarrow{220^\circ} \underset{\text{pyrophosphoric acid}}{H_4P_2O_7} \xrightarrow[\text{Br}_2]{320^\circ\text{C}} \underset{\text{metaphosphoric acid}}{2HPO_3}$$

Sodium metaphosphate is also termed Graham's salt or Calgon (Commercial name). It is soluble in H_2O and precipitates Pb^{2+}, Ag^+ but not Ca^{2+}, Mg^{2+}. Thus, it is used for softening water.

3. It forms 3 series of salts:

(a) $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \;;\quad Ka_1 = 7.5 \times 10^{-3}$

Dihydrogen phosphates are slightly acidic in water.

(b) $H_2PO_4^- \rightleftharpoons H^+ + HPO_2^{2-} \;;\quad Ka_2 = 6.2 \times 10^{-8}$

Monohydrogen phosphates are slightly basic in water.

(c) $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \;;\quad Ka_3 = 1 \times 10^{-12}$

Normal phosphates are appreciably basic in water.

4. Phosphates are estimated quantitatively by adding a solution containing NH_4OH solution of the phosphate and Mg^{2+}. Magnesium ammonium phosphate precipitated is ignited and weighed as $Mg_2P_2O_7$.

Concept Ladder

- H_3PO_4 i.e. phosphoric acid has its pure compound in colourless solid form.
- When all three H^+ ions removed, orthophosphate ion PO_4^{3-} is form, which is also commenly known as phosphate.

Rack your Brain

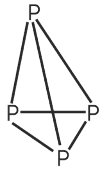
Name the compound formed as esters by orthophoric acid.

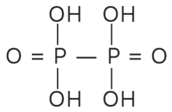
$$2NH_4^+ + 2Mg^{2+} + 2PO_4^{3-} \rightarrow 2MgNH_4PO_4 \overset{\Delta}{\rightarrow} Mg_2P_2O_7 + 2NH_3 + H_2O$$

(II) Hypophosphoric acid $H_4P_2O_6$:

$H_4P_2O_6$ contains P(+4) and is prepared by hydrolysis and oxidation of red phosphorous by NaOCl.

$$P_4 + 4H_2O \xrightarrow[(\text{NaOCl})]{+\,4O_2} 2H_4P_2O_6$$

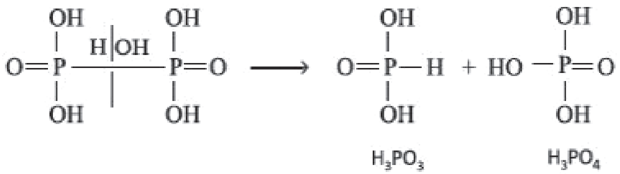




$$O = \underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{P}} - \underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{P}} = O$$

Hypophosphoric acid

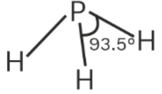
On hydrolysis $H_4P_2O_6$ forms both H_3PO_3 and H_3PO_4



$$H_4P_2O_6 + H_2O \longrightarrow H_3PO_3 + H_3PO_4$$

Phosphine PH_3

PH_3 is a colourless, extremely toxic gas which smells of rotten fish. It is highly reactive and not soluble in H_2O. Its aqueous solutions are neutral.



The bond angle in H – P – H is 93.5° which suggests the presence of almost pure p orbitals.

Preparation:

PH_3 can be formed by hydrolysing metal phosphides or hydrolysing white phosphorous in basic media.

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

Another method also produces small amounts of highly inflammable P_2H_4. Therefore, PH_3 is removed in the following manner:

$$PH_3 + HI \rightarrow \underset{\text{Phosphonium Iodide}}{PH_4I} \xrightarrow{+KOH} KI + H_2O + \underset{(\text{Pure})}{PH_3}\uparrow$$

Properties :

Concept Ladder

A French chemist Philippe once generated a regular supply of heat over Phosphorous (P_4) with an aqueous solution of K_2CO_3, results in colourless gaseous substance called phosphine (due to its rotting fish odour).

Rack your Brain

What is the bond angle between H—P—H in phosphine?

Q.7 PH_3 has lower boiling point than NH_3. Why?

A.7 The electronegativity of N (3.0) is much higher than that of P (2.1). Therefore, NH_3 undergoes extensive intermolecular H-bonding and hence it exists as an associated molecule. To break these H-bonds, a large amount of energy is needed. On the other hand, PH_3 does not undergo H-bonding and thus exists as discrete molecules. Therefore, the boiling point of PH_3 is much lower than that of NH_3.

1. Phosphine is stable in air but catches fire at 150°C.

$$PH_3 + 2O_2 \xrightarrow{150°C} H_3PO_4$$

2. It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2.

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

3. Solution of PH_3 in H_2O decomposes in presence of light giving red P and H_2.
4. Formation of metallic phosphides:

$$3CuSO_4 + 2PH_3 \rightarrow \underset{\text{Black}}{Cu_3P_2} \downarrow + 3H_2SO_4$$

$$3AgNO_3 + PH_3 \rightarrow \underset{\text{Black}}{Ag_3P} \downarrow + 3HNO_3$$

5. PH_3 is weakly basic and forms phosphonium salts with anhydrous acids while NH_3 readily forms NH_4X in aqueous solutions of the acids.

$$PH_3 + HX \rightarrow PH_4X\left(X = Cl, Br, I\right)$$

Uses:

It is used for making 'Holme's signal'. CaC_2 and Ca_3P_2 are contained in containers. Containers are pierced and thrown in sea when gases evolved, burn and serve as a signal.

Halides:

1. PCl_5 is a yellowish white powder while PCl_3 is a colourless liquid and is widely used in organic chemistry.

$$\underset{\text{White}}{P_4} + \underset{\text{Dry}}{6Cl_2} \xrightarrow{\Delta} 4PCl_3$$

$$P_4 + \underset{\substack{\text{Thionyl} \\ \text{Chloride}}}{8SOCl_2} \rightarrow 4PCl_3 + 4SO_2 + S_2Cl_2$$

$$\underset{\text{White}}{P_4} + \underset{\text{Dry,excess}}{10Cl_2} \rightarrow 4PCl_5$$

Concept Ladder

PH_3 possesses the characteristics to cause high environmental demages, it acts as a Lewis base when its lone pair electron is donated in reaction with hydrogen iodide.

Rack your Brain

Why PCl_4^+ can exists but PCl_4^- cannot?

Previous Year's Questions

A compound 'X' upon reaction with H_2O produces a colourless gas 'Y' with rotten fish smell. Gas 'Y' is absorbed in a solution of $CuSO_4$ to give Cu_3P_2 as one of the products. Predict the compound 'X'.

[NEET-2019]

(1) Ca_3P_2
(2) NH_4Cl
(3) As_2O_3
(4) $Ca_3(PO_4)_2$

$$P_4 + \underset{\substack{\text{Sulphuryl}\\ \text{Chloride}}}{10SO_2Cl_2} \rightarrow 4PCl_5 + 10SO_2$$

$$PCl_3 + Cl_2\left(\text{or} S_2Cl_2\right) \rightarrow PCl_5$$

2. PCl_3 fumes in moisture.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 \uparrow + 3HCl \uparrow$$

$$\text{While, } PCl_5 + \underset{\text{Moist air}}{H_2O} \rightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

Concept Ladder

The main use of ammonium sulphate is as a fertilizer for alkaline solids. Ammonium ion forms a small amount of acid, which lowers pH balance of the soil.

3. In solid state it is ionic therefore conducts electricity, while in gaseous and liquid state PCl_5 is trigonal bipyramidal. While in solid state it is ionic and hence conducts electricity

$$2PCl_5 \rightleftharpoons \underset{\text{Tetrahedral}}{\left[PCl_4\right]^+} + \underset{\text{Octahedral}}{\left[PCl_6\right]^-}$$

4. PF_5 forms an unusual trigonal bipyramid where equatorial and axial bonds interchange their positions in short time. This is called pseudo rotation.

Rack your Brain

Why calcium ammonium nitrate does not form soil acid where as ammonium sulphate do?

Fertilizers:

They are the compounds of N, P and K which are soluble in H_2O and easily assimilated by plants without causes any damage to them.

I. Nitrogenous Fertilizers:

(i) Ammonium sulphate ($(NH_4)_2SO_4$) :

Ammonium sulphate is made by passing NH_3 and CO_2 gases into a slurry of $CaSO_4$ in water:

$$2NH_3 + CO_2 + H_2O \rightarrow \left(NH_4\right)_2 CO_3 \xrightarrow{+CaSO_4} CaCO_3 + \left(NH_4\right)_2 SO_4$$

In soil, the action is:

$$\left(NH_4\right)_2 SO_4 \xrightarrow{\text{soil}} NH_3 \xrightarrow{\text{nitrifying bacteria}} \text{Nitrates}\left(\text{easily taken up by plants}\right)$$

Excess of nitrogenous fertilizers makes the soil acidic.

(ii) Calcium Ammonium Nitrate (CAN):

$$NH_3 \xrightarrow[\text{Process}]{\text{Ostwalds}} HNO_3 \xrightarrow{CaCO_3} Ca(NO_3)_2$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

$Ca(NO_3)_2.NH_4NO_3$ formed is known as Calcium Ammonium Nitrate (CAN). It is more soluble in H_2O and does not make soil acidic.

Concept Ladder

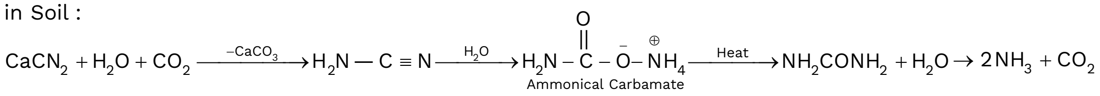
Urea plays an important role in the metabolism of nitrogen containing compounds by animals.

(iii) Nitrolim ($CaCN_2$ + C) :

Preparation:

$$CaCO_3 \xrightarrow[CO_2]{\Delta} CaO \xrightarrow[\text{heat}]{+C} CaC_2 \xrightarrow[1200°C]{+N_2} \underbrace{\underset{\text{White}}{CaN-C\equiv N} + \underset{\text{Black}}{C}}_{\text{Nitrolim (Grey)}}$$

Action in Soil :



$$CaCN_2 + H_2O + CO_2 \xrightarrow{-CaCO_3} H_2N-C\equiv N \xrightarrow{H_2O} \underset{\text{Ammonical Carbamate}}{H_2N-\overset{\overset{\large O}{||}}{C}-\overset{-}{O}-\overset{\oplus}{N}H_4} \xrightarrow{\text{Heat}} NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2$$

Nitrolim is a slow fertilizer and produces more permanent effect.

(iv) Urea (NH_2CONH_2) :

Urea has high nitrogen content (46%) and is soluble in H_2O. Therefore, it is quick acting but is easily washed away.

$$2NH_3 + CO_2 \xrightarrow[\text{Chighpressure}]{180°-200°} \underset{\substack{\text{Ammonium}\\ \text{Carbamate}}}{NH_2COONH_4} \rightarrow \underset{\text{Urea}}{NH_2CONH_2} + H_2O$$

II. Phosphatic Fertilizers :

Phosphate rocks like fluorapatite [$3Ca_3(PO_4)_2.CaF_2$] are insoluble and useless for plants. Thus, they are processed for formation of useful fertilizers.

$$3Ca_3(PO_4)_2.CaF_2 \xrightarrow{+7\,H_2SO_4\,(\text{conc.})} \underset{\substack{\text{Triple Superphosphate}\\ \text{(of lime)}}}{3Ca(H_2PO_4)_2} + 7CaSO_4 + 2HF$$

Group 16 (Oxygen family)

Introduction :

The elements Oxygen (O), Sulphur (S), Selenium (Se), Tellurium (Te) and Polonium (Po) constitute group 16 of the periodic table.

Group 16 elements are also known as Chalcogens, means ore forming, because many metals are found as oxides and sulphides and a few as selenides and tellurides.

Concept Ladder

Sulphur has greater tendency for catenatin than oxygen.

Occurrence :

1. Oxygen is the most abundant element and is found both in free as well as in combined state.
2. Oxygen makes up 46.6% by mass of the earth's crust and dry air contains 21.0% oxygen by volume.
3. Sulphur occurs less abundantly and constitutes 0.034% by mass of the earths crust.
4. Sulphur occurs mainly in combined form of sulphates and sulphides.
5. Onion, garlic, mustard, eggs, proteins hair and wool, the organic materials also contain sulphur.
6. Polonium is radioactive in nature.

Rack your Brain

Arrange the ions of group 16 elements according to their atomic size.

Electronic configuration :

Element	symbol	Atomic Number	Atomic Electronic Configuration	Brief represention of electronic configuration
Oxygen	O	8	$1s^2\ 2s^2\ 2p^4$	$[He]\ 2s^2\ 2p^4$
Sulphur	S	16	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$	$[Ne]\ 3s^2\ 3p^4$
Selenium	Se	34	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^4$	$[Ar]\ 3d^{10}\ 4s^2\ 4p^4$
Tellurium	Te	52	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^4$	$[Kr]\ 4d^{10}\ 5s^2\ 5p^4$
Polanium	Po	84	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^4$	$[Xe]\ 5d^{10}\ 6s^2\ 6p^4$

Trends in physical and chemical properties :

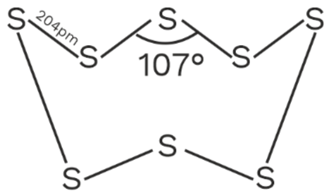
Physical properties :

1. Physical state :

Oxygen is gas while all others are solids.

2. Molecular structure :

Oxygen molecule is diatomic while the molecules of other element are more complex. Sulphur, selenium and tellurium exists as staggered 8-atom rings.



Crown shaped puckered ring of S_8.

3. Atomic and ionic radii :

It increases on moving down the group due to increase in the number of electron shells.

4. Ionization enthalpy :

The ionization energies of the elements of oxygen family are less than those of nitrogen family. This is due to the reason that pnicogens has exactly half-filled orbitals and thus configuration is stable. As we move from oxygen to polonium, the ionization energy decreases due to increase in atomic size.

5. Melting and boiling point :

M.P. and B.P. increases with the increases in atomic numbers because of the increase in magnitude of Vander waals forces.

6. Electronegativity :

Elements of group 16 are more electronegative than corresponding elements of group 15 due to their smaller atomic size.

7. Metallic and non-metallic character :

They have very less metallic character due to high ionisation energy. Their metallic character increases down the group from oxygen to polonium because of decrease in ionization energy.

Concept Ladder

The value of electron gain enthalpy with negative sign for sulphur is higher than that of oxygen.

Rack your Brain

Name the element(s) of group 16 which is amphoteric in nature.

Previous Year's Questions

Which is the correct thermal stability order for H_2E (E = O, S, Se, Te and Po)?

[NEET-2019]

(1) $H_2Se < H_2Te < H_2Po < H_2O < H_2S$
(2) $H_2S < H_2O < H_2Se < H_2Te < H_2Po$
(3) $H_2O < H_2S < H_2Se < H_2Te < H_2Po$
(4) $H_2Po < H_2Te < H_2Se < H_2S < H_2O$

8. Electron gain enthalpy :

The elements of oxygen family have high electron gain enthalpy. The value decreases from sulphur to polonium.

9. Allotropy :

All the elements of 16th group show allotropy. Oxygen exists in two non-metallic forms i.e. O_2 and O_3. Sulphur provides a very good example of an element that exhibits allotropy.

10. Catenation :

Oxygen has some but sulphur has greater tendency for catenation.

$$\underset{(H_2O_2)}{H-O-O-H}, \qquad \underset{(H_2S_2)}{H-S-S-H}$$

Concept Ladder

The boiling point order among H_2O, HCl and NH_3 is $H_2O > NH_3 > HCl$, it is because H_2O is capable of showing more stronger H-bonding than NH_3, while HCl has no H-bonding.

Some properties of group 16 elements.

Properties	O	S	Te	Se	Elements Po
Atomic No.	8	16	34	52	84
Atomic mass	16.00	32.06	77.96	127.60	210
Covalent radius (pm)	74	104	117	137	140
Ionic radius M^{-2} (pm)	140	184	198	221	230(approx)
Density at 298 K (g cm^{-3})	1.32 (at m.p.)	2.06 (for-rohmbic from)	4.19 (for hexagonal gray allotrope)	6.25	—
Melting point K	55	386 (for momoclinic from)	490	723	527
Boiling point K	90	718	958	1263	1233
Ionization enthalpy (I) KJ mol^{-1}	1310	1000	941	870	812
Electronegativity	3.50	2.5	2.48	2.1	2.0
Electron gain enthalpy DH / kJ mol^{-1}	-141	-200	-195	-190	-183

Oxygen and its compounds

Preparation :

O_2 is a colourless, odourless and tasteless gas which is partially soluble in water. Liquid dioxygen is pale blue in colour and the solid is also blue. It is paramagnetic due to presence of unpaired electrons.

1. It is prepared industrially by the electrolysis of acidic or alkaline H_2O or by Claud's Process(fractional distillation of liquid air)
2. In laboratory it is prepared from thermal decomposition of

$$2KClO_3 \xrightarrow{MnO_2\ \text{heat}} 2KCl + 3O_2$$

$$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + 2NO_2 + 1/2O_2$$

3. It can also be made by catalytic decomposition of hypochlorites:

$$2HOCl \xrightarrow{Co^{2+}\text{catalyst}} 2HCl + O_2 \uparrow$$

$$\underset{\text{bleaching powder}}{2CaOCl_2} \xrightarrow{\Delta} 2CaCl_2 + O_2 \uparrow$$

Uses:

Most of the O_2 is used in the steel making industry. Some of it is used in oxy-acetylene welding and as an oxidant in rockets. It is an essential constituent of life.

Concept Ladder

Oxygen does not show oxidation state of +4 and +6, which S does so.

Previous Year's Questions

Which of the following does not give oxygen on heating?

[NEET-2013]

(1) $K_2Cr_2O_7$
(2) $(NH_4)_2Cr_2O_7$
(3) $KClO_3$
(4) $Zn(ClO_3)_2$

Q.8 Why OF_6 does not exist but SF_6 exists?

A.8 Due to absence of d-orbitals in the valence shell, oxygen cannot show an oxidation state of +6 and hence does not form OF_6. In contrast, S contains d-orbitals in the valence shell and hence can show a maximum oxidation state of +6. Since F_2 is a very strong oxidising agent, it oxidises sulphur to its maximum oxidation state of +6 and thus forms SF_6.

[a] Oxides and their general properties

Dioxygen reacts with practically all elements to form oxides. The reactions are usually exothermic and once started often continues spontaneously.

- If an element exists in several oxidation states, then generally lower ones are basic and higher ones are acidic.

$$\underset{\text{neutral}}{N_2O}, NO, N_2O_3, \underset{\text{acidic}}{NO_2}, N_2O_5$$

$$\underset{\text{basic}}{CrO}, \underset{\text{amphoteric}}{Cr_2O_3}, \underset{\text{acidic}}{CrO_3}$$

$$\underset{\text{morebasic}}{PbO}, \underset{\text{lessbasic}}{PbO_2}$$

- The order of acidic strength of oxides can be obtained as follows:

$$K_2O,\ CaO,\ MgO,\ CuO,\ H_2O,\ SiO_2,\ CO_2,\ N_2O_5,\ SO_3$$

$$\longleftrightarrow$$

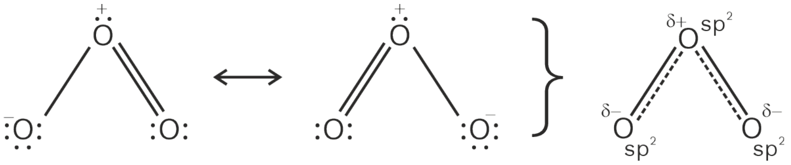
most basic most acidic

The further apart two oxides are in the series, the more stable the compound formed when they react together.

Example : $CaO + H_2O + SO_3 \rightarrow$ morestable $CaSO_4$ ($CaO.SO_3$)

[b] Ozone O_3

O_3 is an unstable, dark blue diamagnetic toxic gas. The colour is due to intense absorption of red light, It also absorbs strongly in the UV region.



For each O atom, of the three sp^2 orbitals two are occupied by two lone pairs and one forms σ– bond. The remaining 4 electrons form π– bonds. The π system is thus $4e^-3$ centre bond.

Concept Ladder

Tendency to show -2 oxidation state diminishes from S to Po in group 16 elements.

Rack your Brain

Why oxygen exists as a diatomic gas at room temperature while other elements as solid?

Preparation:

O_3 is prepared by the action of a silent electric discharge upon dioxygen in an ozoniser.

Bond order = 1.5 for O – O bonds.

Chemical Properties:

1. O_3 turns starch iodide paper blue.
2. The amounts of O_3 in a gas mixture is determined by passing gas into KI solution buffered with a borate buffer (pH 9.2) Iodine liberated is titrated with sodium thiosulphate.

$$O_3 + 2K^+ + 2I^- + H_2O \rightarrow I_2 + 2KOH + O_2$$

Alternatively, it is decomposed catalytically and the change in volume measured.

$$\underset{2\text{volume}}{2O_3} \rightarrow \underset{3\text{volume}}{3O_2}$$

3. Hg in the presence of ozone is oxidized to sub-oxide and starts sticking to glass and loses its meniscus. This is used as a test for ozone called 'Tailing of Mercury'.
4. O_3 is an extremely powerful oxidising agent, second only to F_2.

$$3PbS + 4O_3 \rightarrow 3PbSO_4$$

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

$$2KOH + 5O_3 \rightarrow \underset{\substack{\text{Potassium}\\ \text{ozonide}\\ (\text{Orange solid})}}{2KO_3} + \frac{1}{2}O_2 + H_2$$

5. O_3 reduces peroxides

$$O_3 + BaO_2 \rightarrow BaO + 2O_2$$

$$O_3 + H_2O_2 \rightarrow H_2O + 2O_2$$

Uses

O_3 is used as a disinfectant for water. Its advantage over chlorine is that it avoids unpleasant smell and taste of chlorine, since any excess O_3 decomposes to O_2.

Concept Ladder

O_3 is used as a disinfectant and as a germicide. It is also used for purifying air in crowded places such as cinema halls, tunnels and underground railway station.

Rack your Brain

Why two O—O bond length in the ozone molecule are same?

Previous Year's Questions

The angular shape of ozone molecule (O_3) consists of

[AIPMT]

(1) 1 sigma and 1 pi bond
(2) 2 sigma and 1 pi bond
(3) 1 sigma and 2 pi bond
(4) 2 sigma and 2 pi bond

[c] Hydrogen Peroxide H_2O_2

Pure H_2O_2 is a colourless liquid (like water), more hydrogen bonded than water (and thus has highest boiling point)

Concept Ladder

H_2O_2 is used as an oxidizer, bleaching agent and antiseptic.

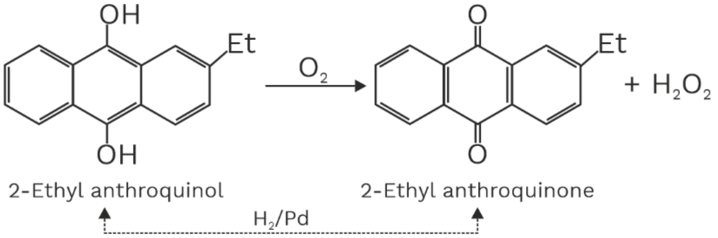
Preparation:

1. At one time H_2O_2 was obtained by electrolysis of H_2SO_4 or $(NH_4)_2SO_4$ using high current density.

$$2SO_4^{2-} \xrightarrow{\text{electrolysis}} S_2O_8^{2-} + 2e^-$$

$$\underset{\substack{\text{Peroxodisulphuric}\\ \text{acid}}}{H_2S_2O_8} + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$$

2. Now, it is produced industrially by a cyclic process.



H_2O_2 is extracted with water as 1% solution which is concentrated to 30% solution.

Rack your Brain

How H_2O_2 can be produced by using cyclic process?

3. In laboratory

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2 \xrightarrow{\text{cool}} Na_2SO_4.10H_2O_2 \quad \text{crystals}$$

$$BaO_2 + CO_2 + H_2O \rightarrow BaCO_3 \downarrow + H_2O_2 \;(\text{Merck's Process})$$

Chemical Properties :

1. H_2O_2 decomposes in presence of impurities like Fe^{2+}, Fe^{3+}, Ni^{2+}, Pt. to undergoes a disproportionation reaction :

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Glycerol or acetanilide is added to check its decomposition.

Previous Year's Questions

The O—O—H bond angle in H_2O_2 is **[AIPMT]**

(1) 106° (2) 109°28’
(3) 120° (4) 97°

2. In most of its reactions H_2O_2 acts as a strong oxidising agent (slow in acidic medium while fast in alkaline).

$$H_2O_2 + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2H_2O$$

$$H_2O_2 + 2\underbrace{\left[Fe(CN)_6\right]^{4-}}_{\text{Ferrocyanide}} \rightarrow 2\underbrace{\left[Fe(CN)_6\right]^{3-}}_{\text{Ferricyanide}} + 2OH^-$$

$$H_2O_2 + SO_3^{2-} \rightarrow SO_4^{2-} + H_2O$$

3. H_2O_2 is forced to act as a reducing agent with stronger oxidising agents and O_2 is evolved.

$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2 \uparrow$$

H_2O_2 is useful to counteract chlorine:

4. H_2O_2 is a mild bleaching agent for hair feathers due to the oxidation reaction:

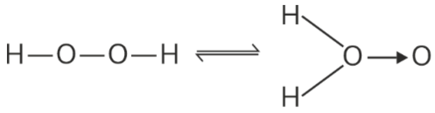
$$H_2O_2 \rightarrow H_2O + [O]$$

5. Qualitative Analysis: It is detected qualitatively by its action on KI.

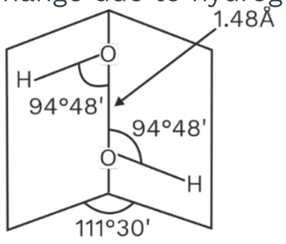
$$2KI \xrightarrow{H_2O_2} 2KOH + I_2$$

Structure:

It is proposed H_2O_2 is a tautomeric mixture of two forms:



It shows restricted rotation about O—O bond due to repulsion between two H's. The structure is same in liquid and gaseous forms, but angles and bond lengths change due to hydrogen bonding.



Structure of H_2O_2 in gas phase

Concept Ladder

H_2O_2 is a reactive oxygen species and the simplest peroxide, a compound having an oxygen – oxygen single bond structure.

Rack your Brain

Name the structure of H_2O_2?

Previous Year's Questions

Hydrogen peroxide molecules are **[AIPMT]**

(1) monoatomic and form X_2^{2-} ions
(2) diatomic and form X^- ions
(3) diatomic and form X_2^- ions
(4) monoatomic and form X^- ions

Sulphur and its Compounds

Allotropy:

Sulphur has the maximum number of allotropic structures. The two common crystalline forms are :

(i) α-Rhombic Sulphur:

It is a yellow solid stable at room temperature, M.P. 11.8°C and specific gravity 2.06 g/cc.

(ii) β –Monoclinic Sulphur:

It is a colourless solid stable above 95.5°C, M.P. 120°C and specific gravity 1.98g/cc.

At 95.5°C (transition temperature both forms are stable). Both α and β forms contain puckered S_8 rings in crown conformation.

Concept Ladder

α-sulphur is insoluble in water but dissolves to some extent in benzene, alcohol and ether.

(iii) Engels Sulphur ($\sum$ - sulphur):

It is unstable and has S_6 rings in chair conformation.

$$Na_2S_2O_3 + conc.HCl \xrightarrow{Toluene} 2S + 2NaCl + O_2 + H_2O$$

(iv) Plastic Sulphur (χ - sulphur):

It is elastic, dark coloured and obtained liquid sulphur into water. It can be moulded with fingers.

Rack your Brain

How mono-clinic sulphure is prepared. Draw its structure?

(v) Colloidal Sulphur:

It is prepared by passing H_2S gas into an oxidising solution like HNO_3, $FeCl_3$

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

Extraction:

Sulphur is obtained from natural gas plants (which contain) and from metal sulphide ores (especially iron pyrites) which produce SO_2.

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S$$

Concept Ladder

α-sulphur is stable below 369 K and transform into β-sulphur above this temperature.

Uses

Almost 90% of S produced is used to manufacture H_2SO_4 .The rest is used in vulcanizing of rubber,making fungicides, gunpowder etc.

[a] Hydrogen sulphide H_2S (Sulphuretted Hydrogen)

It is a colourless, poisonous gas, soluble in H_2O and smell of rotten eggs.

Preparation:

It is easier to make H_2S by the action of mineral acids on metal sulphides.

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S\uparrow$$

$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + \underset{\text{pure}}{3H_2S}\uparrow$$

Chemical Properties:

1. It burns with blue flame.

$$2H_2S + \underset{\text{excess}}{3O_2} \rightarrow 2H_2O + 2SO_2$$

A saturated solution of H_2S is slowly oxidized by air and Sulphur is deposited.

$$2H_2S + O_2\left(\text{limited}\right) \rightarrow 2H_2O + 2S$$

2. It is a very weak dibasic acid.

$$H_2S + NaOH \rightarrow NaHS + H_2O;$$

$$NaHS + NaOH \rightarrow Na_2S + H_2O$$

The two salts NaHS, Na_2S are basic and soluble in water.

3. $H_2S + \underset{\text{dil. solution}}{NH_3} \rightarrow (NH_4)HS\left[\text{not}\,(NH_4)_2\,S\right]$

Yellow $(NH_4)_2S$ is a mixture of ammonium polysulphide and is made by dissolving sulphur in colourless $(NH_4)HS/NH_3$ solution. This solution is used to precipitate metal sulphides in qualitative analysis.

4. H_2S is a reducing agent and reduces Cl_2 to Cl^-, H_2SO to SO_2, $FeCl_3$ to $FeCl_2$ and itself gets oxidized to S.

$$H_2S + Cl_2 \rightarrow 2HCl + S$$

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

Concept Ladder

H_2S is more acidic than H_2O and PH_3. Thermal stability of H_2 o is much higher than that of H_2S.

Rack your Brain

Why H_2S has greater molecular mass than H_2O, former is gas while latter is present in liquid form at room temperature?

Previous Year's Questions

Acidity of diprotic acids in aqueous solutions increases in the order **[NEET-2014]**

(1) $H_2S < H_2Se < H_2Te$
(2) $H_2Se < H_2S < H_2Te$
(3) $H_2Te > H_2S > H_2Se$
(4) $H_2Se < H_2Te < H_2S$

[b] Sulphur Dioxide (SO_2) :

SO_2 is a colourless poisonous gas with a choking smell. It is highly soluble in water and almost completely present as $SO_2.6H_2O$ in water and only 1% as H_2SO_3. Liquid SO_2 has also been used as a non-aqueous solvent.

Concept Ladder

H_2S acts only as a reducing agent while SO_2 can act both as a reducing and oxidising agent.

Preparation:

1. It is prepared by burning S or H_2S in air.

$$S + O_2 \rightarrow SO_2$$

$$2H_2S + \underset{\text{excess}}{3O_2} \rightarrow 2SO_2 + 2H_2O$$

2. It is also prepared by roasting various metal sulphides in smelters.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

Rack your Brain

Why bleaching by SO_2 is temporary?

Chemical Properties :

1. Most of SO_2 is oxidized to SO_3 by the contact process and used to manufacture H_2SO_4.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3\ ;\ \Delta_rH^{\oplus} = -196.6\text{kJ / mol}$$

2. Bleaching action:

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

Bleaching by SO_2 is temporary as reduced colour is reoxidised by air to give black coloured matter.

Also, H_2SO_4 produced during bleaching may be harmful to fibres.

$$\underset{\text{coloured}}{X-OH} + SO_2 \rightarrow \underset{\text{colourless}}{XHSO_3} \xrightarrow{+HCl} XCl \xrightarrow{+H_2O} \underset{\text{coloured}}{XOH} + HCl$$

Cl_2 although has a permanent effect as it produces [O].

Previous Year's Questions

Nitrogen dioxide and sulphur dioxide have some properties in common. Which property is shown by these compounds, but not by the other?

[NEET-2015]

(1) Is soluble in water.
(2) Is used as a food preservative.
(3) Forms 'acid-rain'.
(4) Is a reducing agent.

3. It shows reducing properties in presence of moisture.

$$SO_2 + Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$$

$$5SO_2 + 2KIO_3 + 4H_2O \rightarrow K_2SO_4 + 4H_2SO_4 + I_2$$

Although with stronger reducing agents it acts as an oxidising agent.

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S\downarrow$$

$$3Fe + SO_2 \rightarrow 2FeO + FeS$$

Detection of SO_2:

It may be detected in three ways in the laboratory :

1. By its choking smell
2. It turns filter paper moistened with $K_2Cr_2O_7/H^+$ green.

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

Structure:

$3d_{z^2}$ orbital of S cannot be used to form π bond as its symmetry is wrong. Instead of $3d_{xz}$ orbital on S is used to make the second π bond with $2p_z$ orbital on the second O atom. Although, it is surprising that both π bonds have the same energy.

Concept Ladder

Burning of sulphur or sulphide ores in air generates SO_2.

Rack your Brain

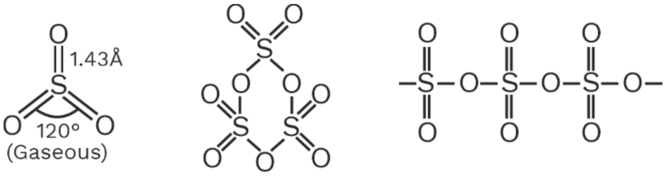
What happen when SO_2 gas is passed through an aqueous solution of a Fe(III) salt.

Q.9 How SO_2 is an air pollutant?

A.9 SO_2 acts as an air pollutant because of the following reasons : (i) SO_2 is strongly irritating to the respiratory tract. SO_2 at a concentration of 5 ppm causes throat and eye irritation (resulting in cough, tears and redness in eyes). It causes breathlessness and affects larynx, i.e., voice box.

[c] Sulphur Trioxide (SO_3) :

It is the anhydride of H_2SO_4 and is solid at room temperature. It has three forms:



In gaseous state, SO_3 has a planar triangular structure involving sp^2 hybrid sulphur atom. The lone pair of sulphur atom forms coordinate bond (σ). Therefore, bond angle is exactly 120°. Solid SO_3 possesses either cyclic trimer (α – form) or infinite helical chains (β – form).

Preparation:

1. It is manufactured on a huge scale by the Contact Process. Practically all of it is converted to H_2SO_4 in the same process :

$$2SO_2 + O_2 \xrightarrow{Pt/V_2O_5} 2SO_3$$

2. $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$

Chemical Properties:

1. $2SO_3 \xrightarrow{1000°C} 2SO_2 + O_2$

2. $SO_3 + \underset{\text{vapour}}{H_2O} \rightarrow \underset{\text{densemist}}{H_2SO_4}$

SO_3 is used to prepare oleum (mainly pyrosulphuric acid $H_2S_2O_7$)

$$SO_3(g) + \underset{98\%}{H_2SO_4} \rightarrow \underset{\text{oleum/fuming sulphuric acid}}{H_2S_2O_7}$$

3. SO_3 is used to make sulfamic acid NH_2SO_3H (the only strong acid that can exist as a solid at room temperature).

$$\underset{\text{Urea}}{NH_2CONH_2} + SO_3 + H_2SO_4 \rightarrow 2NH_2SO_3H + CO_2$$

Concept Ladder

- All the S—O bonds in SO_3 have equal length due to resonance.
- SO_3 exists in 3 allotropic forms α-SO_3, β-SO_3, γ-SO_3.

Rack your Brain

Why SO_3 is not absorbed directly in water to form H_2SO_4 in contact process?

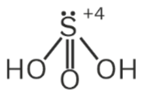
Concept Ladder

SO_2 may be regarded as an anhydride of sulphurous acid (H_2SO_3) while SO_3 is regarded as an anhydride of sulphuric acid (H_2SO_4).

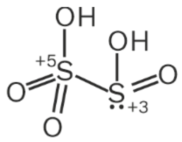
[d] Oxo Acids of Sulphur:

Some oxo acids of Sulphur ending in – ous have S in the oxidation state (+IV) and form salts ending in –ite. Some acid ending in –ic have S in the oxidation state (+VI) and form salts ending in –ate. Four main series exist which are:

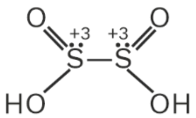
(I) Sulphurous Acid Series:



Sulphurous acid H_2SO_3



Disulphurous (Pyrosulphurous) acid $H_2S_2O_5$



Dithionous acid $H_2S_2O_4$

The most important acid (according to the use) in this series is sulphurous acid (H_2SO_3):

Preparation:

It is only known in solution form (like carbonic acid) and as discussed SO_2 solution in water gives 1% H_2SO_3.

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

Chemical Properties of SO_3^{2-} ion.

1. H_2SO_3 being dibasic forms salt of bisulphites (HSO_3^-) and sulphites (SO_3^-).HSO_3^- however undergoes internal dehydration to form $S_2O_5^{2-}$ ion.

$$2HSO_3^- \overset{heat}{\rightleftharpoons} \underset{\text{disulphite}}{S_2O_5^{2-}} + H_2O$$

2. S(+IV) in SO_3^- and HSO_3^- is a moderately strong reducing agent and forms sulphates on oxidation.

$$SO_3^{2-} + H_2O_2 \rightarrow SO_4^{2-} + H_2O$$

$$H_2SO_3 + H_2O + 2FeCl_3 \rightarrow H_2SO_4 + 2FeCl_2 + 2HCl$$

while with sulphur, sulphites form thiosulphates:

$$SO_3^{2-} + S \xrightarrow{OH^-} \underset{\text{thiosulphate}}{S_2O_3^{2-}}$$

Rack your Brain

Define number of oxo acids formed by sulphure?

Concept Ladder

Sulphourous acid is an intermediate species in the formation of acid rain from sulphur dioxide.

Previous Year's Questions

Which of the following oxoacid of sulphur has —O—O— linkage

[NEET-2020]

(1) H_2SO_3, sulphurous acid

(2) H_2SO_4, sulphuric acid

(3) $H_2S_2O_8$, peroxodisulphuric acid

(4) $H_2S_2O_7$, pyrosulphuric acid

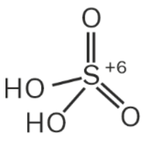
Sulphites and hydrogen sulphites liberates SO_2 on treatment with dilute acids

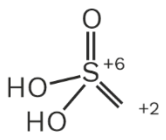
$$SO_3^{2-}\left(\text{or } HSO_3^{2-}\right) \xrightarrow{H^+(\text{dil})} SO_2\uparrow$$

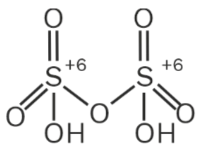
3. SO_3^{2-} acts as an oxidising agent with a strong RA like H_2S.

$$SO_3^{2-} + 2S^{-2} + 6H^+ \rightarrow 3S\downarrow + 3H_2O$$

(II) Sulphuric Acid Series:


Sulphuric acid
H_2SO_4


Thiosulphuric acid
$H_2S_2O_3$


Pyrosulphuric acid (oleum)
$H_2S_2O_7$

(i) Sulphuric acid [Oil of Vitriol] H_2SO_4:

It is the most important acid used in the chemical industry. It is a colourless syrupy liquid with B.P. 338°C and freezes into crystals at 10.5°C . It is strongly hydrogen bonded.

Preparation

1. In ancient days it was prepared from $FeSO_4.7H_2O$ (Green vitriol).

$$\underset{\text{green vitriol}}{2\left(FeSO_4.7H_2O\right)} \xrightarrow{\text{heat}} Fe_2O_3 + SO_2 + 13H_2O + \underset{\text{oil of vitriol}}{H_2SO_4}$$

2. Lead Chamber Process

Was used to manufacture H_2SO_4 industrially but the process is now obsolete as it only produced 78% H_2SO_4. NO_2 is used as a homogeneous catalyst to oxidise SO_2 in the presence of water. NO produced combines with air to produce NO_2 which is reused. Thus, NO and NO_2 act as oxygen carriers

$$\begin{tikzcd} NO_2 + SO_2 + H_2O \arrow[r] & H_2SO_4 + NO \arrow[d] \arrow[r] & +\frac{1}{2}O_2 \\ & NO_2 \arrow[ul, dashed] & \end{tikzcd}$$

Concept Ladder

H_2SO_4 is considered as the **King of Chemicals.** In ancient days, it was called oil of vitriol (Green Vitriol).

Rack your Brain

Write down the main process for manufacturing of sulphuric acid.

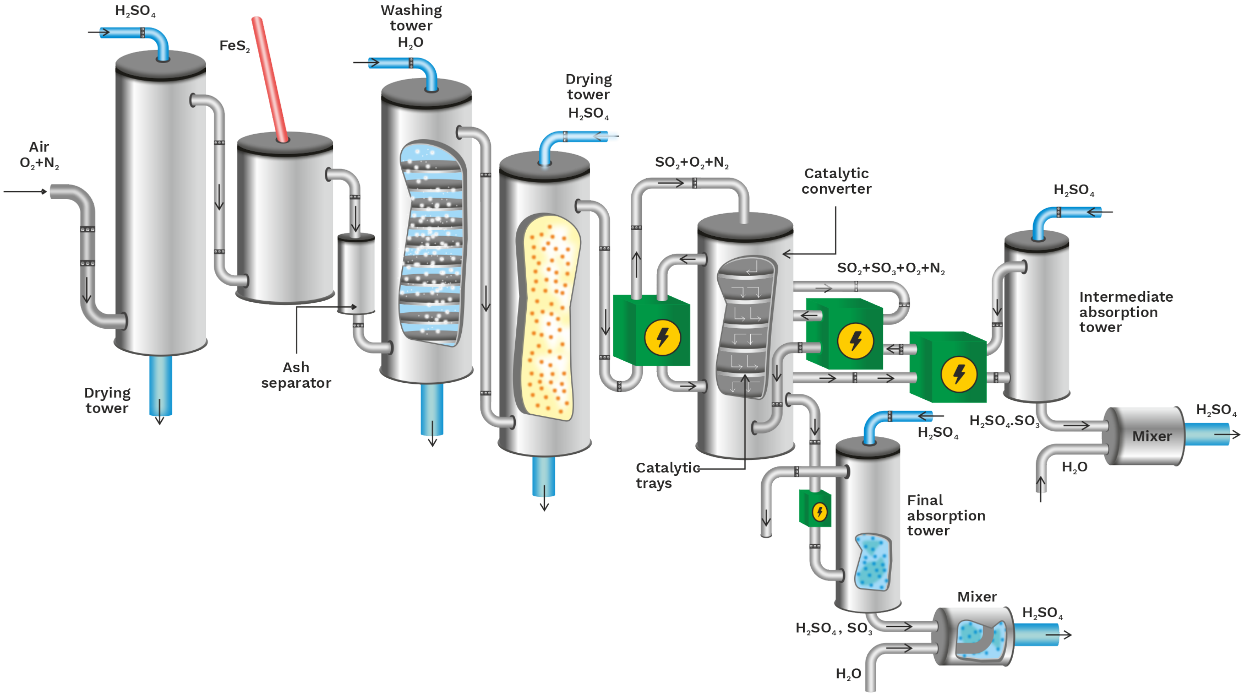
Previous Year's Questions

Oleum is **[AIPMT]**

(1) caster oil
(2) oil of vitriol
(3) fuming H_2SO_4
(4) none of these

3. Contact Process:

This process is most important commercial process for the manufacture of H_2SO_4. It is used widely.



Flow diagram for the manufacture of sulphuric acid

(i) SO_2 is first collected from burning of sulphur or sulphide ores.
(ii) SO_2 is then oxidized.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The forward rxn is exothermic and is favoured by high pressure, low temperature and excess of oxygen. A catalyst (activated V_2O_5) is used to obtain a reasonable conversion.

(iii) SO_3 is then passed into 98% H_2SO_4 forming pyrosulphuric acid ($H_2S_2O_7$) called oleum. Dilution of oleum with water gives concentrated H_2SO_4 (98%).

Previous Year's Questions

Identify the correct formula of oleum from the following :

[NEET-2019]

(1) $H_2S_2O_7$ (2) H_2SO_3
(3) H_2SO_4 (4) $H_2S_2O_8$

Chemical Properties :

1. H_2SO_4 due to its low volatility is used to manufacture more volatile acids.

$$\underset{M=metal;X=F,Cl,NO_3}{2MX+H_2SO_4} \rightarrow 2HX+H_2SO_4$$

2. H_2SO_4 is a powerful dehydrating agent especially for gases.
   It dehydrates HNO_3 forming NO_2^+

$$2H_2SO_4+HNO_3 \rightarrow \underset{\text{Nitronium ion}}{NO_2^+}+H_3O^+ +2HSO_4^-$$

It removes elements of H_2O from organic compounds.

$$2EtOH+H_2SO \rightarrow Et-O-Et+H_2SO_4.H_2O$$

$$(COOH)_2+H_2SO_4 \rightarrow CO+CO_2+H_2SO_4.H_2O$$

H_2SO_4 mixes with H_2O to evolve large amount of heat. If H_2O is poured into concentrated acid, the heat evolved causes violent splashing. Thus, to dilute strong acids like H_2SO_4, acid is poured into water while stirring (not water into acid).

3. H_2SO_4 is a quite strong oxidising agent.

$$2Br^- +\underset{(conc.)}{H_2SO_4} \longrightarrow 2H_2O+SO_2+Br_2$$

$$\underset{(conc.)}{2H_2SO_4}+C \rightarrow CO_2+2SO_2+2H_2O$$

4. Pure H_2SO_4 is a non-aqueous solvent and a sulphonating agent.

$$C_6H_6+HO.SO_3H \rightarrow \underset{\text{Benzenesulphonicacid}}{C_6H_5SO_2OH}+H_2O$$

Concept Ladder

- H_2SO_4 has high boiling point due to H-bonding. It acts as a strong dibasic acid.
- Metals those are more electropositive than hydrogen react with dil. H_2SO_4 to evolve H_2 gas but less electropositive metals on heating with conc. H_2SO_4 evolve SO_2.

Rack your Brain

Why $KMnO_4$ should not be dissolved in conc. H_2SO_4?

Q.10 In solution of H_2SO_4 when SO_3 is bubbled, a compound 'A' is formed, which further reacts with H_2O to give H_2SO_4. Explain this process with equation?

A.10 H_2SO_4 absorbs SO_3 forming oleum (A) which reacts with H_2O to form H_2SO_4.

$$H_2SO_4+SO_3 \longrightarrow \underset{\text{Oleum, A}}{H_2S_2O_7} \xrightarrow{H_2O} 2\ H_2SO_4$$

Uses:

1. It is used in making superphosphate fertilizer.
2. It is used in removal of oxides from the surfaces of metals like Fe, Cu before electroplating or galvanizing.
3. It is used as a dehydrating agent. oxidising agent and as strong acid.

(ii) Thiosulphuric acid ($H_2S_2O_3$):

It is unstable and decomposes in H_2O into a mixture of S, H_2S, SO_2 and H_2SO_4 while the salts (thiosulphates) are stable. Large colourless hexagonal crystals are formed which are highly soluble in water.

sodium thiosulphate ($Na_2S_2O_3.5H_2O$) is the most important thiosulphate also called hypo.

Preparation:

$$\underset{\text{Neutral/alkaline}}{SO_3^{2-} + S} \xrightarrow{\text{boiling}} S_2O_3^{2-}$$

Chemical Properties:

1. Hypo solutions are used for iodine titrations in volumetric analysis.

$$2Na_2S_2O_3 + I_2 \rightarrow \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + 2NaI$$

In iodometric estimation oxidising agents like $CuSO_4$, $K_2Cr_2O_7$ are treated with KI which liberates I_2 which is determined by hypo as above.

$$2CuSO_4 + 4KI \rightarrow 2K_2SO_4 + Cu_2I_2 + I_2$$

2. $Na_2S_2O_3$ is used to destroy excess Cl_2 on fabrics after they have been bleached and called as antichlor.

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \rightarrow 2NaHSO_4 + 8HCl$$

It is also used to remove the taste from heavily chlorinated drinking water.

3. Hypo is used in photography for ‘fixing’ prints

Concept Ladder

$H_2S_2O_3$ is a dibasic acid. It does not exist in free state, salts are quite stable and are reducing in nature.

Rack your Brain

How many P—O—P bonds are there in (i) $H_4P_2O_7$ (ii) P_4O_{10}?

Previous Year’s Questions

Which is the strongest acid in the following?

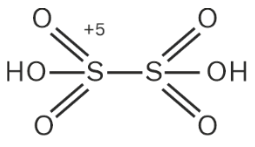
[NEET-2013]

(1) $HClO_4$
(2) H_2SO_3
(3) H_2SO_4
(4) $HClO_3$

and films. It dissolves unreacted $AgNO_3$, AgBr salts.

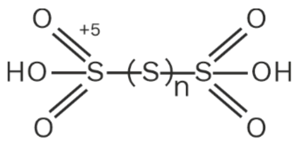
$$Na_2S_2O_3 + 2AgBr \rightarrow Ag_2S_2O_3 \downarrow \overset{+Na_2S_2O_3}{\rightarrow} \text{soluble complexes } Na_3\left[Ag\left(S_2O_3\right)_2\right]$$

(iii) Thionic Acid Series:



Dithionic acid

$H_2S_2O_6$



Polythionic acid

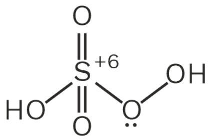
$H_2S_nO_6$

Concept Ladder

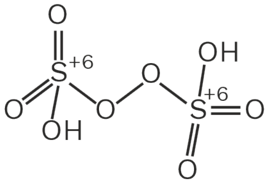
The chemical name for the following acids are : (i) H_2SO_5 Peroxymonosulphuric acid or Caro's acid, (ii) $H_2S_2O_8$ Peroxydisulphuric acid or Marshall's acid, (iii) $H_2S_2O_6$ Dithionic acid

(iv) Peroxo Acid Series

They contain the peroxo linkage —O—O—.



Peroxo monosulphuric acid (Caro's Acid) H_2SO_5



Peroxo disulphuric acid $H_2S_2O_8$ (Marshell's Acid)

Q.11 Why is sulphurous acid acts as reducing agent?

A.11 As Sulphur atom contains a lone pair of electrons, sulphurous acid can be easily oxidised to sulphuric acid. Therefore, it acts as a reducing agent.

$$H_2O + Br_2 + H_2SO_3 \longrightarrow 2\ HBr + H_2SO_4$$

Q.12 Write one chemical reaction to show that conc. H_2SO_4 can act as an oxidising agent.

A.12 Concentrated sulphuric acid oxidises carbon to CO_2.

$$C + 2\ H_2SO_4(\text{conc.}) \xrightarrow{\Delta} CO_2 + 2\ SO_2 + 2\ H_2O$$

Group 17 (Halogen Family)

Introduction :

The elements Fluorine, Chlorine, Bromine, Iodine and Astatine constitute group 17 of the periodic table.

Electronic configuration :

Element	symbol	Atomic Number	Electronic Configuration	Brief representation of electronic configuration
Fluorine	F	9	$1s^2 2s^2 2p^5$	$[He]\ 2s^2\ 2p^2$
Chlorine	Cl	17	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	$[Ne]\ 3s^2\ 3p^5$
Bromine	Br	35	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$	$[Ar]\ 3d^{10}\ 4s^2\ 4p^5$
Iodine	I	53	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^5$	$[Kr]\ 4d^{10}\ 5s^2\ 5p^5$
Astatine	At	85	$1s^2 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^5$	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$

Occurrence :

1. Fluorine is less abundant in earth's crust than chlorine.
2. Fluorine is available mainly as insoluble fluorides.
3. Fluorine occurs to the extent of 0.07% of the earth's crust.

The important minerals of fluorine :

1. Fluorspar or fluorite : CaF_2
2. Cryolite : Na_3AlF_6
3. Fluorapatite: $3Ca_3\ (PO_4)_2\ .\ CaF_2$

Physical properties :

1. **Electronic configuration :** Their valence shell electronic configuration is $ns^2\ np^5$ or $ns^2\ np_x^{\ 2}\ np_y^{\ 2}\ np_z^{\ 1}$ where n = 2 to 6.

2. **Atomic and ionic radii :** The atomic radii increase from fluorine to iodine down the group due to increase in number of shells.

Concept Ladder

- Due to its very small size fluorine does not acts as central atom in formation of interhalogen compounds.
- It is the most electronegative element in the whole periodic table.

3. **Ionization enthalpy :** Ionization energy of these elements are higher than those of the corresponding elements of group 16 due to increase nuclear charge.

4. **Electronegativity :** With increase in atomic number down the group, the electronegativity decreases. The decreasing order of electronegativity is F > Cl > Br > I.

5. **Electron gain enthalpy :** The decreasing order of negative electron gain enthalpy is Cl > F > Br > I.

6. **Oxidation state :** All the halogens show an oxidation state of –1. Except fluorine, all halogens show positive oxidation state also.

7. **Metallic character :** All the halogens are non-metallic in nature due to their high ionization enthalpies and high electronegativities. The non-metalic character gradually decreases down the group.

8. **Bond dissociation energy :** Bond dissociation energy of fluorine is lower than those of chlorine (Cl – Cl) and bromine (Br – Br) because of inter electronic repulsions present in the small atom of fluorine. Hence, bond energy decreases in the order : $Cl_2 > Br_2 > F_2 > I_2$

9. **Bond length :** As the size of the halogen atom increases the bond length of X – X bond in X_2 molecule increases from F_2 to I_2.

10. **Melting point and boiling point :** It increases from F to I due to an increase in the VWF of attraction which increases down in the group.

11. **Density :** The density of halogen increases on moving down the group.

12. **Colour :** All halogens are coloured. The colour

Concept Ladder

Fluorine is better oxidising agent than chlorine, although it has less electron affinity. Chlorine has highest electron affinity in element in whole periodic table.

Rack your Brain

Why electron gain enthalpy of fluorine is less negative than that of chlorine?

Previous Year's Questions

Which one of the following orders is correct for the bond dissociation enthalpy of halogen molecules?

[NEET-2016]

(1) $Br_2 > I_2 > F_2 > Cl_2$
(2) $F_2 > Cl_2 > Br_2 > I_2$
(3) $I_2 > Br_2 > Cl_2 > F_2$
(4) $Cl_2 > Br_2 > F_2 > I_2$

darkness depends on the rise of atomic number from fluorine to iodine.

F : Light yellow; Cl : Yellow green;

Br : Raddish brown; I : Deep violet

The colour is due to the adsorption of energy from visible light by their molecules to excite outer electrons for higher energy levels.

Chemical Properties

1. **Reactivity :**

All the halogens are chemically very reactive elements. This is due to their low dissociation energy. Fluorine is the most reactive and iodine is the least reactive halogen.

2. **Thermal stability :**

Thermal stability of hydrides decreases from HF to HI. i.e. HF > HCl > HBr > HI.

3. **Oxidising power :**

The oxidising power decreases on moving down the group. i.e. $F_2 > Cl_2 > Br_2 > I_2$.

Conversely, I^- is the strongest reducing agent while F^- is the weakest reducing agent.

4. **Hydrogen halides :**

All the halogens combine directly with H_2 to form covalent molecular hydrides but their reactivity progressively decreases from fluorine to iodine.

5. **Bond strength, bond length and thermal stability:**

Since, size of halogen atom increases from F to I down the group, bond length of H–X bond increases down the group.

HF < HCI < HBr < HI

Bond energy has inverse relationship with bond length i.e. larger the bond length, lower the bona strength and vice versa. Thus, order of bond strength is HF > HCl > HBr > HI

Bond strength provides a direct idea of thermal stability. Higher the bond dissociation

Concept Ladder

Standard reduction potential of halogens are positive and decreases down the group. Thus, halogens acts as strong oxidising agents and their oxidising power decreases from fluorine to iodine.

Previous Year's Questions

The variation of the boiling points of the hydrogen halides is in the order HF > HI > HBr > HCl.
What explains the higher boiling point of hydrogne fluoride?

[NEET-2015]

(1) There is strong hydrogen bonding between HF molecules.

(2) The bond energy of HF molecules is greater than in other hydrogen halides.

(3) The effect of nuclear shielding is much reduced in fluorine which polarises the HF molecule.

(4) The electronegativity of fluorine is much higher than for other elements in the group.

energy greater will be thermal stability. Thus, thermal stability follows the order.

HF > HCl > HBr > HI

5. **Reducing character :**

The reducing character of hydrogen halides increases down the group as, HF < HCl < HBr < HI

$$2HX \longrightarrow H_2 + X_2$$

A less thermally stable compound has more tendency to release hydrogen easily and show greater reducing property. Since thermal stability of hydrogen halides decreases from HF to HI, their reducing power increases from HF to HI.

6. **Acidic strength :**

In gaseous state, hydrogen halides are covalent. But in aqueous solutions, they ionize and behave as acids. The acidic strength of these acids increases down the group and hence follows the order.

HF < HCl < HBr < HI

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

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

Reaction with H_2O :

1. $2H_2O + 2F_2 \longrightarrow 4HF + O_2$

Rack your Brain

Explain why halogens are strong oxidising agents.

Previous Year's Questions

Among the following, the correct order of acidity is

[NEET-2016]

(1) $HClO_2 < HClO < HClO_3 < HClO_4$
(2) $HClO_4 < HClO_2 < HClO < HClO_3$
(3) $HClO_3 < HClO_4 < HClO_2 < HClO$
(4) $HClO < HClO_2 < HClO_3 < HClO_4$

Q.13 Sea is the greatest source of halogens. Comment.

A.13 Sea water contains Cl, Br and I of Na, K, Mg and Ca, but mainly NaCl (2.5% by mass). Dried up sea beds contain NaCl and carnallite, $KCl.MgCl_2.6H_2O$. Certain seaweeds contain upto 0.5% of iodine as sodium iodide and chile saltpetre ($NaNO_3$) contains upto 0.2% of sodium iodate. Therefore, sea is the greatest source of halogens.

2. $3H_2O + 3F_2 \longrightarrow 6HF + O_3$

3. $Cl_2 + H_2O \longrightarrow HCl + HClO$
(Hypochlorous acid)

4. $Br_2 + H_2O \longrightarrow HBr + HBrO$
(Hypobromous acid)

5. $2HClO \longrightarrow 2HCl + O_2$,
$2HBrO \longrightarrow 2HBr + O_2$

6. $I_2 + KI = KI_2 + I^- = I_3^-$

Reaction with hydrogen :

1. $H_2 + F_2 \xrightarrow{200°C} 2HF$ (very violent)
$H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$
$H_2 + Br_2 \xrightarrow[\text{Pt. catalyst}]{\text{Heat}} 2HBr$
$H_2 + I_2 \xrightleftharpoons{\text{heat}} 2HI$ (Poor yield)

2. Bleaching action of halogen : Cl_2 acts as a bleaching agent. Its bleaching action is permanent Cl_2 water can also acts as ink remover.

3. Reaction with other halides :
$2KBr\ (aq) + Cl_2\ (g) \longrightarrow 2KCl\ (aq) + Br_2\ (g)$
$2\ KI\ (aq) + Cl_2\ (g) \longrightarrow 2KCl\ (aq) + I_2\ (g)$

Anomalous behaviour of fluorine :

Fluorine differs from other members of its own sub-group due to the following reasons.

1. Small size of the atom in comparison to the sizes of Cl, Br and I atoms.
2. Higher electronegativity.
3. Absence of d-orbitals in its valence shell.
4. Higher positive reduction potential.

The main points of difference are :

1. Fluorine shows only a negative oxidation state

Concept Ladder

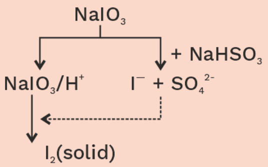
Among halogens, fluorine provides the largest variety of inter-halogen compounds.

Rack your Brain

Arrange hydrogen halides in the increasing order of there dipole moments.

Previous Year's Questions

Which of the following statements is not true for halogens?
[NEET-2018]
(1) All form monobasic oxyacids
(2) All are oxidizing agents.
(3) All but not fluorine, show positive oxidation states.
(4) Chlorine has the highest electron-gain enthalpy.

<table>
<tr><th colspan="4">Reaction with</th></tr>
<tr><th>F_2</th><th>Cl_2</th><th>Br_2</th><th>I_2</th></tr>
<tr><th colspan="4">Preparation Of Gas</th></tr>
<tr>
<td>Light - yellow gas
Most reactive element known strong O.A.
Moisson was awarded Noble prize for his methods of preparing F_2 :
$CaF_2 + \text{conc. } H_2SO_4 \longrightarrow HF$
$HF + KF \longrightarrow K^+ [HF_2]^-$</td>
<td>Yellow green gas
toxic, has pungent suffocating odour
Lab
$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$
Deacon's Process :
It is them dried with CaO, P_4O_{10} or H_2SO_4
$HCl + O_2 \xrightarrow{CuCl_2} Cl_2 + H_2O$
Commercially it is also obtained by electrolysis of NaCl(aq) in the manufacture of NaOH or elect. of NaCl(l) in the manufacture of Na</td>
<td>Brown liquid
Obtained from Sea water and brine lakes by passing Cl_2 as follows:
$Cl_2 + 2Br^- \longrightarrow Cl^- + Br_2$
$Br_2 + 3Na_2CO_3 \longrightarrow NaBr + NaBrO_3 + 3CO_2$
$NaBr + NaBrO_3 \xrightarrow{H^+} HBr + HBrO_3$
$Br_2 \xleftarrow{CuCl_2} HBr + HBrO_3$</td>
<td>Violet solid
Crystallizes as black flakes has slight lustre.
Chile saltpetre is mainly $NaNO_3$ but contains traces of $NaIO_3$ $NaNO_3$ is crystallised out and left $NaIO_3$ is divided into two parts


Purification is done by sublimation.</td>
</tr>
<tr><th colspan="4">H_2O</th></tr>
<tr>
<td>$F_2 + H_2O \longrightarrow 2H^+ + 2F^- + \frac{1}{2} O_2$
(OA)
(spontaneous and strongly exothermic)</td>
<td>$Cl_2 + H_2O \underset{K^+}{\overset{\text{Cold } OH^-}{\rightleftharpoons}} ClO^- + Cl^-$
$Cl_2 + 3H_2O \xrightarrow{\text{hot } OH^-} ClO_3^- + Cl^-$</td>
<td>$Br_2 + H_2O \xrightarrow{OH^-} Br^- + BrO^-$</td>
<td>Sparingly soluble in water but dissolves if I^- are present (as soluble I_3^- forms)
$I^- + I_2 \longrightarrow I_3^-$</td>
</tr>
<tr><th colspan="4">NH_3</th></tr>
<tr><td colspan="4">X_2 reacts with NH_3 to give NH_2 and NH_4X (X= F, Cl, Br)</td></tr>
<tr><th colspan="4">Others</th></tr>
<tr><td colspan="4">All halogens oxidise H_2S to S ; form SO_2X_2 with SO_2 ; trihalides with As, Sb, Bi; penta halides (except I) with As, Sb, Bi .</td></tr>
<tr><th colspan="4">Uses</th></tr>
<tr>
<td>Used in making freon (CFC's)</td>
<td>Used as a bleaching agent
$Cl_2 + H_2O \longrightarrow HOCl$
and make poisonous gases like SO_2Cl_2</td>
<td>it is used to make flame retardant and in organic chemistry.</td>
<td>It is used to make tincture of iodine (I_2 + KI) and in titrations.</td>
</tr>
</table>

of –1 due to maximum value of electronegativity. It never shows any positive oxidation state. The other halogen show negative as well as positive oxidation states, i.e. between –1 and +7.

2. Fluorine is most reactive as bond dissociation energy of F – F bond is low. X – X bond is stronger in Cl_2 and Br_2.

3. 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.

4. Fluorine does not have vacant d-orbital in valence shell therefore it does not combine with F^- ion to form polyfluoride ions like Cl^-, Br^{3-}, I_5^- etc.

Compounds of Halogen :

Chlorine: (Cl_2)

Occurrence :

1. Chlorine is widely distributed in nature in the combined state in the form of chlorides of various metals.

2. Common Salt (NaCl) is the most important chloride which occurs in sea water, lakes and in rocks.

The other important chloride minerals are :

1. Sylvine (Potassium Chloride) KCl
2. Carnalite, KCl, $MgCl_2$, $6H_2O$
3. Chlorapatite, $3Ca_3(PO_4)_2$ $CaCl_2$
4. Horn Silver, AgCl

Preparation :

1. By oxidation of conc. HCl

Concept Ladder

Fluorine and oxygen compounds are called oxygen fluorides, but not fluorine oxides.

Rack your Brain

Why I_2 is more soluble in KI than in water?

Previous Year's Questions

Which of the following elements is extracted commercially by the electrolysis of an aqueous solution of its comopund?

[AIPMT]

(1) Cl (2) Br
(3) Al (4) Na

$PbO_2 + 4\ HCl \longrightarrow PbCl_2 + 2\ H_2O + Cl_2$

$2\ KMnO_4 + 16\ HCl \longrightarrow 2\ KCl + 2MnCl_2 + 8\ H_2O + 5\ Cl_2$

2. Weldon's process : By heating pyrolusite with conc. HCl

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

3. Deacon Process :

HCl(g) is oxidised by atm. oxygen in presence of a catalyst $CuCl_2$ at 400°C (723 K).

$4\ HCl + O_2 \xrightarrow[400°C]{CuCl_2} 2\ Cl_2 + 2\ H_2O$

Physical Properties :

It is yellowish green gas, poisonous in nature, soluble in water. Its aqeous solution is known as chlorine water which on careful cooling gives chlorine hydrate $Cl_2\ 8H_2O$.

Chemical Properties :

1. Bleaching action and oxidising property.
2. $Cl_2 + H_2O \longrightarrow HOCl + HCl$

$HOCl \longrightarrow HCl + O$

The bleaching action of chlorine is permanent and is due to its oxidising nature.

3. $SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$
4. Action of hydrogen :

$H_2 + Cl_2 \longrightarrow 2HCl$

5. Displacement reactions :

$2\ KBr + Cl_2 \longrightarrow 2\ KCl + Br_2$

$2\ KI + Cl_2 \longrightarrow 2\ KCl + I_2$

6. Action of NaOH :

$2\ NaOH + Cl_2 \longrightarrow NaOCl_2 + H_2O$

Concept Ladder

Deacon's process is superior to Weldon's process as in Deacon's process, chlorine is obtained by the oxidation of HCl with air in presence of cupric chloride heated at 400°C.

Rack your Brain

What is the cause of bleaching action of chlorine in water?

Previous Year's Questions

The correct order of increasing bond angles in the following species is

[AIPMT]

(1) $Cl_2O < ClO_2 < ClO_2^-$
(2) $ClO_2 < Cl_2O < ClO_2^-$
(3) $Cl_2O < ClO_2^- < ClO_2$
(4) $ClO_2^- < Cl_2O < ClO_2$

$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$

7. Combination with non metals

$2\,As + 3\,Cl_2 \longrightarrow 2\,AsCl_3$

$2\,S + Cl_2 \longrightarrow S_2Cl_2$

$2\,B + 3\,Cl_2 \longrightarrow 2BCl_3$

$2\,Sb + 3\,Cl_2 \longrightarrow 2\,SbCl_3$

$P_4 + 10\,Cl_2 \longrightarrow 4\,PCl_5$

$P_4 + 6\,Cl_2 \longrightarrow 4\,PCl_3$

8. Other important reactions

Reaction with ammonia

$8\,NH_3 + 3Cl_2 \longrightarrow N_2 + 6\,NH_4Cl$

Reaction with hydrocarbons

$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$

Oxidizing nature of chlorine

$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$

$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2\,HCl$

$H_2S + Cl_2 \longrightarrow 2\,HCl + S$

$SO_2 + Cl_2 + 2\,H_2O \longrightarrow 2\,HCl + H_2SO_4$

Uses of Chlorine :

It is used as :

1. Bleaching agent
2. Disinfectant
3. In the manufacture of $CHCl_3$, CCl_4, DDT, BHC. (Insecticides) etc.
4. In the manufacture of synthetic plastic such as PVC.
5. Poisonous gas phosgene ($COCl_2$), tear gas (CCl_3NO_2), Mustard gas ($ClC_2H_4SC_2H_4Cl$).

Concept Ladder

Bleaching of flowers by Cl_2 is permanent, while that by SO_2 is temporary.

Rack your Brain

Arrange the following oxoacids of chloride in increasing order of their acidic strength.
HOCl, HOClO, $HOClO_2$, $HOClO_3$

Previous Year's Questions

Which of the following displaces Br_2 from an aqueous solution containing bromide ions?

[AIPMT]

(1) I_2 (2) I_3^-
(3) Cl_2 (4) Cl^-

6. Refrigerant such as freon (CCl_2F_2).

7. Extraction of Metals like Au and Pt.

Hydrogen Chloride (Hydrochloric Acid) HCl :

Preparation :

1. HCl is prepared by dissolving hydrogen chloride gas in water.

2. Hydrogen chloride gas required in turn can be prepared by the following methods.

$$H_2\,(g) + Cl_2\,(g) \xrightarrow{\text{sunlight}} 2\,HCl\,(g)$$

HCl gas can also be obtained by burning hydrogen in chlorine.

Laboratory Method :

1. In the laboratory HCl is prepared by mixture of NaCl and conc. H_2SO_4

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$$

2. HCl(g) is dried by passing through cone, H_2SO_4 collected by upward displacement of air.

Properties :

1. HCl is a covalent compound but when dissolved in H_2O it ionizes to form hydrogen ions or chloride ions or hydronium ions.

$$HCl(g) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-$$

2. It reacts with metal to form their respective chlorides and H_2(g).

$$\text{Metal} + HCl \longrightarrow \text{Metal} + \text{Hydrogen chloride}$$

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

Reaction with NH_3 :

$$NH_3 + HCl \longrightarrow NH_4Cl$$

1. It reacts with metal carbonates, bicarbonates, sulphides, sulphites, thiosulophates and nitrites

Concept Ladder

HCl also known as muriatic acid , is an aqueous solution of hydrogen chloride. It is a colourless solution with a distinctive pungent smell.

Rack your Brain

Explain why ClF_3 exists but FCl_3 does not?

Previous Year's Questions

Elements of which the following groups will form anions most readily?

[AIPMT]

(1) Oxygen family
(2) Nitrogen family
(3) Halogens
(4) Alkali metals

etc to form their respective chlorides.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

$$NaHSO_3 + HCl \longrightarrow NaCl + H_2O + SO_2$$

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

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$$

2. It is used for dissolving noble metals like Au, Pt etc.

$$3Pt + 16H^+ + 4NO_3^- + 12Cl \longrightarrow 3PtCl_4^{2-} + 4NO + 8H_2O$$

$$Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$

Uses :

1. In the preparation of chlorides, chlorine, aqua-regia etc.
2. To manufacture glucose from corn strach.
3. In medicine and in galvanizing.
4. In the production of dyes, paints, photographic chemicals etc.

Interhalogen Compounds :

1. These compounds are regarded as halides of more electropositive (i.e. less electronegative) halogens.

Concept Ladder

As chlorine is second most electronegative element in the periodic table, it can form compounds as carbonates, bicarbonates, sulphides and nitrates.

Rack your Brain

Write the components used in the formation of aquaregia.

Q.14 How can you prepare Cl_2 from HCl and HCl from Cl_2. Write reactions only.

A.14 HCl can be oxidised to Cl_2 by a number of oxidising agents such as MnO_2, $KMnO_4$, $K_2Cr_2O_7$, etc.

$$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + Cl_2 + 2\,H_2O$$

Cl_2 can be reduced to HCl by its reaction with H_2 in presence of diffused sun-light.

$$H_2 + Cl_2 \xrightarrow{\text{Diffused sunlight}} 2HCl$$

or $Cl_2 + H_2S \longrightarrow 2\,HCl + S$

HOCl/HClO Hypochlorous acid	$HClO_2$ Chlorous acid	$HClO_3$ Chloric acid	$HClO_4$ Perchloric acid
General characterlstlcs			
Very weak acid Only known in aqueous solution. NaOCl is Well know Unstable	weak acid (stronger than HClO) Only exists in solution.	Known as salts and in aqueous Not very stable and detonates of heated $2HClO_3 \longrightarrow 2ClO_2 + H_2O + 1/2O_2$	One of the strongest acids known. Both salts and acids are well known, can infact be isolated in anhydrous from ($HClO_2 . 2H_2O$)
Preparation			
Shake halogen with freshly precipitated HgO $2HgO + H_2O + 2Cl_2 \longrightarrow HgO.HgCl_2 + 2HOCl$	$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + H_2ClO_2$ $BaSO_4$ is filtered off	$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_3$ $BaSO_4$ is filtered off	$Ba(ClO_4)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_4$
NaOCl is made industrially by electrolysis of cold brine (NaOH solution) or by : $1/2X_2 + OH^- \xrightarrow[<RT]{Cold} XO^- + HX$	Chlorites are made from ClO_2 and NaOH ClO_2 and Na_2O_2 (See Chlorine Dioxide)	Chloraets are formed by : $X_2 + OH^- \xrightarrow{Hot} XO_3^- + X^-$	$NaClO_3 + H_2O \xrightarrow{Electrolysis} NaClO_4 + H_2$
Reactions			
$\underset{+1}{3XO^-} \xrightarrow{hot} \underset{+V}{2XO_3^-} + \underset{+1}{X^-}$	$ClO_2^- \xrightarrow{OH^-} stable$	$ClO_3^- \xrightarrow{400°C} stable$	$2HClO_4 \xrightarrow[-H_2O]{P_2O_5} Cl_2O_7$
$2HClO \xrightarrow{-H_2O} Cl_2O$	$2ClO_2 \xrightarrow[\Delta]{2OH^-} ClO_3^- + ClO_2^- + H_2O$ makes solution yellow $2HClO_2 \xrightarrow{-H_2O} Cl_2O_3$	$ClO_3^- \xrightarrow{low\ temp} ClO_4^- + Cl^-$ $2HClO_3 \xrightarrow{-H_2O} Cl_2O_5$	
Uses			
Used in bleaching and as a disinfectant (especially NaOCl)	Chlorites are also used as bleaches	Chlorates are used to make fire works, matches, $NaClO_3$ is a powerful weedkiller: Solid $NaClO_3$ has also been used to make bombs.	Half of perchlorate is used as NH_4ClO_4 in shuttle launch. $KClO_4$ is used in fireworks and flared.

2. Types of interhalogen compound :

AB type	:	ClF, BrF, BrCl, ICl, IBr
AB_3 type	:	ClF_3, BrF_3, ICl_3
AB_5 type	:	BrF_5, IF_5
AB_7 type	:	IF_7

Preparation :

1. $Cl_2 + F_2 \xrightarrow{437K} 2\ ClF$
2. $Cl_2 + 3F_2 \xrightarrow{573K} 2\ ClF_3$
3. $I_2 + 3Cl_2 \longrightarrow 2\ ICl_3$
4. $Br_2 + 3F_2 \longrightarrow 2\ BrF_3$
5. $I_2 + Cl_2 \longrightarrow 2\ ICl$
6. $Br_2 + 5SF_2 \longrightarrow 2\ BrF_5 + 5S$

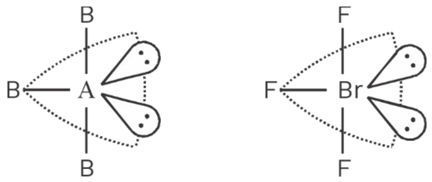
Structure :

1. AB Type :

The central halogen, i.e., the bigger halogen atom (A) is sp^3 hybridised. The molecules are linear due to the presence of three lone pairs on A atom.

2. AB_3 Type :

The central halogen atom is sp^3d hybridised. The molecules have a bent T-shaped geometry instead of trigonal bipyramidal due to the presence of two lone pairs.



Structure of BrF_3

3. AB_5 Type :

The central halogen atom is sp^3d^2 hybridised leading to a square pyramidal geometry instead of octahedral geometry as there present 1 lone pair on the halogen atom A.

Concept Ladder

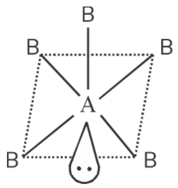
In general interhalogen compounds are more reactive than pure halogens except fluorine because A—B bond is weaker than B—B bond.

Rack your Brain

Why interhalogen compounds are strong oxidizing agents.

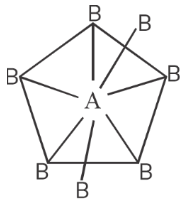
Concept Ladder

Four types of interhalogen compounds are :
(i) XX' : ClF, BrF, BrCl etc.
(ii) XX'_3 : ClF_3, BrF_3, IF_3 etc.
(iii) XX'_5 : ClF_5, BrF_5, IF_5 etc.
(iv) XX'_7 : IF_7



4. AB_7 Type :

The central halogen atom (A) is sp^3d^3 hybridised and the molecules shows the expected pentagonal bipyramidal shape since there are no lone pairs.



Characteristics of Interhalogen Compound :

1. These may be gases (ClF, BrF, ClF_3, IF_7), liquids (BrF_3, BrF_5, IF_5) or solids (ICl, IBr, IF_3, ICl_3).

2. The interhalogen molecules are diamagnetic in nature.

3. With increase in ΔEN between A and B, thermal stability of AB type compounds increases. The more polar is the A – B bond and hence greater is the thermal stability.

   IF > BrF > ClF > ICl > IBr > BrCl

4. A_2 or B_2 molecules are less reactions than AB type compounds. Since AB bond is weaker than A–A & B–B bonds. These order of reactivity of some interhalogen compounds has been found as : $ClF_3 > BrF_5 > IF_7 > BrF_3 > IF_5 > BrF$

6. Hydrolysis gives halogen acid and oxyhalogen acid. The oxyhalogen acid is of larger halogen atom.

$$AB + H_2O \longrightarrow HAO + HB$$

$$ICl + H_2O \longrightarrow HIO + HCl$$

Concept Ladder

The interhalogen compounds of iodine and fluorine are thermally more stable while the compounds of iodine and chlorine or iodine and bromine are less stable.

Rack your Brain

Write the general formula used for formation of interhalogen compounds.

Concept Ladder

AB type interhalogen compounds are ClF, BrF, BrCl, ICl, IBr.

$$ICl_3 + 2H_2O \longrightarrow HIO_2 + 3HCl$$

$$BrF_5 + 3H_2O \longrightarrow HBrO_3 + 5HF$$

$$IF_7 + 6H_2O \longrightarrow H_5IO_6 + 7HF$$

7. The interhalogens of AB type add at olefinic double bond sites.

$$-CH = CH - + ICl \longrightarrow -CHI - CHCl-$$

Uses Of Interhalogen Compounds :

1. ClF_3 and BrF_3 are also used as fluorinating agents.

2. Interhalogen compound are used for the preparation of polyhalides.

3. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$$U_{(s)} + 3ClF_{3(l)} \longrightarrow UF_{6(g)} + 3ClF_{(g)}$$

4. Interhalogen compounds can be used as non-aqueous solvents. BrF_3 is also used as Lewis acid.

5. Interhalogen compounds of the type XX' (particularly ICl) are used as halogenating agent. ICl is used in the estimation of iodine number of fats and oils.

Concept Ladder

Interhalogen compounds are gases or liquids, volatile and create fume in air. These can be hydrolysed and act as oxidising agents.

Rack your Brain

What are polyhalides? Write some examples of polyhalides in which 2 or 3 different halogens are present.

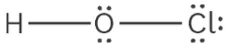
Q.15 Why interhalogens are more reactive than halogens?

A.15 This is because the bond in the interhalogen (X—X') is weaker than X—X and X'—X' bond in the halogens. This is due to less effective overlapping between orbitals of dissimilar atoms than those between similar atoms. However, due to low bond dissociation enthalpy of F—F bond, F_2 is more reactive than its interhalogen compounds.

Oxyacids or Oxoacids of Halogens :

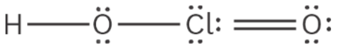
Halogen	Hypohalous acids (x = +1)	Holous acid(x = +3)	Halic acid (x = +5)	Perhalic acid (x = +7)
Cl	HClO	$HClO_2$	$HClO_3$	$HClO_4$
Br	HBrO	—	$HBrO_3$	—
I	HIO	—	HIO_3	HIO_4

Structure : Central halogen atom of all oxyacids of halogen is sp^3 hybridised.

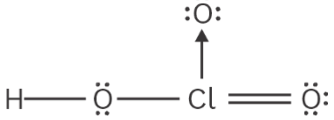


Hypochlorous acid (HClO)

Or



Chlorous acid $(HClO_2)$



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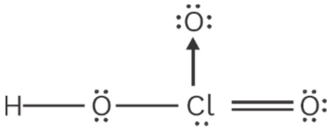
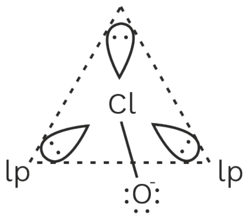


Chloric acid $(HClO_3)$



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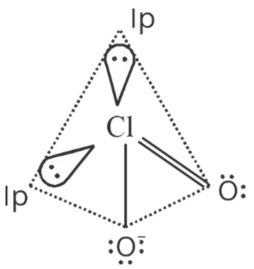

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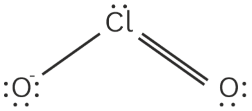
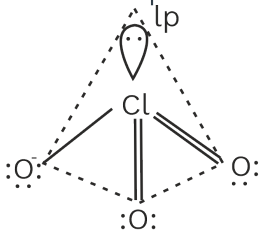


Linear shape of ClO^- ion.

Angular shape of ClO_2^- ion.



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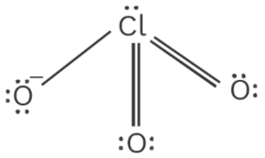
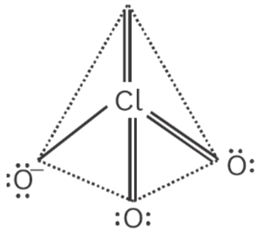


Trigonal pyramidal shape of ClO_3^- ion.



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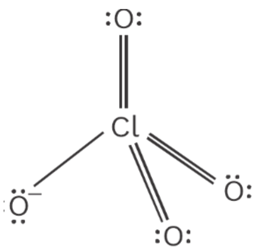


Tetrahedral shape of ClO_4^-

Oxidising power of these oxyacids decreases as the oxidation number of halogen increases.

$HClO > HClO_2 > HClO_3 > HClO_4$

Thermal stability increases with increase in oxidation state of halogen.

$HClO < HOClO < HOClO_2 < HOClO_3$

Hydra – Acids

I Hydrofluoric acid [H_2F_2 or HF] :

1. HF is a colourless, corrosive liquid with pungent smell. It attacks glass and is thus stored in wax bottles or gutta percha bottles.

$$SiO_2 + 6HF \longrightarrow [SiF_6]^{2-} + 2H^+ + 2H_2O$$

(This is also used for etching glass.)

HF is kept in laboratory in KF giving $K^+[F—H—F]^-$ ions.

2. H_2 and F_2 combine with each other very violently even in dark to form HF. Thus special methods are employed in its preparation.

Industrially it is made by heating CaF_2 with strong H_2SO_4. The reaction is endothermic, hence the need for heating as SiO_2 impurities are removed from CaF_2 otherwise they consume much of HF produced.

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

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

$$SiF_4 + 2HF_{(aq)} \rightarrow H_2[SiF_6]$$

3. Two thirds of HF produced are used to make chlorofluoro carbons (Freons) used as refrigerating fluids.

$$CCl_4 + 2HF \xrightarrow{\text{anhydrous conditions} SbCl_5} \underset{\text{freon}}{CCl_2F_2} + 2HCl$$

Concept Ladder

Unlike other halogen acids, hydro fluoric acids attacks silica and glass. With silica it forms silicon tetrafluoride and hydro thio salicylic acid.

Rack your Brain

Why on heating H_2F_2 with a mixture of MnO_2 and H_2SO_4 no gas is involved?

Previous Year's Questions

Which of the statements given below is incorrect?

[NEET-2015]

(1) O_3 molecule is bent.
(2) ONF is isoelectronic with O_2N^-.
(3) OF_2 is an oxide of fluorine.
(4) Cl_2O_7 is an anhydride of perchloric acid.

4. In liquid form HF is used as a non - aqueous solvent.

$$2HF(l) \rightarrow [H_2F]^+ + F^-$$

II. Hydrochloric acid [HCl]

1. At one time HCl was made exclusively by ‘salt cake’ method.

$$\underset{\text{Rock salt}}{NaCl} + \text{conc.}H_2SO_4 \xrightarrow{\Delta} HCl(g) + NaHSO_4$$

$$NaHSO_4 + NaCl \rightarrow HCl(g) + Na_2SO_4$$

2. Highly pure HCl is made by bringing H_2 and Cl_2 in a special combustion chamber. (Direct combination is explosive)

$$Cl_2 + H_2 \rightarrow 2HCl$$

3. In laboratory :

$$2NH_4Cl + \underset{\text{conc.}}{H_2SO_4} \rightarrow 2HCl + (NH_4)_2SO_4$$

4. Cl cannot be dried over P_2O_5 or quick lime because it reacts with them:

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

$$P_4O_{10} + 3HCl \rightarrow POCl_3 + 3HPO_3$$

Hence it is dried by passing through conc. H_2SO_4

5. HCl(g) is colourless, weak reducing agent (is oxidized by strong oxidising agents like MnO_2, $KMnO_4$, $K_2Cr_2O_7$) and highly soluble in water.

III HBr and HI

1. They are prepared by reaction of phosphoric acid on metal bromides or iodides (similar to salt cake process)

$$NaI + H_3PO_4 \rightarrow HI + NaH_2PO_4$$

Concept Ladder

HBr and HI cannot be prepared by heating bromides and iodides with concentrated H_2SO_4 while HCl can.

Rack your Brain

How HCl is considered to be strong acid.

Previous Year’s Questions

Bleaching powder reacts with a few drops of conc. HCl to give

[AIPMT]

(1) chlorine
(2) hypochlorous acid
(3) calcium oxide
(4) oxygen

2. The usual laboratory process is :

$$\underset{\text{Red}}{2P} + 3Br_2 \longrightarrow 2PBr_3 \longrightarrow 6HBr + 2H_3PO_3$$

$$\underset{\text{Red}}{2P} + 3I_2 \longrightarrow 2PI_3 \xrightarrow{+6H_2O} 6HI + 2H_3PO_3$$

3. HBr is not very stable and acts as a strong reducing agent while HI is least stable and thus a more powerful reducing agent.

$$2HNO_3 + 2HI \longrightarrow 2NO_2 + I_2 + 2H_2O$$

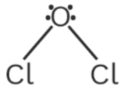
$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O$$

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

Oxides

The bonds in oxides are largly covalent as there is only a small difference in electronegativity between the halogens and oxygen. Most halogen oxides are unstable and tend to explode when subjected to shock. Stability of oxides increases down the group and higher oxidation states are more stable than lower oxidation states.

I Dichloro oxide [Cl_2O]



Cl_2O is a yellow – brown gas which condenses to an orange liquid (bp = 2°C). It is the anhydride of hypochlorous acid (HClO).

1. Cl_2O is prepared by passing dry chlorine over freshly precipitated mercuric oxide.

$$HgO + \underset{\text{dry}}{2Cl_2} \longrightarrow HgCl_2 + Cl_2O$$

2. It is soluble in water

$$Cl_2O + H_2O \rightleftharpoons \underset{\text{Hypochlrous acid}}{2HOCl(aq)}$$

Concept Ladder

HF is the weakest acid among hydro halo acids.
$HF < HCl < HBr < HI$

Rack your Brain

With what neutral molecule ClO^- is isoelectronic?

Previous Year's Questions

The correct order of increasing bond angles in the following species is :

[AIPMT]

(1) $Cl_2O < ClO_2 < ClO_2^-$
(2) $ClO_2 < Cl_2O < ClO_2^-$
(3) $Cl_2O < ClO_2^- < ClO_2$
(4) $ClO_2^- < Cl_2O < ClO_2$

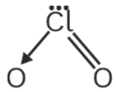
3. It explodes in presence of NH_3 or a reducing agent or on heating.

$$3Cl_2O + 10NH_3 \longrightarrow 2N_2 + 6NH_4Cl + 3H_2O$$

4. It is a strong oxidising agent.

$$Cl_2O + 2HCl \longrightarrow 2Cl_2 + H_2O$$

II Chlorine Dioxide [ClO_2]



It is a yellow gas, condenses to deep red liquid, explodes above −40°C and in presence of reducing agents. It is paramagnetic being an odd electron molecule but does not dimerises as the odd electron is delocalised.

1. It explodes when mixed with reducing agents. The safest laboratory preparation is form sodium chlorate and oxalic acid as this automatically dilutes the gas with CO_2.

$$2NaClO_3 + 2(COOH)_2 \longrightarrow 2ClO_2 + 2CO_2 + (COONa)_2 + 2H_2O$$

2. $2ClO_2 + H_2O \longrightarrow \underbrace{HClO_3 + HClO_2}_{\text{dark green solution}} +$ heat

3. It is used to manufacture $NaClO_2$ which is used for bleaching paper textile.

$$2\,ClO_2 + 2\,NaOH + H_2O_2 \longrightarrow 2\,NaClO_2 + O_2 + 2\,H_2O$$

$$2ClO_2 + 2\,NaOH \longrightarrow \underset{\text{chlorite}}{NaClO_2} + \underset{\text{chlorate}}{NaClO_3} + H_2O$$

4. ClO_2 is a powerful oxidising about and a bleaching agent and is used to purify water.

Concept Ladder

ClO_2 is a powerful oxidising and bleaching agent. It has an angular structure with O—Cl—O bond angle of 117.6°. The molecule is supposed to contain a 3 electrons bond.

Rack your Brain

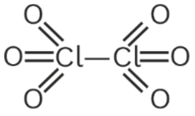
Write equation when ClO_2 reacts with alkalies.

Q.16 What happens when Cl_2 is passed through a hot concentrated solution of a base like $Ba(OH)_2$?

A.16 On treatment with $Ba(OH)_2$, Cl_2 undergoes disproportionation to form barium chloride, $Ba(ClO_3)_2$.

$$6\,Ba(OH)_2 + 6\,\overset{0}{Cl_2} \xrightarrow{\text{Hot}} 5\,Ba\overset{-1}{Cl_2} + Ba(\overset{+5}{Cl}O_3)_2 + 6\,H_2O$$

III Dichlorine Hexoxide [Cl_2O_6]



The exact structure is unknown

It is a dark red liquid which freeze at –180°C to a yellow solid. It is diamagnetic in nature due to absence of unpaired electrons and exists as a dimer. The structure is guessed to be as shown but the exact structure is unknown.

1. It is obtained from ClO_2 and O_3.

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2$$
$$2ClO_3 \rightleftharpoons Cl_2O_6$$

2. Hydrolysis with water or alkali gives chlorate and perchlorate

$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$
$$Cl_2O_6 + 2NaOH \longrightarrow \underset{\text{Chlorate}}{NaClO_3} + \underset{\text{Perchlorate}}{NaClO_4} + H_2O$$

3. It is a strong oxidising agent which explodes on contact with grease.

4. Reaction with anhydrous HF is reversible:

$$Cl_2O_6 + HF \rightleftharpoons FClO_2 + HClO_4$$

IV Dichlorine Heptoxide [Cl_2O_7]

Cl_2O_7 is a colourless oily liquid which is moderately stable and less reactive than others. It is the only exothermic oxide of Cl and the anhydride of perchloric acid $HClO_4$. It is anhydride of perchloric acid and made by dehydrating perchloric acid with P_2O_5 or H_3PO_4.

$$2HClO_4 \xrightarrow{P_4O_{10}} Cl_2O_7 + H_2O$$

Concept Ladder

In vapour state, Cl_2O_6 exists as ClO_3 molecule which is para magnetic while in liquid state it is in dimeric form having even no. of electron hence diamagnetic in nature.

Previous Year's Questions

Which one of the following oxides is expected to exhibit paramagnetic behaviour?

[AIPMT]

(1) CO_2
(2) SiO_2
(3) SO_2
(4) ClO_2

Bleaching Powder:

Bleaching powder is actually written as $Ca(OCl)_2.Ca(OH)_2.CaCl_2.2H_2O$. It is a pale-yellow powder having a strong smell of chlorine and soluble in water. However, a clear solution is never formed due to the presence of impurities.

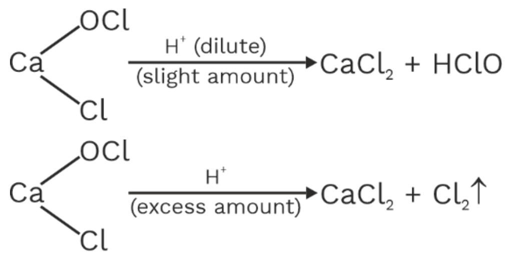
Preparation:

It is made by passing Cl_2 into slaked lime.

$$Ca(OH)_2 + Cl_2 \rightarrow Ca(OCl)Cl + H_2O$$

Chemical Properties:

1. Bleaching action



$$Ca(OCl)Cl \xrightarrow[\text{(slight amount)}]{H^+ \text{ (dilute)}} CaCl_2 + HClO$$

$$Ca(OCl)Cl \xrightarrow[\text{(excess amount)}]{H^+} CaCl_2 + Cl_2\uparrow$$

2. Oxidising action

$$CaOCl_2 + H_2S \rightarrow CaCl_2 + H_2O + S$$

3. It converts acetone into chloroform.

Concept Ladder

Bleacing powder is also termed as calcium chloro hypochlorite, because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid.

Rack your Brain

Name the porcesses used for manufacturing of bleaching powder?

Q.17 Halogens have maximum negative electron gain enthalpy. Explain why?

A.17 Halogen have high effective nuclear charge due to its smallest size in their respective periods. Therefore, they readily accept one electron to acquire the stable electronic configuration of the nearest noble gas. In other words, a halogen atom can accepts an electron therefore larger amount of energy is released, thus halogens have max imum negative electron gain enthalpies.

Group 18 (Noble gases)

Introduction :

1. The elements Helium, Neon, Argon, Krypton, Xenon and Radon constitute group 18 (or zero) of the periodic table.

2. All the noble gases, except He have eight electrons (closed shell) with electronic configuration ns^2np^6 where n = 2 to 6. Helium, however has only two electrons and hence its electronic configuration is $1s^2$.

Concept Ladder

The zero group occupies the intermediate position between the elements of VII A and I A groups.

Electronic Configuration :

Element	Symbol	Atomic Number	Electronic Configuration
Helium	He	2	$1s^2$
Neon	Ne	10	$1s^2 2s^2 2p^6$ OR $[He]\ 2s^2 2p^6$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$ OR $[Ne]\ 3s^2 3p^6$
Krypton	Kr	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ OR $[Ar]3d^{10} 4s^2 4p^6$
Xenon	Xe	54	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$ OR $[Kr]\ 4d^{10} 5s^2 5p^6$
Radon	Rn	86	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$ OR $[Xe]\ 4f^{14} 5d^{10} 6s^2 6p^6$

Occurrence :

1. Except radon (radioactive) all noble gases are present in the atmosphere throughout the universe in the free state to the extent of 1% by volume. Helium is also found as natural gas **Ramsay** discovered. He in cleveite (a uranium ore) i.e. on the earth.

2. The gas is obtained when these minerals are either heated at 1273 K in vacuum or heated with H_2SO_4. Helium and argon are also found in the dissolved gases of some mineral.

Rack your Brain

Why noble gases are monoatomic in nature?

3. Argon is the most abundant noble gas in the atmosphere (0.934% by volume).

The relative abundances of other gases in the atmosphere are :

He = 5.24×10^{-4}, Ne = 1.82×10^{-3}

Ar = 93.4×10^{-2} , Kr = 1.45×10^{3}

and Xe = 8.70×10^{-6} % by volume

Concept Ladder

Noble gases are also termed as inert gases or the rare gases of the atmosphere.

Physical Properties of Noble Gases

1. Physical state :

All the elements of group 18 are colourless, odourless and tasteless.

2. Atomic radii :

The atomic radii of noble gases increases on moving down-the group and their atomic radii correspond to the vander waal's radii.

Order : He < Ne < Ar < Kr < Xe < Rn

Rack your Brain

Explain why electron gain enthalpy of noble gases is zero?

3. Melting point and boiling point :

M.P. and B.P. increases from He to Rn, because of increase in magnitude of vander waal's forces.

Order : He < Ne < Ar < Kr < Xe < Rn

4. Ionisation energy and electron gain enthalpy :

Noble gases have stable ns^2 np^6 fully filled electronic configuration so, these have no tendency to add or lose electron. Therefore ionisation energy of noble gas is very high. On the other hand their electron gain enthalpy is zero.

Order : He > Ne > Ar > Kr > Xe > Rn

Concept Ladder

Noble gases have lowest boiling point in comparision to the elements of their respective periods.

5. Solubility in water :

They are slightly soluble in water their solubility generally increases with the increase in atomic number down the group.

Order : He < Ne < Ar < Kr < Xe < Rn

6. Liquification of gases :

It is difficult to liquify inert gases as their atoms are holded by weak VWF.

7. Ease of liquification increases from He to Rn.

8. He has the lowest B.P. (4.18 K) of any known substances. The ease of liquification increases from He to Rn due to increase in inter-molecular forces.

9. The zero group of the periodic table constitutes Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xenon (Xe) and Radon (Rn).

10. Noble gases do not have chemical reactivity and at ordinary temperature they are present in gaseous form and therefore, these are called **Inert gases**.

Order : He < Ne < Ar < Kr < Xe < Rn

11. Ability to diffuse :

All the noble gas are able to diffuse through glass, rubber, plastic, material and some metals.

Order : He > Ne > Ar > Kr > Xe > Rn

Uses Of Noble Gases :

Helium :

1. Helium is a non–inflammable and light gas therefore, it is used in filling balloons for meteorological observations.
2. It is also used in gas cooled nuclear reactors.
3. Liquid helium (boiling point 4.2 K) is used as Cryogenic agent for carrying out various experiments at low temperatures.

Neon :

1. Ne is used in fluorescent bulbs and discharge tubes for advertisement display purposes.

Concept Ladder

Helium forms no real chemical compounds. Among noble gases only Xenon forms chemical compounds.

Rack your Brain

Noble gases can form compounds only with two elements. Name them?

Concept Ladder

Helium — oxygen mixture is used for artificial respiration in deep seas diving and in treatment of asthma.

2. Neon is also used in televisions set, spark plug, warning signals etc.

3. Glow of different coloured 'neon signs' can be produced by mixing neon with other gases.

Argon :

1. Ar is mainly used to provide an inert atmosphere high temp. metallurgical processes (alloys or arc welding of metals) and for filling electric bulbs. It is also used in the laboratory to handle substances that are air sensitive.

2. This gas is used in gas chromatography.

3. It is mixed with neon to obtain different coloures in neon sign lamps.

Krypton And Xenon :

1. Kr and Xe are used in light bulbs designed for special purpose.

2. These are also used for high speed photography.

3. Krypton-85 is used to measure thickness of sheets of metals and plastics.

Radon :

1. Radon being radioactive is used in nuclear processes.

2. It is also used in treatment of cancer and other tumors.

3. It is used for detecting dislocations and defects in metals and other solids.

Concept Ladder

The two methods used for preperation of argon gas is Ramsay method and Rayleigh method.

Previous Year's Questions

Identify the incorrect statement, regarding the molecule XeO_4 :

[NEET-2013]

(1) XeO_4 molecule is square planar.
(2) There are four $p\pi$-$d\pi$ bonds.
(3) There are four sp^3-p, σ bonds.
(4) XeO_4 molecule is tetrahedral.

Q.18 Why do not helium, neon and argon form chemical compounds?

A.18 Since the ionization enthalpies of He, Ne and Ar are sufficiently higher than those of oxygen and fluorine.

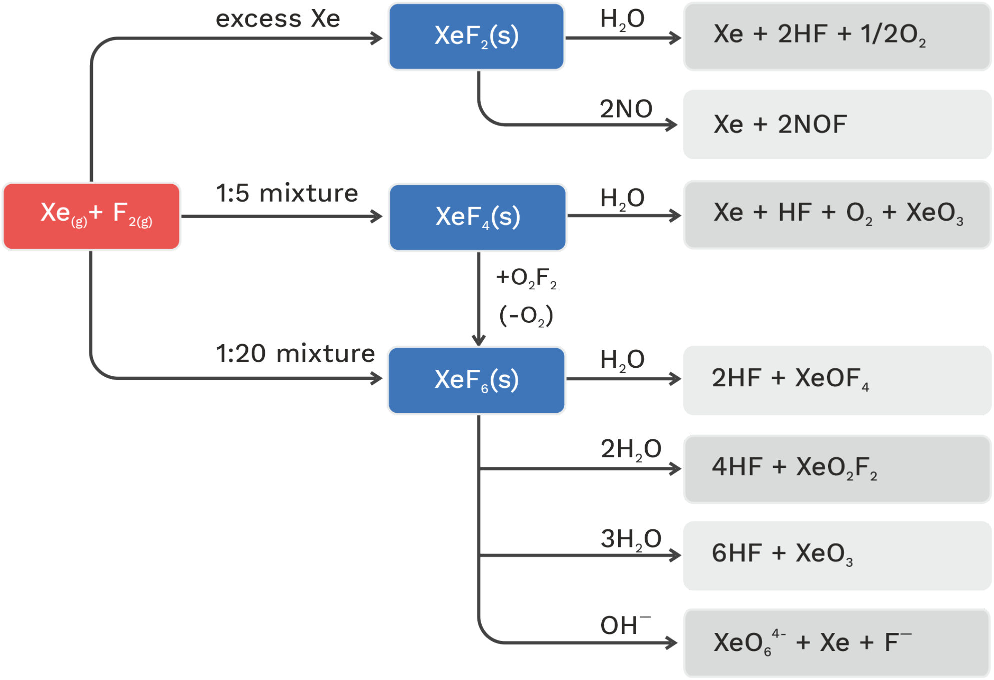
Chemistry of Xenon

Xe reacts directly only with F_2. Oxygen compounds can be obtained from the fluoride.

1. Xenon fluorides are white solid which are extremely powerful oxidising and fluorinating agents. They sublime readily at room temperature and are hydrolysed even by traces of water. Thus, they are stored in Ni containers.

Concept Ladder

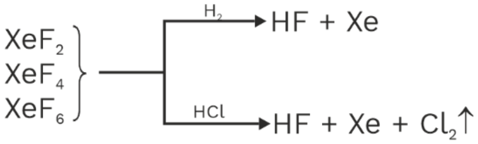
Structures of Xenon fluorides cannot be explained by valence bond approach.



XeO_3 is a hygroscopic white explosive solid. $XeOF_4$ is a colourless volatile liquid.

$$2NaHXeO_4 \xrightarrow{+2OH^-} Na_4XeO_6 + Xe + 2H_2O + O_2$$

2. All xenon fluorides react with hydrogen and oxidise Cl^- to Cl_2. I^- to I_2 and Ce(III) to Ce(IV)



3. Xenon fluorides reacts with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoro anions.

$$XeF_2 + PF_5 \rightarrow [XeF]^+[PF_6]^-$$

$$XeF_4 + SbF_5 \rightarrow [XeF_3]^+[SbF_6]^-$$

$$XeF_4 + MF \rightarrow M^+[XeF_7]^-$$

$$(M = Na, K, Rb, Cs)$$

4. Xe compounds show a variety of shapes:

XeF_2 is linear, XeF_4 is square planar, XeF_6 is a capped octahedron, XeO_3 is pyramidal, $XeOF_4$ is square pyramidal, XeO_2F_2 is see saw shaped, $XeOF_2$ is bent T – shaped, XeO_4 is tetrahedral, XeO_3F_2 is trigonal bipyramidal and $[XeO_6]^{4-}$ ion is octahedral.

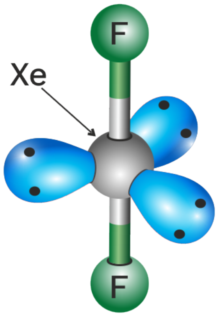
Previous Year's Questions

Which compound has planar structure?

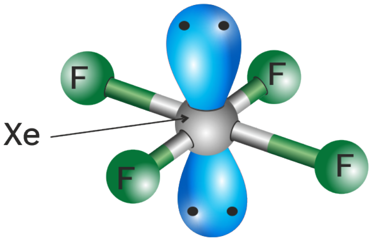
[AIPMT]

(1) XeF_4 (2) $XeOF_2$

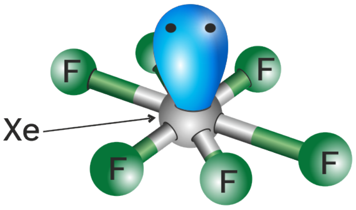
(3) XeO_2F_2 (4) XeO_4



XeF: Linear



XeF_4: Square planar



XeF_6: Distorted octahedral

Q.19 What prompted Bartlett to the discovery of noble gas compounds?

A.19 Since PtF_6 oxidises O_2 to O_2^+, Bartlett thought that PtF_6 should also oxidise Xe to Xe^+ because the ionization enthalpies of O_2 (1175 kJ mol^{-1}) and Xe (1170 kJ mol^{-1}) are quite close.

Q.20 In the preparation of H_2SO_4 by Contact Process, why is SO_3 not absorbed directly in water to form H_2SO_4?

A.20 A dense fog of H_2SO_4 is formed which is difficult to condense.

Q.21 PH_3 forms bubbles when passed slowly in water but NH_3 dissolves. Explain why?

A.21 Due to high electronegativity (3.0) and small size of N, NH_3 forms H-bonds with water and hence it is water soluble. Whereas, due to its lower electronegativity (2.1) of P and its bigger size than N, PH_3 does not form H-bonds with H_2O. As a result, it does not dissolve in H_2O and hence escapes as bubbles.

Q.22 In PCl_5, phosphorus is in sp^3d hybridised state but all its five bonds are not equivalent. Justify your answer with reason.

A.22 Since each axial P—Cl bond is repelled by three bond pairs and each equatorial P—Cl bond is repelled by only two bond pairs, therefore, axial bonds are longer (240 pm) than equatorial bonds (202 pm). Thus, all the five P—Cl bonds in PCl_5 are not equivalent.

Q.23 Why is nitric oxide paramagnetic in gaseous state but the solid obtained on cooling it is diamagnetic?

A.23 Nitric acid has 15 electrons i.e. it has one unpaired electron and hence it is paramagnateic in the gaseous state. but in both solid as well as in liquid it exists as a dimer and hence is diamagnetic in nature.

Q.24 Give the reason to explain why ClF_3 exists but FCl_3 does not exist.

A.24 Because of bigger size, Cl can accommodate three small F atoms around it while F being smaller cannot accommodate three bigger sized Cl atoms around it.

Q.25 SF_6 is known but SH_6 is not. Why?

A.25 H_2 being a very weak oxidising agent cannot oxidise S to its maximum oxidation state of +6 but in case of fluorine (strongest oxidising agent) it oxidises S to its maximum oxidation state of +6, thus SF_6 is known but SH_6 is not known.

Q.26 The majority of noble gas compounds are those of xenon. Explain.

A.26 Except Rn which is radioactive, Xe has the lowest I.E. among inert gases and therefore it can be easily oxidised by strong oxidising agents like O_2 and F_2. That is why majority of inert gas compounds are those of Xe.

Q.27 Arrange the hydrides of group 17 elements in order of their increasing acid strength.

A.27 As the size of halogen increases down the group from F to I, the bond dissociation energy of the H—X bond decreases. Consequently, the tendency of H—X bond to release a proton in water increases. In other words, the acid strength increases in the order : HF < HCl < HBr < HI.

Q.28 Why does argon not form diatomic molecules like oxygen and nitrogen?

A.28 All the orbitals (which are occupied by the electrons) are completely filled in Ar and hence it has no tendency to share electron with other atom of argon to form diatomic molecules. Oxygen and Nitrogen on the other hand, have unpaired electrons and hence share these electrons with other O and N atom respectively forming O_2 and N_2 molecules

Summary

Group 15 (N-family)

1. Hydrides
  - (i) Bond angle : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
  - (ii) Basic character : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
  - (iii) Boiling point : $PH_3 > AsH_3 > NH_3 > SbH_3 > BiH_3$
  - (iv) Thermal stability : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
  - (v) Reducing character : $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

2. (i) NF_3 is not hydrolysed due to absence of vacant d-orbital.
  - (ii) PF_3 and PF_5 are not hydrolysed because P—F bond is stronger than P—O bond.

3. NF_3 is not lewis base although it has lone pair of e^- due to high electronegativity of fluorine.

4. N_2O is called laughing gas.

5. P_4S_3 is used in strike anywhere matches.

6. Fuming HNO_3 is conc. $HNO_3 + NO_2$.

7. PH_3 Poisonous gas having fish like smell.

8. Holmes signal ships is $CaC_2 + Ca_3P_2$

9. Match box side has red P + Sb_2S_3 + sand. Tip of match stick has $K_2Cr_2O_7$ + S + white P or $KClO_3$ or red Pb.

Group 16 (O–family)

1. Acidic character
  - (i) $SO_2 > SeO_2 > TeO_2 > PoO_2$
  - (ii) $SO < SO_2 < SO_3$

2. (i) Pyrosulphuric acid ($H_2S_2O_7$) has S—O—S linkage.
  - (ii) Marshall's acid has O—O linkage.
  - (iii) $S_2O_8^{2-}$ does not have S—S linkage.

3. Catalyst used in manufacture of H_2SO_4 by Lead Chamber process is oxides of nitrogen and in contact process is V_2O_5.

Group 17 (X–family)

1. Electronegativity : F > Cl > Br > I

2. Bond energy : $Cl_2 > Br_2 > F_2 > I_2$

3. Oxidising power : $F_2 > Cl_2 > Br_2 > I_2$

4. I_2 is soluble in water due to formation fo I^{3-} polyhalide ion.

5. Halide of metals in their higher oxidation states are more covalent than those formed in lower oxidation state. e.g. $SnCl_4$ is more covalent than $SnCl_2$.

6. Hydrogen fluroide is not stored in glass bottles because it reacts with them. It is stored in copper, wax or guttapercha bottle.

7. $KClO_3$ is added in fire crackers as oxidising agent.

8. Tincher of iodine is I_2 + KI dissolved in rectified spirit.

9. F_2 is called super halogen due to its high reactivity.

10. Br_2 or Cl_2 turn moist starch KI paper blue because they displace I_2 from KI and this I_2 reacts with starch to give blue complex.

11. AgF is soluble in water but AgCl, AgBr and AgI are not.

Group 18 (Noble gases)

1. Discovery of noble gases.
He – Lockyer and Janassen
Ar – Lord Rayleigh and Ramsey
Kr – Ramsay and Travers
Xe – Ramsay and Travers
Ra – Doron

2. Only He forms interstitial compounds with metals.

3. O-He (1 : 4) mixture is used for treatment of asthama and for artificial respiration in deep sea diving because unlike N, He is not soluble in blood even at high pressure.