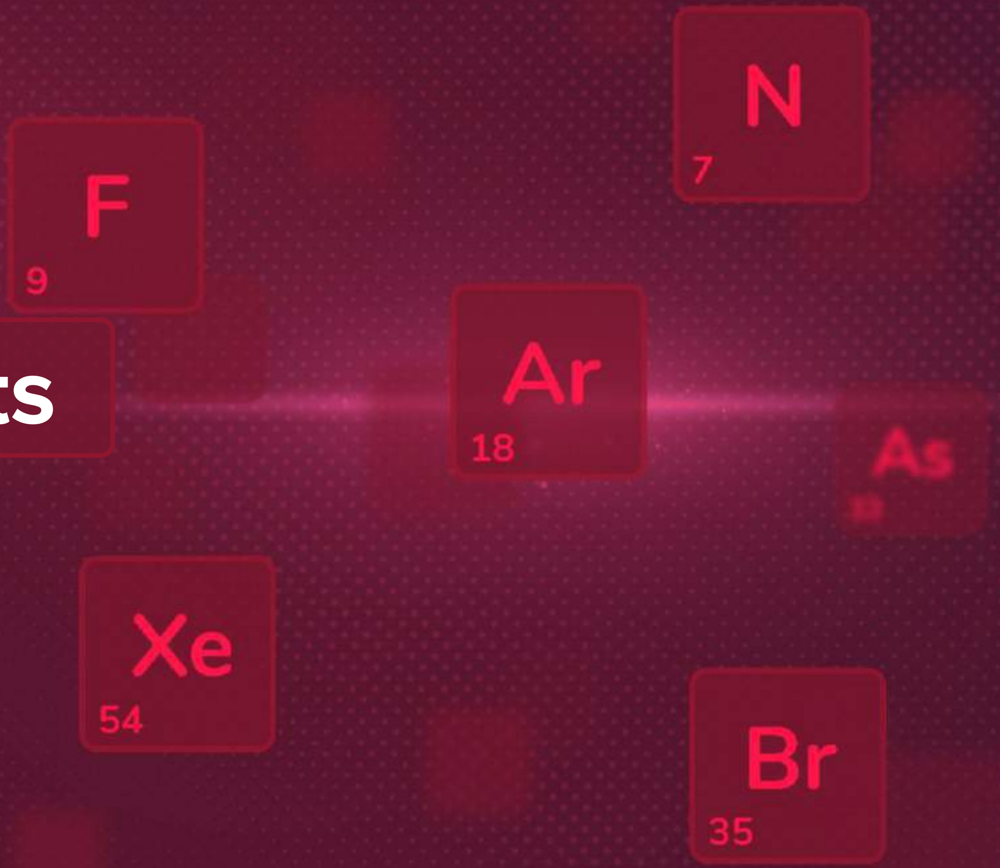
BYJU'S Classes

p-Block Elements



p-Block Elements

Group **13 to 18** of the periodic table of elements constitute the p-block.

Recall!

General **valence shell** electronic configuration

$ns^2\ np^{1-6}$

Except He: $1s^2$

p-Block Elements

The highest oxidation state of p-block elements is equal to **(group number-10).**

p-Block Elements

In groups 13 to 16

Down the group

Stability of
O.S. = Highest group O.S. – 2 ↑

Due to **inert pair effect**

Recall!

Inert pair effect

Due to **poor shielding** of intervening **d & f-**orbitals

Increased Z_{eff} holds **ns^2** electrons **tightly**

ns^2 electrons **do not participate** in bonding

Point to be Noted

The inert-pair effect predominates only in the **sixth period** of the p-block.

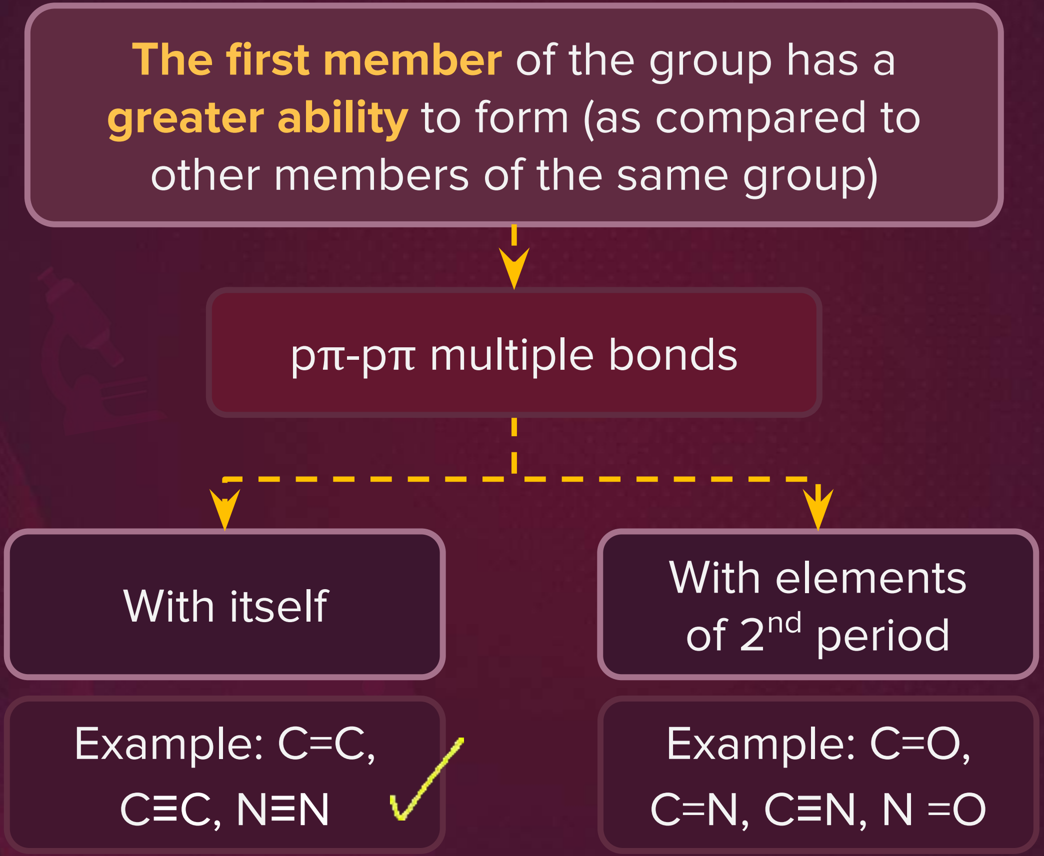
Anomalous Behaviour

The **first member** of each group from 13-17 of the p-block elements

Differs in many respects from the other members of their respective groups.

This is because of the **small size**, **high electronegativity, and absence of d-orbitals**.

Anomalous Behaviour



The first member of the group has a **greater ability** to form (as compared to other members of the same group)

pπ-pπ multiple bonds

With itself

Example: C=C, C≡C, N≡N ✓

With elements of 2^{nd} period

Example: C=O, C=N, C≡N, N =O

p-Block Elements

p-Block elements

- Group 13
- Group 14
- Group 15
- Group 16
- Group 17
- Group 18

p-Block elements

- Group 13
- Group 14
- Group 15
- Group 16
- Group 17
- Group 18

✓

Group 13 and 14 were done in class 11th.

Group 15 Elements

- Nitrogen (N_{7}^{14})
- Phosphorus (P_{15}^{31})

Non-metals

- Arsenic (As_{33}^{75})
- Antimony (Sb_{51}^{122})

Metalloids

- Bismuth (Bi_{83}^{209})

Metals

Group 15 Elements

Nitrogen(N)

Liquid nitrogen uses – Coolant, cold storage, cryotherapy

Phosphorus(P)

Phosphorus over matchstick

When you rub the match stick on the box, you get friction, which means you get heat. This heat causes a small amount of the phosphorus chain to be broken apart and then it starts burning.

Group 15 Elements

Arsenic(As)	Antimony(Sb)	Bismuth(Bi)
Poisonous	Used in batteries, cable	Used in alloys

Group 15 elements

- Occurrence
- Atomic properties
- Physical properties
- Chemical properties

Occurrence

Nitrogen

1. Molecular nitrogen comprises **78%** of earth's atmosphere by **mass**.
2. It is an essential constituent of **proteins** and **amino acids**.
3. It occurs as **sodium nitrate**, $NaNO_3$ (known as Chile saltpetre) & potassium nitrate (Indian saltpetre).

Phosphorus

1

Phosphorus occurs in minerals of the apatite family, **$Ca_9(PO_4)_6.CaX_2$** (X = F, Cl, or OH) which are the main components of phosphate rocks.

Example

Fluorapatite $Ca_9(PO_4)_6.CaF_2$

2

Phosphorus is an essential constituent of **animal and plant matter**.

Organic matter: Source of phosphorus

Other Elements

Arsenic, antimony, and **bismuth** are found mainly as sulphide minerals.

Atomic properties

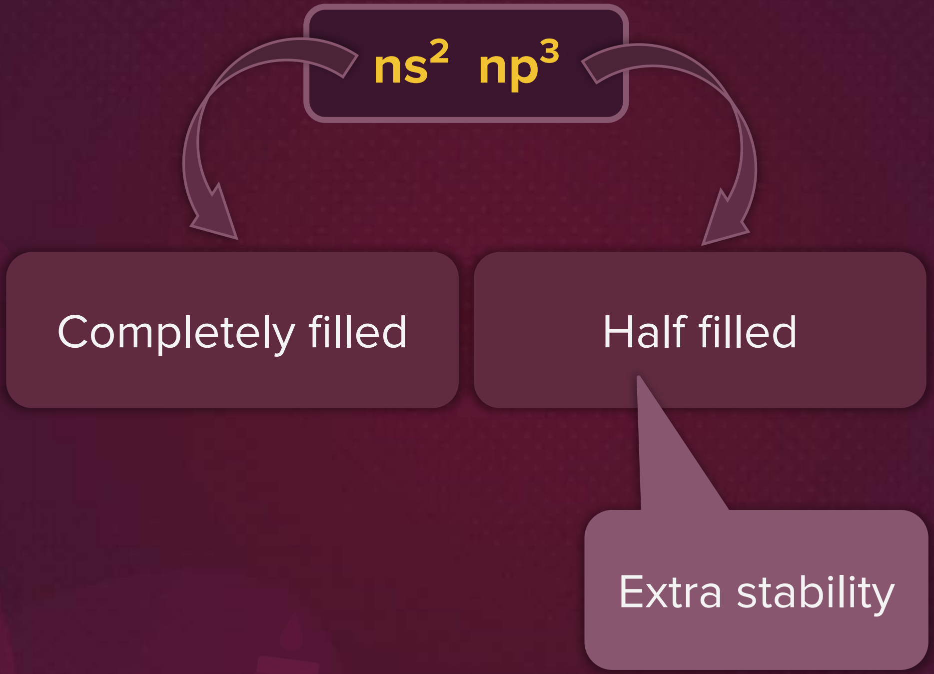
- Electronic configuration
- Covalent & ionic radii
- Ionisation enthalpy
- Electronegativity

Electronic Configuration

Valence shell electronic configuration

$ns^2\ np^3$

Electronic Configuration



$ns^2 \; np^3$

Completely filled

Half filled

Extra stability

Electronic Configuration

Elements	Electronic configuration
Nitrogen	[He] $\underbrace{2s^2\ 2p^3}$
Phosphorus^{15}	[Ne] $\underbrace{3s^2\ 3p^3}$
Arsenic	[Ar] $3d^{10}$ $\underbrace{4s^2\ 4p^3}$
Antimony	[Kr] $4d^{10}$ $\underbrace{5s^2\ 5p^3}$
Bismuth	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^3$

Covalent and Ionic Radii

N < P < As < Sb < Bi

Down the group

Covalent and ionic radii ↑

In a particular oxidation state ✓

Covalent Radii

Down the group

From N to P

There is a **considerable increase**

From As to Bi

Only a **small increase** in covalent radius

Covalent Radii

Reason

Due to the presence of completely-filled

d and f

d or f

in heavier members

Ionisation Enthalpy

Down the group

Atomic size ↑

Ionisation enthalpy ↓

N > P > As > Sb > Bi

Ionisation Enthalpy

Order

Group 15 elements > Group 14 elements

Reason

Group 15 elements → $ns^2\ np^3$

Group 14 elements →

Because of **extra stable half-filled p-orbital** and **smaller size**

Ionisation Enthalpy

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

$\Delta_i H_1$ < $\Delta_i H_2$ < $\Delta_i H_3$ ✓

The order of successive ionisation enthalpies

$$A^{+} \longrightarrow A^{2+} + e^{-}$$

Electronegativity

Down the group

Atomic size ↑

Electronegativity ↓

N > P > As > Sb > Bi

In heavier elements, the difference is not that much pronounced.

Which of the following is the correct order of the specified property?

BOARDS

a $\mathrm{N < P < As > Sb < Bi}$
(First ionisation enthalpy)

b $\mathrm{N > P > As > Sb}$
(Electronegativity)

c $\mathrm{N > P > As > Sb}$
(Covalent radii)

d None of these

In option (a); First ionisation enthalpy is the energy required to remove the outermost electron and on moving down the group, size is increasing and electron is moving away from the nucleus which means the effective nuclear charge is decreasing on the outermost electron and hence, down the group, first ionisation enthalpy decreases regularly which means option (a) is not correct as it has random order here.

In option (b); Electronegativity is the tendency of an atom to attract the shared pair of electrons towards itself and it should regularly decreases on going down the group so option (b) is the correct answer.

In option (c); As we go down the group atomic size increases so covalent radii should increase on going down from N to Sb and hence option (c) is incorrect.

a $N < P < As > Sb < Bi$
(First ionisation enthalpy)

b $N > P > As > Sb$
(Electronegativity)

c $N > P > As > Sb$
(Covalent radii)

d None of these

Hence, option (b) is the correct answer.

Physical Properties

Physical Properties

- Atomicity
- Physical state
- Metallic character
- Boiling points
- Melting points
- Allotropy

1. Atomicity

All the elements of group 15 are **Polyatomic**

Physical Properties

2. State

N_2 → **Diatomic** gas

All other are → **Solids**

Physical Properties

3. Metallic character

It's the tendency to lose electrons and as we are moving down the group, size increase and hence the tendency to lose electrons increases i.e., ionisation enthalpy and electronegativity decreases and hence the metallic character increases.

Down the group

Metallic character ↑

N < P < As < Sb < Bi

Physical Properties

4. Boiling points ▷

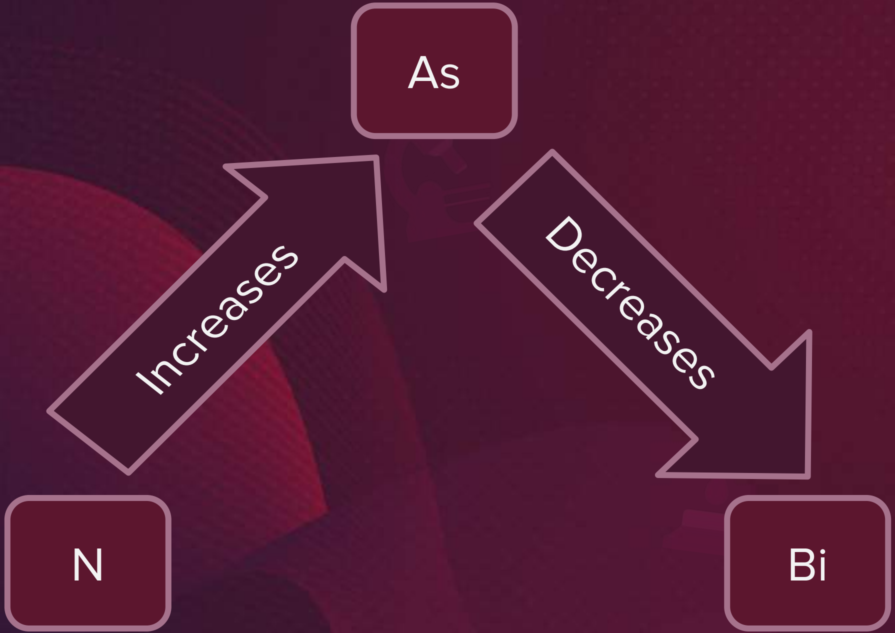
In general,

Down the group → Boiling point ↑

$$\text{N} < \text{P} < \text{As} < \underbrace{\text{Bi} < \text{Sb}}_{\text{Exception}}$$

Physical Properties

5. Melting points


As

Increases

Decreases

N

Bi

Physical Properties

6. Allotropy

When element exist in two or different forms, their different structural modifications called allotropes out of which one of the form is the most stable form.

All elements show allotropy

Except nitrogen

Which of the following element does **not** show **allotropy**?

a P

b Bi

c Sb

d N

Solution

In group 15 elements, all elements show allotropy except nitrogen.

Hence, option (d) is the correct answer.

The **melting** point of group 15 elements:

BOARDS

a Decreases on moving down the group

b Increases on moving down the group

c First decreases upto As and then increases.

d First increases upto As and then decreases.

1) For boiling point, the graph was increasing up to Sb and then there was a gradual decrease from Sb to Bi.

2) For melting point , the graph is increasing up to As and then decreases from As to Bi.

Hence, option (d) is the correct answer.

- **a** Decreases on moving down the group
- **b** Increases on moving down the group
- **c** First decreases upto As and then increases.
- **d** First increases upto As and then decreases.

Anomalous Properties of Nitrogen

Nitrogen differs from rest of the members of this group due to:

1 Smaller size

2 High electronegativity

3 High ionisation enthalpy

4 Unavailability of d-orbitals

Anomalous Properties of Nitrogen

Anomalous properties of nitrogen

- Bonding
- Covalency

Bonding

The catenation tendency is **weaker** in nitrogen.

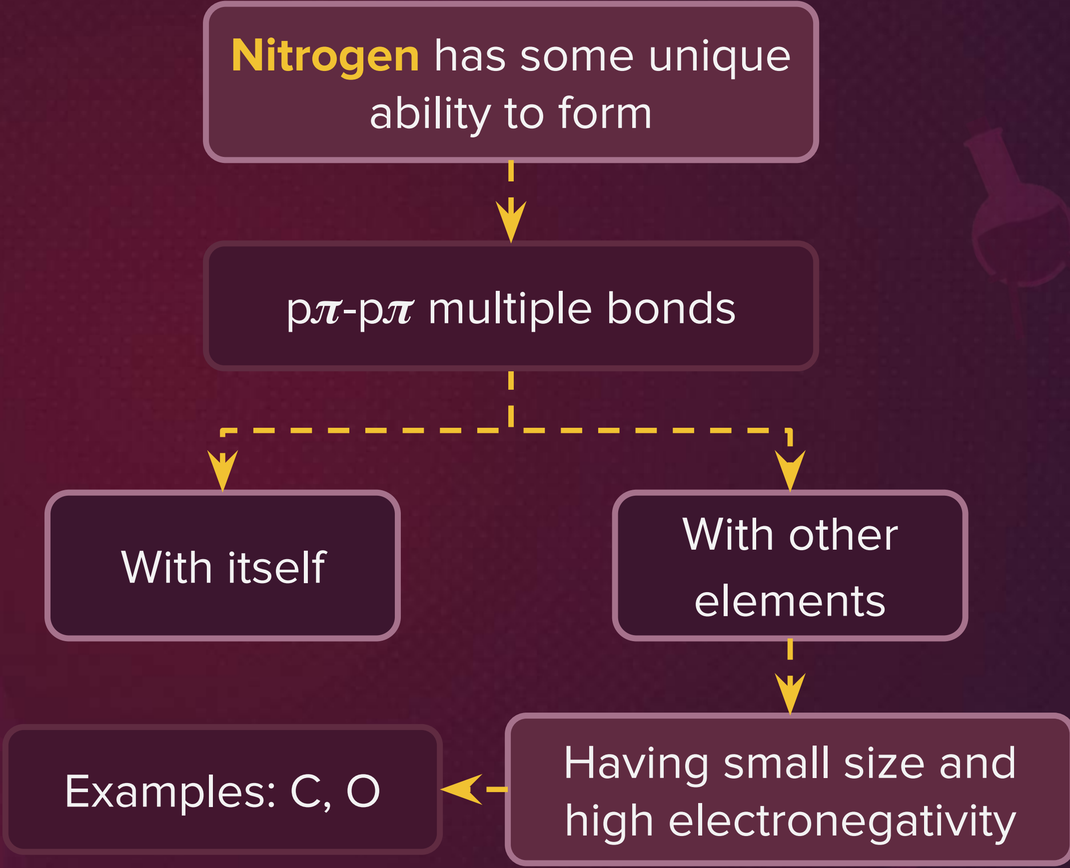
A single N-N bond is **weaker** than a single P-P bond.

Anomalous Properties of Nitrogen

Reason ▷

High interelectronic repulsion of the non-bonding electrons

Owing to the **small bond length**



Nitrogen has some unique ability to form

pπ-pπ multiple bonds

With itself

With other elements

Having small size and high electronegativity

Examples: C, O

Anomalous Properties of Nitrogen

pπ–pπ bonding

Heavier elements

Do not form pπ-pπ bonds

As their atomic orbitals are so **large,** and they **diffuse**

So that they cannot have **effective overlapping**

Anomalous Properties of Nitrogen

Nitrogen exists as **diatomic molecule**

With a triple bond (one sigma and two pi)

$N \equiv N$

Covalency

Another factor that affects the chemistry of nitrogen in the **absence of d-orbitals** in its valence shell.

Anomalous Properties of Nitrogen

Besides restricting its covalency to **4,** nitrogen **cannot form a pπ-dπ** bond.

No d-orbital

It has one s and three p-orbitals for bonding

Heavier elements can form

dπ-pπ bond

Eg: **$R_3P{=}O$ or $R_3P{=}CH_2$**
(R: Alkyl group)

Which of the following properties increases down the group for nitrogen family?

BOARDS

- Electron gain enthalpy decreases down the group and Ionisation enthalpy also decreases due to increase in size on moving down the group.
- Boiling point in general increases on moving down the group.
- Electronegativity also decreases on going down the group

Hence, option (c) is the correct answer.

a	Electron gain enthalpy
b	Ionisation enthalpy
c	Boiling point
d	Electronegativity

Which of the following is the correct electronic configuration for arsenic?

BOARDS

a $[Kr]\ 4d^{10}\ 5s^{2}\ 5p^{3}$

b $[Ar]\ 3d^{10}\ 4s^{2}\ 4p^{2}$

c $[Ar]\ 3d^{10}\ 4s^{1}\ 4p^{3}$

d $[Ar]\ 3d^{10}\ 4s^{2}\ 4p^{3}$

Hence, option (d) is the correct answer.

There is considerable increase in the covalent radius from N to P. However, there is only a small increase from Sb to Bi (of 7 pm). What is the reason?

BOARDS

- a Poor shielding by completely filled d- and f-orbitals in Bi
- b Similar electronegativity of Sb and Bi
- c The Bi being last element of the group
- d Similar densities of Sb and Bi

From N to P there is a considerable increase in radius but less increase in size from Sb to Bi is due to poor shielding by completely filled d- and f-orbitals in Bi.

- **a** Poor shielding by completely filled d- and f-orbitals in Bi
- **b** Similar electronegativity of Sb and Bi
- **c** The Bi being last element of the group
- **d** Similar densities of Sb and Bi

Hence, option (a) is the correct answer.

In which of the following cases does the **inert-pair effect** plays an important role?

BOARDS

- a P
- b Bi
- c Sb
- d As

As we move go down the group, inert pair effect becomes more predominant so Bismuth is the correct answer as its $6s^2$ electrons becomes inert.

Hence, option (b) is the correct answer.

a P

b Bi

c Sb

d As

Which of the following is **correct** statement?

BOARDS

a The valence shell electronic configuration of group 15 element is $ns^2 np^4$

b Ionisation enthalpy increases down the group

c All the elements of group 15 are polyatomic

d Metallic character decreases down the group.

Hence, option (c) is the correct answer.

The **incorrect** statement is:

a A single N-N bond is weaker than a single P-P bond.

b Nitrogen exists as a diatomic molecule.

c Electronic configuration of N is $[He]2s^2\,2p^3$.

d None of these

Hence, option (d) is the correct answer.

Group 15 Elements

Chemical Properties

- Oxidation states and trends in a chemical reactivity
- Reactivity towards hydrogen (hydrides)
- Reactivity towards oxygen
- Reactivity towards halogens
- Reactivity towards metals

Oxidation States and Stability

Common oxidation states

- -3
- +3
- +5

Oxidation States and Stability

Common oxidation states

-3

Reason

Down the group

Stability of **-3** oxidation state

Decreases

Due to **increase** in size and metallic character

Oxidation States and Stability

+3

Down the group

Stability of **+3** oxidation state

Increases

Bi^{3+} > Sb^{3+} > As^{3+}

Reason

Due to increase in the **inert-pair effect** down the group

Oxidation States and Stability

+5

Down the group

Stability of **+5** oxidation state

Decreases

As^{5+} > Sb^{5+} > Bi^{5+}

The only well-characterised Bi (V) compound

BiF_5

Other Oxidation States

Nitrogen

Exhibits

Large number of oxidation states from **-3 to +5**

When it reacts with oxygen

Other Oxidation States

Nitrogen

Compound	O.S. of N
NH_3	-3
N_2	0
N_2O	+1
NO	+2
N_2O_3	+3
NO_2/N_2O_4	+4
N_2O_5	+5

Other Oxidation States

Phosphorus

H_3PO_2

Shows **+1** and **+4** oxidation states in some oxoacids

Disproportionation

Nitrogen

All oxidation states from **+1 to +4**

tend to disproportionate in an **acid** solution.

$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$$

Disproportionation

Phosphorus

All intermediate oxidation states

disproportionate into **+5 and –3**

both in **alkaline** and **acidic medium**

Disproportionation

As, Sb and Bi

The **+3** oxidation state becomes increasingly **stable**

with respect to **disproportionation**

Which ordering of compounds is according to the decreasing order of the **oxidation states** of nitrogen?

BOARDS

- **a** HNO_3, NO, NH_4Cl, N_2
- **b** HNO_3, NO, N_2, NH_4Cl
- **c** HNO_3, NH_4Cl, NO, N_2
- **d** NO, HNO_3, NH_4Cl, N_2

Hence, option (b) is the correct answer.

Which gas is obtained during the disproportionation reaction of HNO_2?

BOARDS

- a NO_2
- b NO
- c O_2
- d N_2

Hence, option (b) is the correct answer.

Group 15 Elements

Chemical Properties

- Oxidation states and trends in chemical reactivity
- **Reactivity towards hydrogen (hydrides)**
- Reactivity towards oxygen
- Reactivity towards halogens
- Reactivity towards metals

Chemical Properties

All the elements form hydrides of the type

EH_3

E = N, P, As, Sb or Bi

Properties of Hydrides

Stability

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Predicted from the bond dissociation enthalpy data

Properties of Hydrides

Hydrides	$\Delta_{diss}H^0$ (E–H) (kJ mol^{-1})
NH_3	389
PH_3	322
AsH_3	297
SbH_3	255
BiH_3	—

$\Delta_{diss}H^0$: Bond dissociation enthalpy

Properties of Hydrides

Reducing character

$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

Ammonia (NH_3) — Mild reducing agent

BiH_3 — Strong reducing agent

Properties of Hydrides

Stability

Order of bond dissociation enthalpy

N-H > P-H > As-H > Sb-H > Bi-H

↓

Can lose hydrogen easily

↓

Has more **reducing power**

Properties of Hydrides

Basicity

$NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$

Properties of Hydrides

Boiling point

$PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

van der Waals forces in bigger **Sb** molecules **dominates the H-bonding** in ammonia

Properties of Hydrides

Melting point

NH_3 > SbH_3 > AsH_3 > PH_3

Reactivity Towards Oxygen

All the elements form two types of oxides

E_2O_3 and E_2O_5

E = N, P, As, Sb or Bi

Reactivity Towards Oxygen

The oxide in the higher oxidation state of the element

is **more acidic**

than that of the lower oxidation state

Reactivity Towards Oxygen

$N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5$

$\xrightarrow{\hspace{4cm}}$

acidic char. ↓s

Down the group

Acidic character ↓

$N_2O_3 > P_2O_3 > As_2O_3 > Sb_2O_3 > Bi_2O_3$

$\xrightarrow{\hspace{4cm}}$

For E_2O_3 Type Oxides

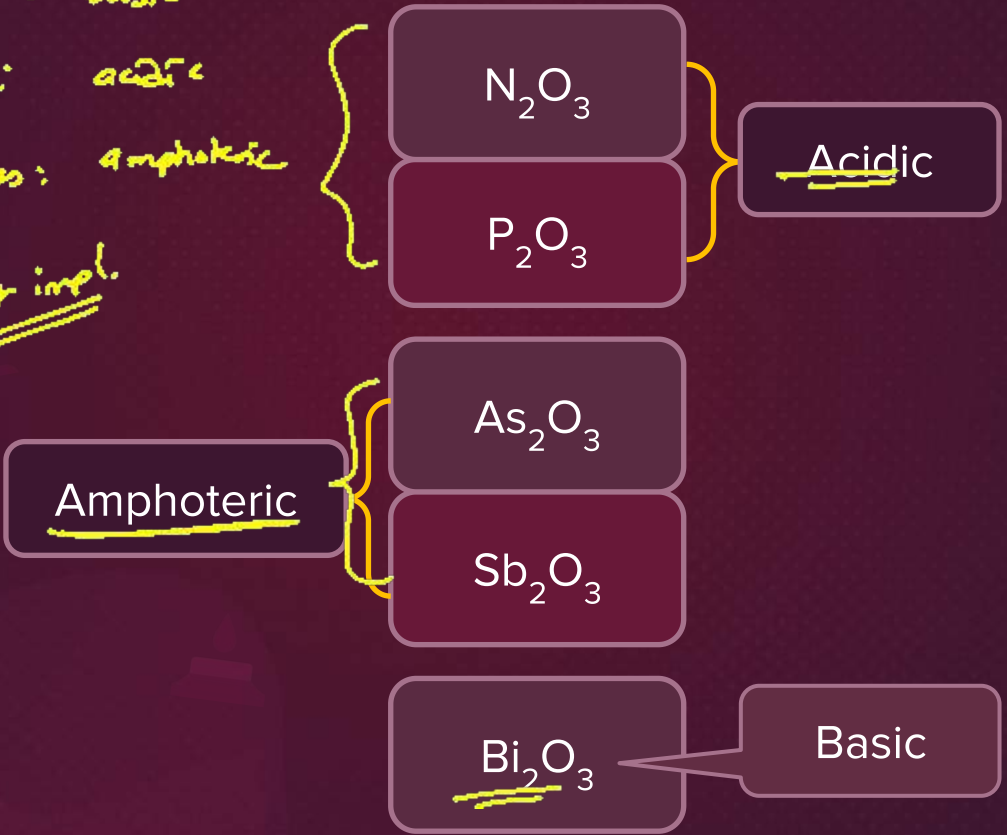
for ox. no. $\leq +3$

metal oxides : tend to be basic

non-metal " : acidic

metalloid oxides : amphoteric

most imp.



N_2O_3

P_2O_3

Acidic

As_2O_3

Sb_2O_3

Amphoteric

Bi_2O_3

Basic

Note

The oxides in lower oxidation state (i.e., **+3**) will act as **reducing reagents**.

Down the group

Reducing power ↓

Group 15 Elements

Chemical Properties

- Oxidation states and trends in chemical reactivity
- Reactivity towards hydrogen (hydrides)
- Reactivity towards oxygen
- **Reactivity towards halogens**
- Reactivity towards metals

Reactivity Towards Halogens

These elements react to form two series of halides

EX_3 and EX_5

E = N, P, As, Sb or Bi

Reactivity Towards Halogens

Trihalides (MX_3)

Except **NX_3**

All trihalides are stable

NF_3 is the only stable halide of nitrogen

Reactivity Towards Halogens

Pentahalides (MX_5)

All elements form pentahalides

Except **nitrogen (N)**

Due to the non-availability of d-orbital

Reactivity Towards Halogens

Pentahalides are **more covalent** than trihalides.

Reason

Polarising power

Elements in '**+5**' O.S > Elements in '**+3**' O.S

Covalent

more

Note

Stability of halides

For a given element of group 15

F > Cl > Br > I

Based on the compounds of group 15 elements, the incorrect statement is:

BOARDS

a Bi_2O_5 is more basic than N_2O_5

b NF_3 is more covalent than BiF_3

c PH_3 boils at a lower temperature than NH_3

d The N–N single bond is stronger than the P–P single bond

Solution

Hence, option d is the correct answer.

In case of nitrogen, NCl_3 is possible but not NCl_5 while in case of phosphorus, PCl_3 as well as PCl_5 are possible. It is due to:

$2s^2\,2p^3$

$3s^2\,3p^3\,\boxed{3d}$

✓

- **a** Availability of vacant d-orbitals in P but not in N
- **b** Lower electronegativity of P than that of N
- **c** Lower tendency of H-bond formation in P than that in N
- **d** Occurrence of P in solid state but N in gaseous state at room temperature

Solution

Hence, option a is the correct answer.

Reactivity Towards Metals

All these elements **react with metals** to form

↓

their binary compounds exhibiting **–3** oxidation state

Reactivity Towards Metals

Examples

Ca_3N_2
(Calcium nitride)

Ca_3P_2
(Calcium phosphide)

Na_3As
(Sodium arsenide)

Zn_3Sb_2
(Zinc antimonide)

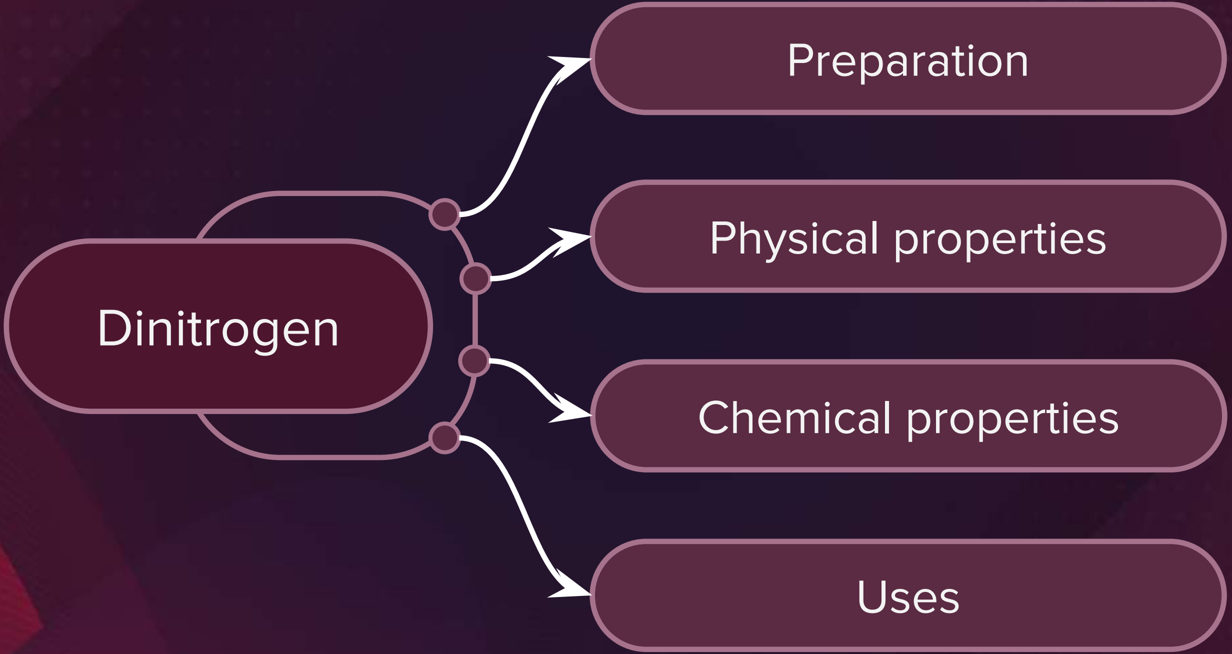
Mg_3Bi_2
(Magnesium bismuthide)

Nitrogen-Containing Compounds

Nitrogen-Containing Compounds

- Dinitrogen (N_2) ✓
- Ammonia (NH_3)
- Oxides of nitrogen
- Oxoacids of nitrogen

Dinitrogen (N_2)



Dinitrogen

Preparation

Physical properties

Chemical properties

Uses

Preparation of Dinitrogen (N_2)

Industrial

From liquefied air by fractional distillation

B.P. 77.2 K

Liquid dinitrogen distils out first, leaving behind liquid oxygen

B.P. 90 K

Preparation of Dinitrogen (N_2)

In the laboratory

Obtained by making **ammonium nitrite** and then warming it.

$$NH_4Cl\ (aq) + NaNO_2\ (aq) \longrightarrow NH_4NO_2\ (aq) + NaCl\ (aq)$$

By heating ammonium nitrite

$$NH_4NO_2\ (aq) \longrightarrow N_2\ (g)\uparrow + 2H_2O\ (\ell)$$

Preparation of Dinitrogen (N_2)

By thermal decomposition

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

Barium azide

Very pure

$$2NaN_3\,(s) \xrightarrow{\Delta} 2Na\,(s) + 3N_2\,(g)$$

Sodium azide

Very pure

Physical Properties

1. Colourless, odourless, tasteless, and non-toxic gas

2. Has very low solubility in water

Physical Properties

N_2 is inert at room temperature

because of the high bond enthalpy of **N≡N** bond.

Reactivity **increases** rapidly with rise in **temperature**, beyond 1500°C.

Chemical Properties

At higher temperatures

With metals

It directly combines with some metals to form predominantly **ionic nitrides.**

With non-metals

It forms covalent nitrides

Chemical Properties

Examples

$$6Li(s) + N_2(g) \xrightarrow{\Delta} 2Li_3N(s)$$

$$3Mg(s) + N_2(g) \xrightarrow{\Delta} Mg_3N_2(s)$$

Chemical Properties

Haber's process

N_2 combines with **hydrogen** at about 773 K, P = 202600 kPa, in the presence of a catalyst (Fe_3O_4 mixed with K_2O, SiO_2, and Al_2O_3)

Industrial manufacture of NH_3

Chemical Properties

Examples

$$N_2\,(g) + 3H_2\,(g) \overset{\Delta}{\rightleftharpoons} 2NH_3\,(g)$$

$$\Delta_r H^0 = -92\ \text{kJ mol}^{-1}$$

Chemical Properties

3

Dinitrogen combines with dioxygen only at a very high temperature

at about 2000 K

to form **nitric oxide** (NO)

$$N_2\,(g) + O_2\,(g) \xrightarrow{\Delta} 2NO\,(g)$$

Assertion: Nitrogen and oxygen are the main components of the atmosphere, but these do not react to form oxides of nitrogen.
Reason: The reaction between nitrogen and oxygen requires high temperature.

BOARDS

a Both the assertion and reason are correct, and the reason is the correct explanation for the assertion.

b Both the assertion and reason are correct, but the reason is not the correct explanation for the assertion.

Assertion: Nitrogen and oxygen are the main components of the atmosphere, but these do not react to form oxides of nitrogen.
Reason: The reaction between nitrogen and oxygen requires high temperature.

BOARDS

c The assertion is incorrect, but the reason is correct.

d Both the assertion and the reason are incorrect.

Solution

Hence, option a is the correct answer.

Uses

1

In the **manufacture of ammonia** and other industrial chemicals containing nitrogen

Example

Calcium cyanamide

Uses

2

It also finds use where, an **inert atmosphere** is required.

Example

In the iron and steel industry, **inert diluent** for reactive chemicals

Uses

3

Liquid dinitrogen is used as a **refrigerant**

to preserve biological materials, food items, and in cryosurgery

Extra pure N_2 can be obtained by heating:

a $NH_4Cl + NaNO_2$

c $(NH_4)_2Cr_2O_7$

b NH_4NO_2

[✓ d] $Ba(N_3)_2$

Solution

Very pure nitrogen can be obtained by the thermal decomposition of $Ba(N_3)_2$ or NaN_3.

Hence, option d is the correct answer.

Nitrogen is best obtained by the thermal decomposition of which one of the following?

a ✗ $NH_4Cl \xrightarrow{\Delta} NH_3\uparrow + HCl\uparrow$

b ✗ $\underset{-3}{N}H_4\underset{+5}{N}O_3 \xrightarrow{\Delta} N_2O\uparrow + 2H_2O\uparrow$

c $AgNO_3 \xrightarrow{\Delta} Ag + NO_2 + \frac{1}{2}O_2\uparrow$

[✓ d] $NH_4NO_2 \xrightarrow{\Delta} N_2\uparrow + 2H_2O\uparrow$

Solution

Hence, option d is the correct answer.

The correct statement with respect to dinitrogen is:

BOARDS

a N_2 is paramagnetic in nature

b It can combine with dioxygen at 25 °C

c Liquid dinitrogen is not used in cryosurgery

d It can be used as an inert diluent for reactive chemicals

N_2 is diamagnetic.

Dinitrogen combines with dioxygen only at **very high temperature** (at about 2000 K) to form nitric oxide

Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery

Use in iron and steel industry, inert diluent for reactive chemicals.

Hence, option (d) is the correct answer.

Which of the following order is **wrong**?

a $NH_3 < PH_3 < AsH_3$ - acidic

b Li < Be < B < C - 1st I.P.

c $Al_2O_3 < MgO < Na_2O < K_2O$ - basic

d $Li^+ < Na^+ < K^+ < Cs^+$ - ionic radius

Hence, option (b) is the correct answer.

The **basic character of hydrides** of the V group elements **decreases** in the order:

BOARDS

a $NH_3 > PH_3 > AsH_3 > SbH_3$

b $SbH_3 > AsH_3 > PH_3 > NH_3$

c $SbH_3 > PH_3 > AsH_3 > NH_3$

d $NH_3 > SbH_3 > PH_3 > AsH_3$

Hence, option (a) is the correct answer.

Which of the following statement is **not correct** for **nitrogen**?

BOARDS

a Its electronegativity is very high.

b d-orbitals are available for bonding.

c It is a typical non-metal.

d Its molecular size is small.

Hence, option (b) is the correct answer.

What is the **sum of the highest and lowest oxidation states** for nitrogen family?

BOARDS

a 3

b 4

c 2

d 5

Hence, option (c) is the correct answer.

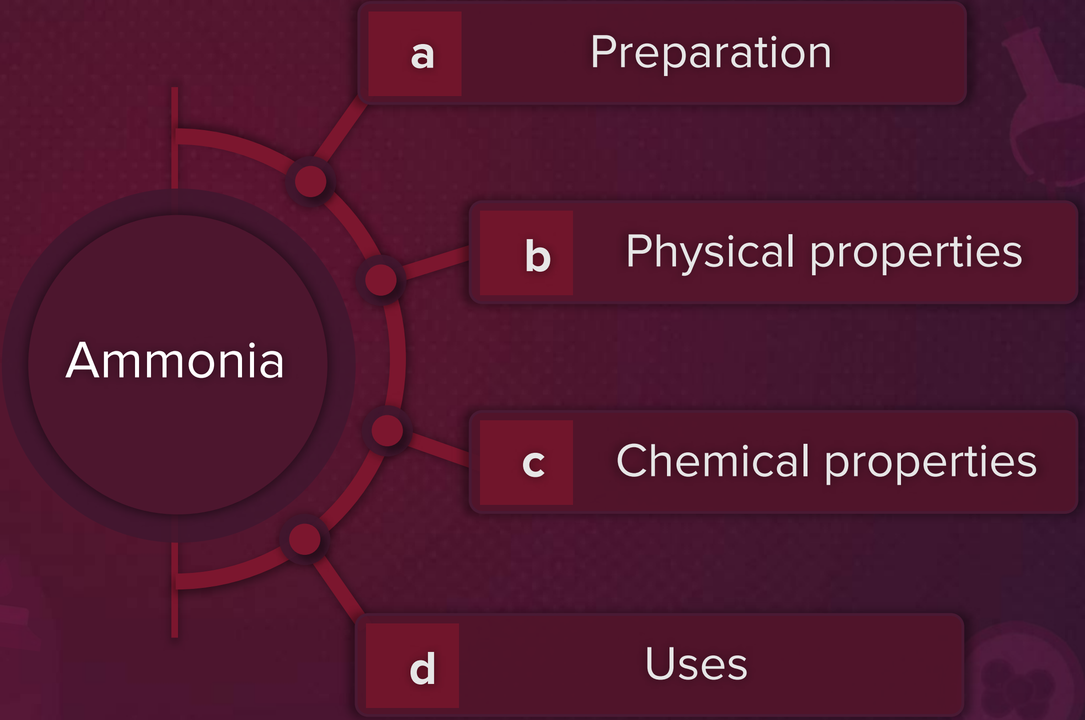
Nitrogen-Containing Compounds

Nitrogen-Containing Compounds

- Dinitrogen (N_2)
- Ammonia (NH_3)
- Oxides of nitrogen
- Oxoacids of nitrogen

Nitrogen-Containing Compounds

Ammonia (NH_3)



Ammonia

a Preparation

b Physical properties

c Chemical properties

d Uses

Ammonia finds great applications in the hair dye industry.

Ammonia (NH_3)

a Preparation

1

Ammonia is present in small quantities in air and soil.

It is formed by the decay of **nitrogenous organic matter.**

Example = Urea

Ammonia (NH_3)

$$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

Ammonia (NH_3)

On small scale

2

Obtained from **ammonium salts** that decompose

When treated with **caustic soda** or calcium hydroxide

Ammonia (NH_3)

On small scale

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$$

Haber's Process

On large scale

Manufactured by **Haber's process**

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$\Delta_r H^0 (298\text{ K}) = -92\text{ kJ mol}^{-1}$$

As per Le Chatelier's principle, "**high pressure** would **favour** the formation of ammonia".

Haber's Process

Optimum conditions for the production of ammonia

Pressure
(20-26 × 10^5 Pa)

Temperature
($\sim$723 K)

Haber’s Process

Catalyst

The **activation barrier** for the dissociation of N_2 and H_2 in the gas phase is **very high.**

Without a catalyst, the reaction between N_2 and H_2 occurs **slowly.**

Iron oxide with small amount of K_2O and Al_2O_3

Earlier, iron was used as a catalyst with **molybdenum (Mo)** as a promoter.

Ammonia (NH_3)

b Physical properties

1 Colourless gas

2 Pungent odour

3 Freezing point is 195.5 K

4 Boiling point is 240 K

Ammonia (NH_3)

5

In solid and liquid state

It is associated through **hydrogen bonds.**

Same as water

Ammonia (NH_3)

In solid and liquid state

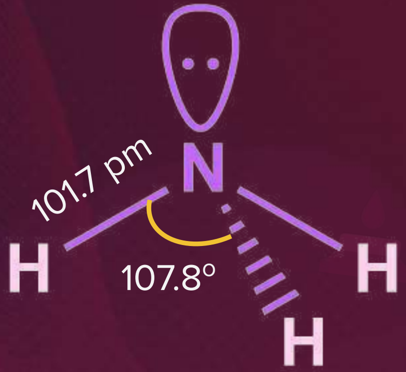
Due to this **association**

It has **higher melting and boiling points** than expected.

Ammonia (NH_3)

Structure

Trigonal pyramidal



Ammonia (NH_3)

Solubility

Highly soluble in water

$$NH_3\,(g) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

The aqueous solution is **weakly basic** due to the formation of OH^-.

Ammonia (NH_3)

C Chemical properties

Chemical Properties

- Ammonia as base
- Thermal decomposition of ammonium salts

Chemical Properties

- Ammonia as base
  - Reaction with acids
  - Reaction with metal salt
  - Complex formation

Ammonia (NH_3)

Ammonia as base

Reaction with acids

1

It forms ammonium salts with acids.

$$NH_3\,(g) + HCl\,(aq) \longrightarrow NH_4Cl\,(aq)$$

$$2NH_3\,(g) + H_2SO_4\,(aq) \longrightarrow (NH_4)_2SO_4\,(aq)$$

Ammonia (NH_3)

Ammonia as base

Reaction with metal salt

As a **weak base**, it precipitates the hydroxides of many metals from their salt solutions.

Ammonia (NH_3)

Ammonia as base

$$ZnSO_4\,(aq) + 2NH_4OH\,(aq) \downarrow Zn(OH)_2\,(s) + (NH_4)_2SO_4\,(aq)$$

White ppt

$$FeCl_3\,(aq) + NH_4OH\,(aq) \downarrow Fe_2O_3.x\,H_2O\,(s) + NH_4Cl\,(aq)$$

Brown ppt

Chemical Properties

Ammonia with $ZnSO_4$

The products, zinc hydroxide is shown by the white precipitates. In this reaction, ions of sulphate and hydroxide are exchanged. Hence, it is a double decomposition reaction.

Chemical Properties

Ammonia as base

Complex formation

The presence of a **lone pair** of electrons on the nitrogen atom of ammonia

Makes it a **Lewis base**

Chemical Properties

It donates the electron pair and forms **linkage with metal ions.**

The formation of such complex compounds finds applications in **detection of metal ions.**

Chemical Properties

Complex formation

$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$

Blue

Deep blue

$Cd^{2+}(aq) + 4NH_3(aq) \longrightarrow [Cd(NH_3)_4]^{2+}(aq)$

Colourless

Chemical Properties

Complex formation

$$Ag^{+}(aq) + Cl^{-}(aq) \rightleftharpoons AgCl(s)$$

Colourless

White ppt

$$AgCl(s) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]Cl(aq)$$

White ppt

Colourless

Chemical Properties of Ammonia

Chemical Properties

- Ammonia as base
- Thermal decomposition of ammonium salts

Ammonium salts **decompose** quite readily on heating.

Chemical Properties of Ammonia

Example: Cl^-, CO_3^{2-} or SO_4^{2-}

If the anion is **not oxidising,** then **ammonia** is evolved.

$$(NH_4)_2SO_4\,(aq) \longrightarrow 2NH_3\,(g) + H_2SO_4\,(aq)$$

$$NH_4Cl \longrightarrow NH_3 + HCl$$

Chemical Properties of Ammonia

Example:

NO_2^- or NO_3^-

If the anion is **more oxidising** then NH_4^+ is oxidised to **N_2 or N_2O.**

$$NH_4NO_2\,(aq) \xrightarrow{\Delta} N_2\,(g) + 2H_2O\,(l)$$

$$NH_4NO_3\,(aq) \xrightarrow{\Delta} N_2O\,(g) + 2H_2O\,(l)$$

Uses of Ammonia

d Uses

1 Used to produce various **nitrogenous fertilisers**

- Ammonium nitrate
- Ammonium sulphate
- Ammonium phosphate
- Urea

etc.

Fertilisers

Uses of Ammonia

Refrigerant

2

Liquid ammonia is also used as a **refrigerant.**

$$Al + N_2 \xrightarrow{\Delta} (A) \xrightarrow{H_2O} (B) \xrightarrow{K_2HgI_4/OH^-} (D)\ \text{(brown ppt.)}$$

What is (D)?

a $H_2N - Hg - Hg - I$

b $H_2N - Hg - O - Hg - I$

c $H_2N - O - Hg - Hg - I$

d $H_2N - Hg - I - Hg - O$

$$\mathrm{Al} + \mathrm{N_2} \xrightarrow{\Delta} (\mathrm{A}) \xrightarrow{\mathrm{H_2O}} (\mathrm{B}) \xrightarrow{\mathrm{K_2HgI_4/OH^-}} (\mathrm{D})\ (\text{brown ppt.})$$

a	$H_2N - Hg - Hg - I$
b	$H_2N - Hg - O - Hg - I$
c	$H_2N - O - Hg - Hg - I$
d	$H_2N - Hg - I - Hg - O$

Hence, option (b) is the correct answer.

Regular use of which of the following fertilisers increases the acidity of soil?

BOARDS

- a Ammonium sulphate
- b Potassium nitrate
- c Urea
- d Superphosphate of lime

Hence, option (a) is the correct answer.

NH_3 **can't** be obtained by:

BOARDS

a Heating of NH_4NO_3 or NH_4NO_2

b Heating of NH_4Cl or $(NH_4)_2\ CO_3$

c Heating of NH_4NO_3 with NaOH

d Reaction of AlN or Mg_3N_2 or $CaCN_2$ with H_2O

Hence, option (a) is the correct answer.

Oxides of Nitrogen

Nitrogen forms a
number of oxides

In **different** oxidation states

Oxides of Nitrogen

- Dinitrogen oxide (N_2O)
- Nitrogen monoxide (NO)
- Dinitrogen trioxide (N_2O_3)
- Nitrogen dioxide (NO_2)
- Dinitrogen tetroxide (N_2O_4)
- Dinitrogen pentoxide (N_2O_5)

Dinitrogen Oxide (N_2O)

$$NH_4NO_3\ (aq) \xrightarrow{\Delta} N_2O\ (g) + 2H_2O\ (\ell)$$

This reaction was involved in the Beirut, Lebanon blast.
On August 4, 2020, one of the world's biggest-ever, non-nuclear explosions destroyed much of Beirut's port and devastated swaths of the capital. The blast was caused by a fire in a warehouse which Lebanese authorities admit held a vast stockpile of ammonium nitrate for six years.

Dinitrogen Oxide (N_2O)

Preparation

$$NH_4NO_3\ (aq) \xrightarrow{\Delta} \mathbf{N_2O}\ (g) + 2H_2O\ (\ell)$$

Dinitrogen Oxide (N_2O)

Oxidation state

N_2O

$$2x + -2 = 0$$

$$x = +1$$

O.S of nitrogen

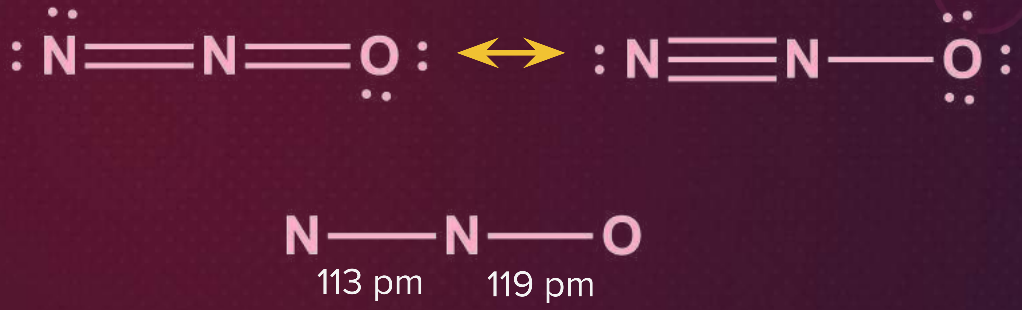
Dinitrogen Oxide (N_2O)

Physical appearance and chemical nature

1. Stable
2. Relatively unreactive
3. Colourless gas
4. Neutral oxide

Dinitrogen Oxide (N_2O)

Structure



Note

N_2O is used as an **anesthetic** and also known as **laughing gas.**

Oxides of Nitrogen

- Oxides of Nitrogen
  - Dinitrogen oxide (N_2O)
  - Nitrogen monoxide (NO)
  - Dinitrogen trioxide (N_2O_3)
  - Nitrogen dioxide (NO_2)
  - Dinitrogen tetroxide (N_2O_4)
  - Dinitrogen pentoxide (N_2O_5)

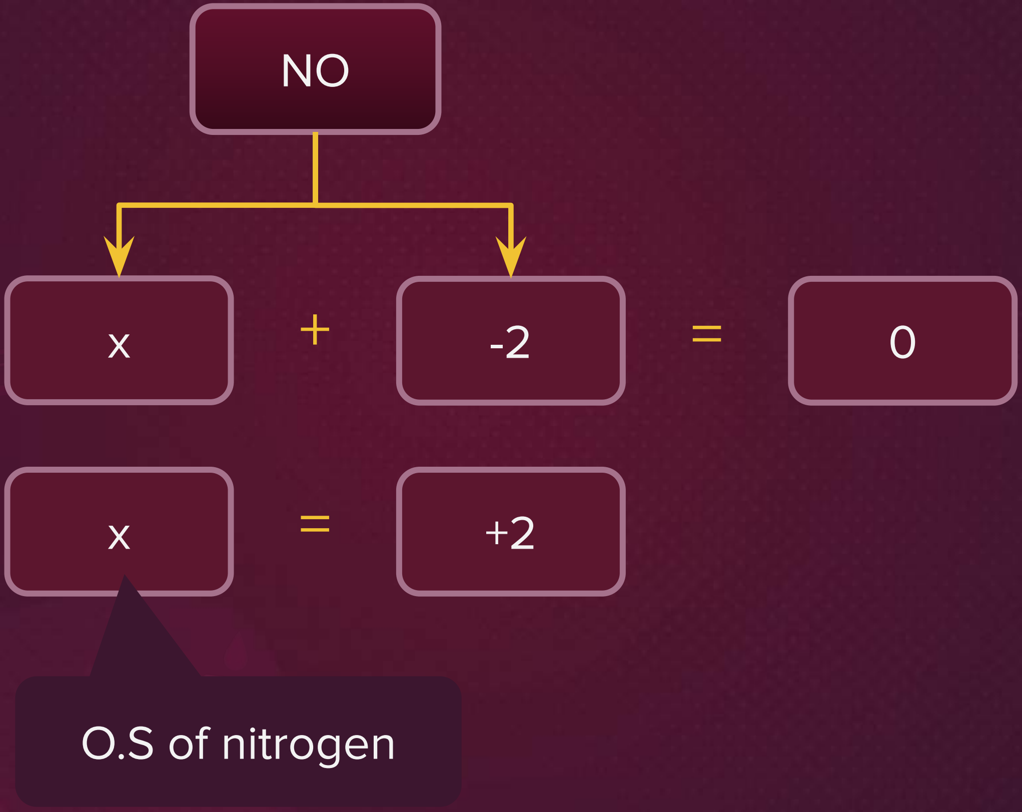
Nitrogen Monoxide (NO)

Preparation

$$2NaNO_2\,(aq) + 2FeSO_4\,(aq) + 3H_2SO_4\,(aq) \downarrow Fe_2(SO_4)_3\,(aq) + 2NaHSO_4\,(aq) + 2H_2O\,(l) + 2\mathbf{NO}\,(g)$$

Nitrogen Monoxide (NO)

Oxidation state



NO

$$x + (-2) = 0$$

$$x = +2$$

O.S of nitrogen

Nitrogen Monoxide (NO)

Physical appearance and chemical nature

1. Colourless gas

2. Neutral oxide

Nitrogen Monoxide (NO)

Physical appearance and chemical nature

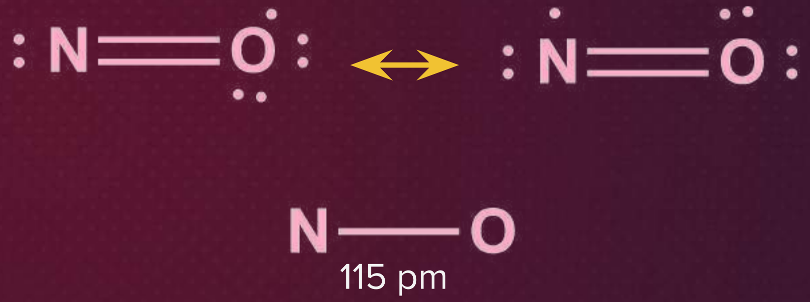
3

Reacts instantly with O_2 to give NO_2

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

Nitrogen Monoxide (NO)

Structure



$:N=\overset{\cdot}{\underset{\cdot\cdot}{O}}: \longleftrightarrow :\dot{N}=\ddot{O}:$

Nitrogen Monoxide (NO)

Nature

It is an **odd electron molecule.** Hence, the **gas** is **paramagnetic** in nature.

Which of the following properties is **not shown by NO**?

BOARDS

a It is paramagnetic in liquid state.

b It is a neutral oxide.

c It combines with oxygen to form nitrogen dioxide.

d Its bond order is 2.5.

Hence, option (a) is the correct answer.

?

Ammonia can be **dried** by:

BOARDS

a Conc. H_2SO_4

b P_4O_{10}

c CaO

d Anhydrous $CaCl_2$

Hence, option (c) is the correct answer.

Reaction of ammonia with excess Cl_2 gives:

BOARDS

- a NH_4Cl and N_2
- b NH_4Cl and HCl
- c NCl_3 and NH_4Cl
- d NCl_3 and HCl

Hence, option (d) is the correct answer.

Hydrolysis of nitrides of s-block elements (for e.g., Ba_3N_2, Ca_3N_2, Li_3N) will yield:

BOARDS

- a NH_3 + Metal hydroxide
- b Only NH_3
- c NH_3 + HNO_3
- d NH_4OH

Hydrolysis of nitrides of s-block elements (for e.g., Ba_3N_2, Ca_3N_2, Li_3N) will yield:

- **a** NH_3 + Metal hydroxide
- **b** Only NH_3
- **c** $NH_3 + HNO_3$
- **d** NH_4OH

Hence, option (a) is the correct answer.

Oxides of Nitrogen

Oxides of Nitrogen

- Dinitrogen oxide (N_2O)
- Nitrogen monoxide (NO)
- Dinitrogen trioxide (N_2O_3)
- Nitrogen dioxide (NO_2)
- Dinitrogen tetroxide (N_2O_4)
- Dinitrogen pentoxide (N_2O_5)

Dinitrogen Trioxide (N_2O_3)

Preparation

By condensing **equimolar amounts** of NO and NO_2 together or by reacting NO with the appropriate amount of O_2.

$$NO + NO_2 \longrightarrow N_2O_3$$

$$4NO + O_2 \longrightarrow 2N_2O_3$$

Dinitrogen Trioxide (N_2O_3)

Oxidation state

N_2O_3

$$2x + 3 \times (-2) = 0$$

$$x = +3$$

O.S of nitrogen

Dinitrogen Trioxide (N_2O_3)

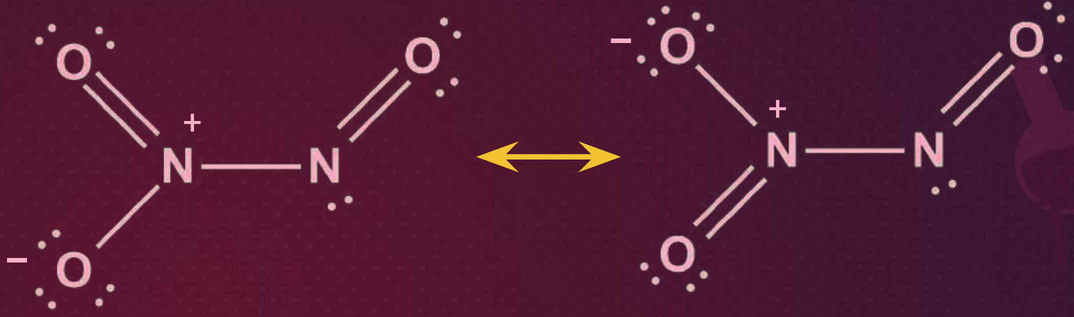
Physical appearance and chemical nature

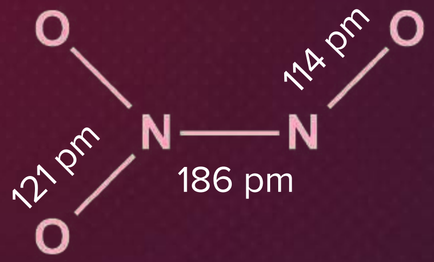
1. Blue solid
2. Acidic

It is **anhydride of HNO_2**

Dinitrogen Trioxide (N_2O_3)

Structure





Planar

The reaction of **NO with N_2O_4** at 250 K gives:

BOARDS

a	N_2O
b	NO_2
c	N_2O_3
d	N_2O_5

Hence, option (c) is the correct answer.

The pale blue liquid obtained by equimolar mixture of two gases at –30°C is:

- a N_2O
- b NO_2
- c N_2O_3
- d N_2O_5

Hence, option (c) is the correct answer.

Nitrogen Dioxide (NO_2)

Preparation

Laboratory method

$$2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 2PbO + O_2$$

Nitrogen Dioxide (NO_2)

Oxidation state

NO_2

$$x + 2 \times (-2) = 0$$

$$x = +4$$

O.S. of nitrogen

Nitrogen Dioxide (NO_2)

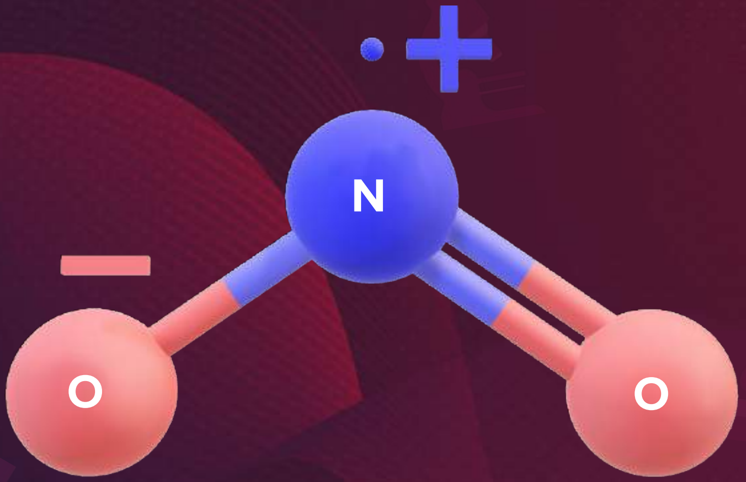
Physical appearance and chemical nature

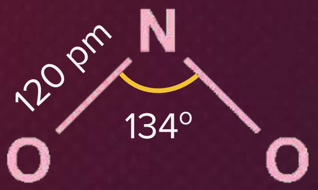
1 Red-brown poisonous gas

2 Very reactive

Nitrogen Dioxide (NO_2)

Structure





Bent

The following are **neutral** oxides, **except:**

BOARDS

a NO

b N_2O

c CO

d NO_2

Hence, option (d) is the correct answer.

Dinitrogen Tetroxide (N_2O_4)

Preparation

$$2NO_2\,(g) \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4\,(s)$$

Paramagnetic, brown

Diamagnetic, colourless

NO_2-N_2O_4 system is a **strong oxidising agent**

Dinitrogen Tetroxide (N_2O_4)

Oxidation state

N_2O_4

$2x + 4 \times (-2) = 0$

$x = +4$

O.S. of nitrogen

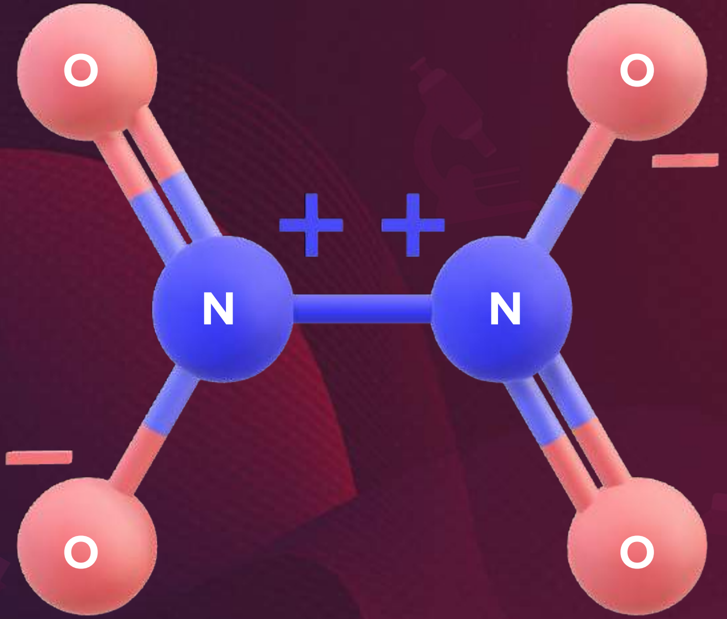
Dinitrogen Tetroxide (N_2O_4)

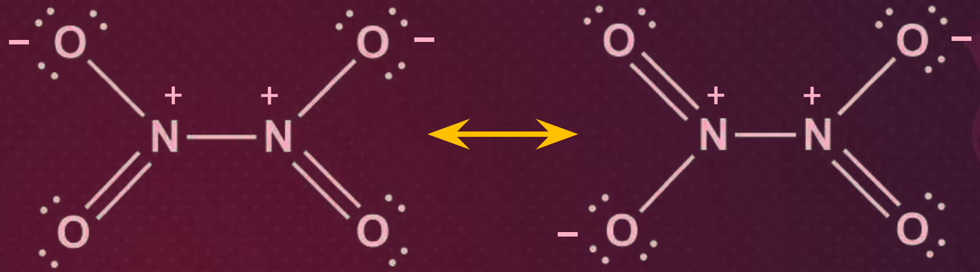
Physical appearance and chemical nature

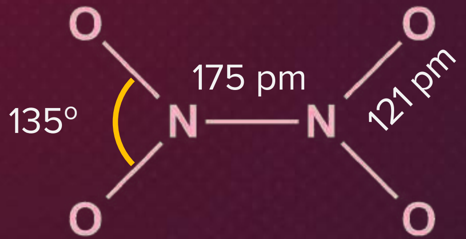
1. Colourless solid/liquid
2. Acidic

Dinitrogen Tetroxide (N_2O_4)

Structure







Planar

Which of the following statements is **wrong**?

BOARDS

a The stability of hydrides decreases from NH_3 to BiH_3 in group 15 of the periodic table

b Nitrogen cannot form dπ-pπ bond

Which of the following statements is **wrong**?

BOARDS

c The single N–N bond is weaker than the single P–P bond.

d N_2O_4 has two resonance structure.

Hence, option (d) is the correct answer.

Dinitrogen Pentoxide (N_2O_5)

Preparation

$$4HNO_3\ (aq) + P_4O_{10}\ (s) \longrightarrow 4HPO_3\ (aq) + 2N_2O_5\ (s)$$

Dinitrogen Pentoxide (N_2O_5)

Oxidation state

N_2O_5

$$2x + 5 \times (-2) = 0$$

$$x = +5$$

O.S. of nitrogen

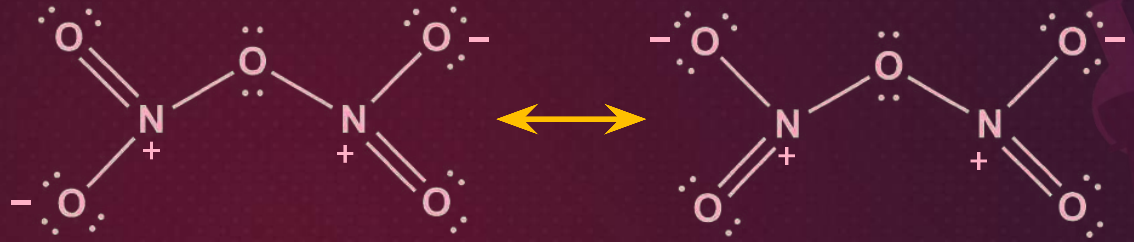
Dinitrogen Pentoxide (N_2O_5)

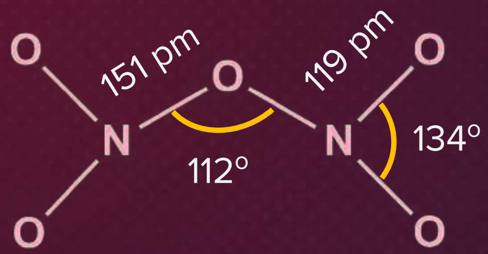
Physical appearance and chemical nature

1. Colourless, deliquescent solid
2. Acidic
3. Anhydride of HNO_3
4. Strong oxidising agent

Dinitrogen Pentoxide (N_2O_5)

Structure





Planar

Among the oxides of nitrogen such as N_2O_3, N_2O_4 and N_2O_5, the molecule(s) having N-N **bond** is/are:

BOARDS

- a N_2O_3 and N_2O_5
- b N_2O_4 and N_2O_5
- c N_2O_3 and N_2O_4
- d Only N_2O_5

Hence, option (c) is the correct answer.

Which of the following is a **mixed acid anhydride**?

BOARDS

a NO

b NO_2

c N_2O_5

d N_2O

Hence, option (b) is the correct answer.

The gas that is **acidic in nature** is:

BOARDS

- a NO
- b N_2O
- c NO_2
- d Both (a) and (c)

Hence, option (c) is the correct answer.

Oxoacids of Nitrogen

Nitrogen forms oxoacids such as

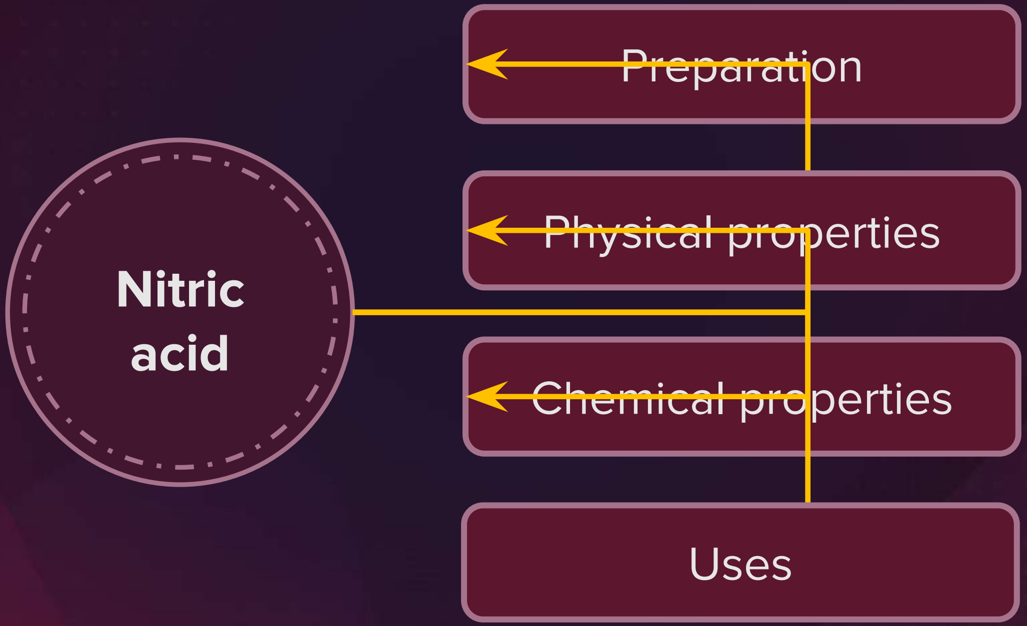
$H_2N_2O_2$
(Hyponitrous acid)

HNO_2 (Nitrous acid)

HNO_3 (Nitric acid)

Most important

Nitric Acid (HNO_3)



Nitric acid

Preparation

Physical properties

Chemical properties

Uses

Nitric Acid (HNO_3)

Preparation

On a large scale

Ostwald's process

Catalytic oxidation of NH_3 by atmospheric oxygen.

Nitric Acid (HNO_3)

On a large scale

Step 1

$$4NH_3\,(g) + \underset{\text{(from air)}}{5O_2\,(g)} \xrightarrow[\text{500 K, 9 bar}]{\text{Pt/Rh gauge catalyst}} 4NO\,(g) + 6H_2O\,(g)$$

Nitric Acid (HNO_3)

On a large scale ▷

Step 2

The nitric oxide so formed, combines with oxygen to give NO_2

$$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$$

Nitric Acid (HNO_3)

On a large scale ▷

Step 3

The nitrogen dioxide so formed, dissolves in water to give HNO_3

$$3NO_2\ (g) + H_2O\ (\ell) \longrightarrow 2HNO_3\ (aq) + NO\ (g)$$

Recycled

Nitric Acid (HNO_3)

On a large scale ▷

Step 4

By **distillation**, aqueous HNO_3 can be concentrated up to ≈ **68%** by mass

It can be further concentrated to **98%** by mass by **dehydration** with concentrated H_2SO_4.

Nitric Acid (HNO_3)

Physical properties

1. **Colourless** liquid

2. Freezing point is **231.4 K** and boiling point is **355.6 K**.

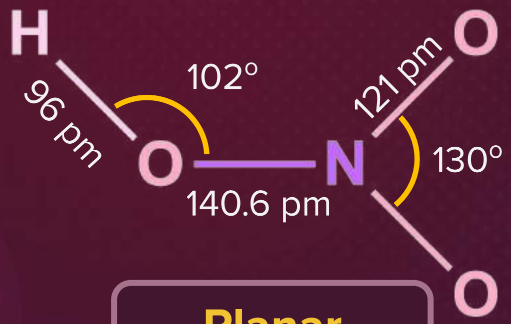
Nitric Acid (HNO_3)

3

In gaseous state

↓

HNO_3 exists as a **planar** molecule



Planar

Concentrated nitric acid, upon long standing, turns **yellow-brown** due to the **formation** of:

BOARDS

- a NO
- b NO_2
- c N_2O
- d N_2O_4

Hence, option (b) is the correct answer.

Nitric Acid (HNO_3)

Nitric acid

- Preparation
- Physical properties
- Chemical properties
- Uses

Nitric Acid (HNO_3)

Reactivity

With water

With metals

With non-metals and their compounds

Nitric Acid (HNO_3)

Reactivity with water

In aqueous solution ▷ Nitric acid behaves as a **strong acid**, releasing hydronium and nitrate ions

$$HNO_3\,(aq) + H_2O\,(\ell) \longrightarrow H_3O^+\,(aq) + NO_3^-\,(aq)$$

Nitric Acid (HNO_3)

Reactivity with metals

Concentrated nitric acid is a **strong oxidising agent.**

It attacks most metals

Except, **noble** metals
Example: Au, Pt

The **products** of oxidation depend upon

- Concentration of the acid
- Temperature
- Nature of the material undergoing oxidation

Nitric Acid (HNO_3)

1

HNO_3 is an excellent **oxidising agent**. Metals like copper and zinc which are insoluble in HCl, dissolve in HNO_3.

Nitric Acid (HNO_3)

Example

$$3Cu + 8HNO_3 \textbf{ (dil.)} \longrightarrow 3Cu(NO_3)_2 + 2\textbf{NO} + 4H_2O$$

$$Cu + 4HNO_3 \textbf{ (conc.)} \longrightarrow Cu(NO_3)_2 + 2\textbf{NO}_2 + 2H_2O$$

Nitric Acid (HNO_3)

Example

$$4Zn + 10HNO_3\ \textbf{(dil.)} \longrightarrow 4Zn(NO_3)_2 + \mathbf{N_2O} + 5H_2O$$

$$Zn + 4HNO_3\ \textbf{(conc.)} \longrightarrow Zn(NO_3)_2 + 2\mathbf{NO_2} + 2H_2O$$

Nitric Acid (HNO_3)

2 Some metals, such as gold, are insoluble even in HNO_3, but **dissolve in aqua regia**.

Aqua regia

1 A mixture of **25%** conc. HNO_3 and **75%** conc. HCl.

Nitric Acid (HNO_3)

2

The **enhanced ability** of aqua regia to dissolve metals arises from the **oxidising power** of HNO_3 and the ability of Cl^- to form **complexes** with metal ions.

Nitric Acid (HNO_3)

Some metals (example: **Cr, Al**) do not dissolve in concentrated nitric acid

because of the formation of a **passive film of oxide** on the surface

When copper is heated with conc. HNO_3 it **produces**?

BOARDS

- a $Cu(NO_3)_2$, NO, and NO_2
- b $Cu(NO_3)_2$ and N_2O
- c $Cu(NO_3)_2$ and NO_2
- d $Cu(NO_3)_2$ and NO

Hence, option (c) is the correct answer.

Nitric Acid (HNO_3)

Reactivity

- With water
- With metals
- With non-metals & their compounds

Iodine to iodic acid

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

Carbon to carbon dioxide

$$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$$

Nitric Acid (HNO_3)

Sulphur to sulphuric acid

$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

Phosphorus to phosphoric acid

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Brown Ring Test

Depends on the ability of Fe^{2+} to **reduce nitrates to nitric oxide**

Nitric oxide formed reacts with Fe^{2+} to form

Brown coloured complex

Brown Ring Test

Process

Add dilute **ferrous sulphate** solution to aqueous solution containing **nitrate ion**

Then carefully add **conc. sulphuric acid** along the sides of the test tube

Brown Ring Test

2

A **brown ring** at the interface between the solution and H_2SO_4 layer

Indicates the **presence of nitrate ion** in the solution

Brown Ring Test

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{(Brown)}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

Nitric Acid (HNO_3)

Uses

Used for the manufacture of **fertilisers** (NH_4NO_3)

For the manufacture of **other nitrates** that are used in **explosives**

Substances burn **more readily in N_2O** than in air because N_2O:

BOARDS

a Is reactive at high temperature

b Dissociates to give more nitrogen than in air

c The activation energy is increased on increasing temperature

d Dissociates more readily than O_2

Hence, option (d) is the correct answer.

The reaction of zinc with dilute and concentrated nitric acid, respectively, produces:

BOARDS

a NO_2 and NO

b NO and N_2O

c NO_2 and N_2O

d N_2O and NO_2

Hence, option (d) is the correct answer.

The mixture of concentrated **HCl and HNO_3** made in **3:1** ratio contains:

BOARDS

- a ClO_2
- b NOCl
- c NCl_3
- d N_2O_4

Hence, option (b) is the correct answer.

Allotropic Forms of Phosphorus

Important allotropic forms

- White phosphorus
- Red phosphorus
- Black phosphorus

Properties of White Phosphorus

Physical properties

1. Translucent white **waxy** solid
2. **Poisonous**
3. **Insoluble** in water but soluble in carbon disulphide
4. **Glows** in the dark (chemiluminescence)

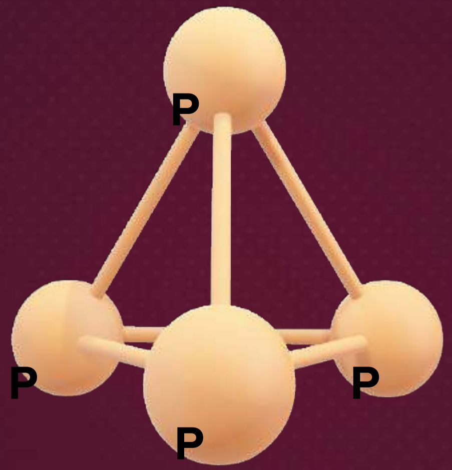
Properties of White Phosphorus

Bioluminescence

Glows in the dark
(chemiluminescence)

White Phosphorus

Structure



Consists of discrete **tetrahedral P_4** molecule

White Phosphorus

Chemical properties ▷

1 Stability

White phosphorus is thermodynamically **less stable**

because of **angular strain** in the **P_4** molecule

Angles are only **60°**

Result ▷

More reactive than the other solid phases

Under normal conditions

Properties of White Phosphorus

Chemical properties

In an inert atmosphere of CO_2

2

Dissolves in **boiling NaOH** solution to giving **PH_3**

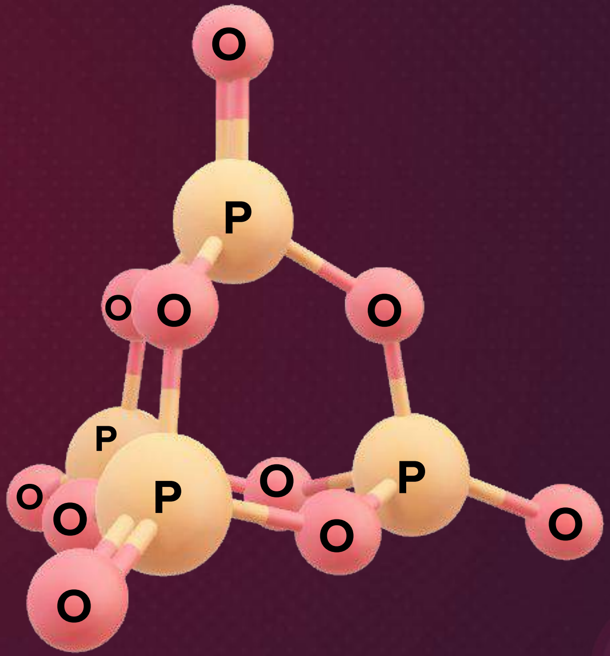
$$P_4\,(s) + 3NaOH\,(aq) + 3H_2O\,(l) \longrightarrow PH_3\,(g) + 3NaH_2PO_2\,(aq)$$

White Phosphorus

3

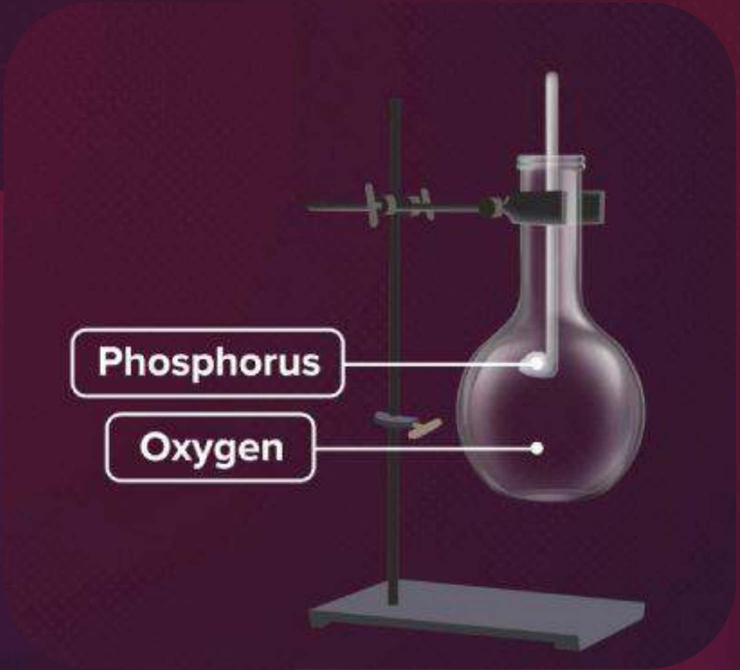
Readily **catches fire** to give **white fumes** of P_4O_{10}

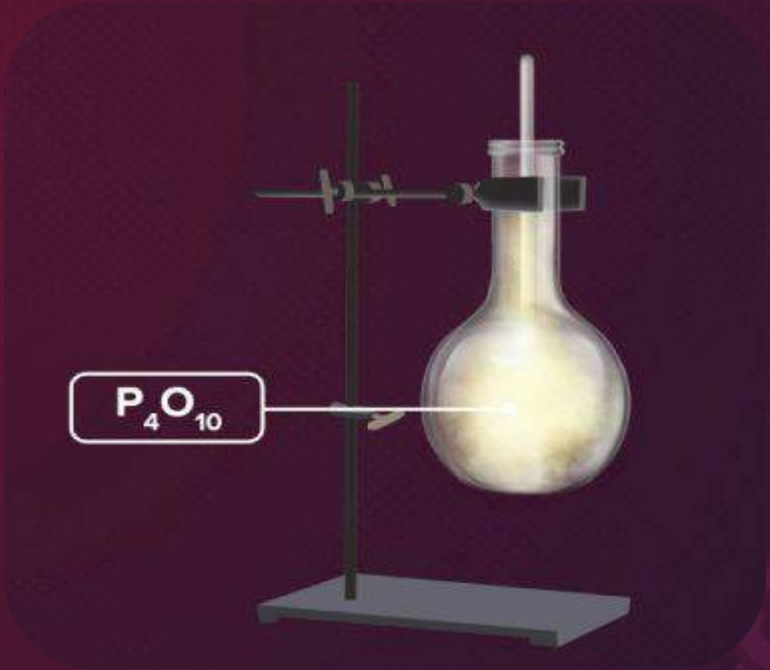
$P_4\ (s) + 5O_2\ (g) \longrightarrow P_4O_{10}\ (s)$



White Phosphorus

P_4 reacting with oxygen ▷



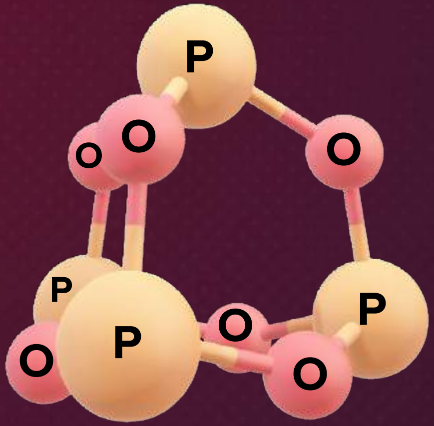


Properties of White Phosphorus

What happens if **limited air** is supplied?

Reaction with limited air

$P_4\,(s) + 3O_2\,(g) \longrightarrow P_4O_6\,(l)$



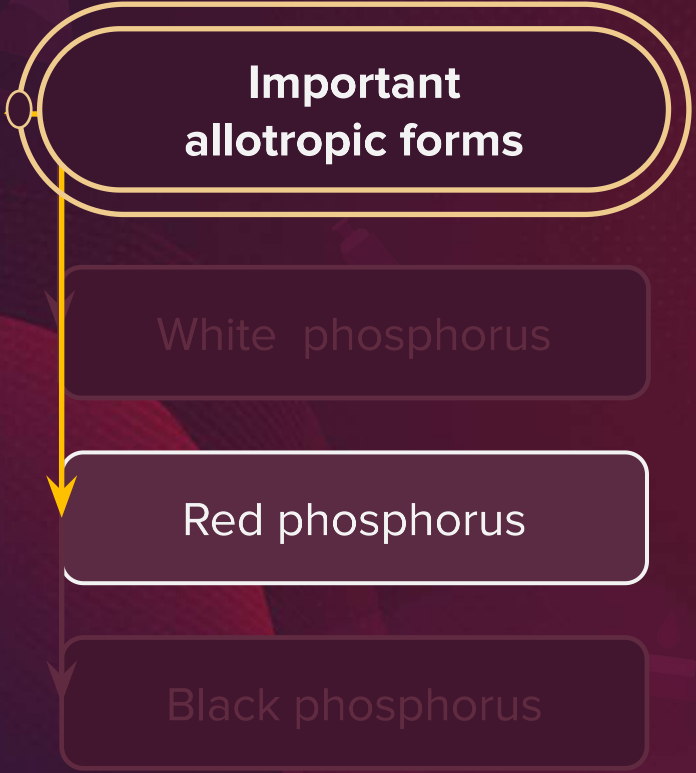
The reaction of P_4 with X leads selectively to P_4O_6. The X is:

BOARDS

- a Dry O_2
- b A mixture of O_2 and N_2
- c Moist O_2
- d O_2 in the presence of aqueous NaOH

Hence, option (b) is the correct answer.

Allotropic Forms of Phosphorus



Important allotropic forms

White phosphorus

Red phosphorus

Black phosphorus

Red phosphorus

Red Phosphorus

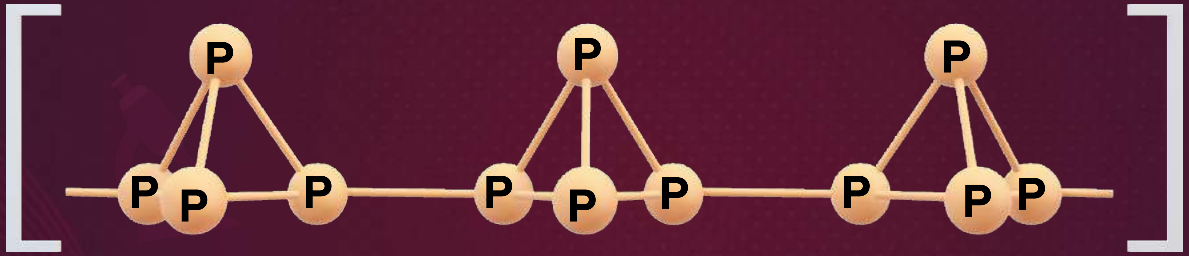
Preparation

Heating white phosphorus at 573 K in an **inert** atmosphere for several days

$$\text{White phosphorus} \xrightarrow[\text{Several days}]{\Delta} \text{Red phosphorus}$$

Properties

Structure



It is polymeric, consisting of chains of P_4 **tetrahedra** linked together, forming a giant molecule.

Properties

Due to this highly polymerised structure, **red phosphorus** is less reactive.

Physical properties

1 **Iron grey lustre**

2 **Non-poisonous**

3 **Insoluble** in **water** as well as in **carbon disulphide**

4 Does **not glow** in the dark

Red Phosphorus

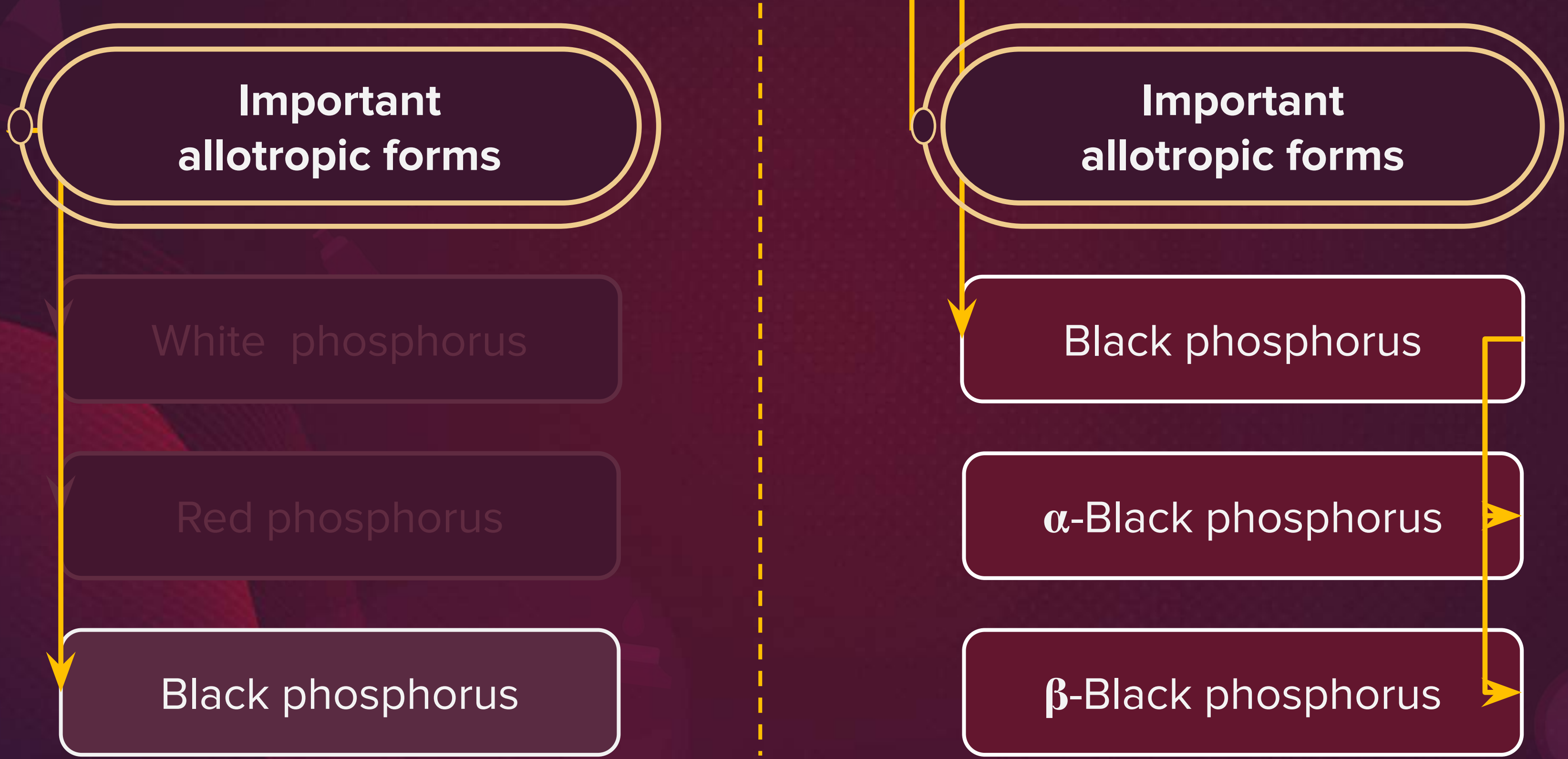
Chemical properties

1

$$\textbf{Red}\ \text{phosphorus} \xrightarrow[\Delta]{\text{High pressure}} \textbf{Black}\ \text{phosphorus}$$

Unlike white phosphorus, red **phosphorus** does not ignite readily in air and shows **no reaction with NaOH.**

Allotropic Forms of Phosphorus



Important allotropic forms

- White phosphorus
- Red phosphorus
- Black phosphorus

Important allotropic forms

- Black phosphorus
  - α-Black phosphorus
  - β-Black phosphorus

α-Black Phosphorus

Preparation

$$\textbf{Red}\ \text{phosphorus} \xrightarrow[\Delta]{\text{Sealed tube at 803 K}} \boldsymbol{\alpha}\textbf{-Black}\ \text{phosphorus}$$

α-Black Phosphorus

Properties

1. Can be sublimed in air
2. Has opaque **monoclinic** or **rhombohedral** crystals
3. Does **not oxidise** in air

β-Black Phosphorus

Preparation

White phosphorus $\xrightarrow[\text{473 K}]{\text{Under high pressure}}$ **β-Black** phosphorus

Properties

It does not burn in air up to 673 K.

Thermally **most stable**

Important

Thermal stability order

White phosphorus < Red phosphorus < Black phosphorus

Thermodynamically most stable allotrope of phosphorus is:

BOARDS

a Red

b White

c Black

d Yellow

Hence, option (c) is the correct answer.

Phosphorus-Containing Compounds

Phosphorus-Containing Compounds

- Phosphine (PH_3)
- Phosphorus halides
- Oxoacids of phosphorus

Phosphine (PH_3)

Phosphine

- Preparation
- Physical properties
- Chemical properties
- Uses

Preparation

1

Reaction of calcium phosphide with water

$$Ca_3P_2\,(s) + 6H_2O\,(l) \rightarrow 3Ca(OH)_2\,(aq) + 2PH_3\,(g)$$

Preparation

2

Reaction of calcium phosphide with dilute HCl

$$Ca_3P_2\,(s) + 6HCl\,(l) \rightarrow 3CaCl_2\,(aq) + 2PH_3\,(g)$$

Preparation

In laboratory

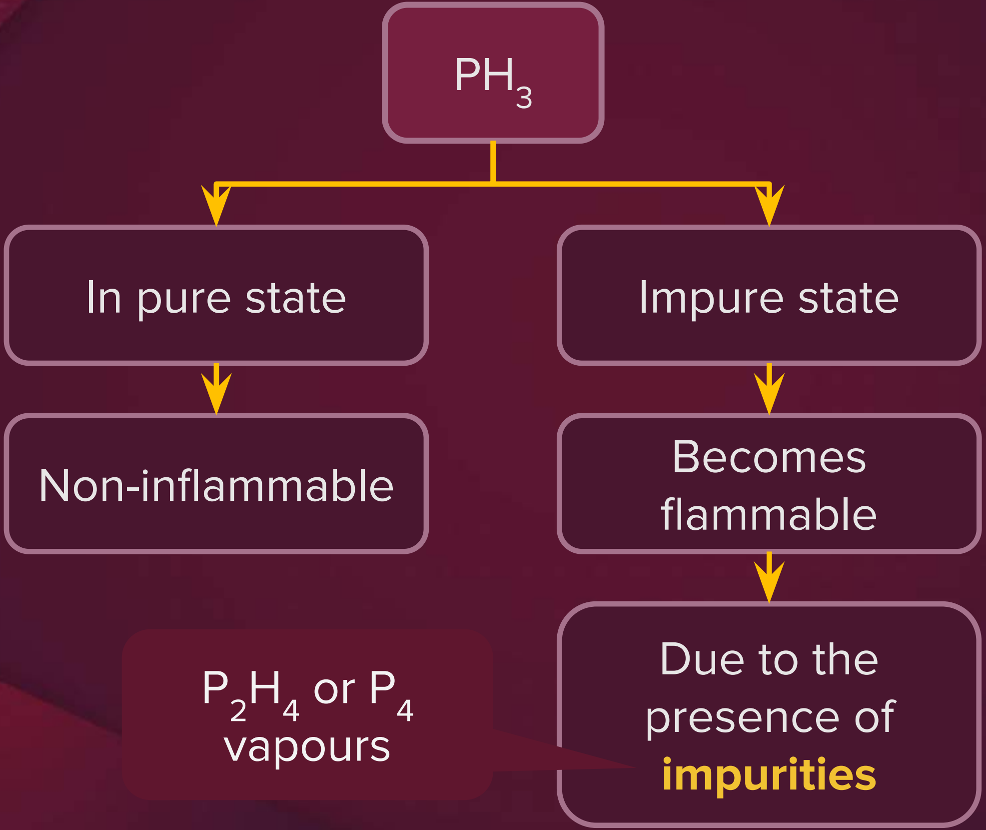
White phosphorous

$$P_4\ (s) + 3NaOH\ (aq) + 3H_2O\ (l) \downarrow PH_3\ (g) + \mathbf{3NaH_2PO_2}\ (aq)$$

In an **inert atmosphere** of CO_2

Point to be Noted

In pure state



PH_3

In pure state

Non-inflammable

Impure state

Becomes flammable

Due to the presence of **impurities**

P_2H_4 or P_4 vapours

Preparation

Purification

Absorbed in HI to form **phosphonium iodide (PH_4I)**

which on treating with **KOH,** it gives off **phosphine**

$$PH_4I\ (aq) + KOH\ (aq) \longrightarrow KI\ (aq) + H_2O\ (aq) + PH_3\ (g)$$

Physical Properties

1. **Colourless** gas
2. **Rotten fish-like** smell
3. Highly **poisonous**
4. Explodes in contact with traces of **oxidising agents**

   ↓

   Example: HNO_3, Cl_2, and Br_2 vapours
5. It is slightly soluble in water but soluble in organic solvents.

Chemical Properties

1

The solution of PH_3 in water decomposes in the presence of light

giving **red phosphorus** and **H_2**

Chemical Properties

2

When absorbed in **copper sulphate or mercuric chloride solution**, the corresponding **phosphides** are obtained.

$$3CuSO_4\,(aq) + 2PH_3\,(g) \longrightarrow Cu_3P_2(aq) + 3H_2SO_4\,(aq)$$

$$3HgCl_2\,(aq) + 2PH_3\,(g) \longrightarrow \mathbf{Hg_3P_2}\,(aq) + 6HCl\,(aq)$$

Uses

1. The spontaneous combustion of phosphine is technically used in **Holme’s signals**
2. Smoke screens

Uses

3

Containers containing **calcium carbide** and **calcium phosphide** are pierced and thrown in the sea

when the gases evolved burn serve as a **signal.**

Phosphorus-Containing Compounds

- Phosphine (PH_3)
- **Phosphorus halides**
- Oxoacids of phosphorus

Phosphorus-Containing Compounds

- Phosphorus halides
  - Phosphorus trichloride

Phosphorus Trichloride (PCl_3)

Phosphorus trichloride

- Preparation
- Physical properties
- Chemical properties

Preparation

1

Obtained by passing **dry chlorine** over heated white phosphorus

$$P_4\,(s) + 6Cl_2\,(g) \longrightarrow 4PCl_3\,(\ell)$$

Preparation

2

Obtained by the action of **thionyl chloride** with white phosphorus

✓

$$P_4\,(s) + 8SOCl_2\,(\ell) \longrightarrow 4PCl_3\,(\ell) + 4SO_2\,(g) + 2S_2Cl_2\,(\ell)$$

$$P_4 + SOCl_2 \longrightarrow PCl_3 + SO_2 + S_2Cl_2$$

Physical Properties

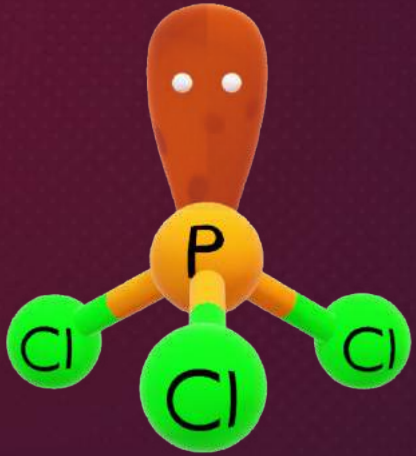
It is a **colourless oily liquid**.

Chemical Properties

Structure

1

Pyramidal shape in which phosphorus is **sp^3 hybridised.**



Chemical Properties

2

Hydrolyses in the presence of moisture

$$\overset{+3}{P}Cl_3\,(\ell) + 3H_2O\,(\ell) \rightarrow H_3PO_3\,(aq) + 3HCl\,(aq)$$

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

$$\boxed{x = +3}$$

Chemical Properties

3

Reacts with organic compounds containing **–OH group**

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

$$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

Chemical Properties

4

It also acts as a reducing agent when treated with **SO_3** and **conc. H_2SO_4.**

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

$$PCl_3 + 2H_2SO_4 \longrightarrow SO_3HCl + SO_2 + 2HCl + HPO_3$$

The **product formed** in the reaction of $SOCl_2$ with white phosphorus is?

- a PCl_3
- b SO_2Cl_2
- c SCl_2
- d $POCl_3$

Solution

a PCl_3

b SO_2Cl_2

c SCl_2

d $POCl_3$

Hence, option a is the correct answer.

What may be expected to happen when phosphine gas is mixed with chlorine gas?

- **a** PCl_3 and HCl are formed, and the mixture warms up
- **b** PCl_5 and HCl are formed, and the mixture cools down
- **c** $PH_3.Cl_2$ is formed with warming up
- **d** $PH_3.Cl_2$ is formed with warming up

Solution

Hence, option (a) is the correct answer.

PCl_3 reacts with water to form:

a PH_3

b H_3PO_3 and HCl

c $POCl_3$

d H_3PO_4

Solution

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

Hence, option (b) is the correct answer.

One mole of PCl_3 is dissolved in excess of water. The number of moles of NaOH required to neutralise this solution completely is:

- a 6
- b 7
- c 5
- d 4

Solution

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

H_3PO_3 is dibasic so 2 moles for this and 3 mole for HCl and hence total mole = 5

Hence, option (c) is the correct answer.

White phosphorous on reaction with NaOH gives PH_3 and:

BOARDS

$$P_4 + NaOH + H_2O \longrightarrow PH_3 + \boxed{NaH_2PO_2}$$

a Na_2HPO_3 ✗

[✓ b] NaH_2PO_2 ✓

c NaH_2PO_3 ✗

d Na_3PO_4 ✗

Sodium hypophosphite

Solution

Hence, option (b) is the correct answer.

Which of the following may ignite spontaneously in air?

BOARDS

a White phosphorus

b Red phosphorus

c Black phosphorus

d Nitrogen

Solution

White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the P_4 molecule where the angles are only 60°. It readily catches fire in air to give dense white fumes of P_4O_{10}.

Hence, option (a) is the correct answer.

White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a:

BOARDS

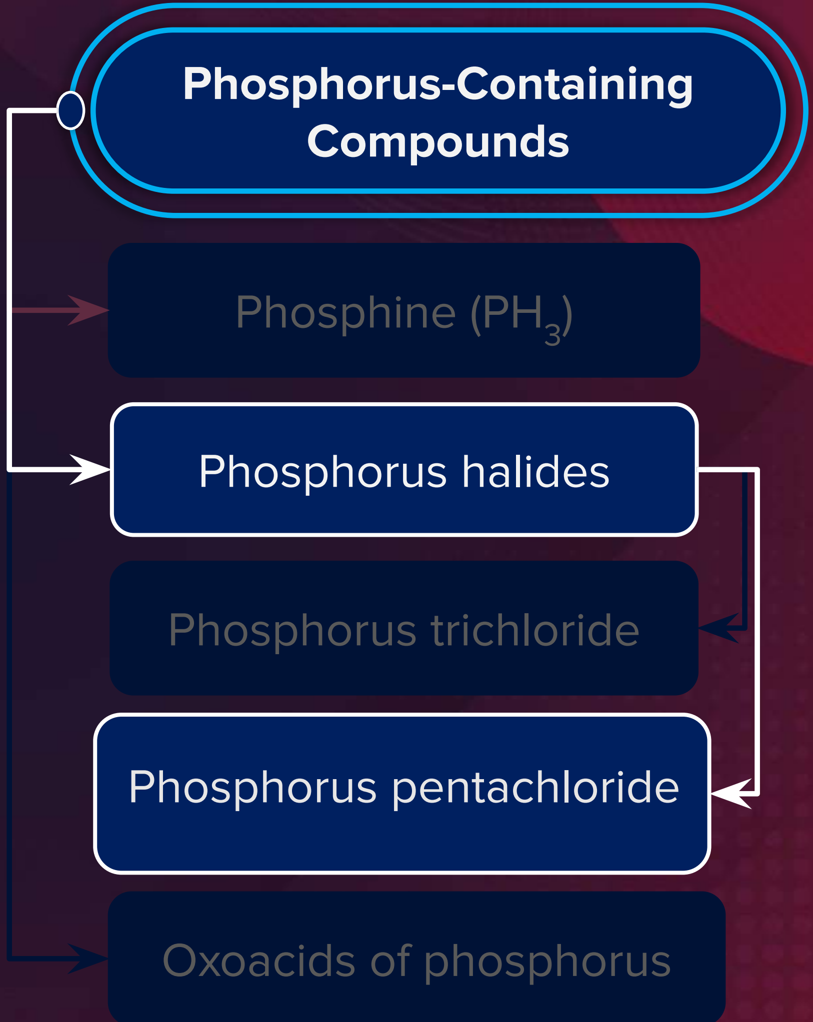
- a Dimerisation reaction
- b Disproportionation reaction
- c Condensation reaction
- d Precipitation reaction

Solution

P_4 (s) + 3NaOH (aq) + $3H_2O$ (l) $\longrightarrow$ PH_3 (g) + $\mathbf{3NaH_2PO_2}$ (aq)

P undergoes reduction as well as oxidation and hence disproportionation

Hence, option (b) is the correct answer.



Phosphorus-Containing Compounds

- Phosphine (PH_3)
- Phosphorus halides
  - Phosphorus trichloride
  - Phosphorus pentachloride
- Oxoacids of phosphorus

Phosphorus Pentachloride (PCl_5)

Phosphorus pentachloride

- **a** Preparation
- **b** Physical properties
- **c** Chemical properties

Preparation

1

Reaction of white phosphorus with excess of dry chlorine

$$P_4\,(g) + 10Cl_2\,(g) \longrightarrow 4PCl_5\,(g)$$

Preparation

$SOCl_2$

2

Prepared by the action of **SO_2Cl_2** on phosphorus

$$P_4\,(g) + 10SO_2Cl_2 \longrightarrow 4PCl_5\,(g) + 10SO_2$$

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

Physical Properties

PCl_5 is a **yellowish white** powder.

Chemical Properties

$$✓\ \overset{+5}{P}Cl_5 + 4H_2O \longrightarrow \underline{\underline{H_3\overset{+5}{P}O_4}} + 5HCl$$

1

In moist air, it hydrolyses to **$\underline{POCl_3}$** and finally $\underline{\text{gets converted}}$ to **$\underline{\text{phosphoric}}$** $\underline{\text{acid}}$.

$$✓\ PCl_5\,(g) + H_2O\,(\ell) \longrightarrow \underline{\cancel{POCl_3}}\,(g) + \underline{2HCl\,(aq)}$$

$$\underline{\cancel{POCl_3}}\,(aq) + 3H_2O\,(\ell) \longrightarrow \underline{H_3PO_4}\,(aq) + 3\underline{HCl}\,(aq)$$

Chemical Properties

2

When heated, it sublimes but **decomposes** on stronger heating.

$$PCl_5 \xrightarrow{250\ ^\circ C} PCl_3 + Cl_2$$

Chemical Properties

3

It reacts with organic compounds containing –OH group, converting them to **chloro derivatives**.

$$\underline{C_2H_5OH} + \underline{PCl_5} \longrightarrow \underline{\mathbf{C_2H_5Cl}} + \overset{\star}{POCl_3} + \underline{HCl}$$

$$CH_3COOH + PCl_5 \longrightarrow \underline{\mathbf{CH_3COCl}} + \overset{\star}{POCl_3} + HCl$$

Chemical Properties

4

On heating with finely divided metals, PCl_5 gives corresponding **chlorides**.

$$2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$$ ✓

$$Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$$

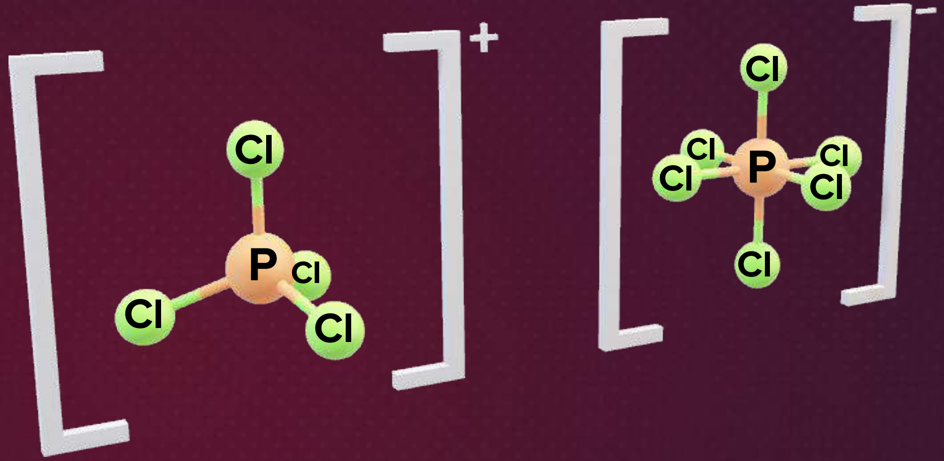
Structure

$$PCl_5 + PCl_5 \rightarrow \boxed{PCl_4^+}\ PCl_6^-$$

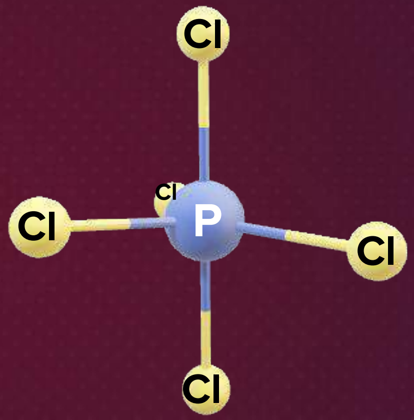
In solid state, it exists as an **ionic solid**

Consisting of **$[PCl_4]^+$ (tetrahedral)** and **$[PCl_6]^-$ (octahedral).**

As **Ionic solid $[PCl_4]^+$ (tetrahedral)** and **$[PCl_6]^-$ (octahedral)**

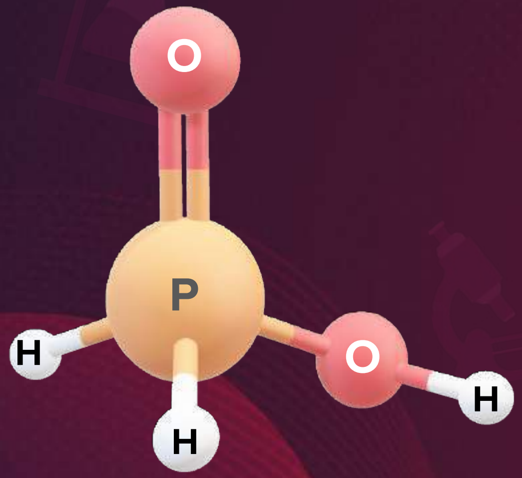


In gaseous and liquid phases, it has a **trigonal bipyramidal** structure.



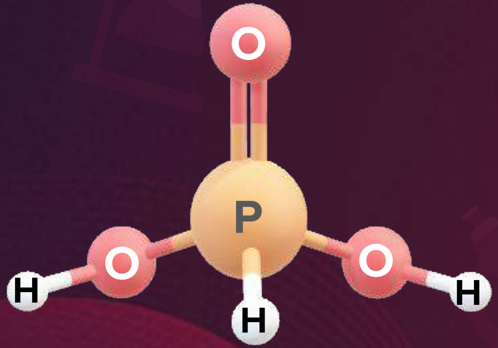
The three equatorial P–Cl bonds are **equivalent**, while the two axial bonds are **longer** than equatorial bonds

Oxoacids of Phosphorus



Name	Hypophosphorous (Phosphinic)
Formula	H_3PO_2
Oxidation	+1
Characteristic	One P-OH Two P-H One P=O
Preparation	White P_4 + alkali

Oxoacids of Phosphorus



Name	Orthophosphorous (Phosphonic)
Formula	H_3PO_3
Oxidation	+3
Characteristic	Two P-OH One P-H One P=O
Preparation	$P_2O_3 + H_2O$

Orthophophorous Acid

Orthophophorous acid (or phosphorous acid) on heating **disproportionates** to give orthophosphoric acid (or phosphoric acid) and phosphine.

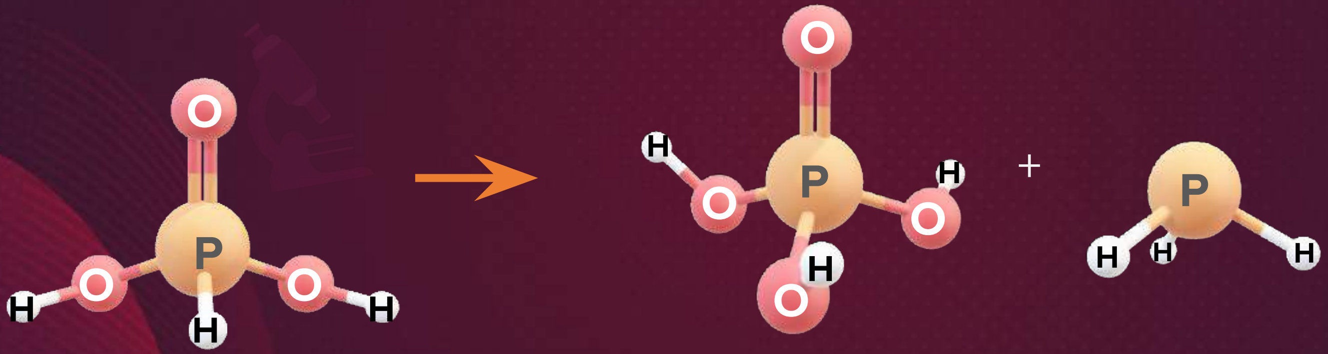
$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

Oxoacids of Phosphorus

+3

+5

-3



Phosphorous acid

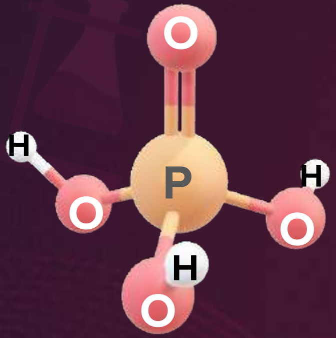
Phosphoric acid

Phosphine

Oxoacids of Phosphorus

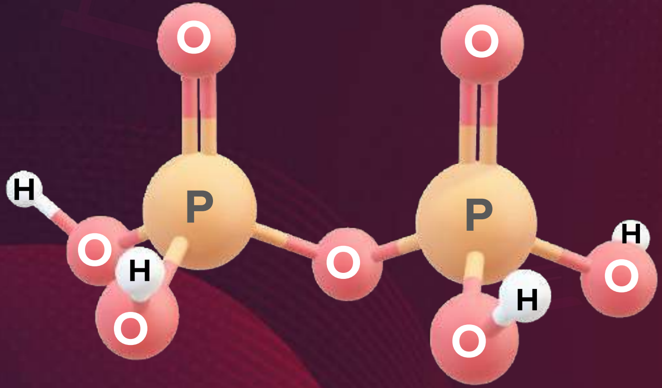
Name	Pyrophosphorous
Formula	
Oxidation	
Characteristic	Four P-OH Two P-H Two P=O One P-O-P
Preparation	$PCl_3 + H_3PO_3$

Oxoacids of Phosphorus



Name	Orthophosphoric
Formula	H_3PO_4
Oxidation	: +5
Characteristic	Three P-OH One P=O
Preparation	$P_4O_{10} + H_2O$

Oxoacids of Phosphorus

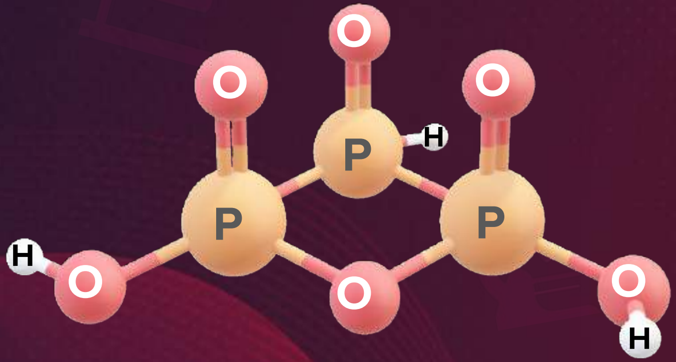


Name	Pyrophosphoric
Formula	$H_4P_2O_7$
Oxidation	+5
Characteristic	Four P-OH Two P=O One P-O-P
Preparation	Heating phosphoric acid

Oxoacids of Phosphorus

Name	Hypophosphoric
Formula	$H_4P_2O_6$
Oxidation	+4
Characteristic	Four P-OH One P-P Two P=O
Preparation	Red P_4 + alkali

Oxoacids of Phosphorus



Name	Metaphosphoric
Formula	$(HPO_3)_n$
Oxidation	+5
Characteristic	Three P-OH Three P=O Three P-O-P
Preparation	Phosphorus acid + Br_2, heat in a sealed tube

Strong reducing behaviour of H_3PO_2 is due to:

BOARDS

a. High electron gain enthalpy of phosphorus

b. High oxidation state of phosphorus

c. Presence of two –OH groups and one P–H bond

d. Presence of one –OH group and two P–H bonds

Solution

Hence, option (d) is the correct answer.

Which is the correct statement for the given acids?

BOARDS

Solution

Can be understood by structures
Phosphinic acid is a monoprotic acid as it contains one P–OH bond
Phosphonic acid is a diprotic acid as it contains two P–OH bonds

Hence, option (a) is the correct answer.

- **a** Phosphinic acid is a monoprotic acid, while phosphonic acid is a diprotic acid.
- **b** Phosphinic acid is a diprotic acid, while phosphonic acid is a monoprotic acid
- **c** Both are diprotic acids.
- **d** Both are triprotic acids.

Which of the following statements is not valid for oxoacids of phosphorus?

a. Orthophosphoric acid is used in the manufacture of triple superphosphate.

b. Hypophosphorous acid is a diprotic acid.

c. All oxoacids contain tetrahedral four coordinated phosphorus.

d. All oxoacids contain at least one P═O unit and one P-OH group.

Solution

Hence, option (b) is the correct answer.

Oxidation states of P in $H_4P_2O_5$, $H_4P_2O_6$, $H_4P_2O_7$ are respectively:

~~BOARDS~~

$\boxed{+4}$

$+4 + 2x + 5(-2) = 0$

$x = +3$

$+4$
$+ 2x$
$+ 7(-2)$
$= 0$

$x = +5$

a +3, +5, +4 ✗

b +5, +3, +4 ✗

c +5, +4, +3 ✗

[✓ d] +3, +4, +5

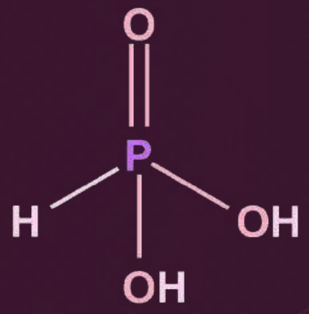
Solution

Hence, option (d) is the correct answer.

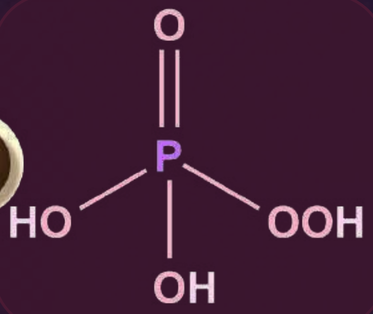
The structural formula of hypophosphorous acid is:

BOARDS

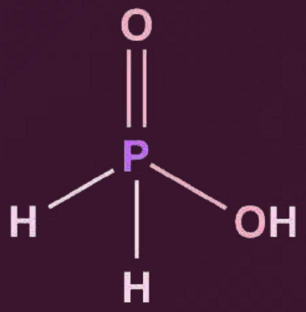
a



b



c



d None of these

Solution

Hypophosphorous acid is H_3PO_2.

Hence, option (c) is the correct answer.

p-Block Elements

p-Block Elements

- Group 13
- Group 14
- Group 15
- **Group 16**
- Group 17
- Group 18

One
Should
See
Tennis
Politely

Group 16 Elements

Oxygen ($^{16}_{8}O$)	Non-metals
Sulphur ($^{32}_{16}S$)	
Selenium	Metalloids
Tellurium	
Polonium	Radioactive metal

Sometimes known as group of **chalcogens**

Note

Polonium is **radioactive** and short-lived (half-life 13.8 days).

Occurrence

Oxygen

Most abundant of all elements ✓

Exists in free form as O_2 and makes up **20.9%** by volume and **23%** by weight of atmosphere

Occurrence

Oxygen

Most of this has been produced by **photosynthesis.**

$$6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2$$

Occurrence

Sulphur

Constitutes **0.034%** by weight of earth's crust and occurs mainly in combined form as numerous sulphide ores and as sulphates (particularly **gypsum**).

Properties of Group-16

Atomic Properties

- Electronic configuration
- Atomic & ionic radii
- Ionisation enthalpy
- Electron gain enthalpy
- Electronegativity

Electronic Configuration

$16 - 10 = 6$

The elements of group 16 have **six** electrons in the outermost shell.

General valence shell electronic configuration

$ns^2 np^4$

Properties of Group-16 Elements

Property	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass	16.00	32.06	78.96	127.60	210.00
State	Gas	Solid	Solid	Solid	Solid
Electronic configuration	[He] $2s^2\ 2p^4$	[Ne] $3s^2\ 3p^4$	[Ar] $3d^{10}\ 3s^2\ 3p^4$	[Kr] $4d^{10}\ 5s^2\ 5p^4$	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$
Radioactive	No	No	No	No	Yes
Melting point (K)	55	393	490	725	520
Boiling point (K)	90	718	958	1260	1235

Atomic and Ionic Radii

Order

O < S < Se < Te

Down the group

Atomic and **ionic radii** ↑

Due to **increase** in number of shells

Ionisation Enthalpy

Down the group

Decreases

O > S > Se > Te

Reason

Due to **increase in size**.

Ionisation Enthalpy

Order

Group 15 elements > Group 16 elements

$ns^2\ np^3$

$ns^2\ np^4$

Because of **extra stable** half-filled p orbital.

Electron Gain Enthalpy

Down the group

↓

S > Se > Te > Po > O

-200 -141

For O

Due to compact nature, it has **less negative** electron gain enthalpy **than S.**

From S to Po

The value again becomes **less negative** up to polonium.

Electronegativity

Next to fluorine, **oxygen** has the highest electronegativity value amongst the elements.

Electronegativity

Order

O > S > Se > Te > Po

Down the group

Decreases

with **increase** in atomic size

Group 16 Elements

Group 16 Elements

- Occurrence
- Atomic properties
- Physical properties
- Chemical properties

Physical Properties

1. Metallic character

Oxygen and sulphur

Selenium and tellurium

Polonium

Metallic Character

Down
the group

Increases

with **increase** in
atomic size

Physical Properties

2. Catenation

→ σ bond strength

σ

$\ddot{O} - \ddot{O}$

O = O

Down the group

S

Decreases ✓

This property is prominently displayed by sulphur (S_8).

Physical Properties

3. Boiling point

Down the group

Increases

O < S < Se < Te > Po

Physical Properties

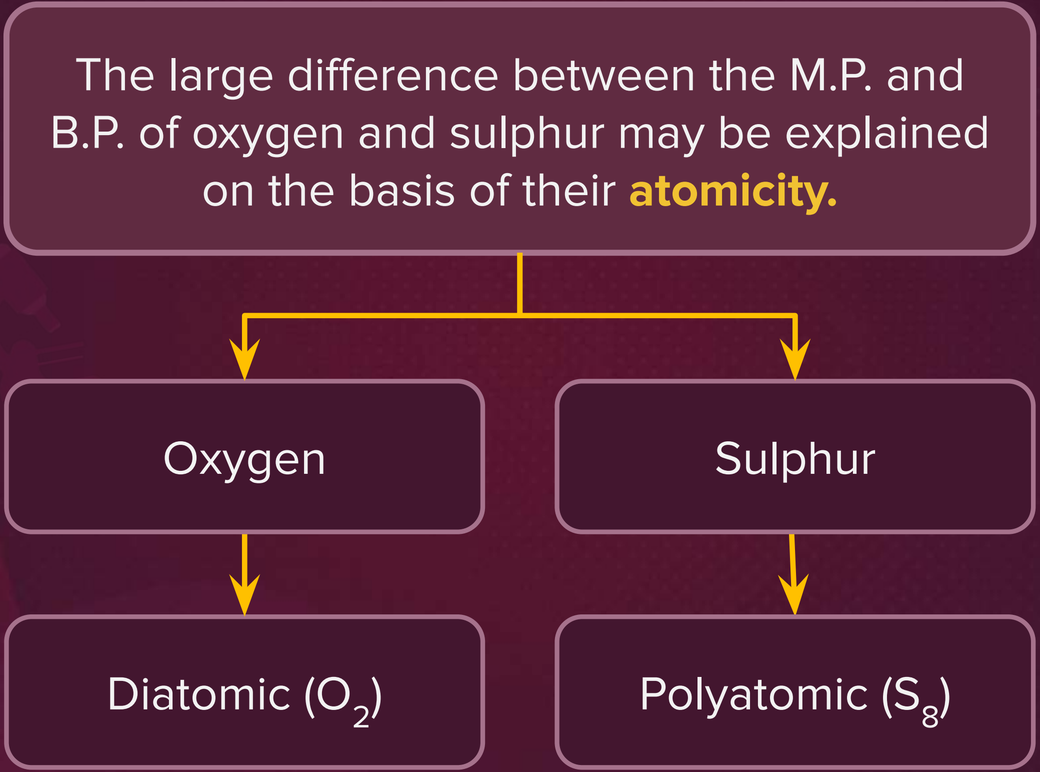
4. Melting point

Down the group

Increases

O < S < Se < Te > Po

Physical Properties



The large difference between the M.P. and B.P. of oxygen and sulphur may be explained on the basis of their **atomicity.**

Oxygen

Diatomic (O_2)

Sulphur

Polyatomic (S_8)

Physical Properties

5. Allotropy

All elements

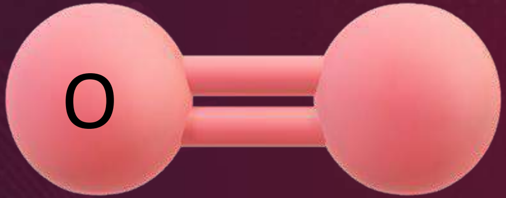
show allotropy.

Physical Properties

Oxygen exists in two allotropic forms

- O_2
- O_3 (unstable and decomposes to O_2)

Allotropes of Oxygen (O)



Dioxygen (O_2)

Ozone (O_3)

Allotropes of Sulphur

$\boxed{S_8}$

S_2 S_4 S_6 S_{20} S_8 S_{10} S_{14}

Sulphur has more allotropic forms than any other element.

This difference arises partly from the extent to which sulphur has **polymerised** and partly from the crystal structure adopted.

Allotropes of Sulphur

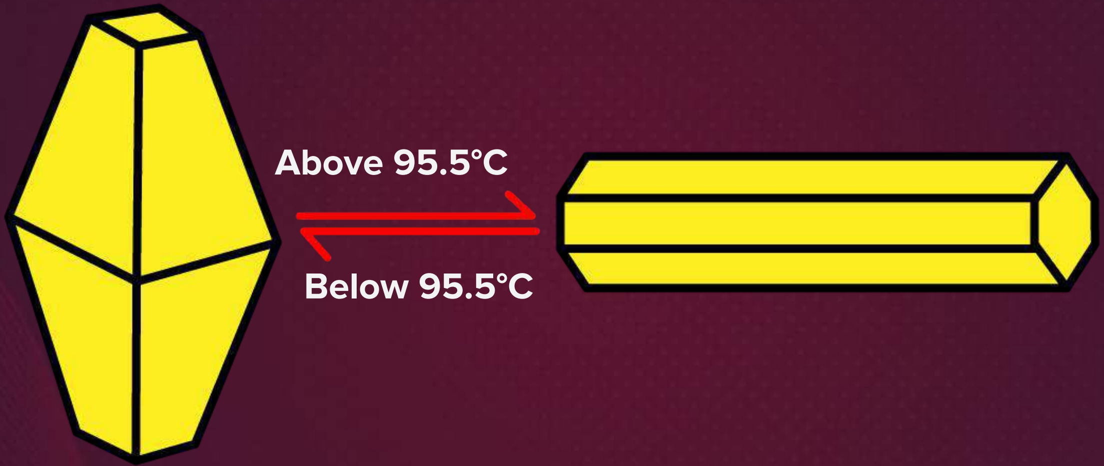
Two common forms are **α or rhombic sulphur** and **β or monoclinic sulphur,** both are stable at 95.5°C (transition temperature).

These two forms change **reversibly** with slow heating or slow cooling.

Rhombic Sulphur

Monoclinic Sulphur

Allotropes of Sulphur



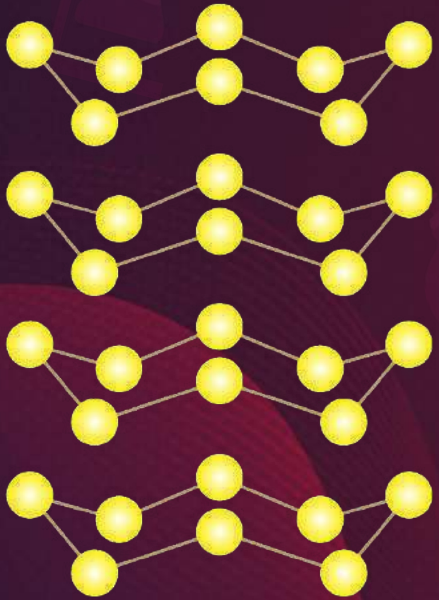
Above 95.5°C

Below 95.5°C

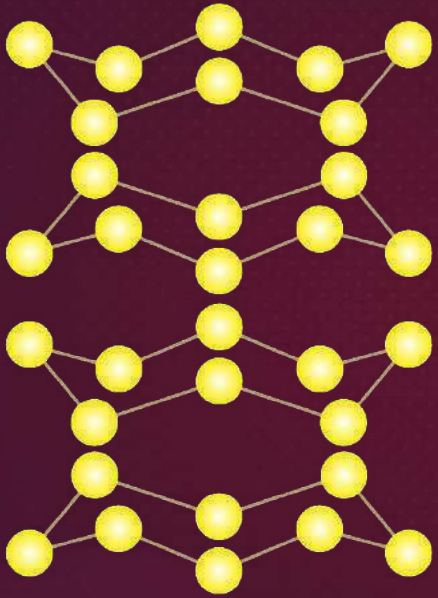
Rhombic sulphur

Monoclinic sulphur

Allotropes of Sulphur



Rhombic sulphur



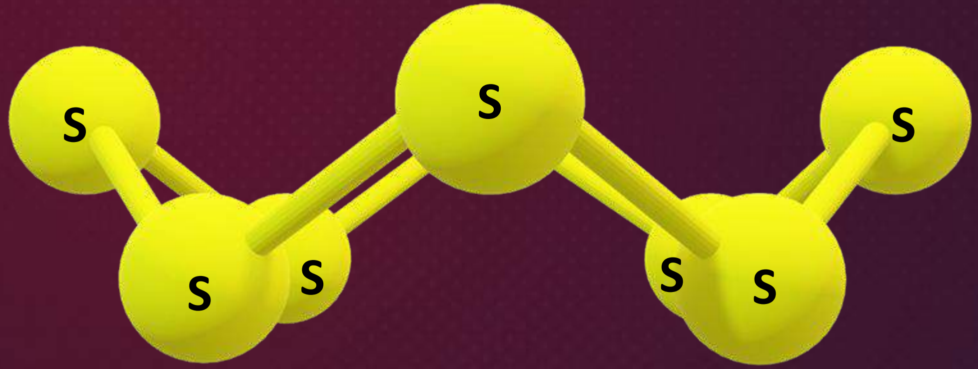
Monoclinic sulphur

A third form known as **γ-monoclinic** sulphur is also present.

Allotropes of Sulphur

All three forms contain **puckered S_8 rings** with a crown conformation.

Crown conformation



Rhombic (α-Sulphur)

1. It is **yellow** in colour and its specific gravity is 2.06.
2. Melting point = **385.8 K**
3. It is readily **soluble in CS_2**.
4. Rhombic sulphur crystals are formed on **evaporating** the solution of roll sulphur in CS_2.
5. It is **insoluble in water** but gets dissolved to some extent in benzene, alcohol and ether.

Monoclinic (β-Sulphur)

1 Its melting point is **393 K** and specific gravity is 1.98.

2 It is **soluble in CS_2**.

3 This form of sulphur is prepared by **melting** rhombic sulphur in a dish and cooling it till crust is formed.

Two holes are made in the crust and the remaining liquid is poured out.

On removing the crust, **colourless, needle-shaped crystals** of β-sulphur are formed.

Allotropes of Sulphur

Both rhombic and monoclinic sulphur have **S_8 molecules,** which are packed to give different crystal structures.

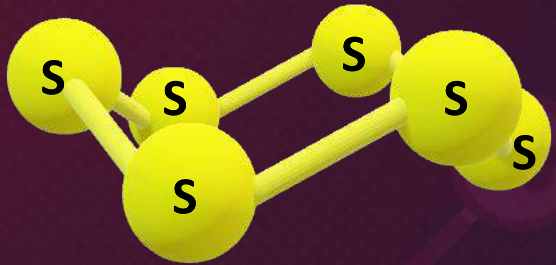
The S_8 ring in both the forms is puckered and has a **crown** shape.

S S S

Several other modifications of sulphur containing **6-20 sulphur** atoms per ring have been synthesised in the last two decades.

In cyclo-S_6, the ring adopts the **chair form.**

Chair conformation



Uses

The S—S bond is important in **biological** system.

It is found in some **proteins** and **enzymes** such as **cysteine**.

Uses

Selenium has a unique property of **photo conductivity.**

It is used in **photocopying** machines and also as a **decolouriser** of glass.

Correct statement about **allotropy of sulphur** is:

BOARDS

$$\text{Rhombic} \xrightleftharpoons{95^\circ C} \text{Monoclinic}$$

- ~~a~~ Monoclinic sulphur is more stable than rhombic sulphur at room temperature. 20 - 25°C
- ~~b~~ Both monoclinic and rhombic sulphur have the same ring structures and crystalline structures. S_8
- [✓ c] Rhombic sulphur exists at room temperature. ✓
- d None of these ✗

The most stable allotropic form of sulphur is Rhombic sulphur. Hence, stable at room temperature.

Hence, option (c) is the correct answer.

Identify the **incorrect** statement:

$S_2 \rightarrow \overset{*}{\pi}3p_x^1 = \overset{*}{\pi}3p_y^1$

$O_2 \rightarrow \overset{*}{\pi}2p_x^1 = \overset{*}{\pi}2p_y^1$

a. Rhombic and monoclinic sulphur have S_8 molecules. T

b. S_8 ring has a crown shape. T

c. S_2 is paramagnetic like oxygen. T

d. The S–S–S bond angles in the S_8 and S_6 rings are the same. F ✓

Hence, option (d) is the correct answer.

Crown shape of S_8 molecule is present in:

BOARDS

- a Rhombic sulphur
- b Monoclinic sulphur
- c Both (a) & (b)
- d None of these

Both rhombic & monoclinic sulphur has crown shape.

Hence, option (c) is the correct answer.

Identify the incorrect statement related to PCl_5 from the following:

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

- a. PCl_5 molecule is non-reactive. ✗
- b. Three equatorial P-Cl bonds make an angle of 120° with each other. T
- c. Two axial P-Cl bonds make an angle of 180° with each other. T
- d. Axial P-Cl bonds are longer than equatorial P-Cl bonds. T

Hence, option (a) is the correct answer.

Which of the following cannot dissociate as $PX_5 \rightleftharpoons PX_3 + X_2$?

NEET BOARDS

a PF_5

b PCl_5

c PBr_5

d PI_5

Hence, option (a) is the correct answer.

Which compound has an ionic nature in solid state?

BOARDS

a PCl_5

b $POCl_3$

c P_4O_{10}

d PCl_3

Hence, option (a) is the correct answer.

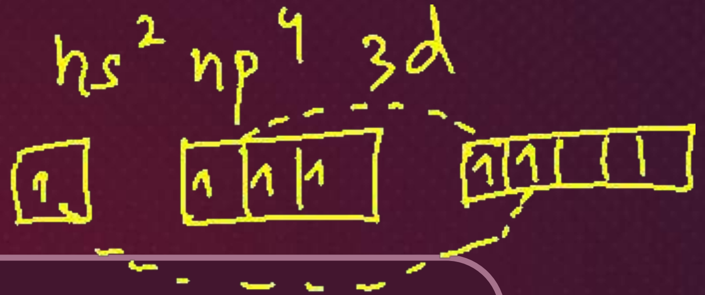
Anomalous properties of oxygen

- Covalency
- Bonding

Covalency

The **absence of d-orbitals** in oxygen **restricts** its covalency to **4** and **rarely increases beyond 2**.

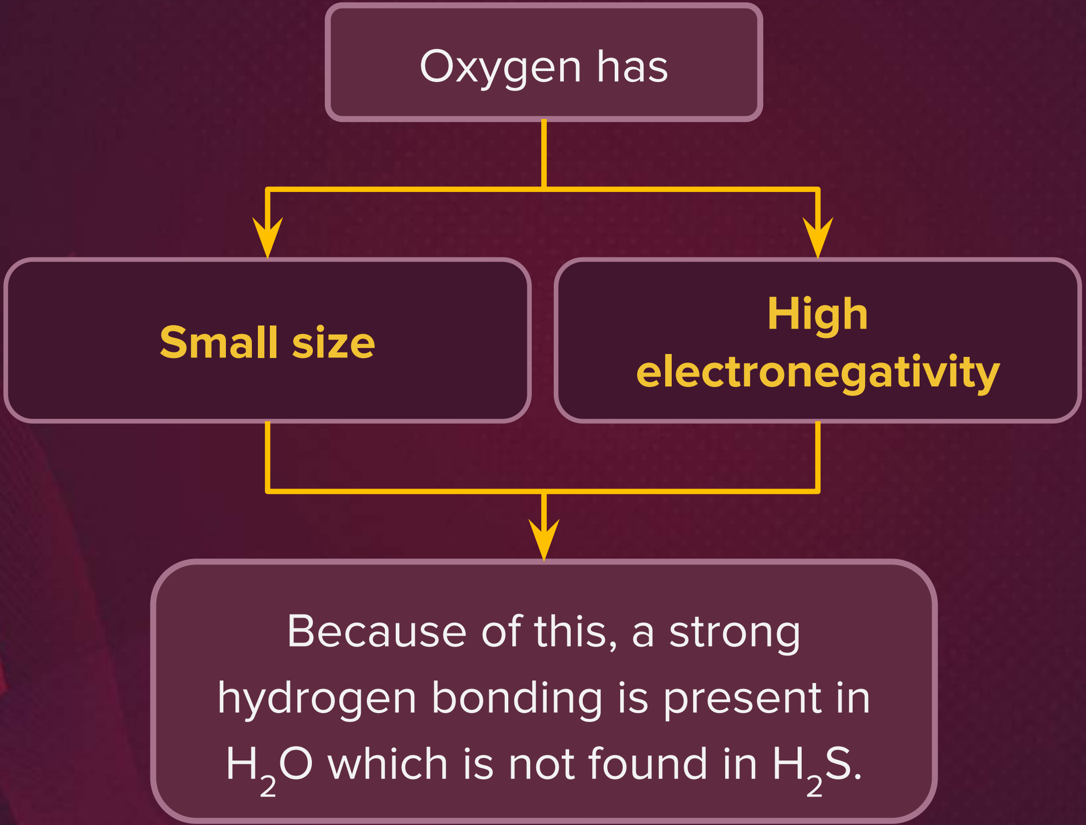
Covalency



In case of **other elements** of the same group,

The valence shell can be **expanded** and covalency **exceeds four**.

Bonding



Oxygen has

Small size

High electronegativity

Because of this, a strong hydrogen bonding is present in H_2O which is not found in H_2S.

Oxidation State & Stability

Oxidation states

- -2
- +2
- +4
- +6

Down the group

Tendency to exhibit **-2** oxidation state ↓

Polonium hardly shows –2 oxidation state.

-2 Oxidation State

Electronegativity of oxygen is very high, therefore it shows only **negative** oxidation states such as **–2.**

Except in the case of **OF_2** where its oxidation states is **+2**.

Oxidation State

Other elements of the group exhibit **+2, +4, +6** oxidation states.

+4 and +6 are **more common**.

+4 Oxidation State

Down the group

Tendency to exhibit +4 oxidation state ↑

Reason

Inert pair effect

+6 Oxidation State

Down the group

Tendency to exhibit **+6** oxidation state ↓

+4 and +6 Oxidation States

+6

SF_6

S, Se, and Te usually show

+4 oxidation in their compounds with **oxygen**

+6 oxidation in their compounds with **fluorine**

↑

Bonding in +4 and +6 oxidation states is primarily **covalent**.

✓

Chemical Properties

Reactivity

- Towards hydrogen
- Towards oxygen
- Towards halogens

Properties of Hydrides

Thermal stability

H_2O > H_2S > H_2Se > H_2Te

Hydrides	$\Delta_{diss}H^0$ of H-E (kJ mol^{-1})
H_2O	463
H_2S	347
H_2Se	276
H_2Te	238

$\Delta_{diss}H^0$: Bond dissociation enthalpy

Properties of Hydrides

Acidity

H_2Te > H_2Se > H_2S > H_2O

K_a	Value
H_2O	1.8×10^{-16}
H_2S	1.3×10^{-7}
H_2Se	1.3×10^{-4}
H_2Te	2.3×10^{-3}

K_a: Dissociation constant

Properties of Hydrides

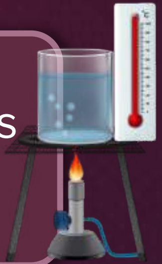
Boiling point

Generally,

Boiling point $\propto$

Down the group → Boiling point ↑

But, H_2O has high **boiling point** as compared to other elements.



Properties of Hydrides

Reducing property

$H_2S < H_2Se < H_2Te$

All the hydrides **except water** possess reducing property.

↓

This character **increases** from **H_2S to H_2Te**.

Assertion: Dinegative anion of oxygen (O^{2-}) is quite common but dinegative anion of sulphur (S^{2-}) is less common. T

Reason: Covalency of oxygen is two. ✓ T

NEET BOARDS

a ✗ If both the assertion and the reason are correct and the reason is a correct explanation of the assertion. ✗

b ✓ If both the assertion and the reason are correct but the reason is not a correct explanation of the assertion.

Assertion: Dinegative anion of oxygen (O^{2-}) is quite common but dinegative anion of sulphur (S^{2-}) is less common.

Reason: Covalency of oxygen is two.

BOARDS

Oxygen is second most electronegative element after fluorine. So, it can easily gain electrons to form dinegative anion (O^{2-}) while sulphur is not so electronegative element as oxygen.

Hence, option (b) is the correct answer.

c If the Assertion is correct but Reason is incorrect

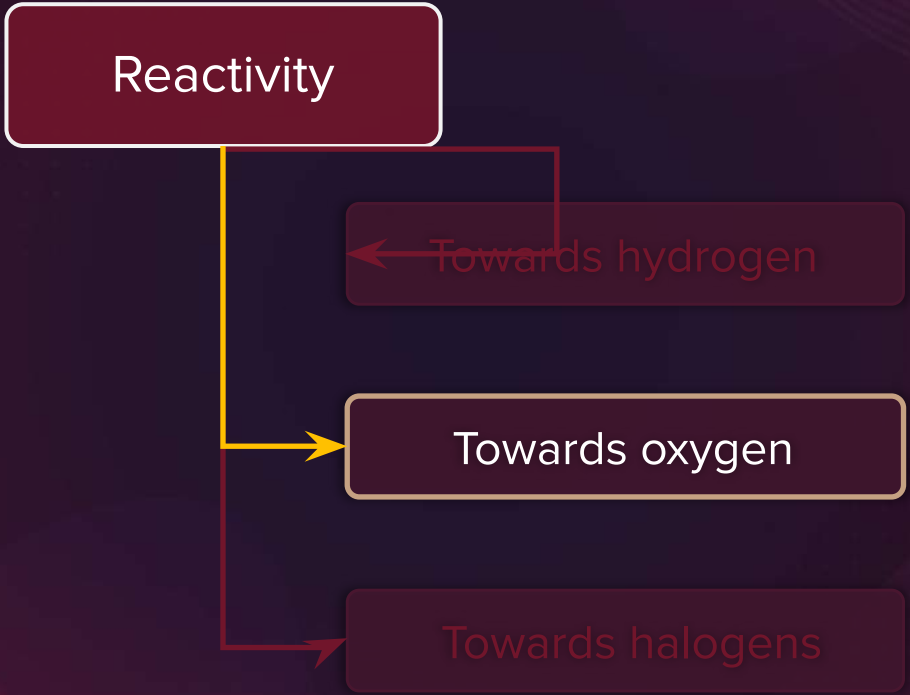
d If both the Assertion and Reason are incorrect.

Acidity of diprotic acids in aqueous solutions **increases** in the order:

- a $H_2S < H_2Se < H_2Te$
- b $H_2Se < H_2S < H_2Te$
- c $H_2Te < H_2S < H_2Se$
- d $H_2Se < H_2Te < H_2S$

Hence, option (a) is the correct answer.

Chemical Properties



Reactivity

Towards hydrogen

Towards oxygen

Towards halogens

Reactivity Towards Oxygen

All these elements form two types of oxides

EO_2 and EO_3

E = S, Se, Te or Po

Sulphur dioxide (SO_2)

Sulphur trioxide (SO_3)

Properties of Oxides

Oxidising power of dioxide

Down the group

Increases

SO_2 is **reducing,** while **TeO_2** is **oxidising agent.**

Properties of Oxides

Oxidising power of trioxide

Down the group

Increases

Trioxides act only as **oxidising agents.**

Properties of Oxides

Both dioxides and trioxides are **acidic** in nature.

Reactivity Towards Halogens

These elements react to form three series of halides.

EX_6, EX_4, EX_2

E = Element of group 16,
X = Halogen

Reactivity Towards Halogens

Stability

Order of stability of halides

Flourides > Chlorides > Bromides > Iodides

Hexahalides

sp^3d^2

EX_6 EF_6

ECl_6 X

EBr_6 X

EI_6 X

1. Amongst hexahalides, **hexafluorides** are the only **stable** halides.
2. All hexafluorides are **gaseous** in nature.
3. They have an **octahedral** structure.

Hexahalides

Sulphur hexafluoride (SF_6) is exceptionally **stable** due to steric reasons.

Sulphur hexafluoride (SF_6)

Tetrafluorides

Tetrafluorides have sp^{3}d hybridisation.

Trigonal bipyramidal structure

One of the **equatorial position** is occupied by a **lone pair** of electrons.

See-saw shape

Dihalides

All elements except **oxygen** form dichlorides and dibromides.

Dihalides

Dihalides are formed by **sp^3** hybridisation.

Thus, they have a **tetrahedral** geometry.

Sulphur dichloride (SCl_2)

Monohalides

S_2Cl_2

The well-known monohalides are **dimeric** in nature.

Examples

S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2, and Se_2Br_2

Monohalides

These dimeric halides undergo **disproportionation**

$$2\overset{+1}{Se_2}Cl_2 \longrightarrow \overset{+4}{SeCl_4} + 3\overset{0}{Se}$$

Different Types of Oxygen- Containing Compounds

Oxygen-containing compounds

- Oxygen (O_2)
- Ozone (O_3)

Preparation of Oxygen

1. Dioxygen is produced industrially by **fractional distillation** of liquid air.

2. **Electrolysis of water** leads to the release of **hydrogen** at the **cathode** and **oxygen** at the **anode**.

Preparation of Oxygen

Electrolysis of water

This is the production of oxygen via electrolysis. Oxygen is produced at anode via oxidation. **This method was most helpful in the COVID crises of second wave in India.**

Preparation of Oxygen

3

It is prepared on a small scale in a laboratory by **thermal** decomposition of **$KClO_3$** (with MnO_2 as catalyst).

$$2KClO_3 \xrightarrow[MnO_2]{150°C} 2KCl + 3O_2 + \text{traces of } Cl_2 \text{ or } ClO_2$$

↓

Catalyst

Preparation of Oxygen

4

By **thermal** decomposition of **oxides of metals**

$$2HgO\,(s) \xrightarrow{450^\circ C} 2Hg\,(\ell) + O_2\,(g)$$

$$2Ag_2O\,(s) \xrightarrow{350^\circ C} 4Ag\,(s) + O_2\,(g)$$

$$2PbO_2\,(s) \xrightarrow{\Delta} 2PbO\,(s) + O_2\,(g)$$

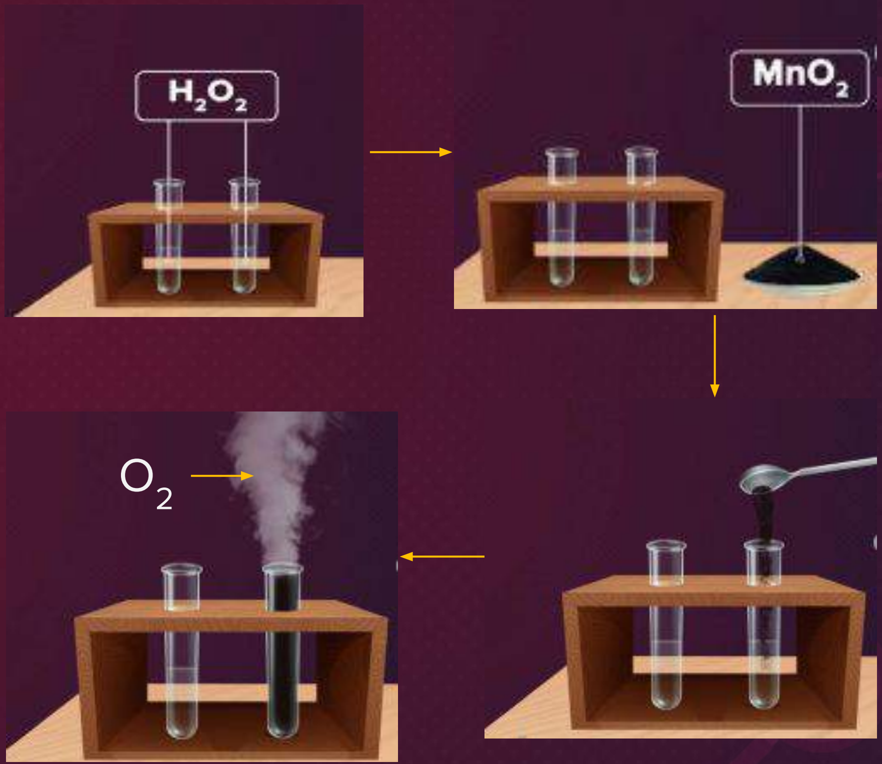
Preparation of Oxygen

5

By decomposition of **hydrogen peroxide**

$$2H_2O_2\,(aq) \xrightarrow{MnO_2} 2H_2O\,(\ell) + O_2\,(g)$$

Decomposition of hydrogen peroxide



Physical Properties

1 **Pale blue** in colour

2 **Odourless gas**

3 Strong supporter of **combustion**

4 Paramagnetic

Uses of Oxygen

Normal respiration

Combustion

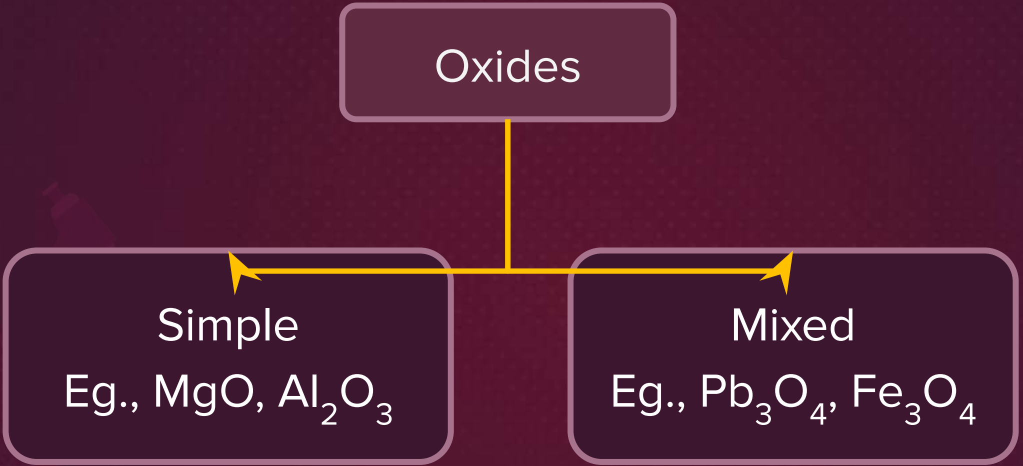
Combustion of fuels, e.g., hydrazines in **liquid oxygen** provides tremendous thrust in **rockets**.

Oxides

Oxygen reacts with most of the elements of the periodic table to form **oxides**.

In many cases one element forms **two or more oxides**. The oxides vary widely in their **nature and properties**.

Oxides



Oxides

Simple

Eg., MgO, Al_2O_3

Mixed

Eg., Pb_3O_4, Fe_3O_4

- Simple oxides
  - Acidic
  - Basic
  - Amphoteric
  - Neutral

Simple Oxides

An oxide that combines with water to give an **acid**

Example

SO_2, Cl_2O_7, CO_2, N_2O_5

$SO_2 + H_2O \longrightarrow H_2SO_3$

Note

Generally, oxides of **non-metals** are **acidic** in nature.

Oxides of some metals in high oxidation states also have **acidic character.**

Example → Mn_2O_7, CrO_3, V_2O_5

Basic Oxides

Oxides that give a **base** with water

Example

Na_2O, CaO, BaO

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Note

In general, **metallic oxides** are **basic.**

Amphoteric Oxides

Al^{+3} Al_2O_3

Some metallic oxides exhibit a **dual behaviour**. They show characteristics of both **acidic as well as basic oxides**.

Such oxides are known as **amphoteric oxides.**

Amphoteric Oxides

Example

Al_2O_3 reacts with **acids** as well as **alkalis**.

$$Al_2O_3\,(s) + 6HCl\,(aq) + 9H_2O\,(\ell) \longrightarrow 2[Al(H_2O)_6]^{3+}\,(aq) + 6Cl^-\,(aq)$$

$$Al_2O_3\,(s) + 6NaOH\,(aq) + 3H_2O\,(\ell) \longrightarrow 2Na_3[Al(OH)_6]\,(aq)$$

Neutral Oxides

Such oxides are known as **neutral oxides**.

Oxides that are **neither acidic nor basic**.

E.g., CO, NO, and N_2O

Which of the following is the correct statement?

- **a** Dioxygen is produced industrially by fractional distillation of liquid air.
- **b** All elements except oxygen form dichlorides and dibromides.
- **c** The absence of d-orbitals in oxygen restricts its covalency to 4.
- **d** All of these

Hence, option (d) is the correct answer.

Which one of the following is the correct decreasing order of boiling points?

BOARDS

- a $H_2Te > H_2O > H_2Se > H_2S$
- b $H_2O > H_2S > H_2Se > H_2Te$
- c $H_2Te > H_2Se > H_2S > H_2O$
- d $H_2O > H_2Te > H_2Se > H_2S$

Among the hydrides of group 16 elements, boiling point of H_2O is higher than H_2S because of strong intermolecular hydrogen bonding. After the decrease in boiling point from H_2O to H_2S, from H_2S to H_2Te, it increases due to increase in size of the atoms from S to Te which increases the magnitude of van der Waal's forces among the molecules. So, the correct order of boiling points is $H_2O > H_2Te > H_2Se > H_2S$

Hence, option (d) is the correct answer.

O_3

- Preparation
- Physical properties
- Chemical properties
- Uses

Preparation of Ozone

Pure and dry stream of oxygen is passed through a silent **electrical discharge**

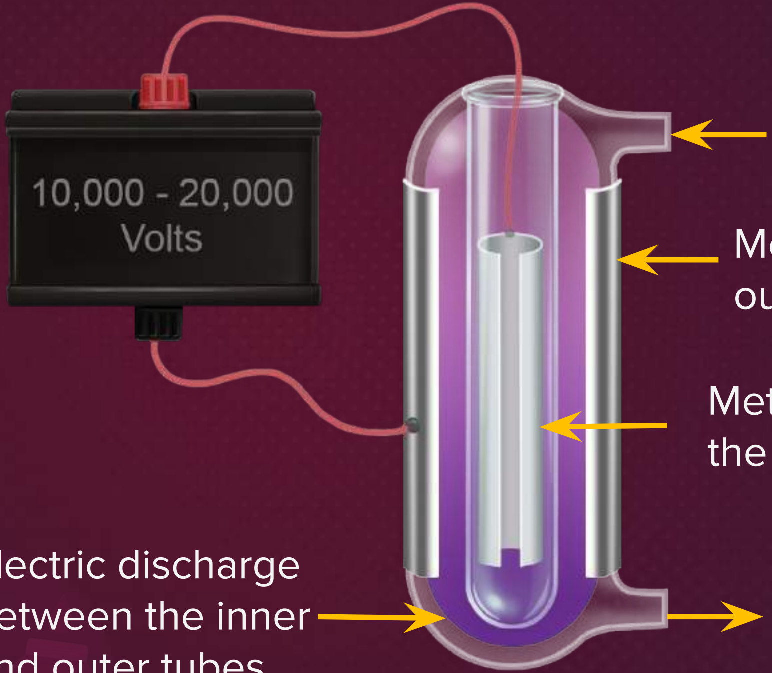
$\Delta H_r^\circ = 2 \times 142 = +284$ kJ

$$3O_2 \rightarrow 2O_3;\ \Delta H^0\ (298\ \text{K}) = +142\ \text{kJ mol}^{-1}$$

Endothermic

Preparation of O_3 via electrical discharge

Purple colour indicates the concentration of the ozone. Dry O_2 gas is passes through the inlet and we obtain an ozone rich gaseous mixture which is purified via ozone concentrator.



Dry O_2 gas

Metal foil outside of the outer glass tube

Metal foil inside of the inner glass tube

Electric discharge between the inner and outer tubes

O_3 in O_2

Note

Silent electrical discharge is used in the preparation of ozone to prevent its **decomposition.**

Preparation of Ozone

Mixture obtained contains **5–10% ozone** by volume, and this mixture is called **ozonised oxygen**.

Higher concentration or pure O_3 can be obtained by **fractional liquefaction** of the mixture.

Physical Properties of Ozone

1

Gas – dark blue ✓
Liquid – blue ✓
Solid – violet ✓

2

It has a **characteristic smell** and is **toxic** in high concentrations (> 100 ppm)

Chemical Properties of Ozone

O_3 is **thermodynamically unstable** with respect to O_2

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

$\Delta G =$

Large negative

Chemical Properties of Ozone

Oxidising agent

Ozone acts as a powerful oxidising agent due to the ease with which it liberates the atoms of **nascent oxygen.**

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

Oxidising Properties

It oxidises I^- to iodine

$$2KI + H_2O + O_3 \longrightarrow 2KOH + O_2 + I_2$$

It oxidises lead sulphide
to lead sulphate

$$PbS\ (s) + 4O_3\ (g) \longrightarrow PbSO_4\ (s) + 4O_2\ (g)$$

Ozone

Buffered with a **borate buffer** (pH = 9.2)

When ozone reacts with an **excess of KI** solution

Iodine is liberated, which can be titrated against a **standard solution of $H_2S_2O_3$**

Estimation of ozone

Initially in KI solution ozone is added. I_2 is liberated, which is estimated by titration with the **hypo solution**. Solution become colourless at the end point.

Ozone Depletion

Particularly,
nitric oxide

NO

Experimentally,
nitrogen oxide
combine very
rapidly with O_3

$$NO\ (g) + O_3\ (g) \longrightarrow NO_2\ (g) + O_2\ (g)$$

Ozone Depletion

There is a possibility that **nitrogen oxides** emitted from the exhaust systems of **supersonic jet aeroplanes** might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

Ozone Depletion

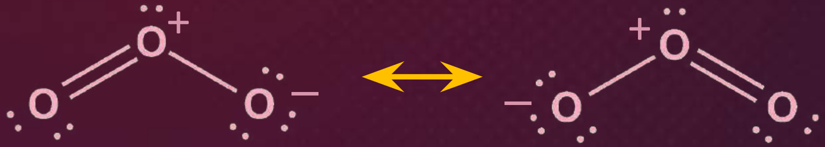
Another threat to this ozone layer is probably posed by the **use of freons**

which are used in **aerosol sprays** and as **refrigerants.**

Ozone Structure

The two O–O bond lengths are **identical**

It is a **resonance hybrid**
of the two main forms



Uses

Used for **sterilising water**

Protects us from **harmful UV radiation** from the sun

Ozone is obtained from oxygen:

BOARDS

a By oxidation at high temperature

b By oxidation using a catalyst

c By silent electric discharge

d By conversion at high pressure

Hence, option (c) is the correct answer.

The correct statements regarding ozone is/are:

BOARDS

- **a** Ozone is thermodynamically less stable with respect to oxygen.
- **b** It acts as a powerful oxidising agent.
- **c** It rapidly reacts with NO (g) and form NO_2 (g) and O_2 (g).
- **d** All of these

Ozone is thermodynamically less stable because it decomposes into oxygen and this decomposition result in the liberation of heat, so its entropy is positive and free energy is negative.

Ozone acts as powerful oxidizing agent because it can easily decompose to give an atom of nascent oxygen which is more reactive than oxygen.

$NO + O_3 \square NO_2 + O_2$

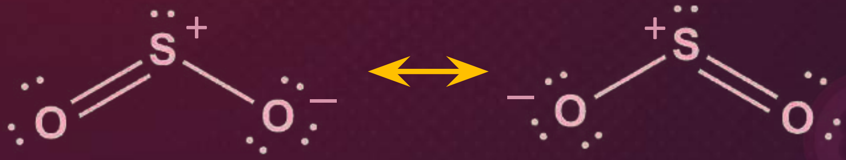
Hence, option (d) is the correct answer.

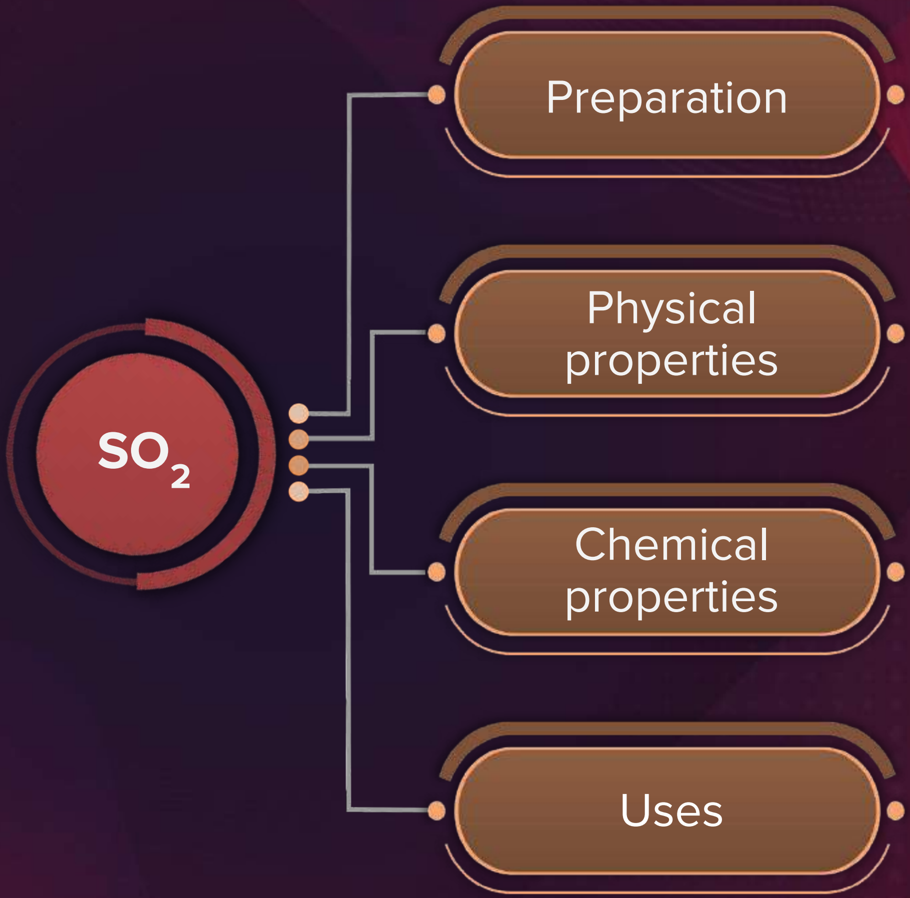
Sulphur Dioxide (SO_2)

Both the bonds are **equivalent**

Molecule of SO_2 is **angular.**

It is a resonance hybrid of the two canonical forms





SO_2

- Preparation
- Physical properties
- Chemical properties
- Uses

Preparation of SO_2

1

SO_2 is formed together with a little (**6–8%**) SO_3 when **sulphur is burnt** in air or oxygen

$$S + O_2 \text{ or air} \xrightarrow{\text{Burn}} SO_2$$

Sulfur is burnt with a blue flame in the glass tube. SO_2 produced get transferred into the jar having universal indicator solution(green colour indicates pH = 7). As the concentration of the SO_2 increases, H_2SO_3 is produced which turns solution red.

Preparation of SO_2

Laboratory method

2

Generated by treating a sulphite with **dil. H_2SO_4**

$$SO_3^{2-}\,(aq) + 2H^+\,(aq) \rightarrow H_2O\,(l) + SO_2\,(g)$$

Physical Properties of SO_2

1. **Colourless gas** with burning sulphur smell
2. Highly **soluble** in water

Chemical Properties of SO_2

1

Sulphur dioxide, when passed through water, forms a solution of **sulphurous acid**.

$$\overset{+4}{S}O_2\,(g) + H_2O\,(\ell) \rightleftharpoons \underline{H_2\overset{+4}{S}O_3}\,(aq)$$

Chemical Properties of SO_2

2

It reacts readily with sodium hydroxide solution, forming **sodium sulphite**.

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

Sodium sulphite then reacts with more sulphur dioxide to form sodium **hydrogen sulphite**

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$$

Chemical Properties of SO_2

3

Oxidised to sulphur trioxide by oxygen in the presence of **vanadium oxide catalyst**

$$2SO_2\,(g) + O_2\,(g) \xrightarrow{V_2O_5} 2SO_3\,(g)$$

Chemical Properties of SO_2

4

It is a powerful **reducing agent**

It converts iron (III) to iron (II) ions

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

Chemical Properties of SO_2

Reduction or decolourisation of acidified potassium permanganate(VII) solution is a **convenient test for SO_2**

Convenient test for the gas

$$\underline{5SO_2} + 2MnO_4^- + 2H_2O$$

$$\downarrow$$

$$\underline{5SO_4^{2-}} + 4H^+ + 2\boxed{Mn^{2+}}$$

Uses

In **refining** petroleum

As an **anti-chlor**

Oxo-Acids of Sulphur

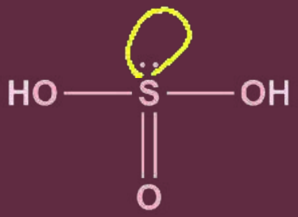
Sulphur forms a number of **oxoacids** such as H_2SO_3, H_2SO_4, $H_2S_2O_7$, $H_2S_2O_8$

Some of these acids are **unstable** and cannot be isolated.

Sulphurous Acid (H_2SO_3)

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

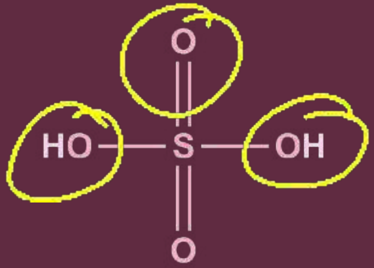
$$x = +4$$

Oxidation state	+4
Structure	 $HO-\underset{\underset{O}{\|}}{\ddot{S}}-OH$

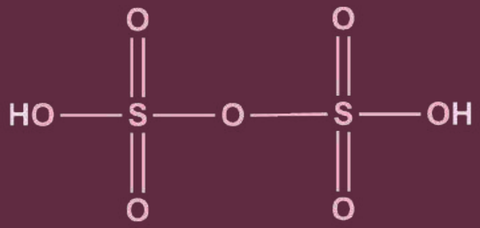
Sulphuric Acid (H_2SO_4)

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

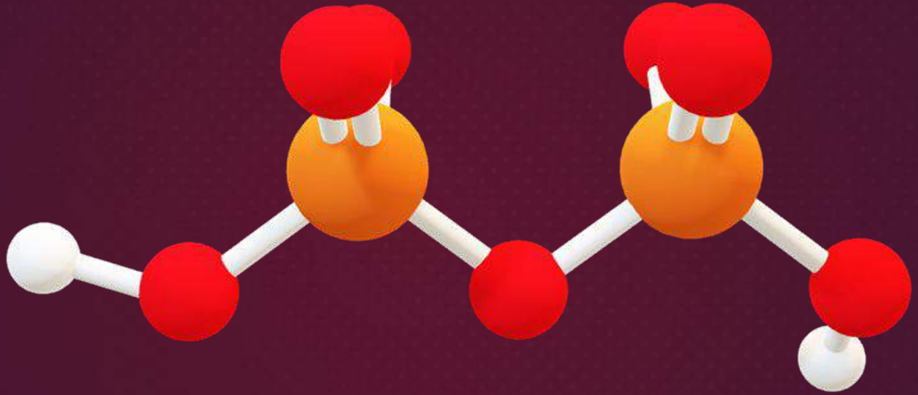
$$\boxed{x = +6}$$

Oxidation state	+6
Structure	

Pyrosulphuric Acid ($H_2S_2O_7$)

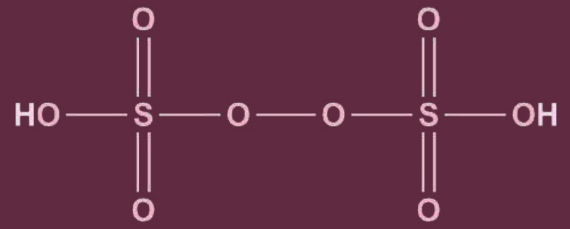
Oxidation state	+6
Structure	

Pyrosulphuric Acid

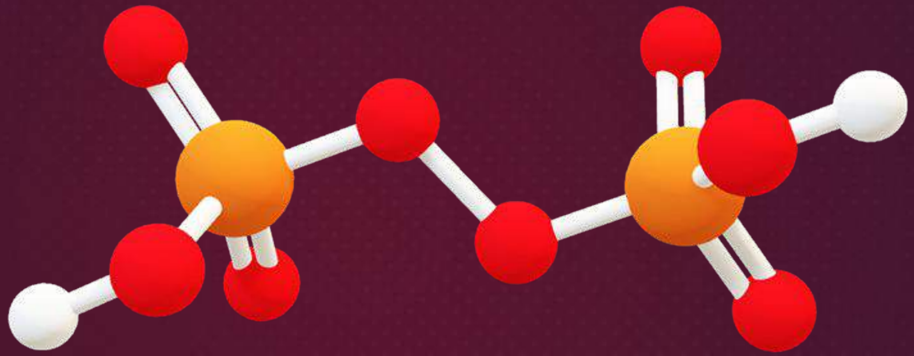


Red ball – Oxygen-atom
Orange ball – Sulphur-atom
White ball – Hydrogen-atom

Peroxydisulphuric Acid ($H_2S_2O_8$)

Oxidation state	
Structure	

Peroxydisulphuric acid



Red ball – Oxygen-atom
Orange ball – Sulphur-atom
White ball – Hydrogen-atom

Sulphuric Acid (H_2SO_4)

H_2SO_4

- Preparation
- Physical properties
- Chemical properties
- Uses

Preparation of Sulphuric acid

Sulphuric acid is manufactured by the **contact process.**

Sulphuric acid obtained by the contact process is **96–98% pure**.

Contact Process

1

Sulphur or sulphide **ore** is burnt in air to generate **SO_2**

$$S + O_2(g) \longrightarrow SO_2(g)$$

SO_2 produced is purified by removing dust and other impurities such as **arsenic compounds,** in a dust precipitator

Contact Process

This the **key step**

2

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

$$2SO_2(g) + O_2(g) \xrightleftharpoons{V_2O_5} 2SO_3(g)$$

$$\Delta_r H = -196.6 \text{ kJ mol}^{-1}$$

Contact Process

This reaction is **exothermic** and **reversible**

The forward direction results in the decrease in volume

So, **Low temperature (not too low)** and **high pressure** are the favourable conditions for maximum yield

Contact Process

3

Absorption of SO_2 in H_2SO_4 to give **oleum ($H_2S_2O_7$)**

Dilution of oleum with water gives **H_2SO_4** of the desired concentration

Preparation of Sulphuric acid

In the industry, **two steps** are carried out simultaneously to make the process a **continuous** one and to **reduce the cost.**

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

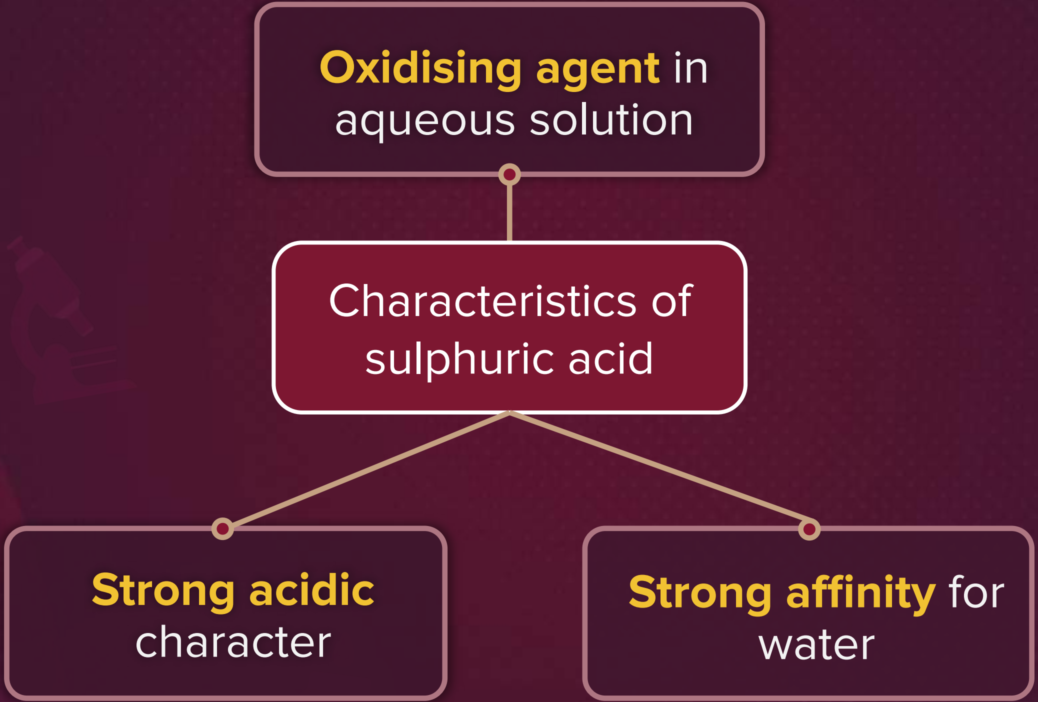
Oleum

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

Physical Properties of Sulphuric acid

1. **Colourless, dense, oily liquid**
2. **Dissolves in water** with the evolution of a larger quantity of heat

Chemical Properties of Sulphuric acid



Oxidising agent in aqueous solution

Characteristics of sulphuric acid

Strong acidic character

Strong affinity for water

Chemical Properties of Sulphuric acid

1

Sulphuric acid ionises in **two steps**

$$H_2SO_4\,(aq) + H_2O\,(\ell) \rightarrow H_3O^+\,(aq) + HSO_4^-\,(aq)$$

$$Ka_1 = \text{very large}\ (Ka_1 > 10)$$

$$HSO_4^-\,(aq) + H_2O\,(\ell) \rightarrow H_3O^+\,(aq) + SO_4^{2-}\,(aq)$$

$$Ka_2 = 1.2 \times 10^{-2}$$

Chemical Properties of Sulphuric acid

Larger value of Ka_1 (**$Ka_1 > 10$**) means that H_2SO_4 is largely dissociated into **H^+ and HSO_4^-** ions

Greater the value of dissociation constant (K_a)

Stronger is the acid

Chemical Properties of Sulphuric acid

2

Concentrated H_2SO_4 is a **strong dehydrating agent**

It removes water from **organic compounds**

Charring of sugar

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

Charring of Sugar

Charring of sugar is a dehydration reaction. As the water molecules are removed from the sugar molecules, the heat generated vapourises water and expands the remaining carbon into a porous, smoking black column.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

Chemical Properties of Sulphuric acid

3

Hot concentrated H_2SO_4 is a moderately strong **oxidising agent** (intermediate between phosphoric and nitric acids)

↓

Both metals and non-metals are oxidised by concentrated sulphuric acid, which is **reduced to SO_2**

Chemical Properties of Sulphuric acid

Examples

$$Cu + 2H_2SO_4\ (conc.) \rightarrow CuSO_4 + SO_2 + 2H_2O$$

$$S + 2H_2SO_4\ (conc.) \rightarrow 3SO_2 + 2H_2O$$

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

Uses of Sulphuric acid

To manufacture **fertilisers**

Petroleum refining

Lead storage batteries

In which pairs of ions both the species contain **S–S bond**?

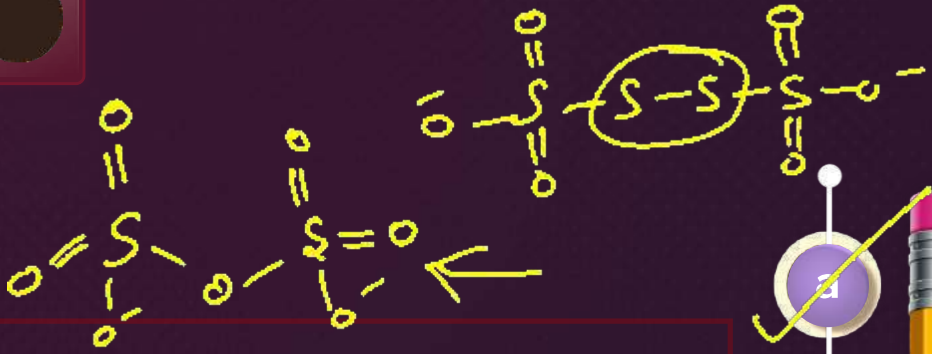
BOARDS

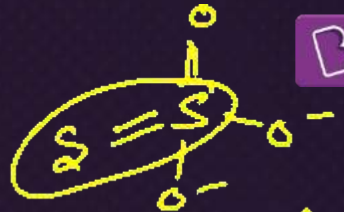
a $S_4O_6^{2-}, S_2O_3^{2-}$

b $S_2O_7^{2-}, S_2O_8^{2-}$

c $S_4O_6^{2-}, S_2O_7^{2-}$

d $S_2O_7^{2-}, S_2O_3^{2-}$





Tetra thionate ↑

Thiosulphate

a ✓ $S_4O_6^{2-}$, $S_2O_3^{2-}$ ✓

b ✗ $S_2O_7^{2-}$, $S_2O_8^{2-}$

Disulphate

c ✗ ✓ $S_4O_6^{2-}$, $S_2O_7^{2-}$ ✗

d ✗ $S_2O_7^{2-}$, $S_2O_3^{2-}$ ✗

Hence, option (a) is the correct answer.

The difference in oxidation states of sulphur atoms present in $H_2S_2O_7$ is:

BOARDS

a 4

b 5

c 3

d 0

a 4

b 5

c 3

d 0

Hence, option (d) is the correct answer.

Which of the following is not oxidised by O_3?

- a KI
- b $KMnO_4$
- c K_2MnO_4
- d $FeSO_4$

Which of the following is not oxidised by O_3?

a KI

b $KMnO_4$

c K_2MnO_4

d $FeSO_4$

Hence, option (b) is the correct answer.

Which of the following chemical reactions depicts the oxidising behavior of H_2SO_4?

BOARDS

- **a** $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
- **b** $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$
- **c** $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
- **d** $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

Which of the following chemical reactions depicts the oxidising behavior of H_2SO_4?

BOARDS

- **a** $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
- **b** $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$
- **c** $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
- **d** $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

Hence, option (a) is the correct answer.

p-Block Elements

- Group 13
- Group 14
- Group 15
- Group 16
- **Group 17**
- Group 18

Free
Classes
Bring
Infinite
Attendance

Group 17 Elements

These are collectively known as the **halogens.**

Greek: halo
Meaning: salt

Greek: gen
Meaning: born

Group 17 Elements

- Occurrence
- Atomic properties
- Physical properties
- Chemical properties

Element	Source
F	• Main Source: **Fluorspar** or **fluorite** (CaF_2) • Another Source: **Fluorapatite** [$3Ca_3(PO_4)_2.CaF_2$] **Cryolite** Na_3AlF_6
Cl	• Most abundant compound of Cl – NaCl (Sea water) • **Carnallite**: $KCl.MgCl_2.6H_2O$
Br	• Bromides occur in sea water and brine lakes.
I	• Iodides occur in low concentration in sea water. • Better source: Natural brines

Atomic Properties

- Electronic configuration
- Covalent and ionic radii
- Ionisation enthalpy
- Electron gain enthalpy
- Enthalpy of dissociation
- Distance (X–X)

Atomic Properties

Electronic configuration

General valence shell **electronic configuration** $ns^{2n}p^5$

Element	Electronic configuration
F	$[He]2s^2 2p^5$
Cl	$[Ne]3s^2 3p^5$
Br	$[Ar]3d^{10} 4s^2 4p^5$
I	$[Kr]4d^{10} 5s^2 5p^5$

Atomic Properties

Covalent and ionic radii

F < Cl < Br < I

Element	Covalent radii (in pm)	Ionic radii (in pm)
F	64	133
Cl	99	184
Br	114	196
I	133	220

Atomic Properties

Ionisation enthalpy

F > Cl > Br > I

Element	Ionisation enthalpy (in kJ/mol)
F	1680
Cl	1256
Br	1142
I	1008

Atomic Properties

Electron gain enthalpy

Cl > F > Br > I

Electron gain enthalpy (in kJ/mol)	Cl	F	Br	I
	-349	**-333**	-325	-296

Maximum negative electron gain enthalpy in their corresponding period

Why does fluorine have a lesser E.G.E than chlorine?

Electron gain enthalpy

Due to small size of fluorine atom

There are **strong inter-electronic repulsions** in the relatively **small 2p** orbitals of fluorine.

Thus, the incoming electron does not experience much attraction.

Atomic Properties

Enthalpy of dissociation (X_2)

Cl–Cl > Br– Br > F–F > I–I

Compound	Enthalpy of dissociation (in kJ/mol)
F–F	158.8
Cl–Cl	242.6
Br–Br	192.8
I–I	151.1

Atomic Properties

Distance X–X

F_2 > Cl_2 > Br_2 > I_2

Compound	**Distance (in pm)**
F_2	143
Cl_2	199
Br_2	229
I_2	266

Physical Properties

- Atomicity
- Melting & boiling points
- Enthalpy of hydration
- Colour
- Solubility

Physical Properties

Atomicity

All halogens exist as **diatomic (X_2)** molecule.

Physical Properties

F_2 < Cl_2 < Br_2 < I_2

	F_2	Cl_2	Br_2	I_2
Melting point	54.4 K	172 K	265.8 K	386.6K
Boiling point	84.9 K	239 K	332.5 K	458.2 K

Physical Properties

$\Delta_{Hyd}H\ (X^-)$: F^- > Cl^- > Br^- > I^-

	F^-	Cl^-	Br^-	I^-
$\Delta_{Hyd}H$ of X^- (in kJ/mol)	515	381	347	305

Smaller the ion

Higher is the hydration energy

Physical Properties

Colour

Element	Colour (at room temperature)
F	Pale green-yellow gas
Cl	Greenish yellow gas
Br	Reddish brown liquid
I	Dark violet solid

Display different colours

This is due to the **absorption of radiations** in visible region, which results in the excitation of outer electrons to a higher energy level.

By absorbing different quanta of radiation, they **display different colours**.

Physical Properties

Solubility

Fluorine and chlorine react with water. Bromine and iodine are only **sparingly soluble** in water.

But bromine and iodine are **soluble** in various **organic solvents** such as CCl_4, CS_2, etc., to give **coloured solutions.**

Chemical Properties

Oxidation states

1

All the halogens exhibit **–1** oxidation state.

However, chlorine, bromine, and iodine exhibit **+1, +3, +5, and +7** oxidation states as well.

Chemical Properties

Oxidation states

2

Higher oxidation states of chlorine, bromine, and iodine are mainly seen when

The halogens are in combination with the **fluorine** and **oxygen** atoms

Examples

In interhalogens, oxides, and oxoacids

Chemical Properties

Oxidation states

3

Fluorine atom has **no d-orbitals** in its valence shell. Therefore, it **cannot expand its octet.**

Being the **most electronegative,** it exhibits only **–1** oxidation state.

Chemical Properties

Reactivity

4

All the **halogens** are **highly reactive**. They react with **metals** and **non-metals** to form **halides**.

Down the group

Reactivity decreeses

The non-metal that does not exhibit positive oxidation state is:

- a Fluorine
- b Oxygen
- c Chlorine
- d Iodine

Hence, option (a) is the correct answer.

Chemical Properties

Oxidising nature

5

The **ready acceptance** of an electron is the reason for the **strong oxidising nature** of **halogens**.

F_2 is the **strongest oxidising halogen,** and it oxidises other halide ions in solution or even in the solid phase.

Chemical Properties

$$F_2 + 2X^- \longrightarrow 2F^- + X_2$$

X = Cl, Br or I

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$$

X = Br or I

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

Chemical Properties

Halogen displacement reaction

Cl_2 is added to the solutions of chloride, bromide and iodide respectively. Colour change is observed in the bromide and iodide test tubes due to the formation of the Br_2 and I_2, while no reaction occurs in the chloride test tube.

Bromine water is added to the solutions of chloride, bromide and iodide respectively. The colour change observed in the iodide test tube is due to the formation of I_2, but no reaction occurs in the chloride and bromide test tubes.

I_2(aq) is added to the solutions of chloride, bromide and iodide respectively. No reaction occurs in any of the test tubes, but the colour change is due to the colour of iodine water, which imparts its colour to the solution.

Chemical Properties

Oxidising ability of halogens in aqueous solution

Down the group ↓

Fluorine oxidises **water to oxygen,** whereas chlorine and bromine react with water to form the corresponding **hydrohalic** and **hypohalous acids.**

→ HOCl, HOBr

Chemical Properties

$$2F_2(g) + 2H_2O(\ell) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$X_2(g) + H_2O(\ell) \rightarrow HX(aq) + HOX(aq)$$

X = Cl or Br

Spontaneous

$$4I^-(aq) + 4H^+(aq) + O_2(g) \rightarrow 2I_2(s) + 2H_2O(\ell)$$

Chlorine water exposed to atmosphere

When exposed to atmosphere for a longer time, the solution become colourless and the pH decreases to 2.52 due to formation of HCl and HOCl.

$Cl_2\,(g) + H_2O\,(l) \rightarrow HCl\,(aq) + HOCl\,(aq)$

Which among the following factors is the most important in making fluorine the strongest oxidising halogen?

BOARDS

- a Hydration enthalpy
- b Ionisation enthalpy
- c Electron affinity
- d Bond dissociation energy

Solution

Chlorine has the highest electron gain enthalpy, so gaseous chlorine can accept electrons easily. Nonetheless, fluorine is the strongest oxidising agent and the oxidising power decreases from F_2 to I_2. This is due to:

1. Low enthalpy of dissociation of F_2 due to weak F-F bond
2. High enthalpy of hydration due to the smaller size of F^- ion.

Enthalpy of hydration plays an important role than the enthalpy of dissociation in making fluorine the strongest oxidising agent.

Thus, the oxidising power of halogens follows the order $F_2 > Cl_2 > Br_2 > I_2$

Hence, option (a) is the correct answer.

Anomalous behaviour of **fluorine** is due to:

1. Small size
2. Highest electronegativity
3. Low F–F bond dissociation enthalpy
4. Non-availability of d-orbitals in valence shell

Anomalous Properties of Fluorine

1. Most of the **reactions of fluorine** are **exothermic** (due to the **small** and **strong bond** formed by it with other elements).

2. It forms **only one oxoacid,** while other halogens form several oxoacids.

Anomalous Properties of Fluorine

3

Hydrogen fluoride is **liquid** (b.p. 293 K) due to strong **hydrogen bonding**.

4

Other hydrogen halides that have **bigger size and less electronegativity** are **gases**.

Chemical reactivity

- Reactivity towards hydrogen
- Reactivity towards oxygen
- Reactivity towards metals
- Reactivity towards other halogens

Reaction with H_2

$X_2 + H_2 \longrightarrow 2HX$

Where X = F, Cl, Br, I

Hydrogen halide

Down the group

Reactivity towards **H_2** ↓

F_2 reacts violently, whereas **I_2** is **slow** at room temperature.

Hydrogen Halides

Stability: HF > HCl > HBr > HI

$\Delta_{diss}H$ (kJ/mol): 574, 432, 363, 295

Acidic strength: HF < HCl < HBr < HI

Acidic strength

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

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 hydrogen fluoride?

BOARDS

a There is strong hydrogen bonding between HF molecules.

b The bond energy of HF molecules is greater than its other hydrogen halides.

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 hydrogen fluoride?

BOARDS

c The effect of nuclear shielding is much reduced in fluorine which polarise the HF molecule.

d The electronegativity of fluorine is much higher for other elements in the group.

Solution

Bond energy is the energy required to break a bond. In the hydrogen halides, HF requires a large amount of energy due to the presence of strong hydrogen bonding. Hence, the boiling point of HF molecule is higher due to the presence of strong hydrogen bonding between HF molecules.

Hence, option (a) is the correct answer.

Oxygen Fluorides

1

Fluorine forms two oxides, **OF_2** and **O_2F_2**.

Only **OF_2** is **thermally stable** at 298 K.

Oxygen Fluorides

2

These oxides are essentially **oxygen fluorides** because of the **higher electronegativity** of **fluorine** than oxygen. Both are **strong fluorinating agents**.

Halogen Oxides

3

Chlorine, bromine, and iodine form oxides in which the **oxidation states** of these halogens vary from **+1 to +7.**

Higher oxides of halogens tend to be **more stable** than the lower ones.

Halogen Oxides

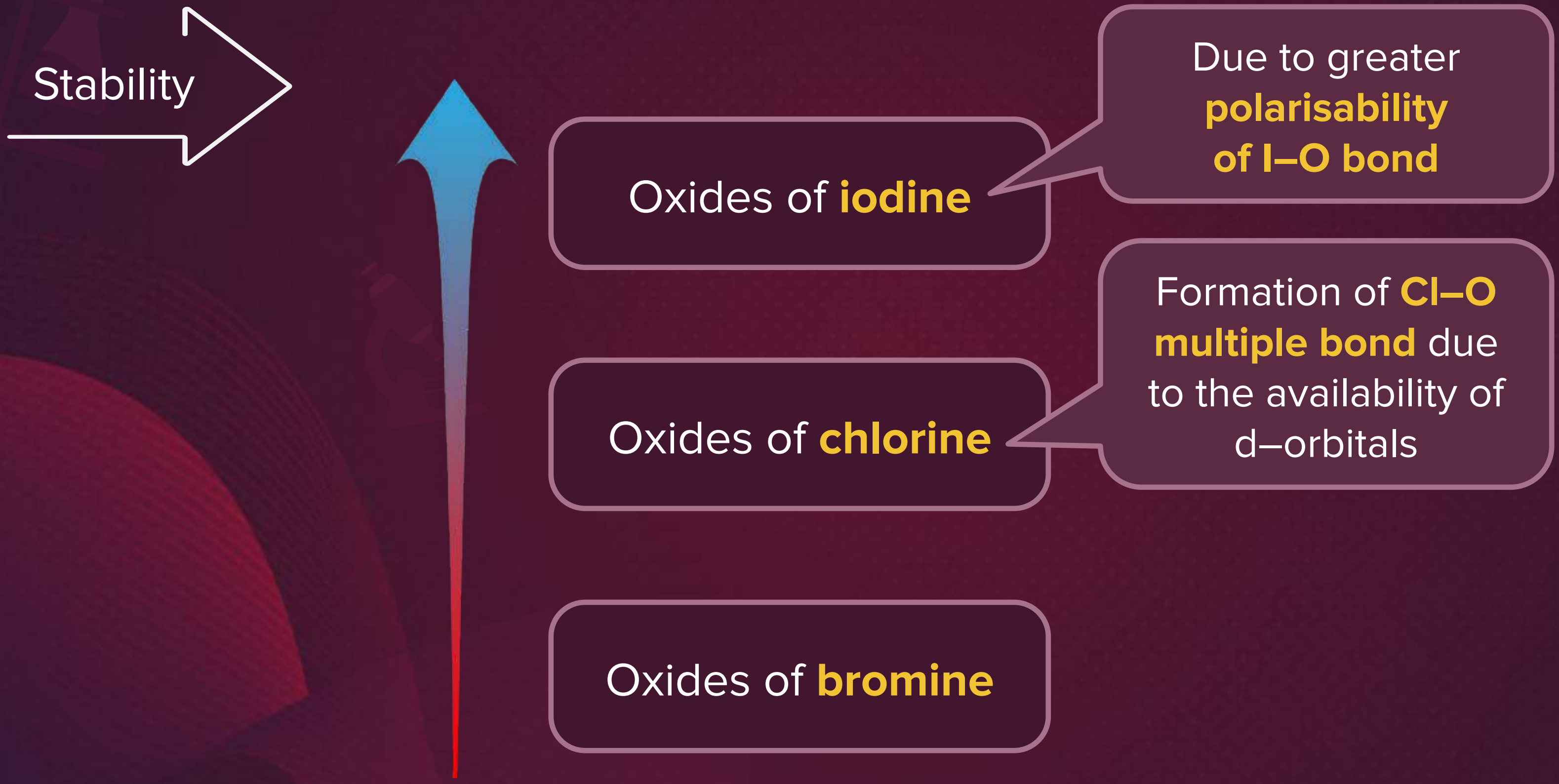
4

Considering **kinetic** and **thermodynamic** factors

Order of stability of **oxides** formed by halogens

Generally, Br < Cl < I

Stability of Halogen Oxides



Stability

Oxides of **iodine**

Due to greater **polarisability of I–O bond**

Oxides of **chlorine**

Formation of **Cl–O multiple bond** due to the availability of d–orbitals

Oxides of **bromine**

Chlorine Oxides

Cl_2O, ClO_2, Cl_2O_6, and Cl_2O_7

Highly reactive oxidising agents and tend to **explode**.

ClO_2 is used as a **bleaching agent** for paper pulp and textiles and in water treatment.

Which of the following chlorine oxides is used as a bleaching agent for paper pulp and textiles?

BOARDS

- a Cl_2O
- b ClO_2
- c Cl_2O_6
- d Cl_2O_7

Solution

Chlorine dioxide, ClO_2 is used as a bleaching agent for paper pulp and textiles.

Hence, option (b) is the correct answer.

Reaction with Metals

Halogens react with metals
to form **metal halides**.

General reaction

$$nX_2 + 2M \longrightarrow 2MX_n$$

Example

$$Br_2\ (\ell) + Mg\ (s) \longrightarrow MgBr_2\ (s)$$

Metal Halides

Ionic character

$MF > MCl > MBr > MI$

Where M = Monovalent metal

Metal Halides

Ionic character

If a metal exhibits **more than one oxidation state**, the metal in higher oxidation state will be **more covalent** than the one in lower oxidation state.

For example,

$SnCl_4$ and **$SbCl_5$** are more covalent than **$SnCl_2$** and **$SbCl_3$** respectively.

Reactivity of Halogens Towards Other Halogens

$$X_2 + X'_2 \longrightarrow 2XX'$$

Halogens combine amongst themselves to form a number of compounds known as **interhalogen compounds.**

Types of interhalogens

$\overset{+1}{X}\overset{-1}{X'}$

$\overset{+3}{X}\overset{-1}{X'_3}$

$\overset{+5}{X}\overset{-1}{X'_5}$

$\overset{+7}{X}\overset{-1}{X'_7}$

More electropositive

where, **X** is a **larger size** halogen

X' is **smaller size** halogen.

More EN −

Chlorine

- Preparation
- Physical properties
- Chemical properties
- Uses

Preparation

1

By heating manganese dioxide with concentrated hydrochloric acid

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

Preparation

Deacon's process

Air is used to **oxidise HCl** the presence of $CuCl_2$ (catalyst) at 723 K.

$$4HCl + O_2 \underset{450^\circ C}{\overset{CuCl_2}{\rightleftharpoons}} 2Cl_2 + 2H_2O + \Delta$$

Reaction is **reversible**

And conversion is **65%**

Chlorine

- Preparation
- Physical properties
- Chemical properties
- Uses

Physical Properties of Cl_2

1. Greenish yellow gas with **pungent and suffocating odour**
2. About **2–5 times heavier** than air
3. **Soluble** in water

Chemical Properties

1

Chlorine reacts with a number of **metals** and **non-metals.**

Examples

$$2Na + Cl_2 \longrightarrow 2NaCl$$

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

Chemical Properties

2 Reaction with **alkali**

$$2NaOH + \overset{0}{Cl}_2 \longrightarrow Na\overset{-1}{Cl} + NaO\overset{+1}{Cl} + H_2O$$

(Cold & dil.)

Hypochlorite

$$6NaOH + 3\overset{0}{Cl}_2 \longrightarrow 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$$

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

(Hot & conc.)

Chlorate

Chemical Properties

3

Reaction with **dry slaked lime**

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

Composition of **bleaching powder** is $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$

Chemical Properties

4

Chlorine water on standing loses its **yellow colour** due to the formation of **HCl and HOCl.**

Hypochlorous acid (HOCl) so formed gives **nascent oxygen,** which is responsible for the oxidising and bleaching properties of chlorine.

Chemical Properties

Oxidising property

Oxidises ferrous to ferric

$$2\overset{+2}{Fe}SO_4 + H_2SO_4 + \overset{0}{Cl_2} \longrightarrow \overset{+3}{Fe_2}(SO_4)_3 + 2H\overset{-1}{Cl}$$

Iodine to iodic acid

$$\overset{0}{I_2} + 6H_2O + 5\overset{0}{Cl_2} \longrightarrow 2H\overset{+5}{I}O_3 + 10H\overset{-1}{Cl}$$

Chemical Properties

Bleaching action

$$Cl_2 + H_2O \longrightarrow HCl + \underset{\displaystyle HCl + O}{\underset{\downarrow}{HOCl}}$$

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

It is a powerful **bleaching agent.**

Bleaching action is due to **oxidation**.

Chemical Properties

Bleaching effect of chlorine is **permanent**.

It bleaches **vegetable or organic matter** in the presence of moisture.

$$\text{Coloured substance} + \text{O} \longrightarrow \text{Colourless substance}$$

Uses

For bleaching **wood pulp**

In the preparation of **poisonous gases** such as phosgene ($COCl_2$), tear gas(CCl_3NO_2) etc.

Select the incorrect statement.

BOARDS

Electron density

a. The basic nature of X$^-$ is in the order ~~$F^- > Cl^- > Br^- > I^-$~~ T

b. The electron gain enthalpy is in the order F > Cl > Br > I. F

c. The ionic character of M–X bond decreases in the order M–F > M–Cl > M–Br > M–I T

d. Among F^-, Cl^-, Br^-, and I^-, F^- has the highest enthalpy of hydration. T

Solution

In general, electron gain enthalpy becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of fluorine and thus, the incoming electron does not experience much attraction. Therefore, the order of electron gain enthalpy of halogens is $Cl^- > F^- > Br^- > I^-$

We know, stronger acid has weaker conjugate base. So, The basic nature of X^- is in the order $F^- > Cl^- > Br^- > I^-$. Hence, option a is correct.

According to Fajan rule, as the size of anion increases, ionic character decreases. So, The ionic character of M–X bond decreases in the order M–F > M–Cl > M–Br > M–I. So, option c is correct.

Solution

Due to small size and high electronegativity, F^- has highest enthalpy of hydration among the halogens. So, option d is correct.

Hence, option b is the correct answer.

Which one of the following is used in the preparation of chlorine?

BOARDS

a Both MnO_2 and $KMnO_4$

b Only $KMnO_4$

c Only MnO_2

d Either MnO_2 or $KMnO_4$

Hence, option a is the correct answer.

The catalyst used in the Deacon's process for the manufacture of chlorine is:

BOARDS

$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$

- a Cu
- b An alloy of copper
- [✓ c $CuCl_2$]
- d CuS

Deacon process is the preparation of chlorine gas using Hydrochloric acid gas with atmospheric oxygen (raw oxygen straight from photosynthesis) using a catalyst (cupric chloride).

Hence, option c is the correct answer.

The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are:

BOARDS

- **a** ClO_2 and ClO_3
- **b** Cl^- and ClO^-
- **c** Cl^- and ClO_2
- **d** ClO^- and ClO_3

Hence, option b is the correct answer.

Among the following which is the strongest oxidising agent?

BOARDS

a Br_2

b I_2

c Cl_2

d F_2

Solution

Fluorine is the most electronegative element and electron gain tendency decreases down the group. Hence, fluorine readily gets reduced to F– ion and is the strongest oxidizing agent. Standard reduction potential (SRP) value of these four halogens is in the order $F_2 > Cl_2 > Br_2 > I_2$.

Thus, fluorine is the strongest oxidising agent.

Hence, option d is the correct answer.

Which one of the following orders is not in accordance with the property stated against it?

BOARDS

- **a** $F_2 > Cl_2 > Br_2 > I_2$: Bond dissociation energy
- **b** $F_2 > Cl_2 > Br_2 > I_2$: Oxidising power
- **c** HI > HBr > HCl > HF: Acidic property in water
- **d** $F_2 > Cl_2 > Br_2 > I_2$: Electronegativity

Bond dissociation energies of halogen, **decrease down the group as the size of the atom increases**. However, the bond dissociation energy of fluorine, is, lower than chlorine and bromine because of interelectronic repulsions present in the small atom of fluorine. So option a is incorrect.

All halogen atoms have a strong tendency to accept an electron due to its electronic configuration i.e., there is the only requirement of one electron to complete their octet. Hence they act as a strong oxidizing agent. However their oxidizing power decreases from F_2 to I_2. So, option b is correct.

Hence, option a is the correct answer.

As we move down the group, the bond strength between halogen and hydrogen, decreases as the size of halogen increases so, liberation of H^+ become easy and hence, acidic nature increases. So, option c is correct.

We know, down the group electronegativity decreases, so option d is the correct.

Hence, option a is the correct answer.

Regarding F^- and Cl^- which of the following statements is/are correct?

F → Hight SRP

✓ (i) Cl^- can give up an electron more easily than F^-. T

✓ (ii) Cl^- is a better reducing agent than F^-.

✗ (iii) Cl^- is smaller in size than F^-. ✗ $F \xrightarrow{+e^-} F^-$ ✓

✗ (iv) F^- can be oxidised more readily than Cl^-.

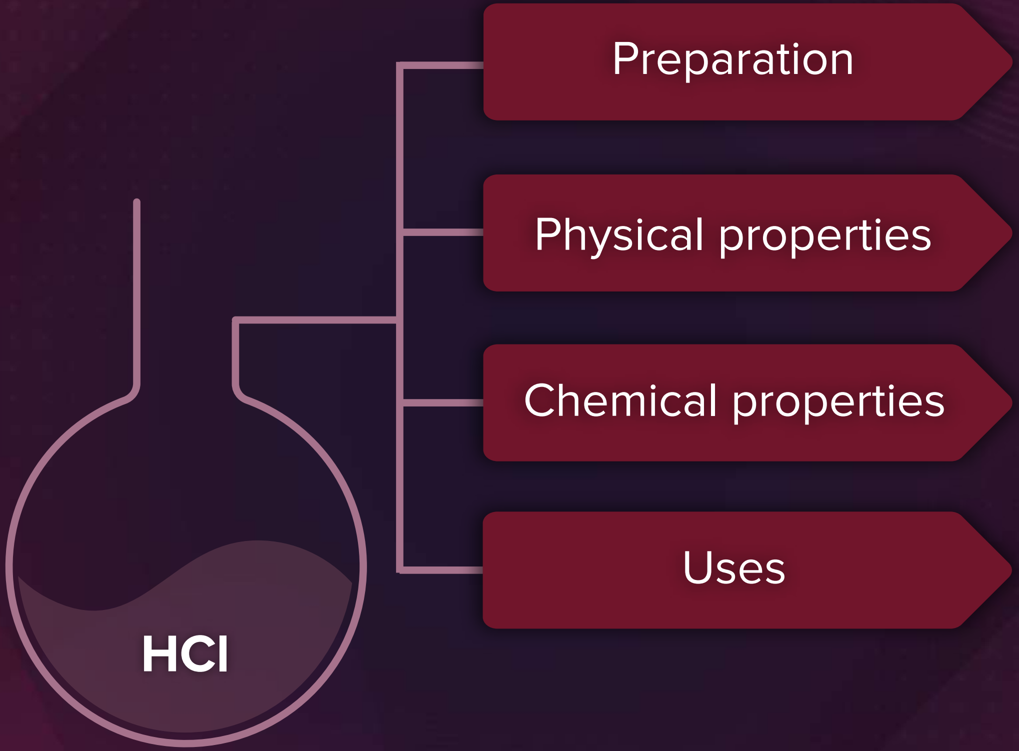
$Cl \underset{\longleftarrow}{\xrightarrow{+e^-}} Cl^-$ ✓

Solution

The electronegativity of F^- ion is the highest, so it accepts an electron, and Cl^- ion can donate an electron relatively more easily. Also, the size of F^- is smaller than chloride ion.

Hence, option a is the correct answer.

- a (i) and (ii)
- b (i), (ii) and (iv)
- c (iii) and (iv)
- d Only (i)



HCl

- Preparation
- Physical properties
- Chemical properties
- Uses

Preparation

Heating sodium chloride with concentrated sulphuric acid

$$\mathrm{NaCl} + \mathrm{H_2SO_4} \xrightarrow{150^\circ\mathrm{C}} \mathrm{NaHSO_4} + \mathrm{HCl}$$

$$\mathrm{NaHSO_4} + \mathrm{NaCl} \xrightarrow{550^\circ\mathrm{C}} \mathrm{Na_2SO_4} + \mathrm{HCl}$$

Physical Properties of HCl

1. **Colourless, pungent** smelling gas

2. Quite **soluble** in water

$$HCl\,(g) + H_2O\,(\ell) \longrightarrow H_3O^{+}\,(aq) + Cl^{-}\,(aq)$$

Physical Properties of HCl

The aqueous solution is called **hydrochloric acid.**

High value of dissociation constant (K_a)

Strong acid in water

$$K_a = 10^7$$

Chemical Properties of HCl

1 Acidic character

It reacts with **NH_3** and gives off white fumes of **NH_4Cl**.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

Chemical Properties of HCl

SB + WA → Salt (Basic)

2

Hydrochloric acid decomposes the **salts of weaker acids.**

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

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

$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$

Uses

In manufacturing **chlorine, NH_4Cl,** and **glucose** (from corn starch)

In **medicines**

As a **laboratory reagent**

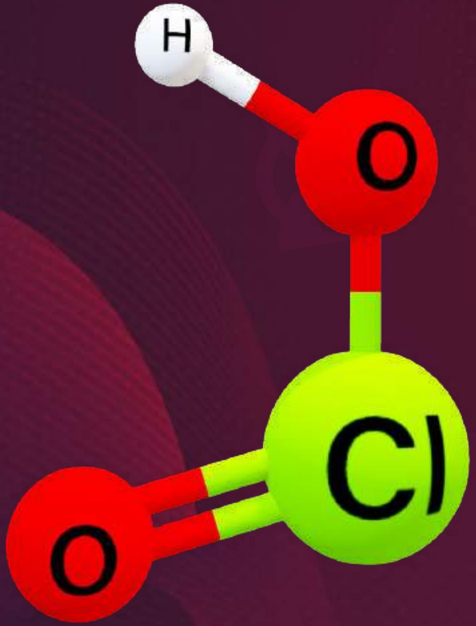
Hypofluorous acid (HOF)

Fluorine is unique among the halogens in forming no species in which it has a formal oxidation state other than **-1**.

The only known oxoacid is **hypofluorous acid, HOF.**

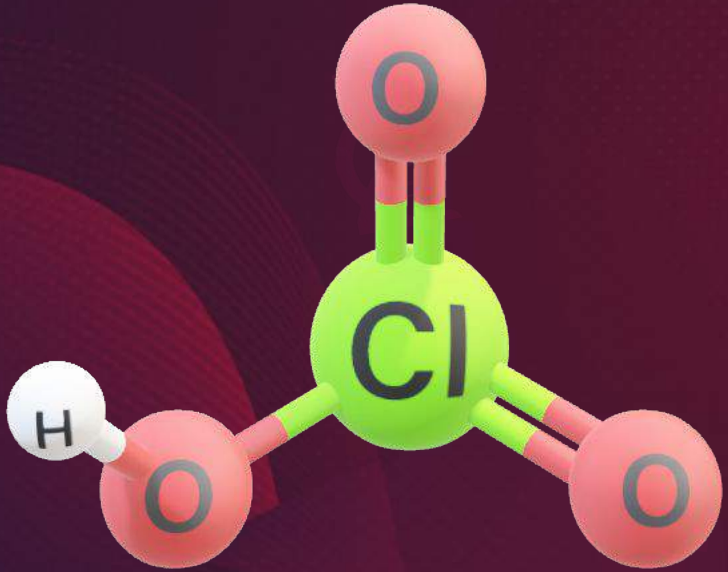
Oxoacids of Chlorine

Chlorous acid



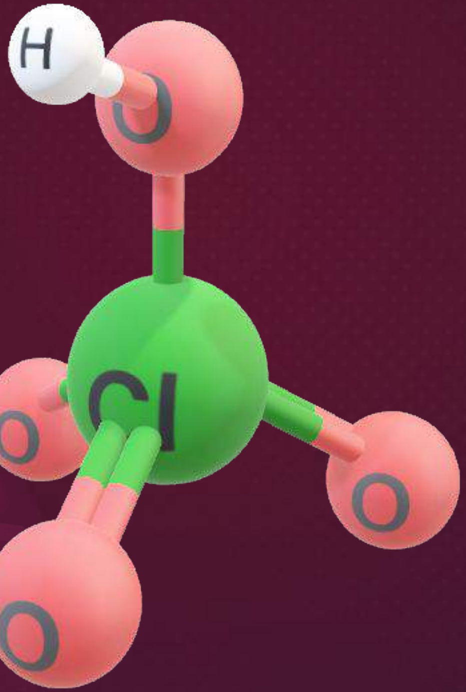
Oxoacids of Chlorine

Chloric acid



Oxoacids of Chlorine

Perchloric acid



Interhalogen Compounds

Halogen atoms have different electronegativities. Due to this **difference** in electronegativities, the halogen atoms combine with each other.

This gives rise to the formation of binary covalent compounds, which are called **interhalogen** compounds.

Interhalogen compounds

- Types & examples
- Preparation
- Physical properties
- Chemical properties
- Uses

Types of Interhalogen Compounds

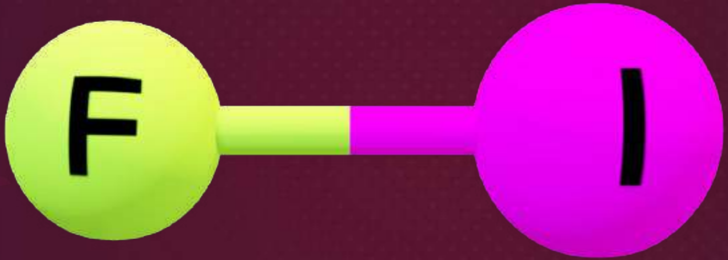
Four types ▷ XX' | XX'_3 | XX'_5 | XX'_7

X Halogen of larger size

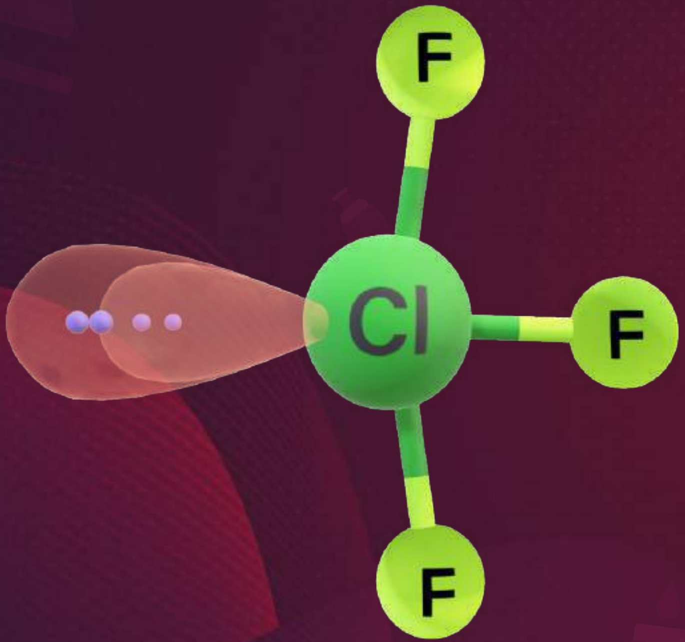
X′ Halogen of smaller size

X is more electropositive than X′

Iodine monofluoride (XX′)



Chlorine trifluoride (XX_3')

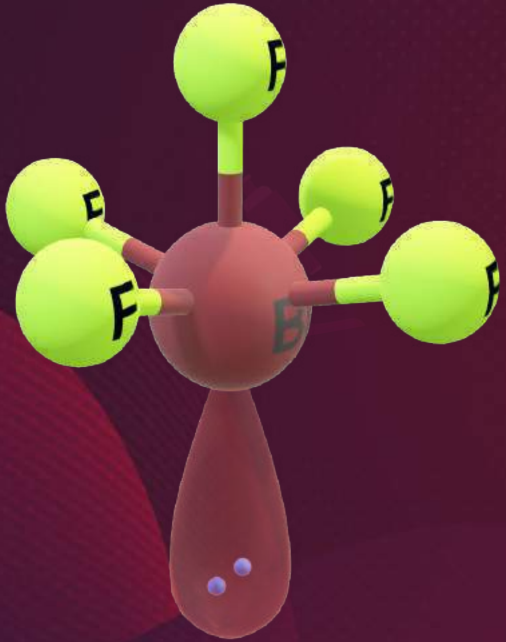


Hybridisation – sp^3d

Geometry – Trigonal Planar

Structure – T-shaped

Bromine Pentafluoride (XX_5')

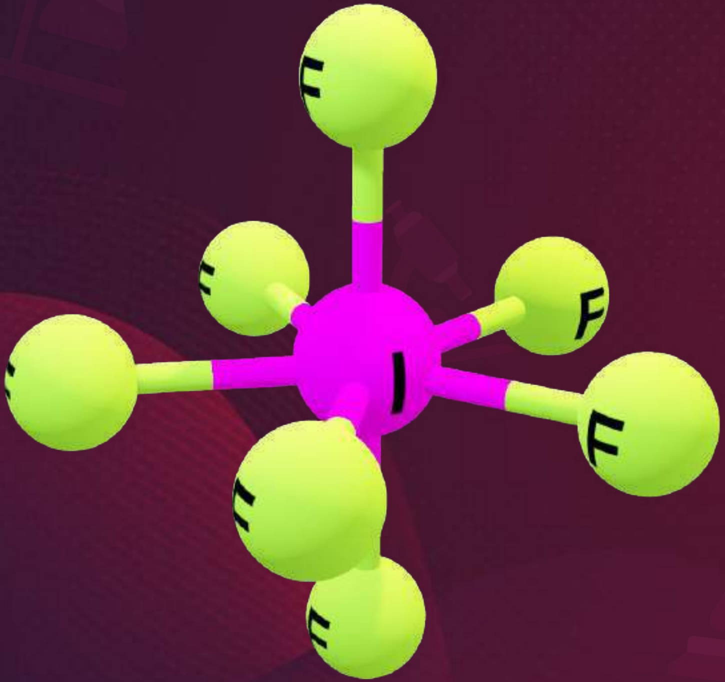


Hybridisation – sp^3d^2

Geometry – Octahedral

Structure – Square Pyramidal

Iodine Heptafluoride (XX_7')

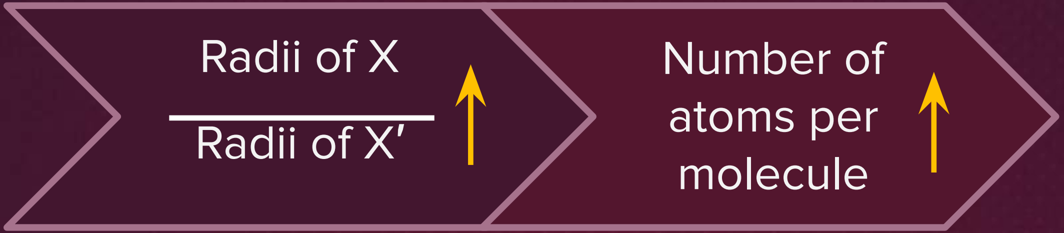


Hybridisation – sp^3d^3

Geometry – Pentagonal Bipyramidal

Structure – Pentagonal Bipyramidal

Interhalogen Compounds



$$\frac{\text{Radii of X}}{\text{Radii of X}'} \uparrow$$

Number of atoms per molecule ↑

Thus, iodine (VII) fluoride should have the **maximum number of atoms** as the ratio of the radii between I and F should be the **maximum**.

That is why its formula is **IF_7** (having the maximum number of atoms).

By the **direct combination** of halogens:

$$\underset{\text{(equal volumes)}}{Cl_2 + F_2} \xrightarrow{473\text{ K}} 2ClF$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573\text{ K}} 2ClF_3$$

$$\underset{\text{(equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl$$

Physical Properties

1

These compounds may be **gases, liquids,** or **solids.**

Gases: ClF, BrF, ClF_3, IF_7

Liquids: BrF_3, BrF_5

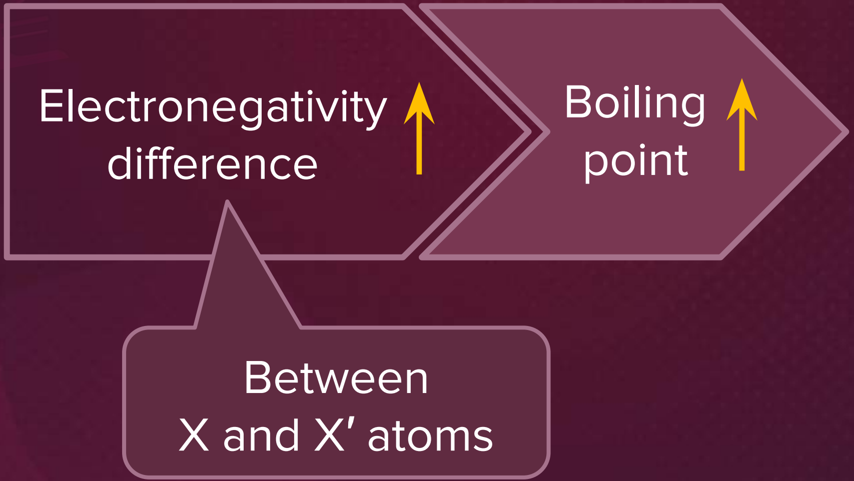
Solids: ICl, IBr, IF_3, ICl_3

Physical Properties

2

All interhalogens are **covalent molecules** and are **diamagnetic** in nature.

3



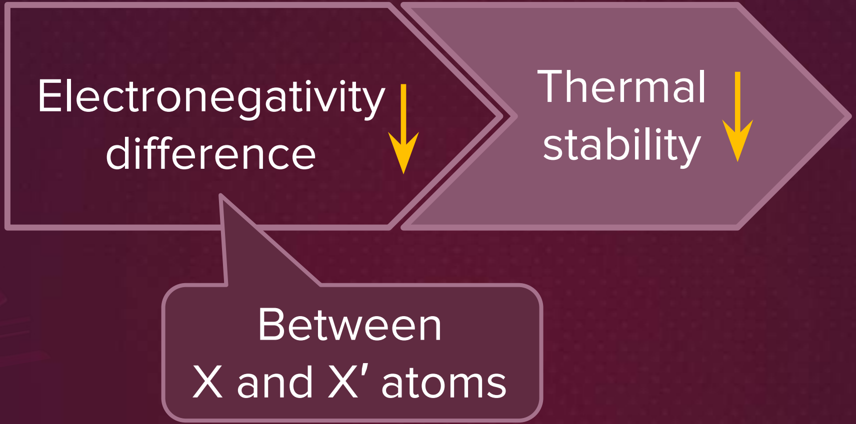
Electronegativity difference ↑

Boiling point ↑

Between X and X′ atoms

Physical Properties

4



Electronegativity difference ↓

Thermal stability ↓

Between X and X′ atoms

Physical Properties

4

$F \rightarrow 4$

$Cl \rightarrow 3$

$I \rightarrow 2.5$

$4 - 2.5 = 1.5$　　$4 - 3$　　$3 - 2.5$

IF > ClF > ICl ✓

1.5　　= 1　　0.5

More polar is the X–X′ bond, more is the **stability of interhalogen.**

Chemical Properties

1

Interhalogen compounds are **more reactive** than the **parent halogens** but **less reactive than F_2.**

This is because the X–X' bond in interhalogens is **weaker** than the X–X bond in halogens except the F–F bond.

Chemical Properties

2

All interhalogen compounds undergo **hydrolysis.**

$$XX' + H_2O \longrightarrow HX' + HOX$$

Chemical Properties

All these undergo **hydrolysis** giving

A **halide ion**

Derived from **smaller** halogen

A **hypohalite** (when XX'), **halite** (when XX'_3), **halate** (when XX'_5), and **perhalate** (when XX'_7) anion

Derived from **larger** halogen

Uses

Interhalogen compounds are very useful **fluorinating agents.**

Interhalogen compounds can be used as **non-aqueous solvents**

Interhalogen compounds

- Types & examples
- Preparation
- Physical properties
- Chemical properties
- Uses

Chemical Properties

1

Interhalogen compounds are **more reactive** than the **parent halogens** but **less reactive than F_2.**

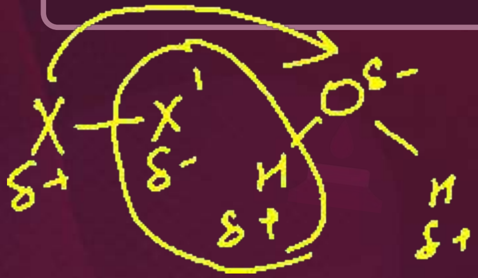
This is because the X–X' bond in interhalogens is **weaker** than the X–X bond in halogens except the F–F bond.

Chemical Properties

2

All interhalogen compounds undergo **hydrolysis.**

$$XX' + H_2O \longrightarrow \underline{HX'} + \underline{HOX} \quad ✓$$



Chemical Properties

All these undergo **hydrolysis** giving

A **halide ion**

Derived from **smaller** halogen

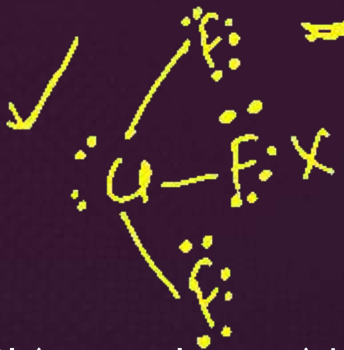
A **hypohalite** (when XX'), **halite** (when XX'_3), **halate** (when XX'_5), and **perhalate** (when XX'_7) anion

Derived from **larger** halogen

The number of lone pairs of electrons present in the central atom of ClF_3 is:

$$H = \frac{1}{2}[V + M - C + A]$$

$$= \frac{1}{2}[7+3] = 5 \quad sp^3d^2$$



- a 4
- b 3
- [✓ c] 2
- d 5

Cl (central atom) has 7 valence electrons, out of which 3 are involved in bond formation with 3 F atoms. 7–3 = 4 valence electrons remain in the form of 2 lone pairs of electrons.

Hence, option c is the correct answer.

Uses

Interhalogen compounds are very useful **fluorinating agents.**

Interhalogen compounds can be used as **non-aqueous solvents**

Match the interhalogen compounds of column-I with their geometry in column-II and assign the correct code:

A-iii
B-i

ClF ClF_3 $H = \frac{1}{2}[7+3] = 5$ sp^3d TBP

BrF_5 $H = \frac{1}{2}[7+5] = 6$ sp^3d^2 Oh

	Column I		Column II
(A)	XX'	(i)	T-shape
(B)	XX'_3	(ii)	Pentagonal bipyramidal
(C)	XX'_5	(iii)	Linear
(D)	XX'_7	(iv)	Square pyramidal
		(v)	Tetrahedral

IF_7 sp^3d^3

Pentagonal bipyramidal

Match the interhalogen compounds of column-I with their geometry in column-II and assign the correct code:

BOARDS

	A	B	C	D
(a)	(iii)	(i)	(iv)	(ii)
(b)	(v)	(iv)	(iii)	(ii)
(c)	(iv)	(iii)	(ii)	(i)
(d)	(iii)	(iv)	(i)	(ii)

Hence, option a is the correct answer.

Group 18
(The Noble Gases)

Hero

Never

Arrived

Kriti

Xeroxed

Randomly

Group 18 elements

- Helium
- Neon
- Argon
- Krypton
- Xenon
- Radon

All these are gases and chemically **unreactive.**

They **form very few compounds**, and are hence termed as noble gases.

Noble Gases

- Occurrence
- Atomic properties
- Physical properties
- Chemical properties
- Uses

Occurrence and isolation

Except **radon**

All noble gases occur in the atmosphere

Order of abundance in air

Ar ✓ > Ne > Kr > He > Xe

Atomic Properties

- Electronic configuration
- Atomic radii
- Ionisation enthalpy

Atomic Properties

Electronic configuration

Except **helium ($1s^2$)**

All noble gases have the general electronic configuration **ns^2np^6.**

Their inactive nature are ascribed to their **closed shell structures.**

02

He

Helium

4.0026

Series
Noble gas

Radioactive
No

Electron Configuration
$1s^2$
2

Atomic Weight
4.0026

State
Gas

Atomic Number
02

Density
0.1785 g/L

Melting point
0.95 K

Boiling point
4.216 K

10

Ne

Neon

20.1797

Series	Radioactive	Electron Configuration
Noble gas	No	[He] $2s^2 2p^6$
Atomic Weight	**State**	2, 8
20.1797	Gas	
Atomic Number	**Density**	
10	0.8999 g/L	

Melting point

24.55 K

Boiling point

27.1 K

18

Ar

Argon

39.948

Series

Noble gas

Radioactive

No

Electron Configuration

[Ne] $3s^2 3p^6$

2, 8, 8

Atomic Weight

39.948

State

Gas

Atomic Number

18

Density

1.7837 g/L

Melting point

83.95 K

Boiling point

87.45 K

36

Kr

Krypton

83.8

Series
Noble gas

Radioactive
No

Electron Configuration
[Ar] $3d^{10}4s^{2}4p^{6}$

2, 8, 8, 18

Atomic Weight
83.800

State
Gas

Atomic Number
36

Density
3.733 g/L

Melting point
116.00 K

Boiling point
120.85 K

54

Xe

Xenon

131.29

Series

Noble gas

Radioactive

No

Electron Configuration

[Kr] $4d^{10}5s^{2}5p^{6}$

2, 8, 18, 18, 8

Atomic Weight

131.29

State

Gas

Atomic Number

54

Density

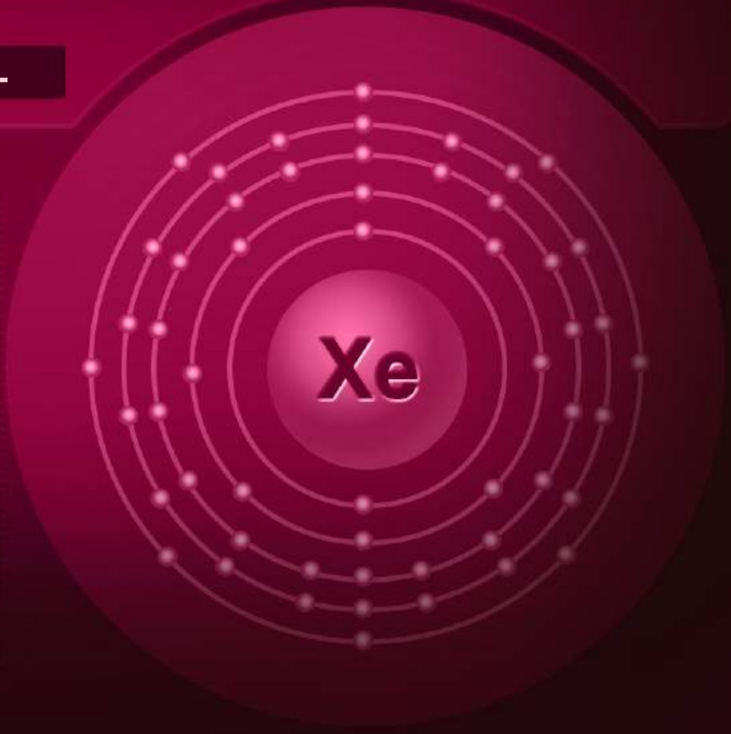
5.887 g/L

Melting point

161.39 K

Boiling point

165.1 K



86

Rn

Radon

222

Series

Noble gas

Radioactive

Yes

Electron Configuration

[Xe] $4f^{14}5d^{10}6s^{2}6p^{6}$

2, 8, 18, 32, 18, 8

Atomic Weight

222

State

Gas

Atomic Number

86

Density

9.75 g/L

Melting point

202 K

Boiling point

211.4 K

Atomic Properties

Atomic Radii

Down the group

Increases

Reason | Increase in the number of shells

He < Ne < Ar < Kr < Xe

Atomic Properties

Ionisation Enthalpy

Due to the stable electronic configuration, they exhibit **very high ionisation enthalpy.**

Down the group

Decreases

He > Ne > Ar > Kr > Xe

Physical Properties

1. All the noble gases are **monoatomic.**
2. **Colourless, odourless,** and **tasteless**
3. **Sparingly** soluble in water

Physical Properties

4

Very low melting and boiling points

This is because the only type of interatomic interaction in these elements is **weak dispersion forces.**

Physical Properties

5

Helium has the **lowest boiling point** of any known substance.

4.2 K

Chemical Properties

Noble gases are
least reactive due to

Completely **filled ns^2 np^6** electronic configuration in their valence shell

High ionisation enthalpy and more **positive electron gain enthalpy**

Reactivity of Noble Gases

The compounds of krypton are fewer. Only the **difluoride (KrF_2)** has been studied in detail.

No true compounds of Ar, Ne, or He are yet known.

Reactivity of Noble Gases

Neil Bartlett, prepared a red compound which is formulated as **$O^{2+}PtF_6^-$.**

He observed that,

$(I.E._1)_{O_2} \approx (I.E._1)_{Xe}$

1175 kJ/mol

1170 kJ/mol

Reactivity of Noble Gases

He also prepared another red-coloured compound **$Xe^+PtF_6^-$** by mixing **PtF_6** and **xenon.**

Many **xenon compounds,** mainly with the most electronegative elements like fluorine and oxygen, have been **synthesised**.

Xenon fluoride compounds

- Preparation
- Properties

Preparation

Xenon forms three binary fluorides, namely **XeF_2, XeF_4, and XeF_6**, by the direct reaction of elements under appropriate experimental conditions.

The products formed depend on the **Xe/F_2 ratio.**

Xe excess

400°C

$$Xe\,(g) + F_2\,(g) \xrightarrow{673\ K,\ 1\ bar} XeF_2\,(s)$$

Xe : F

1 : 5 ratio

$$Xe\,(g) + 2F_2\,(g) \xrightarrow{873\ K,\ 7\ bar} XeF_4\,(s)$$

Xe : F

1 : 20 ratio

$$Xe\,(g) + 3F_2\,(g) \xrightarrow{573\ K,\ 60\text{-}70\ bar} XeF_6\,(s)$$

Properties of Xenon Fluoride compounds

XeF_2, XeF_4, and XeF_6

Colourless crystalline solids

They are **readily hydrolysed** even by traces of water

Powerful **fluorinating agents**

Properties of Xenon Fluoride compounds

Xenon fluorides react with

Fluoride ion **acceptors** to form **cationic species**

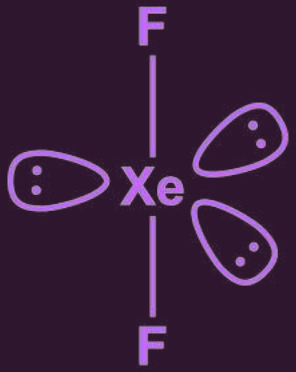
$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$$

Fluoride ion **donors** to form **fluoroanions**

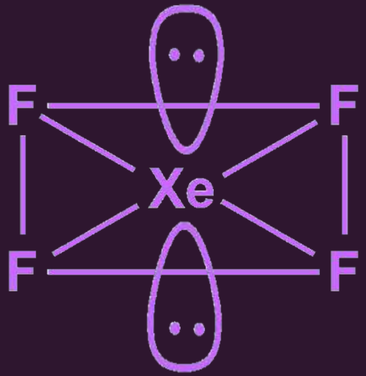
$$XeF_6 + MF \longrightarrow M^+ [XeF_7]^-$$

(M = Na, K, Rb or Cs)

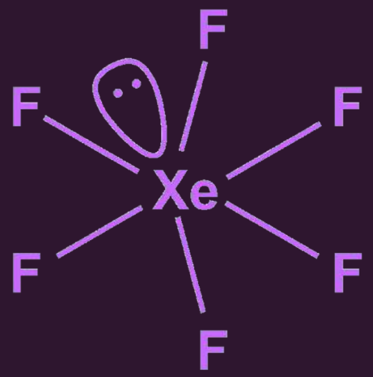
XeF$_2$

Structure	
Hybridisation	
Geometry	
Shape	

XeF_4

Structure	
Hybridisation	
Geometry	
Shape	

XeF_6

Structure	
Hybridisation	
Geometry	
Shape	

The formation of $O_2^+[PtF_6]^-$ is the basis for the formation of xenon fluorides. This is because:

BOARDS

a O_2 and Xe have comparable sizes.

b Both O_2 and Xe are gases.

c O_2 and Xe have comparable ionisation energies.

d O_2 and Xe have comparable electronegativities.

Hence, option c is the correct answer.

Xenon-oxygen compounds

- Preparation
- Properties

Xenon-Oxygen Compounds

Hydrolysis of XeF_4 and XeF_6 with water gives **XeO_3.**

$$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3\,H_2O \longrightarrow XeO_3 + 6\,HF$$

Xenon-Oxygen Compounds

Partial hydrolysis of XeF_6 gives **oxyfluorides, $XeOF_4$**, and **XeO_2F_2**.

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

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

Properties of Xenon-Oxygen Compounds

$$H = \frac{1}{2}[V + M - C + A]$$

$$= \frac{1}{2}[8 + 0] = 4 \quad sp^3 \quad Th$$

Compound	Physical propeties	Molecular structure
XeO_3	Colourless, explosive solid	Pyramidal
$XeOF_4$	Colourless, volatile liquid	Square Pyramidal

$$H = \frac{1}{2}[8 + 4] = 6$$

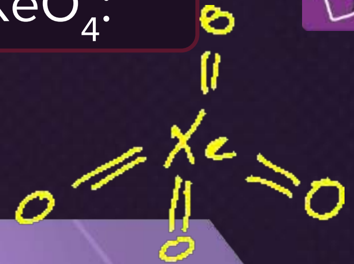
$$sp^3d^2$$

Identify the **incorrect** statement regarding the molecule XeO_4:

BOARDS

$H = \frac{1}{2}[8 + 0 + 0] = 4$ sp^3 Th

$ns^2 np^6$



XeO_4 :

Xe – [(4σ, 4π) bonds, 0 l.p.]
– sp^3 hybridisation – tetrahedral

O - [(1σ, 1π) bond, 2 l.p.]
– sp^2 hybridisation.

1π bond means one electron from O is in p orbital, which means in total there are 4 sp^3-p bonds.

Hence, option a is the correct answer.

- a ✓ XeO_4 molecule is square planar. ✗
- b ✗ There are four pπ-dπ bonds. ✓ T
- c ✗ There are four sp^3-p, σ-bonds. T
- d ✗ XeO_4 molecule is tetrahedral. T

XeO_4 :

Xe – [(4σ, 4π) bonds, 0 l.p.]
– sp^3 hybridisation – tetrahedral

O - [(1σ, 1π) bond, 2 l.p.]
– sp^2 hybridisation.

1π bond means one electron from O is in p orbital, which means in total there are 4 sp^3-p bonds.

Four pπ – dπ bonds are also formed with oxygen atoms by the unpaired electrons. Here, p-orbital is from O and d-orbital is from Xe - atom respectively.

Hence, option a is the correct answer.

Xenon forms the largest number of compounds only with oxygen and fluorine because:

BOARDS

(i) Oxygen and fluorine have very high electronegativity.

(ii) Ionisation energy of Xe is the largest among rare gases.

(iii) Ionisation energy of Xe is low compared to those of other rare gases.

(iv) Low dissociation energy of fluorine molecule compared to those of Cl_2 and Br_2

Oxygen and fluorine are more electronegative elements and act as strong oxidising agents, which means they can easily attract the lone pair of noble gas elements.
Down the group ionisation energy decreases, so Xe has low I.E. compared to other noble gases above it.

Hence, option b is the correct answer.

a (i), (ii), (iii)
b (i), (iii), (iv)
c (iii), (iv)
d (i), (iv)

Uses

Helium is used in filling balloons

Helium is used as a diluent due to its very low solubility in blood.

Helium is used in gas-cooled nuclear reactors

Neon is used in discharge tubes

Argon is used in filling electric bulbs

Argon is used in arc welding of metals and alloys

Which of the following xenon-oxo compounds may not be obtained by the hydrolysis of xenon fluorides?

BOARDS

a XeO_2F_2

b $XeOF_4$

c XeO_3

d XeO_4

Hence, option d is the correct answer.

$$XeF_6 + 1\,H_2O \rightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$$

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

$$XeF_4 + H_2O \rightarrow \boxed{XeO_3} + \underline{Xe + HF + O_2}$$

$$XeF_2 + H_2O \rightarrow Xe + HF + O_2$$

Xenon hexafluoride on partial hydrolysis produces compounds 'X' and 'Y'. Compounds 'X' and ‘Y’ with the oxidation state of Xe in them is respectively:

BOARDS

a $XeOF_4$ (+6) and XeO_3 (+6)

b XeO_2 (+4) and XeO_3 (+6)

c $XeOF_4$ (+6) and XeO_2F_2 (+6)

d XeO_2F_2 (+6) and XeO_2 (+4)

$$\underset{(+6)}{XeF_6} + H_2O \rightarrow \boxed{\underset{(+6)}{XeOF_4}} + 2HF$$

- a. $XeOF_4$ (+6) and XeO_3 (+6) X
- b. X XeO_2 (+4) and XeO_3 (+6)
- c. $XeOF_4$ (+6) and XeO_2F_2 (+6)
- d. XeO_2F_2 (+6) and XeO_2 (+4) X

$$\overset{(+6)}{XeF_6} + 2H_2O \rightarrow \overset{(+6)}{XeO_2F_2} + 4HF$$

Hence, option c is the correct answer.

The correct order of N-compounds in the decreasing order of their oxidation states is:

$NO \rightarrow \boxed{+2}$

$N_2 \rightarrow 0$

$HNO_3 \rightarrow +1 + x + 3(-2) = 0$

$\boxed{x = +5}$

a ✓ $\overset{+5}{HNO_3}, \overset{+2}{NO}, \overset{0}{N_2}, \overset{-3}{NH_4Cl}$

b ✗ $\overset{+5}{HNO_3}, \overset{+2}{NO}, \overset{-3}{NH_4Cl}, \overset{0}{N_2}$

c ✗ NH_4Cl, N_2, NO, HNO_3

d ✗ $\overset{+5}{HNO_3}, \overset{-3}{NH_4Cl}, \overset{+2}{NO}, \overset{0}{N_2}$

$\boxed{x = -3}$ $x + 4(+1) + (-1) = 0$

Hence, option a is the correct answer.

Which of the following statements is not true for halogens?

$HOF, HOCl, HOBr, HOI$

a. All form monobasic oxyacids. T

b. All are oxidising agents. $\overset{0}{X_2} \longrightarrow \overset{-1}{X}$ T

c. Chlorine has the highest electron gain enthalpy. T

d. All halogens show positive oxidation states. X

All the halogens except fluorine show positive oxidation states. This is because, fluorine being the most electronegative element can never have a positive oxidation state.

Hence, option d is the correct answer.

In the structure of ClF_3, the number of lone pair of electrons on central atom ’Cl’ is:

BOARDS

a One

b Two

c Three

d Four

In the structure of ClF_3, the number of lone pairs of electrons on central atom Cl is two. Cl has 7 valence electrons out of which 3 are involved in bond formation with 3 F atoms. 7–3 = 4 valence electrons remains in the form of 2 lone pairs of electrons.

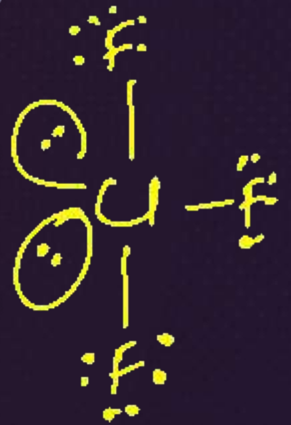
Hence, option b is the correct answer.

- a One
- [✓ b Two]
- c Three
- d Four

$$H = \frac{1}{2}[V + M - C + A]$$

$$= \frac{1}{2}[7 + 3] = 5 \quad sp^3d^2$$

TBP



Which oxide of nitrogen is **not a common pollutant** introduced into the atmosphere both due to natural and human activity?

BOARDS

N_2O_5 is not a common pollutant introduced into the atmosphere both due to natural and human activity.

N_2O, NO, and NO_2 are common pollutants introduced into the atmosphere both due to natural and human activity.

Hence, option a is the correct answer.

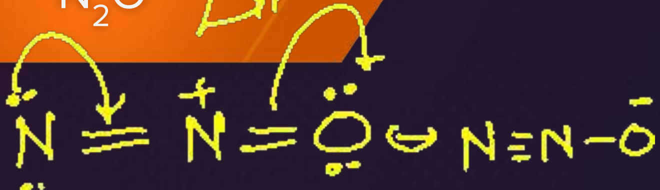
- a N_2O_5
- b NO_2
- c NO
- d N_2O

Among the compounds shown below, which one has a linear structure?

- a NO_2
- b HOCl
- c O_3
- d N_2O

180° ✗

- a NO_2
- b HOCl
- c O_3
- [✓ d] N_2O Linear



Hence, option d is the correct answer.

Which of the following oxides is amphoteric in nature?

$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$

GeO_2/ $SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$

PbO_2/ $SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$

- a SnO_2 ✓
- b SiO_2 Acidic
- c GeO_2 Acidic
- d CO_2 Acidic

CO_2
SiO_2
GeO_2
Acidic

SnO_2
PbO_2
Amphoteric

SnO_2

/ $PbO_2 + 4HCl \rightarrow PbCl_4 + 2H_2O$

Hence, option a is the correct answer.

Which one of the following reactions does not come under hydrolysis-type reaction?

- **a** $SiCl_4 (\ell) + 2H_2O (\ell) \rightarrow SiO_2 (s) + 4HCl (aq)$
- **b** $Li_3N (s) + 3H_2O (\ell) \rightarrow NH_3 (g) + 3LiOH (aq)$
- **c** $2F_2 (g) + 2H_2O (\ell) \rightarrow 4HF (aq) + O_2 (g)$
- **d** $P_4O_{10} (s) + 6H_2O (\ell) \rightarrow 4H_3PO_4 (aq)$

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$Si(OH)_4 \xrightarrow{-2H_2O} SiO_2$

a. $\overset{+4}{SiCl_4}(\ell) + 2H_2O(\ell) \rightarrow \overset{+4}{SiO_2}(s) + 4HCl(aq)$ ✓ Hydrolysis

b. $\overset{+1}{Li_3}\overset{-3}{N}(s) + 3H_2O(\ell) \rightarrow \underset{3}{NH_3}(g) + 3LiOH(aq)$ Hydrolysis

c. $2\overset{0}{F_2}(g) + 2\overset{+1}{H_2}\overset{-2}{O}(\ell) \rightarrow 4\underset{-1}{HF}(aq) + \underset{0}{O_2}(g)$ Redox ✓

d. $P_4O_{10}(s) + 6H_2O(\ell) \rightarrow 4H_3PO_4(aq)$ Hydrolysis

$4x+10(-2)=0$

$\boxed{x=+5}$

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

$(x=+5)$

Hence, option c is the correct answer.

For the second period elements, the correct increasing order of first ionisation enthalpy is:

BOARDS

a Li < Be < B < C < N < O < F < Ne

b Li < B < Be < C < O < N < F < Ne

c Li < B < Be < C < N < O < F < Ne

d Li < Be < B < C < O < N < F < Ne

$\text{Li} < \text{B} < \text{Be} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne}$

$2s^1 \quad 2s^2\,2p^1 \quad 2s^2 \quad 2s^2\,2p^2 \quad 2s^2\,2p^4 \quad 2s^2\,2p^3 \quad 2s^2\,2p^5 \quad 2s^2\,2p^6$

Hence, option b is the correct answer.

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

$H_2Po < H_2Te < H_2Se < H_2S$ TS ∝ Bond. diss. Energy

^ H_2O

- **a** $H_2Po < H_2Te < H_2Se < H_2S < H_2O$ ✓
- **b** $H_2Se < H_2Te < H_2Po < H_2O < H_2S$ ✗
- **c** $H_2S < H_2O < H_2Se < H_2Te < H_2Po$ ✗
- **d** $H_2O < H_2S < H_2Se < H_2Te < H_2Po$ ✗

On going down the group, the thermal stability of H_2E decreases because H–E bond energy decreases.

Hence, option a is the correct answer.

The correct order of atomic radii in group 13 elements is:

BOARDS

B < Ga < Al < In < Tl

B
Al
Ga — 31

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4s^1$

- a B < Al < In < Ga < Tl ✗
- b B < Al < Ga < In < Tl ✗
- c B < Ga < Al < In < Tl ✓
- d B < Ga < Al < Tl < In ✗

Generally, atomic radii increases down the group, but the atomic radius of Ga is less than that of Al due to the poor shielding effect of 3d electrons in Ga.

Hence, option c is the correct answer.

Which one of the following elements is unable to form MF_6^{3-} ion?

B

2d ✗

BF_6^{3-}

BF_4^{-}

- a Ga
- b Al
- c In
- [✓ d] B

B^{3+} has no vacant d orbitals. It has only on s and 3 p orbitals in its valence shell. Hence, it can accept only 4 electron pairs and can form BF_4^{-}.

Hence, option d is the correct answer.

The stability of +1 oxidation state among Al, Ga, In, and Tl increases in the sequence:

a Al < Ga < In < Tl

b Tl < In < Ga < Al

c In < Tl < Ga < Al

d Ga < In < Al < Tl

Al < Ga < In < Tl $\boxed{+x}$ $\boxed{+x-2}$

gp 13 → ns^2np^1 $\boxed{+3}$

Inert Pair effect

- a Al < Ga < In < Tl ✓
- b Tl < In < Ga < Al
- c In < Tl < Ga < Al ✗
- d Ga < In < Al < Tl ✗

As we go down the group, the stability of low oxidation state increases, this is generally due to inert pair effect.

Hence, option a is the correct answer.

+3 Stab

+1 Stab↑