

P - BLOCK

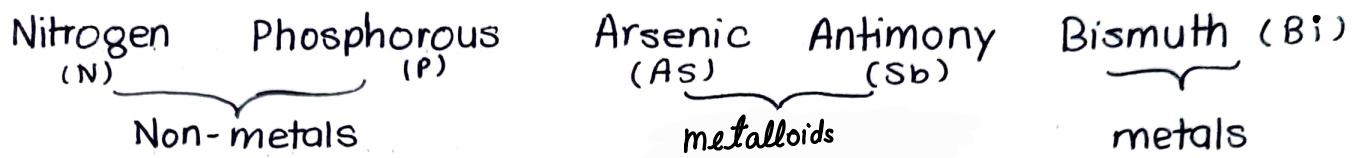
Class 12th

APNI KAKSHA

Rajneesh Dhattarwal

THE P-BLOCK ELEMENTS

GROUP-15 ELEMENTS



I Electronic configuration : ns^2np^3

extra stable electronic configuration due to half-filled p-orbital.

II Atomic and Ionic radii :

- Down the group the atomic / ionic radii increases due to increase in the no. of inner shells or 'shielding effect'.
 - The increase in size from N to P is considerable, while from As to Bi, only a small increase is observed due to the presence of completely filled d/f orbitals which have poor shielding effect.

III Ionisation enthalpy:

- Down the group, Ionisation enthalpy decreases due to gradual increase in atomic size.

NOTE : Because of the extra stable half-filled p-orbitals, electronic configuration and small size, the 1st IE of group -15 is much greater than that of group 14 elements, in the corresponding periods.

- The order of successive ionisation enthalpy as expected is:
 $\Delta i^1 H_1 < \Delta i^1 H_2 < \Delta i^1 H_3$

IV Electronegativity:

- The electronegativity value decreases down the group with increasing atomic size.

V Occurrence :

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- in the form of plants' and animals' 'proteins'.

- (ii) PHOSPHOROUS: in minerals of the apatite family.
eg. fluorapatite $[Ca_5(PO_4)_6 \cdot CaF_2]$
- an essential constituent of animal and plant matter.
 - present in bones as well as in living cells.
- (iii) ARSENIC, ANTIMONY, and BISMUTH are found mainly as 'sulphides'

Q Nitrogen exists as diatomic molecule i.e. N_2 while Phosphorous exists as tetra-atomic molecule ie. P_4 . Explain.

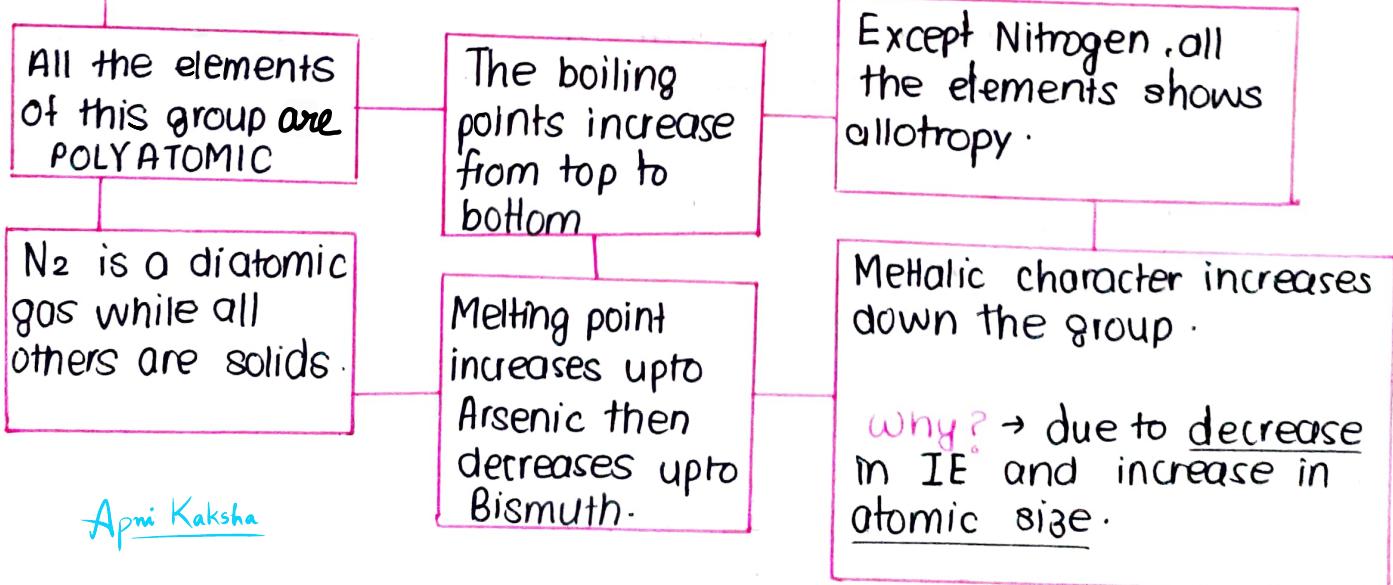
A: It is because phosphorous (P) cannot form $p\pi-p\pi$ multiple bonds because of diffused nature of large $3p$ -orbital, which doesn't lead to effective overlap.

- Nitrogen can form $p\pi-p\pi$ multiple bond because $2p$ orbital is smaller in size and can overlap sideways effectively.

Q Nitrogen is gas at room temperature, while phosphorous is a solid. Explain.

A It is because the atomicity increases from diatomic nitrogen (N_2) to tetra-atomic phosphorous (P_4) which increase the VDW forces largely.

PHYSICAL PROPERTIES :



■ CHEMICAL PROPERTIES

■ OXIDATION STATES

Electronic configuration : $ns^2 np^3$

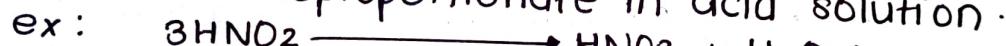
Examples : -3 : $\overset{+6}{\text{Ca}_3}\overset{-6}{\text{N}_2}$ (ionic valency) ; NH_3 (covalency)
+3 : $\overset{+3}{\text{NCl}_3}$; $\overset{+3}{\text{PCl}_3}$
+5 : $\overset{+5}{\text{PCl}_5}$

The tendency to exhibit -3 O.S decreases down the group.
why? due to increase in size and metallic character.

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+3 and +5 are generally the covalency and the tendency to show +3 O.S in comparison to +5 O.S increases down the group. **why?** It is because of inert pair effect. i.e. non-participation of S electrons in bond formation, as when we go down the group, the bonds formed are weaker and thus energy released is not sufficient to cause unpairing of S e⁻s.

NOTE: In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution.



→ Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.

Q: Give reason for the fact that nitrogen shows anomalous behaviour in group 15. Also give chemical evidence for the same.

A: Reasons for anomalous behaviour:

- small size
- high electronegativity
- unique ability to form $p\pi-p\pi$ multiple bonds.
- high ionisation enthalpy.
- non-availability of d-orbitals.

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CHEMICAL EVIDENCE:

- Nitrogen is capable of forming $p\pi-p\pi$ multiple bonds with itself and with other elements, having small size and high - electronegativity (e.g. C, O)

• It is capable of showing -3 O.S as ionic valency (ex. Ca_3N_2)

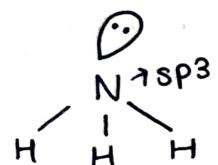
Q. Dinitrogen (N_2) is inert at room temperature. Why?

A. It is because of high bond dissociation enthalpy of triple bond in nitrogen molecule $\{\text{N} \equiv \text{N} \rightarrow \text{N}_2\}$

NOTE: The single N-N bond is weaker than the single P-P bond because of high- inter-electronic repulsion of the non-bonding electrons, owing to the small bond length. As a result, the catenation tendency is weaker in nitrogen.

REACTIVITY TOWARDS HYDROGEN:

All group 15 elements form hybrids of formula ' MH_3 ', which is, trigonal pyramidal in shape. Hybridisation of the element is sp^3 with one lone pair of e⁻s present at one of the vertices of tetrahedron.



shape: trigonal pyramidal
geometry: tetrahedron

HYBRIDES

| | | |
|----------------|---------------|------------|
| NH_3 | \rightarrow | Ammonia |
| PH_3 | \rightarrow | Phosphine |
| AsH_3 | \rightarrow | Arsine |
| SbH_3 | \rightarrow | Stibine |
| BiH_3 | \rightarrow | Bismuthine |

(i) Thermal stability: $\rightarrow \{ \text{how easily it can be decomposed} \}$

Decreases down the group because of increase in size of the element which results in weaker bonds.

(ii) Reducing characteristics: (Reduce hone ka matlab kitni jaldi e⁻ accept kar leta hai)

Increases down the group because the thermal stability decreases as the bond length increases down the group.

NOTE: Ammonia is a mild reducing agent, and BiH_3 is the strongest reducing agent amongst all the hybrides.

(because down the group, there are weaker bonds, so bond length will increase and reducing character increases).

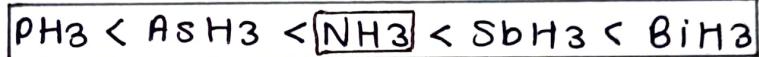
(iii) Boiling point :



Boiling point increases from PH₃ to BiH₃ because of increase in VDW forces, with increase in mass and size.

NH₃ In the group, has exceptionally high boiling point because of its ability to undergo hydrogen bonding.

Therefore, the correct order is



(iv) Basic character:

- NH_3 and other hydrides are basic in nature because of presence of lone pair of e^- s over the central atom.
 - The basic character decreases down the group:

$$\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$$

because of increase in size of the central atom and thus, reduction in its tendency to give lone pair with decrease in electron density.

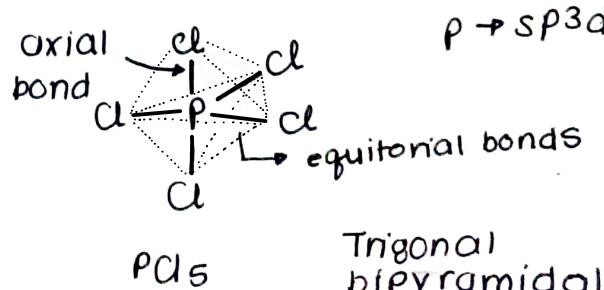
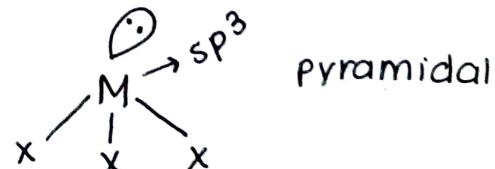
Q PH₃ when passed through water forms bubbles while NH₃ doesn't. Why?

(means PH_3 is insoluble and NH_3 is soluble in H_2O)

A It is because unlike PH₃, NH₃ is soluble in water as it can form H-bond, with H₂O molecules.

■ REACTIVITY TOWARDS HALOGENS

- They form trihalides of the formula MX_3 with pyramidal shape.
 - They form pentahalides of the formula MX_5 with trigonal bipyramidal shape.



Q. All the bonds in PCl_5 are not equivalent. Why?
A. It is because along axial lines, there is greater repulsion. Therefore, to minimize repulsion, axial bonds are elongated i.e. longer than equatorial bonds.

Q. Penta halides are more covalent than trihalides. Explain.
$${}^{+5}\text{MX}_5 \quad {}^{+3}\text{MX}_3$$

A. It is because in penta halides, the oxidation state of the central metal atom, is high and thus its charge density and polarising power, is also high resulting in greater covalent character. (FAZAN'S RULE)

Q. Bromides are more covalent than chlorides. Why?
A. size of bromide > size of chloride

It is because larger the size of an anion, more is its polarisability and hence, greater is the covalent character. (FAZAN'S RULE)

Q. BiF_3 is pre-dominately ionic. Why?

A. $\text{F}^- \rightarrow$ smallest anion, least polarisability
 $\text{Bi} \rightarrow$ largest cation, least charge density, least polarising power.
⇒ least covalent character
⇒ $\text{BiF}_3 \rightarrow$ pre-dominately ionic.

Q. PCl_5 exists while NCI_5 doesn't. Why?

A. It is because unlike P, nitrogen doesn't have vacant d-orbital to which s e's can move after getting unpaired.

Q. RaP=O exists while RaN=O doesn't. Why?

A. It is because nitrogen doesn't have vacant d-orbitals.
 \therefore 8 e's can't get unpaired and nitrogen can't form 5 bonds.

TRY OUT YOURSELF

Q: The H-N-H angle value is higher than H-P-H, H-As-H, H-Sb-H. angles. Why?

REACTIVITY TOWARDS OXYGEN

- All these elements form two types of oxides: M_2O_3 and M_2O_5
- The oxide in the higher O.S. of the element is more acidic than that of lower O.S.
Their acidic character decreases down the group,
 N_2O_3 } \rightarrow ACIDIC As_2O_3 } \rightarrow AMPHOTERIC $Bi_2O_3 \rightarrow$ BASIC
 P_2O_3

REACTIVITY TOWARDS METALS

All these elements react with metals to form their binary compounds exhibiting -3 O.S

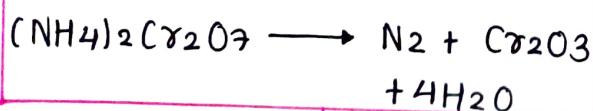


DINITROGEN (N_2)

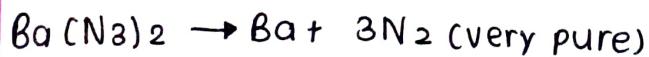
PREPARATION

Commercially produced by liquefaction and fractional distillation of air

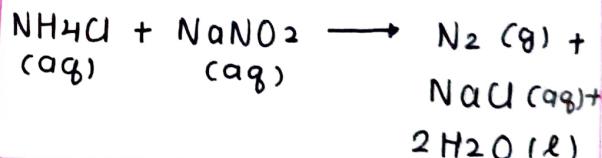
By thermal decomposition of ammonium dichromate



By thermal decomposition of sodium or barium azide



By treating aq. solution of NH_4Cl with sodium nitrite.



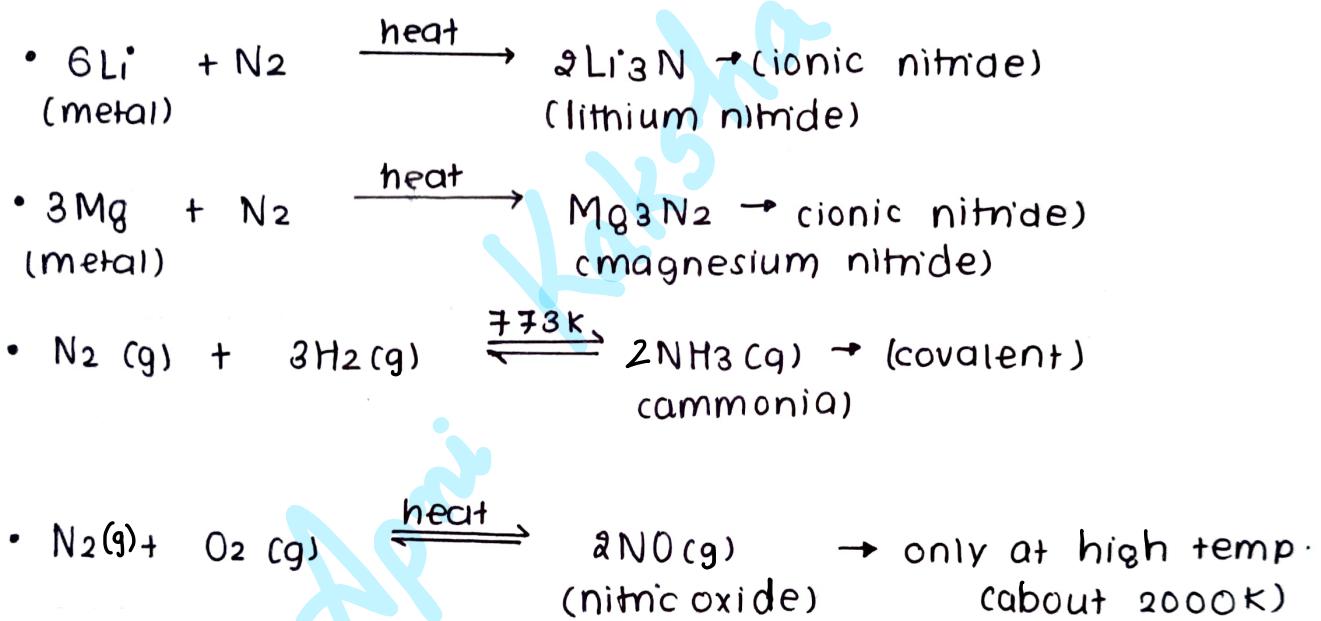
By small amounts of NO and HNO_3 (impurities) formed by passing the gas through aq. H_2SO_4 containing $K_2Cr_2O_7$.

PROPERTIES

colourless, odourless, tasteless and non-toxic gas

is inert at room temperature.

has very low solubility in water and low freezing and boiling point.



USES

in the manufacture of ammonia and other industrial chemicals

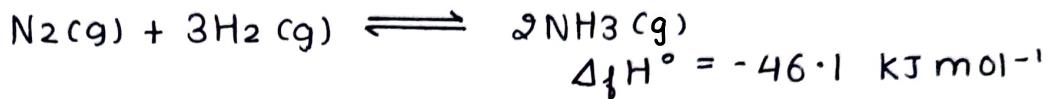
used where inert atmosphere is required

liquid dinitrogen is used as a refrigerant to preserve biological materials, food items etc.

AMMONIA

PREPARATION :

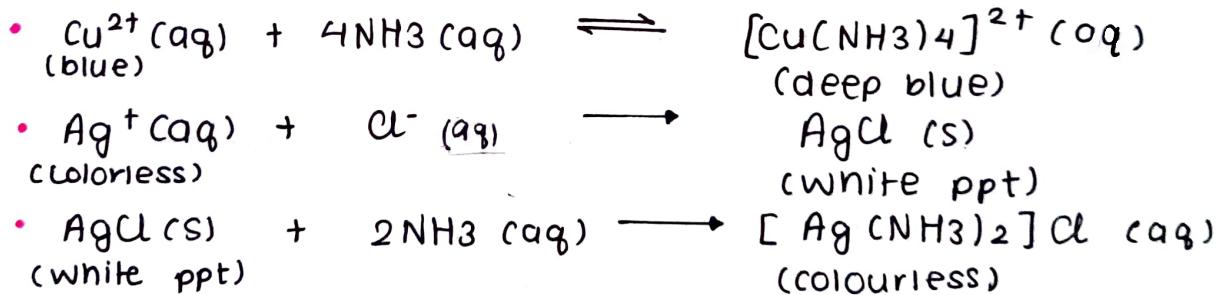
By Haber's Process:



- Conditions:
 - pressure about 200 atm
 - temperature at 700 K
 - catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.

PROPERTIES :

- Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to formation of OH^- ion.
- $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
- It donates the electron pair and form linkages with metal ions and the formation of such complex compounds finds application in detection of metal ions such as Cu^{2+} , Ag^+ :



USES

to produce various nitrogenous fertilizers

ex: ammonium nitrate
ammonium phosphate
ammonium sulphate
urea.

in the manufacture of some inorganic nitrogen compounds.
(ex. HNO_3)

Liq. NH_3 is also used as a refrigerant

OXIDES OF NITROGEN

Refer to Table 7.3 : Oxides of Nitrogen &
Table 7.4 : Structures of Oxides of Nitrogen
of NCERT Textbook, Chemistry (PART-1)

NITRIC ACID: HNO_3 (colourless liquid)

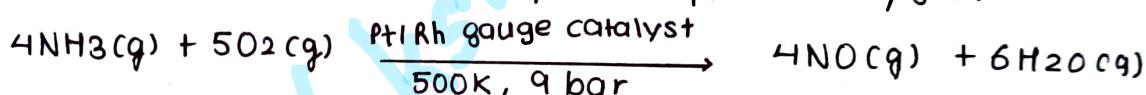
PREPARATION

- In the laboratory, nitric acid is prepared by heating KNO_3 or NaNO_3 and conc H_2SO_4 in a glass retort.

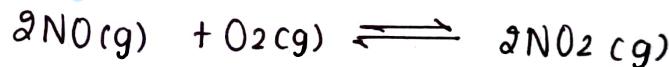


- By Oswald's Process.

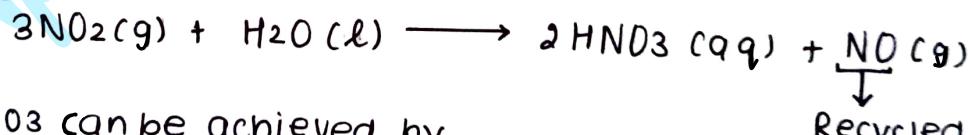
STEP I : catalytic oxidation of NH_3 by atmospheric oxygen.



STEP II : Nitric oxide (NO) thus formed combines with O_2 giving NO_2



STEP III : Nitrogen dioxide (NO_2), so formed, dissolves in H_2O to give HNO_3 .



- * 98% conc. of HNO_3 can be achieved by dehydration with conc. H_2SO_4

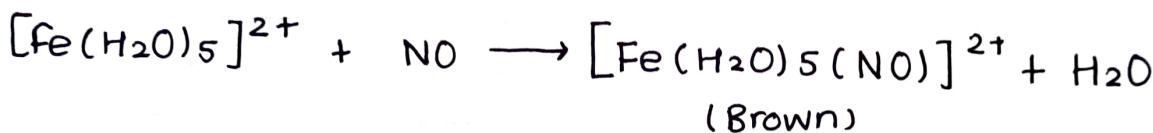
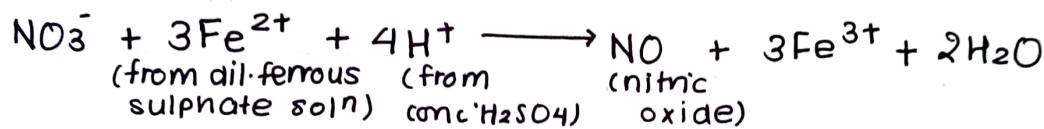
PROPERTIES :

- In aq. solution, HNO_3 behaves as a strong acid giving hydronium and nitrate ions.
$$\text{HNO}_3(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{H}_3\text{O}^+(aq) + \text{NO}_3^-(aq)$$
- Conc. HNO_3 is a strong oxidising agent and attacks most metals except noble metals such as Gold and platinum. The products of oxidation depends upon ;
 - i) conc. of acid
 - ii) the nature of the material undergoing oxidation.
 - (iii) temperature

V. imp:

- $3\text{Cu} + 8\text{HNO}_3$ (dilute) $\rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
- $\text{Cu} + 4\text{HNO}_3$ (conc) $\rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 2\text{H}_2\text{O}$
- $4\text{Zn} + 10\text{HNO}_3$ (dilute) $\rightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$
- $\text{Zn} + 4\text{HNO}_3$ (conc) $\rightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
- Some metals (e.g. Cr, Al) don't dissolve in conc. HNO_3 , because of the formation of a passive film of oxide on the surface. (passivation).
- Conc. HNO_3 also oxidises non-metals and their compounds.
ex: $\text{I}_2 + 10\text{HNO}_3 \rightarrow 2\text{HI}(\text{O})_3 + 10\text{NO}_2 + 4\text{H}_2\text{O}$
 $\text{S}_8 + 48\text{HNO}_3 \rightarrow 8\text{H}_2\text{SO}_4 + 48\text{NO}_2 + 16\text{H}_2\text{O}$

BROWN RING TEST (for nitrate ion)



USES OF HNO_3

in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics.

in the pickling of stainless steel, etching of metals and as an oxidiser in rocket fuels

PHOSPHORUS - ALLOTROPIC FORMS

Allotropic forms of phosphorous are: WHITE, RED & BLACK

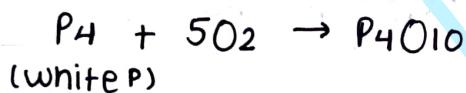
White Phosphorous

- Properties
- translucent white, waxy solid
 - poisonous
 - insoluble in water but soluble in CS_2
 - glows in dark

• It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3 .



• It readily catches fire in air to give dense white fumes of P_4O_{10} .



Red Phosphorous

Preparation: • obtained by heating white phosphorous at 573 K in an inert atmosphere for several days

Properties :

- possesses iron grey lustre
- odourless, non-poisonous
- insoluble in H_2O as well as CS_2
- doesn't glow in dark.

• Black phosphorous : obtained by heating red phosphorous under high pressure. It has two forms:

forms

α - Black

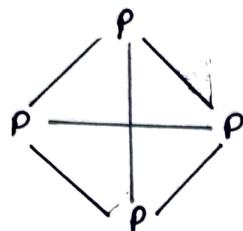
- formed when red P is heated in a sealed tube at 803 K
- doesn't oxidise in air
- has opaque monoclinic

β - Black

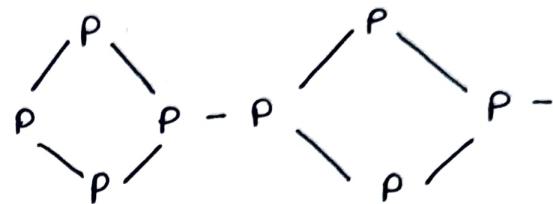
- prepared by heating white P at 473 K under high pressure.
- doesn't burn in air upto 673 K

or rhombohedral crystals.

Q. Compare the structure and reactivity of 2 imp. allotropes of P.



white phosphorous
discrete P_4 units



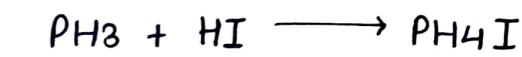
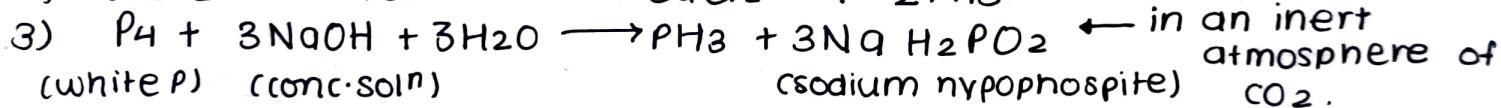
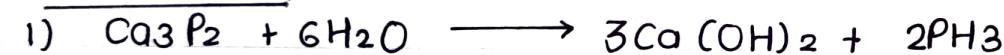
red phosphorous
Polymeric structure of P_4 units

CBSE 2009

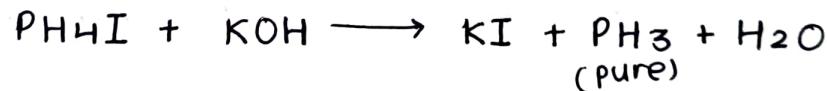
Reactivity: White P is more reactive than red P because of angular strain in the molecule as the bond angle is very small i.e. 60° .

• Phosphine : PH_3

: PREPARATION:



(impure)



(pure)

• colourless gas with rotten fish smell and it's highly poisonous

PROPERTIES

• weakly basic
ex. $PH_3 + HBr \rightarrow PH_4Br$

• slightly soluble in water.

• explodes in contact with traces of oxidising agents like HNO_3 , Cl_2 , and B_2O_3 vapours

: USES:

• It is used in HOLME'S SIGNALS and in SMOKE SCREENS.

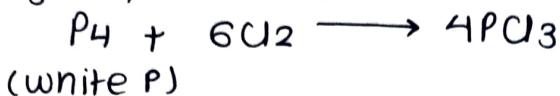
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PHOSPHOROUS HALIDES

PHOSPHOROUS TRICHLORIDE : PCl₃

Preparation:

- 1) By passing dry chlorine over heated white P.



- 2) By action of thionyl chloride (SOCl₂) on white P



Properties:

- 1) It is a colourless oily liquid and hydrolyses in the presence of moisture.



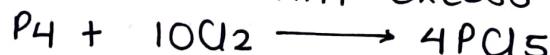
- 2) It reacts with organic compounds containing -OH group.



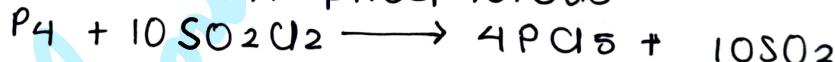
PHOSPHOROUS PENTACHLORIDE : PCl₅

Preparation:

- 1) by reaction of white P with excess of dry chloride

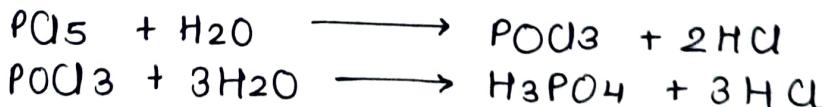


- 2) by action of SO₂O₂ on phosphorous



Properties:

- 1) It is a yellowish white powder & it hydrolyses to POCl₃ and finally gets converted to phosphoric acid.



- 2) When heated, it sublimes but decomposes on stronger heating.



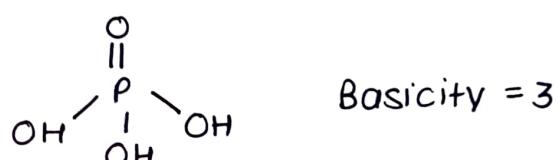
Q. How does PCl_5 exist in solid state?

A. In the solid state, PCl_5 exists as an ionic solid, $[\text{PCl}_4]^+ [\text{PCl}_6]^-$ in which the cation $[\text{PCl}_4]^+$ is tetrahedral and the anion $[\text{PCl}_6]^-$ is octahedral.

OXO- ACIDS OF PHOSPHOROUS

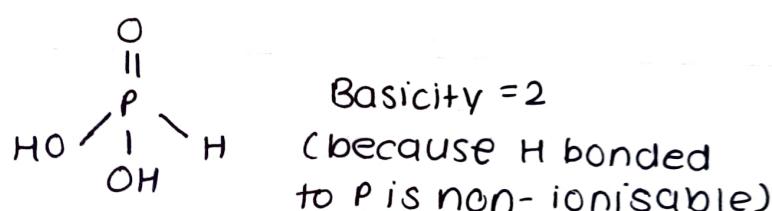
- In all these acids, P atom is tetrahedrally co-ordinated to atleast 1 Oxygen Atom with double bond and atleast 1-OH group.
- H bonded to O only is ionisable.

1) H_3PO_4 : Phosphoric acid



Basicity = 3

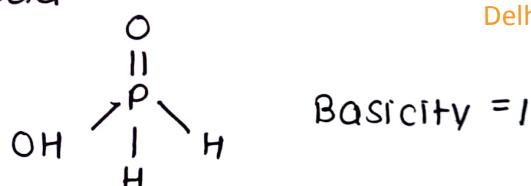
2) H_3PO_3 : Phosphorus acid



Basicity = 2

(because H bonded to P is non-ionisable)

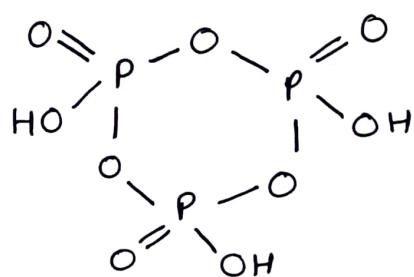
3) H_3PO_2 : Hypo-phosphorus acid



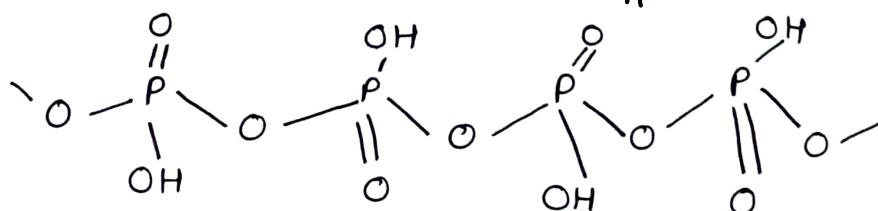
Delhi 2010

Basicity = 1

4) Cyclotrimetaphosphoric acid : $(\text{HPO}_3)_3$

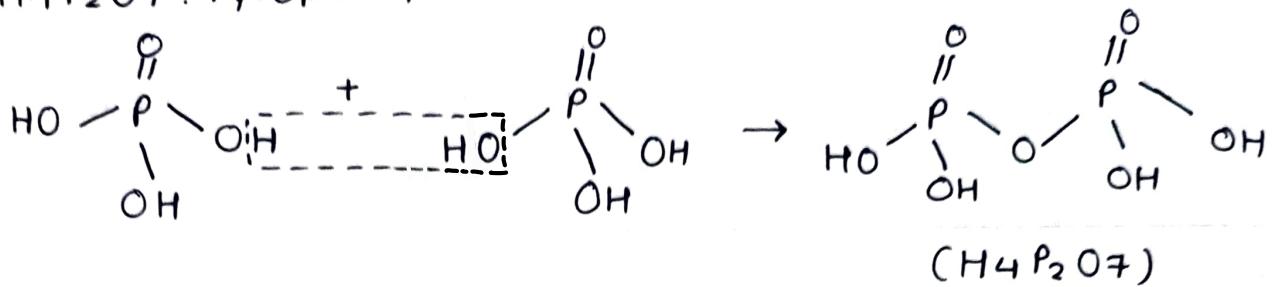


5) Polymetaphosphonic acid : $(\text{HPO}_3)_n$



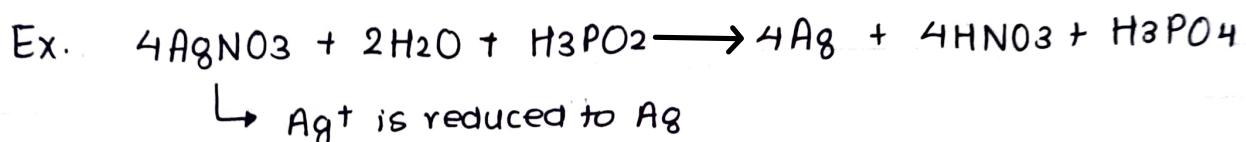
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6) $\text{H}_4\text{P}_2\text{O}_7$: Pyrophosphoric acid



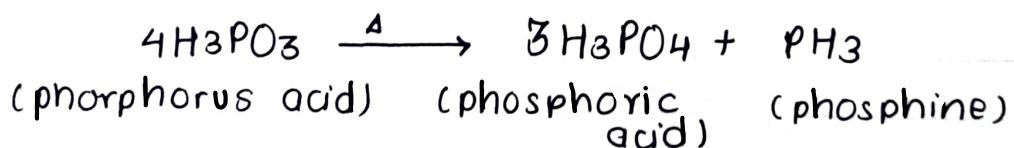
Q Explain the reducing properties of hypo-phosphorous acid? (H_3PO_2)

- A. H bonded to P is non-ionisable but imparts reducing characteristics to the acid.
In H_3PO_2 , 2H are directly bonded to P and hence is reducing in nature.



Q What happens when H_3PO_3 is heated?

- A Orthophosphorous acid (or phosphorus acid) or heating disproportionates to give orthophosphoric acid [or phosphoric acid] and phosphine.



GROUP-16 ELEMENTS {chalcogens}

| Atomic no. | Element | Electronic configuration |
|------------|----------------|---|
| 8 | Oxygen {O} | [He] $2s^2 2p^4$ |
| 16 | Sulphur {S} | [Ne] $3s^2 3p^4$ |
| 34 | Selenium {Se} | [Ar] $3d^{10} 4s^2 4p^4$ |
| 52 | Tellurium {Te} | [Kr] $4d^{10} 5s^2 5p^4$ |
| 84 | Polonium {Po} | [Xe] $4f^{14} 5d^{10} 6s^2 6p^4$ ↳ radioactive |

Occurrence:

SULPHUR: as sulphates such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), baryte (BaSO_4)
as sulphides such as galena (PbS), zinc blende (ZnS) etc.

Electronic Configuration:

The elements of group 16 have $6 e^-s$ in the outermost shell ($ns^2 np^4$)

Atomic and Ionic radii:

Down the group, atomic and ionic radii increases due to increase in the no. of shells.

Ionisation enthalpy (IE):

Ionisation enthalpy decreases down the group due to increase in size.

Q. Elements of group 16 generally show less value of 1st I.E compared to the corresponding periods of group 15. Why?

A. Due to extra stable half-filled p-orbitals electronic configuration of group 15 elements, larger amount of energy is required to remove e^-s compared to grp 16 elements.

Electron Gain Enthalpy (EGE):

EGE becomes less negative down the group (because of ↑ size), but EGE of oxygen is less than that of sulphur.
 Why? because the incoming electron faces greater

inter-electronic repulsions in the small sized 2p orbitals of oxygen atom.

Delhi 2014

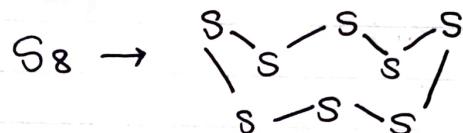
Electronegativity:

Down the group, electronegativity decreases as size increases

NOTE: Next to fluorine, OXYGEN has the highest electronegativity value amongst the elements.

- Their MELTING & BOILING points increases down the group.
(because VDW force \rightarrow ↑ses with increase in mass & size)

Q Oxygen exists as diatomic molecule (O_2) while sulphur exists as S_8 . Why?



Q There exists a large difference b/w the melting and boiling points of oxygen and sulphur. Explain.

A It can be explained on the basis of their atomicity: oxygen exists as a diatomic molecule (O_2) whereas sulphur exists as a polyatomic molecule (S_8).

Q Oxygen exists as gas at room temp. while sulphur as solid. Why?

Delhi 2012, 2010
CBSE 2018

CHEMICAL PROPERTIES

OXIDATION STATES:

- The stability of -2 O's decreases down the group.
(because of decrease in electronegativity).
- The tendency or stability of +4 O's in comparison to +6 O's increases down the group, due to inert pair effect.

Q SF_6 exists while OF_6 doesn't. Why?

A This is because oxygen can't show O's of +6, as it doesn't have vacant d-orbitals.

Q. Give an account of all O.S exhibited by oxygen.

| | | | |
|---|-------------------------------|------|---------------------|
| A | OF ₂ | +2 | |
| | Cl ₂ O | -2 | (most common oxide) |
| | H ₂ O ₂ | -1 | (peroxide) |
| | KO ₂ | -1/2 | (super oxide) |
| | O ₂ F ₂ | +1 | |

Q Compound between O and F (ex. OF₂) is called fluoride, while that between O and Cl (ex. Cl₂O) is called oxide. Why?

A OF₂ (fluoride) : Fluoride is more electronegative than oxygen.
O.S of oxygen : +2 ; O.S of fluorine : -1.

Cl₂O (oxide) : Oxygen is more electronegative than chlorine
O.S of oxygen : -2 ; O.S of fluorine : +1

Q Give reasons and examples of anomalous behaviour of oxygen.

- A 1) Small size → can form pπ-pπ bond.] can form H-bonding
2) High electronegativity
3) Non-availability of vacant d-orbitals.] can't show O.S of +4 and +6.

REACTIVITY TOWARDS HYDROGEN

All the elements from grp. 16 form hydrides of the type H₂E (E = O, S, Se, Te, Po)

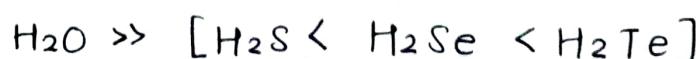
a) Thermal stability :

Down the group, thermal stability decreases as the size/bond length increases and hence H-E bond dissociation enthalpy decreases.

b) Reducing character :

- All hydrides except H₂O possess reducing property.
- Down the group, reducing character increases as thermal stability decreases.

c) Boiling Point :



exceptionally high bp because of H bonding

↳ because of increases in vdw forces due to ↑se in size and mass.

- Reducing character : Depends upon strength of M-H bond
- Boiling Point : Depends upon V.W forces \propto MW (molecular weight) \propto Strength of H-bond

Therefore, the correct order of boiling point is :



CBSE 2012, 2011
Delhi 2011, 2010

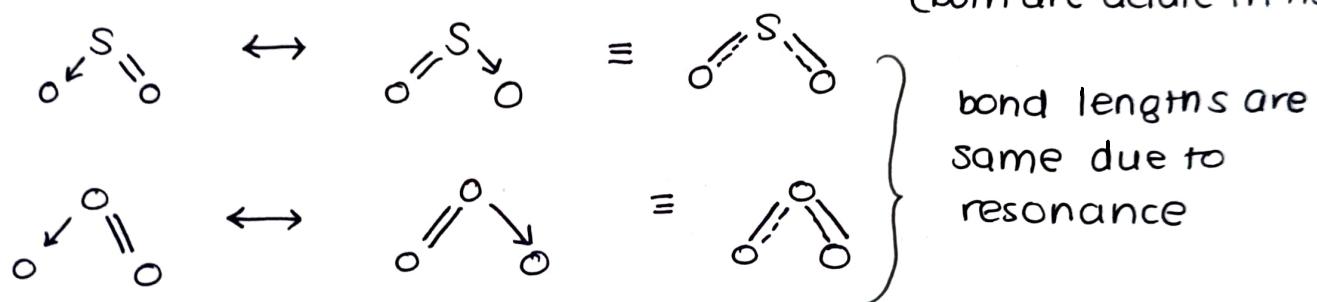
d) Acidic Strength : $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$

Acidic strength increases down the group as bond length \uparrow ses, bond strength \downarrow ses, which makes the release of H^+ easier.

REACTIVITY TOWARDS OXYGEN

1) Group 16 elements form oxides of the formula, MO_2 & MO_3

(both are acidic in nature)



- 2) • The oxides of the formula MO_2 can act as reducing agent, and \therefore themselves undergo a change in O.S from +4 to +6.
 • Down the group, reducing property decreases as the stability of +4 O.S increases due to inert pair effect.

NOTE: SO_2 is reducing while TeO_2 is an oxidising agent.

- 3) O_3 and SO_2 are gases because they exist as discrete molecules while SeO_2 and TeO_2 are solids because they have a polymeric structure with covalent linkages.

REACTIVITY TOWARDS HALOGENS

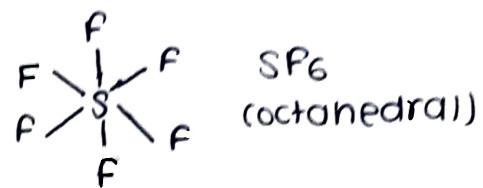
- Group 16 elements form halides of the form MX_6 , MX_4 , MX_2 .
- The stability of the halides decreases in the order:



Apni Kaksha

- Amongst hexahalides, hexafluorides are the only stable halides.

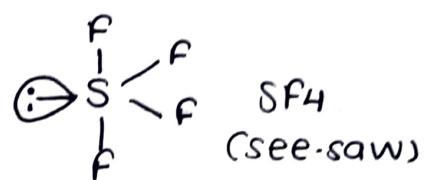
(hexafluorides → gaseous in nature
→ have octahedral structure



- Amongst tetrafluorides, SF₄ → gas; SeF₄ → liquid; TeF₄ → solid

SP₃ hybridisation

trigonal
by-pyramidal
structure



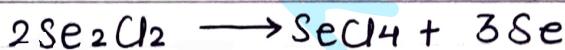
- Dihalides → SP³ hybridisation

→ tetrahedral structure

⇒ All elements except Se form dichlorides and dibromides.

- Monohalides → dimeric in nature (ex. S₂F₂, S₂Cl₂, S₂Br₂, etc)

These dimeric halides undergo disproportionation:

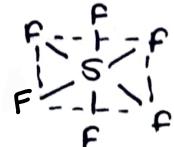


Q. SF₆ exists while Cl₆ doesn't. Why?

A. It is because Cl is not electronegative enough to bring about such high O.S. of +6 in sulphur. Also, its difficult for sulphur to accomodate 6 large-sized Cl. atoms around itself.
(causes steric crowding)

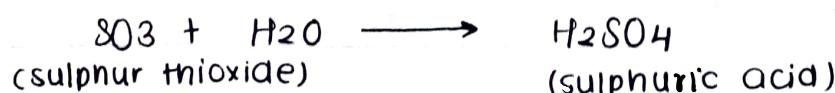
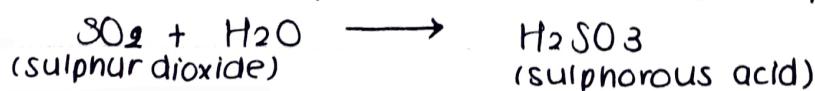
Q. How do you explain the inert nature of SF₆? CBSE 2011, Delhi 2011

A. SF₆ is inert or unreactive because sulphur in SF₆ is sterically protected by six fluorine atoms.



Q. Justify that the oxides of sulphur are acidic in nature.

A. It is because they dissolve in water to produce acid:



Apni Kaksha

Q. Why is H₂O a liquid and H₂S a gas?

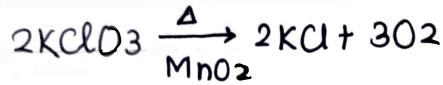
A. H₂O : H-bonding → Aggregation of H₂O molecules due to H-bonding.

H₂S : no H-bonding

DIOXYGEN [O₂]

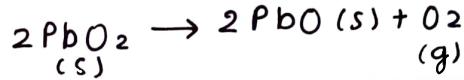
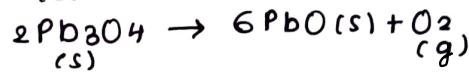
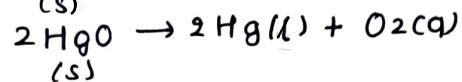
PREPARATION

By heating oxygen containing salts such as chlorates, nitrates and permagnets

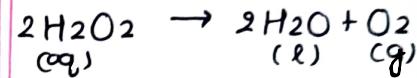


By thermal decomposition of the oxides of metals

↓ low in electrochemical series and higher oxides of some metals



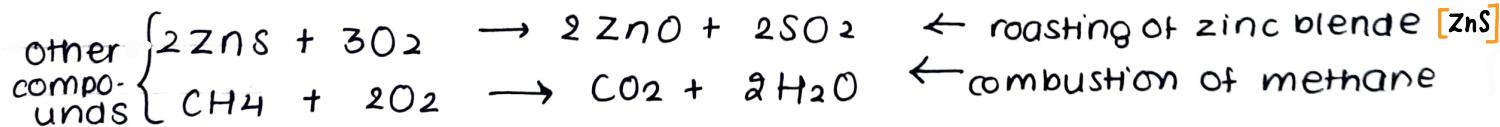
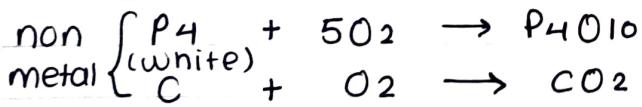
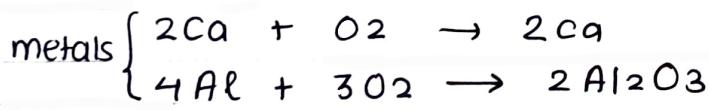
Hydrogen peroxide is readily decomposed into H₂O & O₂ by catalysts such as finely divided metals and manganese dioxide



- On large scale, dioxygen (O₂) is obtained from the electrolysis of water. H₂ is released at CATHODE and O₂ at ANODE.

PROPERTIES

- colourless, odourless gas
- Some of the reactions of O₂ with metals, non-metals and other compounds:



USES

in normal respiration and combustion processes.

used in oxy-acetylene welding, in the manufacture of many metals, particularly steel.

oxygen cylinders are widely used in hospitals, high altitude flying & mountaineering.

Q Dioxygen (O_2) is paramagnetic. Explain.

A Dioxygen (O_2) \rightarrow even no. of electrons

It is because of the presence of 2 unpaired e^- s in the ANTI BONDING π^* molecular orbital of O_2 .

Q Explain how oxygen acts as a vital support for aquatic and marine life?

A It is because dioxygen (O_2) is sufficiently soluble in water.

Q Which of the following doesn't react with O_2 directly

: Zn, Tl, Pt, Fe?

A Pt \rightarrow noble metal

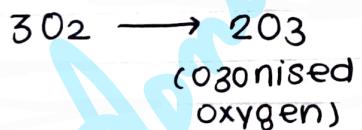
■ OZONE (O_3)

\rightarrow ozone is an allotropic form of oxygen.

\rightarrow The ozone layer protects the earth's surface from an excessive concentration of ultraviolet (UV) radiations.

• PREPARATION

When a slow dry stream of O_2 is passed through a SILENT ELECTRICAL DISCHARGE, conversion of O_2 to O_3 (10%) occurs.



$$\Delta H^\circ = +142 \text{ kJ mol}^{-1}$$

(endothermic rxn)

{ hence, it is necessary to use silent electric discharge to prevent its decomposition }

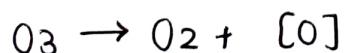
• PROPERTIES

PALE BLUE GAS ; DARK BLUE LIQUID, VIOLET-BLACK SOLID has a characteristic smell and is harmless in small concentration.

Q Explain how ozone acts as a powerful oxidising agent.

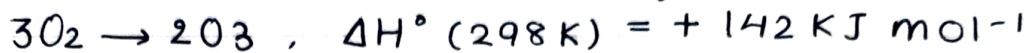
Ans It is because it readily decomposes to release nascent oxygen

CBSE 2011



\hookrightarrow nascent oxygen for oxidation

Q. Ozone is thermodynamically unstable w.r.t oxygen. Justify this statement with the help of following eqn:



Ans: $2\text{O}_3 \rightarrow 3\text{O}_2$, $\Delta H^\circ = -142 \text{ kJ mol}^{-1}$

CBSE 2019

ΔH of the rxn is negative, i.e. $\Delta H < 0$

Entropy of the rxn is increasing i.e. $\Delta S > 0$

We Know, Gibbs energy change $\Delta G = \Delta H - T\Delta S$

$$= (-ve) - T(+ve)$$

$$\Delta G = -ve$$

$$\Rightarrow \Delta G < 0$$

→ reaction is spontaneous i.e. it has a tendency to move in forward direction. Hence, ozone is thermodynamically unstable w.r.t oxygen.

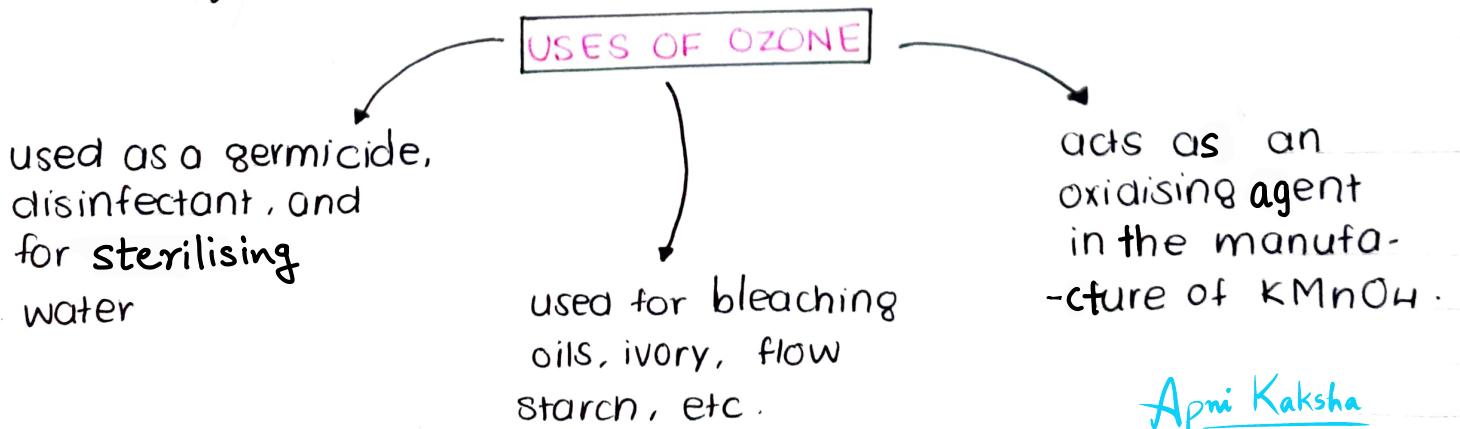
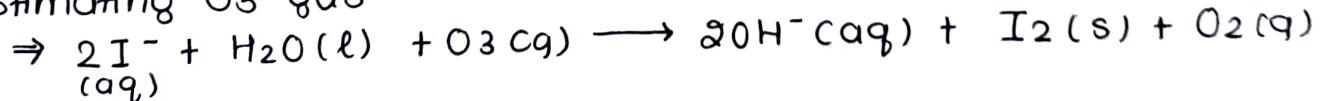
Q. Explain how supersonic jet planes are responsible for the depletion of ozone layer.

Ans. It is because the nitrogen oxides emitted from the exhaust systems of these planes, react very rapidly with ozone and hence deplete it.



Q. How is O₃ estimated quantitatively?

Ans: When Ozone reacts with an excess of potassium iodide (KI) solution buffered with a borate buffer (pH 9.2) iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O₃ gas.



SULPHUR ALLOTROPE FORMS :

1) RHOMBIC SULPHUR (α -sulphur) \leftarrow stable form at room temp. (S_8)

- Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2 .
- Yellow in colour.
- Insoluble in water but dissolves to some extent in benzene, alcohol and ether.
- It's readily soluble in CS_2 .

2) MONOCLINIC SULPHUR (β -sulphur) (S_8)

Preparation : This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing crust, colourless needle shaped crystals of β -sulphur are formed (which is soluble in CS_2).

■ TRANSITION TEMPERATURE :

- β -sulphur is stable above 369 K and transforms into α -sulphur below it.
- Conversely α -sulphur is stable below 369K and transforms into β -sulphur above this.
- At 369K, both the forms are stable. This temp is called transition temperature.

Q. Which form of sulphur shows paramagnetic behaviour?

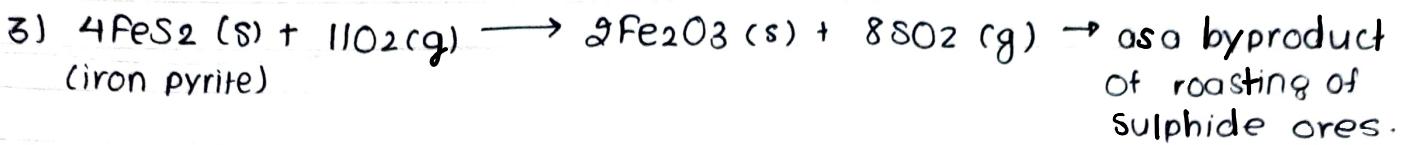
A. In vapour state, sulphur partly exists as S_8 molecule, which has two unpaired electrons in the antibonding π^* orbital like O_2 and hence, exhibit paramagnetism.

CBSE 2019
Delhi 2012

■ SULPHUR DIOXIDE [SO_2] :

■ PREPARATION :-

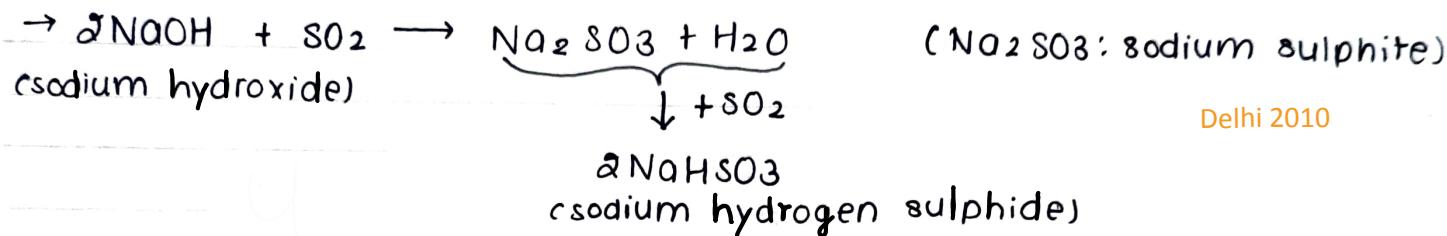
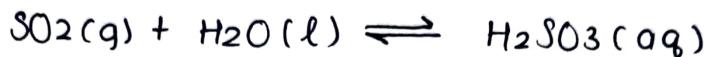
- 1) $S(l) + O_2(g) \rightarrow SO_2(g)$ (traces of sulphur trioxide are also formed)
(sulphur) (air)
- 2) $SO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g)$
(sulphite ion) (from dil. sulphuric acid)



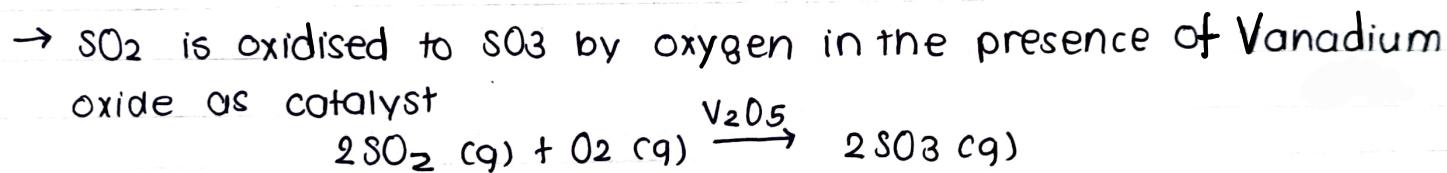
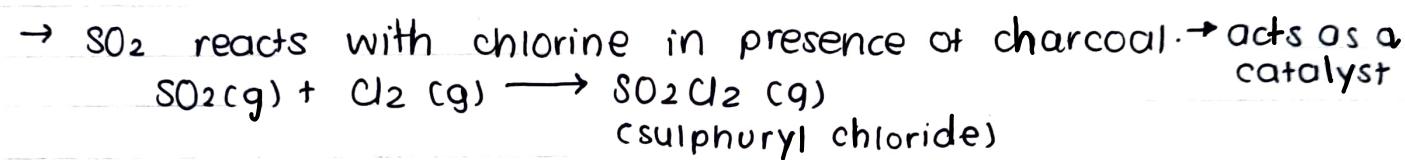
- PROPERTIES :-

→ It is a colourless gas, with pungent smell and is highly soluble in water.

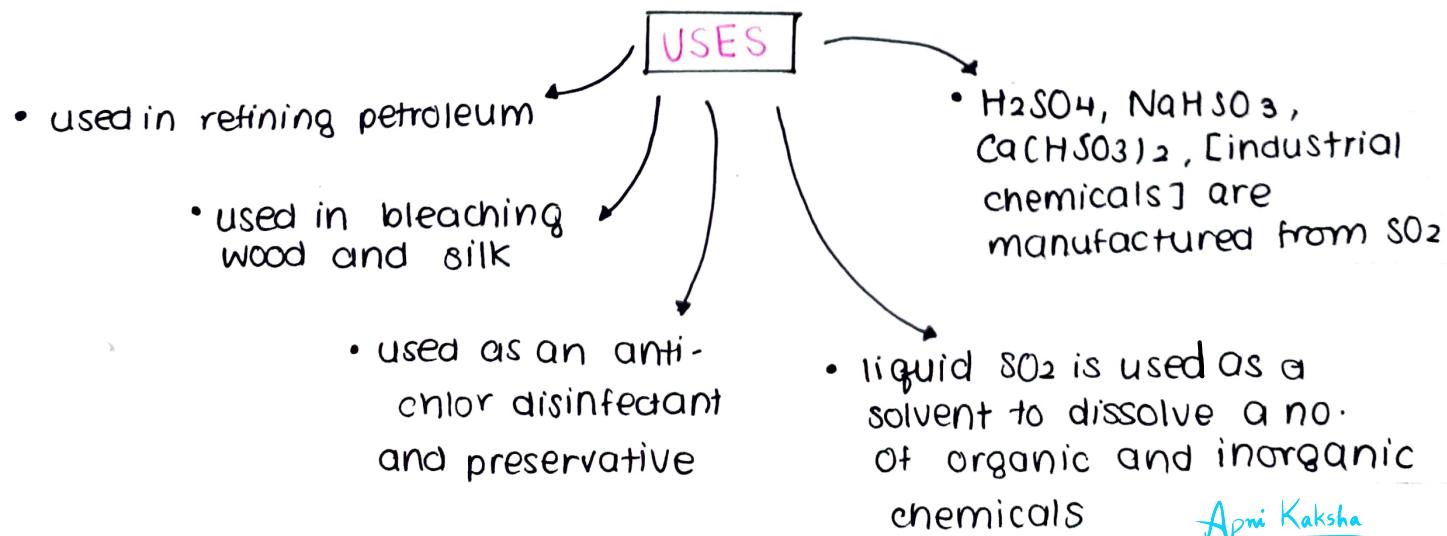
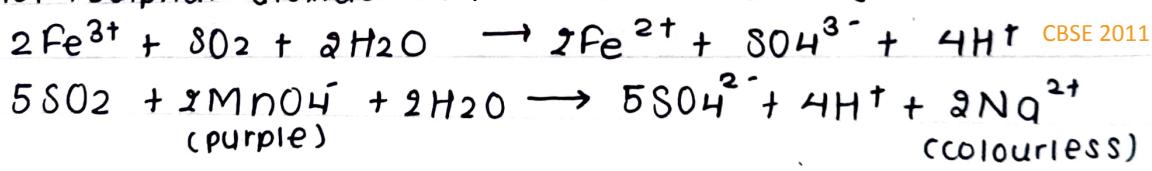
SO_2 when passed through H_2O , forms a solution of sulphurous acid.



Delhi 2010



NOTE When moist sulphur dioxide behaves as a reducing agent;



Try out:

- Q. What happens when SO_2 is passed through an aqueous soln of Fe (III) salt?
- Q. How is the presence of SO_2 detected?
- Q. Comment on the nature of the two S-O bonds formed in SO_2 molecule.

■ OXO-ACIDS OF SULPHUR

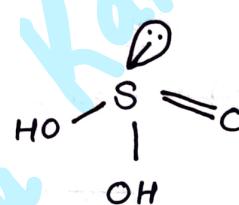
CBSE 2018

- Sulphuric acid : H_2SO_4



CBSE 2014

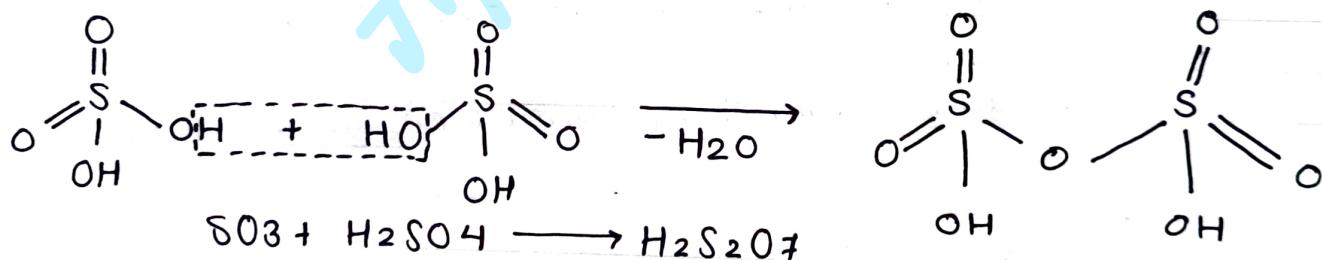
- Sulphurous acid : H_2SO_3



pyramidal structure

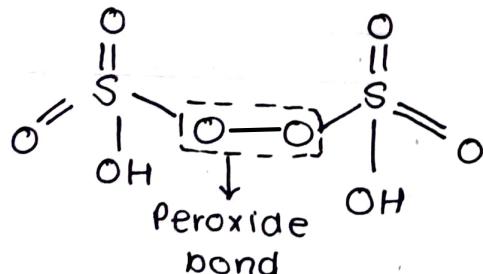
CBSE 2012
Delhi 2014

- Pyrosulphuric acid : $\text{H}_2\text{S}_2\text{O}_7$ (oleum)



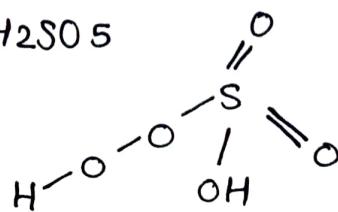
CBSE 2011
Delhi 2012

- Peroxodisulphuric acid : $\text{H}_2\text{S}_2\text{O}_8$



CBSE 2019,
Delhi 2013,2012

- Peroxomonosulphuric acid : $\text{H}_2\text{S}_2\text{O}_5$



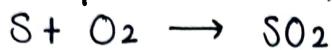
Apni Kaksha

SULPHURIC ACID : H_2SO_4

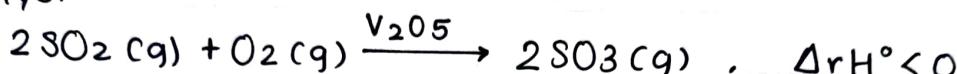
MANUFACTURE :

Sulphuric acid is manufactured by CONTACT PROCESS which involves 3 steps;

S.1 Burning of sulphur or sulphide ores to generate SO_2 .



S.2 SO_2 is catalytically oxidised to SO_3 in the presence of $V_2O_5(s)$ as catalyst.



- (The rxn is exothermic, reversible and the forward rxn leads to decrease in volume).
- (Therefore, low temp and high pressure are fav. cond'n for max yield)

S.3 SO_3 produced in the above step is absorbed in Sulphuric acid to give Oleum.



Oleum is then diluted with water to obtain sulphuric acid of desired concentration.

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

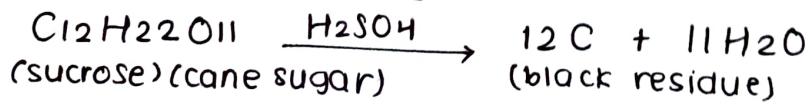
PROPERTIES

- is a colourless, dense, oily liquid
- dissolves in water with the evolution of a large quantity of heat.

→ The chemical reactions of H_2SO_4 are as a result of following characteristics:

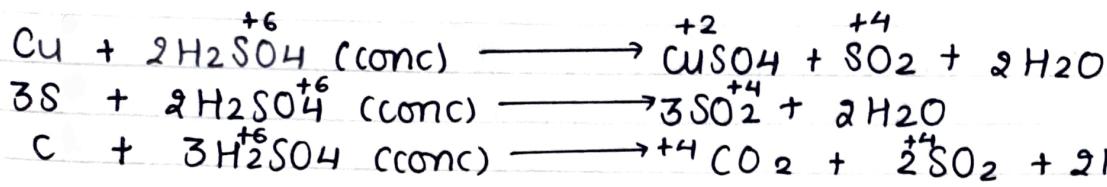
- low volatility
- strong acidic character
- strong affinity for water
- ability to act as an oxidising agent.

→ Conc. H_2SO_4 is a very strong dehydrating agent and thus, causes charring of sugars:



Apni Kaksha

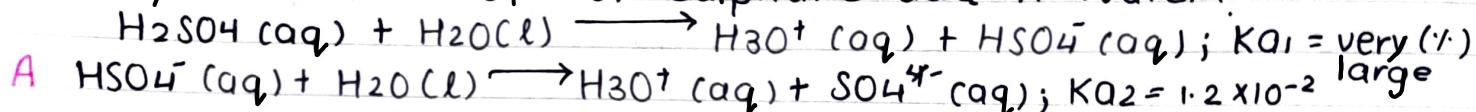
→ Hot conc. H_2SO_4 is a moderately strong oxidising agent.



CBSE 2014,
Delhi 2017

Delhi 2011

Q. Why is $K_{a2} \ll K_{a1}$ for sulphuric acid in water?



A $\text{HSO}_4^- \text{ (aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+ \text{ (aq)} + \text{SO}_4^{2-} \text{ (aq)}; K_{a2} = 1.2 \times 10^{-2}$ large
 $K_{a2} \ll K_{a1}$ because the tendency of bisulphate ion to loose one more H^+ ion is less.

→ The larger value of K_{a1} means that H_2SO_4 is largely dissociated into H^+ and HSO_4^-

→ Greater the value of dissociation constant, the stronger is the acid.

Q. What happens when

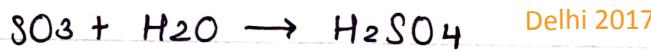
(i) conc. H_2SO_4 is added to calcium fluoride?

→ It forms hydrogen fluoride



(ii) SO_3 is passed through water?

→ It dissolves SO_3 to give H_2SO_4



USES OF H_2SO_4

→ is a very important industrial chemical
 → is used in manufacture of fertilisers.

→ used in manufacture of nitro-cellular products and as an laboratory reagent

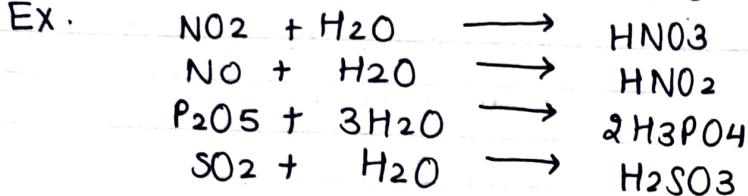
→ used in petroleum refining and manufacture of pigments, paints and dyestuff intermediates.

→ used in detergent industry, metallurgical applications, and in storage batteries.

SIMPLE OXIDES : A binary compound of oxygen with another element is called oxide.

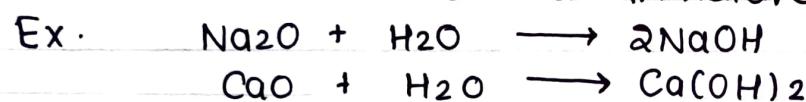
ACIDIC OXIDE

- An oxide that combines with water to give an acid
- Non-metallic oxides are acidic in nature.



BASIC OXIDE

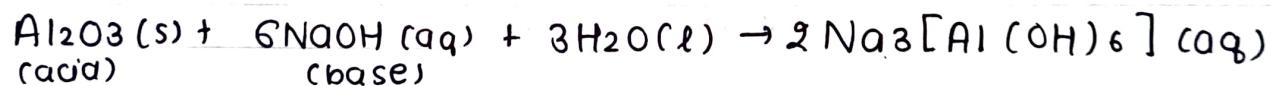
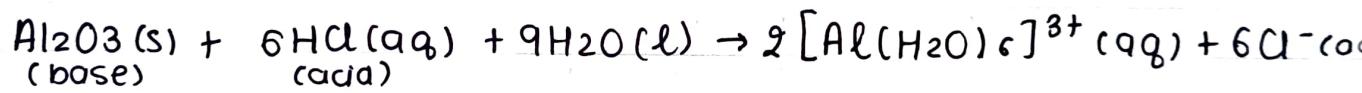
- The oxides which dissolve in water to give alkalies
- Metallic oxides are basic in nature.



AMPHOTERIC OXIDES

- The oxides which react with both acids and bases and show both acidic as well as basic characteristics

Ex:



NEUTRAL OXIDE

- Oxides which are neither acidic nor basic

Ex: CO, NO and N₂O

NOTE: Oxides of some metals in high oxidation state also have acidic character

Ex: Mn₂O₇, Cr₂O₃, V₂O₅

GROUP-17 ELEMENTS

| Atomic no | Element | Electronic Configuration |
|-----------|-----------------------------------|----------------------------------|
| 9 | fluorine (F) | [He] $2s^2 p^5$ |
| 17 | chlorine (Cl) | [Ne] $3s^2 3p^5$ |
| 35 | Bromine (Br) | [Ar] $3d^{10} 4s^2 4p^5$ |
| 53 | Iodine (I) | [Kr] $4d^{10} 5s^2 5p^5$ |
| 85 | Astatine (At) ↓ radioactive | [Xe] $4f^{14} 5d^{10} 6s^2 6p^5$ |

NOTE: Group 17 elements are collectively known as Halogens.
 {Halo means salt and Genes means born. i.e. salt producers}
The halogens are highly reactive non-metallic elements.

- Fluorine:
 - as insoluble fluorides ($\text{CaF}_2 \rightarrow$ fluorspar, $\text{Na}_3\text{AlF}_6 \rightarrow$ cryolite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2 \cdot$ fluor apatite)
 - small quantities are present in soils, river water, plants and bones & teeth of animals.
- Iodine:
 - Certain forms of marine life contain iodine in their systems; various seaweeds, for example, contain upto 0.5% of iodine & chile saltpetre contains upto 0.2% of sodium iodate (NaIO_3)

- Q** Sea is the greatest source of some halogens. Comment.
- A**
- Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium & calcium (mainly NaCl solution).
 - The deposits of dried up seas contain these compounds, e.g. NaCl and carnalite $\rightarrow \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (an ore of Mg)
 - Certain forms of marine life contain iodine in their systems

ELECTRONIC CONFIGURATION

- All these elements have seven electrons in their outermost shell ($ns^2 np^5$)
- ATOMIC AND IONIC RADII
- The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge.

→ Atomic and Ionic radii increase from fluorine to iodine due to increasing number of quantum shells.

• IONISATION ENTHALPY :

→ They have little tendency to lose electrons. Thus, they have very high ionisation energy.

→ Ionisation enthalpy decreases down the group.

↳ Why? due to increase in atomic size

• ELECTRON GAIN ENTHALPY :

→ Halogens have max -ve EGE in the corresponding periods.
↳ Why? These elements have smallest size in their respective periods and therefore max effective nuclear charge. As a result, they readily accept an electron to acquire noble gas configuration.



→ EGE becomes less negative down the group (as size ↑ses)

But...

EGE of fluorine (F) is less than that of chlorine (Cl).

because the incoming e⁻ face greater inter-electronic repulsions in the small sized 2p orbital of fluorine (F)

CBSE 2011

• ELECTRONEGATIVITY :

→ They have VERY HIGH electronegativity due to their small size.

→ Down the group, electronegativity ↓ses as size ↑ses.

∴ Fluorine is the most electronegative element in the periodic table

Apni Kaksha

• PHYSICAL PROPERTIES

1) Fluorine } gases Bromine → liquid Iodine → solid
Chlorine }

2) Their melting and boiling point increases down the group with atomic number. Because VDW forces ↑ses with ↑se in mass.
All halogens are coloured, F₂ → yellow, Cl₂ → greenish yellow
Br₂ → brown, I₂ → violet

CBSE 2012, 2010

- 3) This is due to absorptions of radiations in visible region which results in the excitation of outer electron to higher energy level. By absorbing different quanta of radiation, they display different colours
- 4) Bromine and Iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, CHCl_3 , CS_2 and hydrocarbons to give coloured solutions
- 5) Down the group, from Cl to I, the Bond dissociation Energy decreases in the order $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$, because the bond length increases with the increase in the size of the halogens
 But... Bond dissociation Energy of F-F bond is less than Cl-Cl bond. Why? because of high electron-electron repulsion among the lone pairs in F_2 molecule where they are much close to each other in case of Cl_2 . So the correct order of B.D.E is

$$\boxed{\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2}$$

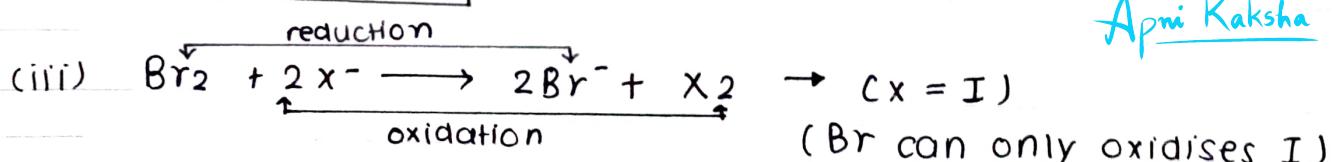
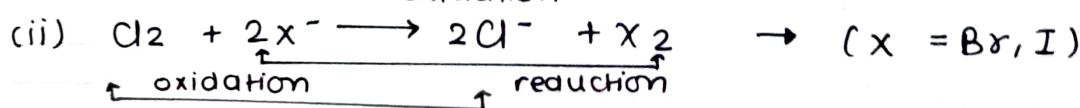
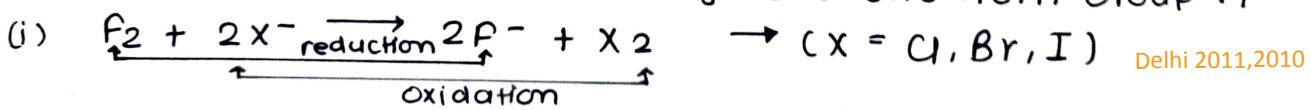
CHEMICAL PROPERTIES

- All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.
- The easy acceptance of an electron is the reason for the strong oxidising nature of halogens.

Delhi 2010

NOTE: F_2 is the strong oxidising halogen, and it oxidises other halide ions in solution or even in the solid phase.
 In general, a halogen oxidises halide ions of higher atomic number.

Ques: Identify X in the following reactions from Group 17.



∴ Order of oxidising power: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

Apni Kaksha

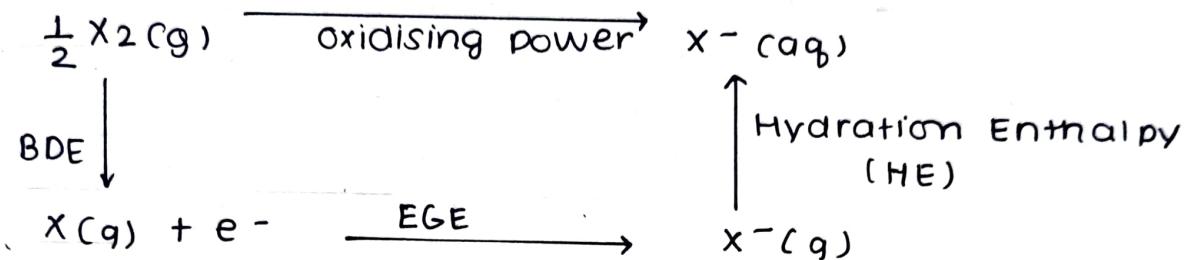
Que: Considering the parameters such as BDE, EGE, Hydration enthalpy. Compare the oxidising power of F_2 and Cl_2

CBSE 2019, 2012, 2014, 2011

Ans: In gas phase, EGE of F < EGE of Cl



- In aq. phase, oxidising power of $P_2 >$ oxidising power of Cl_2
oxidising power: redⁿ tendency to gain e^- .



| | F_2 | Cl_2 |
|----------------|-------|--------|
| BDE (reqd) | low | high |
| EGE (released) | low | high |
| HE (released) | high | low |

{energy reqd \rightarrow must be less} {due to greater charge density of F^- }

\rightarrow Thus, low BDE of F_2 and high HE of F^- more than compensate low EGE of F^- .

Therefore, oxidising power of $F_2 >$ oxidising power of Cl_2
(measured in aqueous phase even though EGE of F < EGE of Cl measured in gaseous phase)

Que: The max O.S for any element is exhibited in its oxides and fluorides. Why?

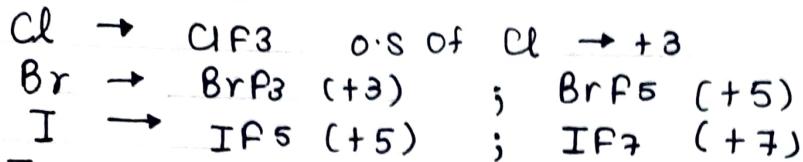
Ans: Because F and O are the most electronegative element of the periodic table and \therefore are able to bring about max. O.S of an element.

Que: F exhibits only -1 O.S while other element also exhibit +1, +3, +5 and +7 O.S. Why?

Apni Kaksha

Ans: F \rightarrow HF ; ClF_3 ; IF_7 {Being most electronegative element, fluorine cannot exhibit any +ve oxidation state}

| | | | |
|----------|------------------|----|----|
| O.S of F | \rightarrow -1 | -1 | -1 |
|----------|------------------|----|----|



CBSE 2012 ,Delhi 2013

- The F atom has no d-orbitals in its valence shell, and ∴ cannot expand its octet. Whereas other halogens, have vacant d-orbitals due to which they can expand their octets to show higher O.S of +3, +5, +7.

ANAMOLOUS BEHAVIOUR OF FLUORINE

Reasons: very small size, highest electronegativity, low F-F BDE and non-availability of d- orbitals in valence shell.

Examples :-

- a) It doesn't show higher O.S like +3, +5, +7.
- b) It forms only 1 oxo-acid while other halogens form a number of oxo-acids
- c) It is capable of forming H-bond due to which HF is a liquid while other halides are gases.

Ques Write the reactions of F_2 and Cl_2 with water.

Ans $2\text{F}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) \rightarrow 4\text{H}^+(\text{aq}) + 4\text{F}^-(\text{aq}) + \text{O}_2(\text{g})$
Fluorine, oxidises water to oxygen.

And.

$X_2(g) + H_2O(l) \rightarrow HX(aq) + HOX(aq)$ (where $X = Cl, Br$)
 Chlorine and Br react with H_2O to form corresponding hydrohalic and hydrohalous acids.

REACTIVITY OF HALOGENS TOWARDS HYDROGEN

All halogens react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to Iodine.

(i) Boiling point :-

$\rightarrow \text{HF} >> [\text{HCl} < \text{HBr} < \text{HI}]$
 (due to H-bonding) (B.p. \uparrow regularly due to \uparrow in
 CBSE 2012 VDW forces)

∴ The correct order is $\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$.

→ but remember the reactivity
of $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

(iii) Stability : $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

Down the group, bond length increases and bond strength decreases.

(iii) Acid Strength : $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

Because bond length \uparrow goes down the group which makes the release of H^+ easier.

REACTIVITY OF HALOGENS TOWARDS METALS

- Halogens react with metals to form metal halides like NaCl , MgBr_2 ,
- The ionic character of the halides decreases in the order $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$ ($\text{M} \rightarrow$ monovalent metal)
- According to Fajan's rule, larger the size of anion, the greater is its polarizability i.e. e⁻ density will be shifted towards cation. Hence, more covalent.
- If a metal exhibits more than one O.S., the halides in higher O.S. will be more covalent than the one in lower O.S.
According to Fajan's rule, greater the charge on cation, greater is the covalent character.

Ex. SnCl_4 is more covalent than SnCl_2 ; PbCl_4 than PbCl_2

REACTIVITY OF HALOGENS TOWARDS OXYGEN

i) Fluorine : forms two oxides OF_2 and O_2F_2

O_2F_2
only thermally
stable at 298 K

* Both are strong
fluorinating
agents.

- * These are essentially OXYGEN FLUORIDES because fluorine is more electronegative than oxygen.
- * O_2F_2 oxidizes plutonium to PuF_6 .

ii) Chlorine: Chlorine oxides Cl_2O , ClO_2 , Cl_2O_6 , and Cl_2O_7

Cl_2O_7
are highly reactive
oxidising agents

Cl_2O_7 tends to explode

NOTE : ClO_2 is used as an BLEACHING AGENT for paper pulp and textiles, and in water treatment.

(iii) Bromine : Bromine oxides : Br_2O , BrO_2 , BrO_3

↓
least stable halogen-oxides ↓
exists only at low temp ↗ are very powerful oxidising agent

(iv) Iodine : Iodine oxides : I_2O_4 , I_2O_5 , I_2O_7

↓
are insoluble solids ↗ decompose on heating

NOTE: $\text{I}_2\text{O}_5 \rightarrow$ very good oxidising agent
 → it is used in carbon monoxide's estimation

NOTE: The higher oxides of halogens tend to be more stable than the lower ones.

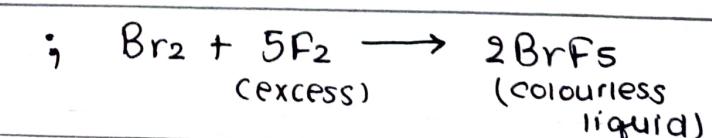
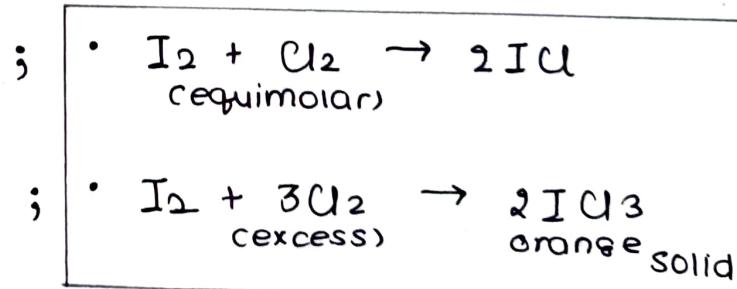
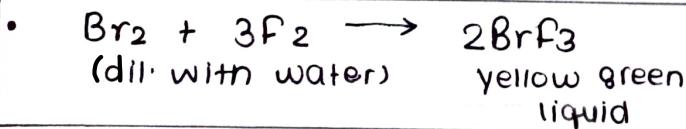
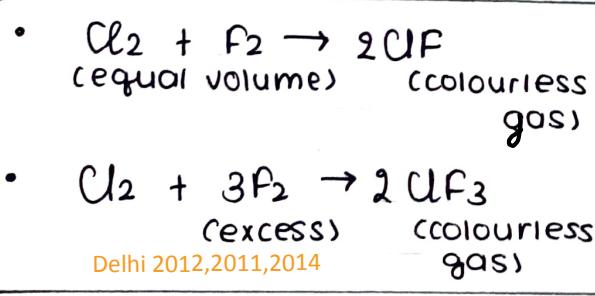
REACTIVITY OF HALOGENS TOWARDS OTHER HALOGENS

→ Halogens combine amongst themselves to form a number of compounds known as **interhalogens** of the type XX' , XX'_3 , XX'_5 , XX'_7
 where $\text{X} \rightarrow$ larger size halogen
 $\text{X}' \rightarrow$ smaller size halogen
 & X is more electropositive than X' .

INTERHALOGEN COMPOUND :-

PREPARATION:

They are formed by direct combination of halogens under appropriate conditions



PROPERTIES:-

Covalent molecules

are volatile solids / liquids at 298K except ClF which is a gas

diamagnetic in nature

IMP:

→ Interhalogen compounds are more reactive than halogens (except fluorine) (polar bond)

↳ Why? Because $X-X'$ bond in interhalogen is weaker than $X-X$ bond in halogens except F-F bond. CBSE 2012, 2011, 2010
(non-polar bond)

That's why they are stronger oxidising agents than halogens except F_2 .

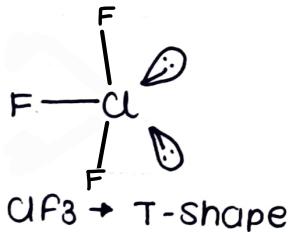
→ All these undergo hydrolysis:

Ex:

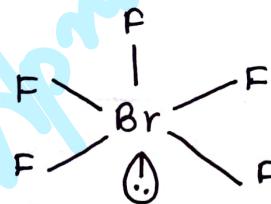


NOTE: Halide ion is derived from the smaller halogen

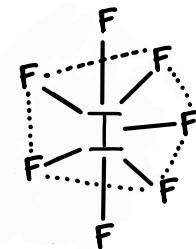
STRUCTURE:



Delhi 2012



$\text{BrF}_5 \rightarrow \text{square pyramidal}$

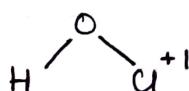


$\text{IF}_7 \rightarrow \text{pentagonal bipyramidal}$

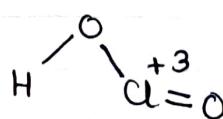
OXOACIDS OF HALOGENS

→ Due to high electronegativity and small size, fluorine (F) forms only 1 oxoacid, HOF Known as **fluoric (I) acid** or **hypoflurous acid**.

OXOACIDS OF CHLORINE

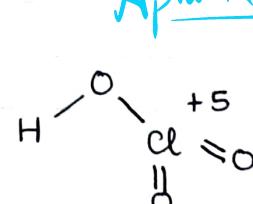


$\text{HOCl} \rightarrow \text{hypochlorous acid}$



$\text{HClO}_2 \rightarrow \text{chlorous acid}$

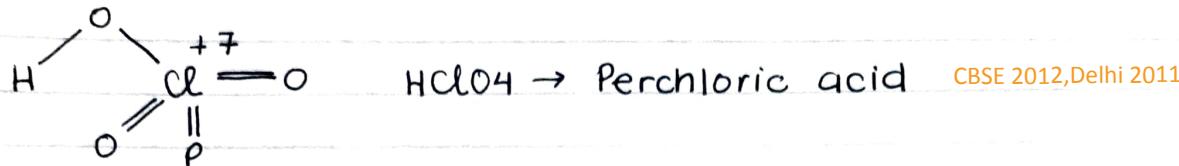
CBSE 2019, 2018



$\text{HClO}_3 \rightarrow \text{chloric acid}$

CBSE 2011, 2013

Apni Kaksha



Q Arrange the following acids in order of their acid strength:

- (i) HCl, HClO, HClO₃, HClO₄

Ans HCl < HClO < HClO₃ < HClO₄

Stability of conjugate base: $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \boxed{\text{ClO}_4^-}$

-ve charge
is dispersed
by 4 oxygen
atom

* STABLE THE CONJUGATE BASE, STRONGER IS THE ACID.

- (ii) HOF, HOCl, HOBr, HOI

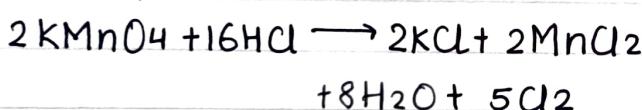
Ans HOF > HOCl > HOBr > HOI

It can be explained on the basis of the fact that F is the most e-ve halogen & ∴ will polarise the -O-H bond to the max, making HOF the strongest acid.

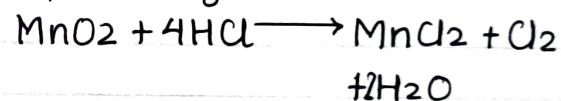
■ CHLORINE

(named on the basis of its color (chloros - greenish yellow))

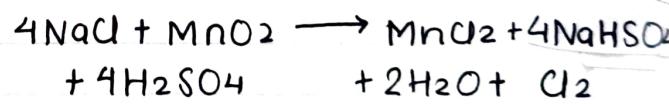
⇒ By action of HCl on



⇒ By heating MnO₂ with conc. HCl



However, a mixture of NaCl and conc. H₂SO₄ is used in place of HCl

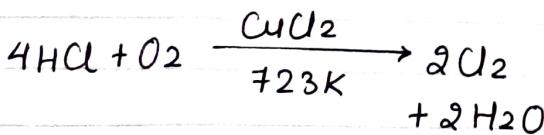


(B)

MANUFACTURE OF CHLORINE

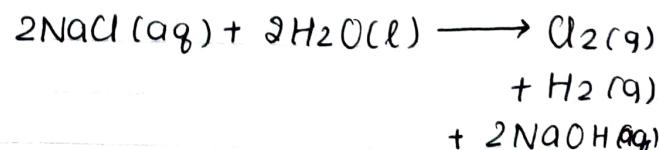
Deacon's Process

By oxidation of HCl gas by atmospheric oxygen in the presence of CuCl₂ (catalyst) at 723 K



Electrolytic Process

Chlorine is obtained by the electrolysis of brine solution. Cl₂ is liberated at anode



(c)

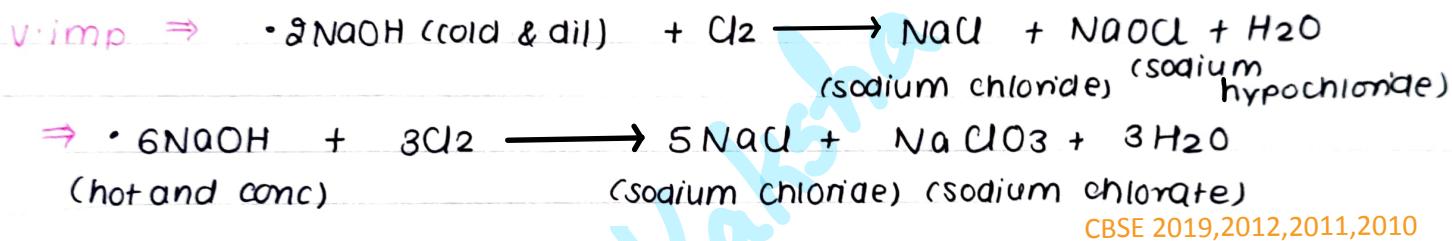
PROPERTIES

greenish yellow gas
with pungent and suffocating odour

about 2-5 times
heavier than
air.

can be liquified easily into
greenish yellow liquid which
boils at 239K
soluble in
water.

→ With excess ammonia, chlorine gives nitrogen and ammonium chloride, whereas with excess chloride, nitrogen trichloride (explosive) is formed.



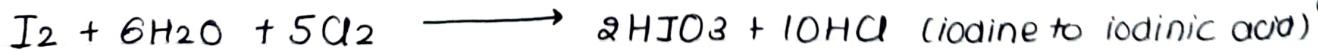
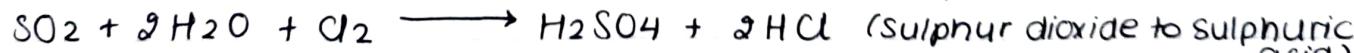
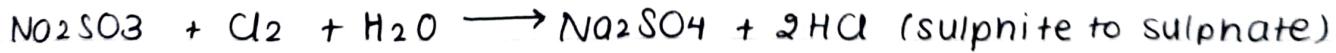
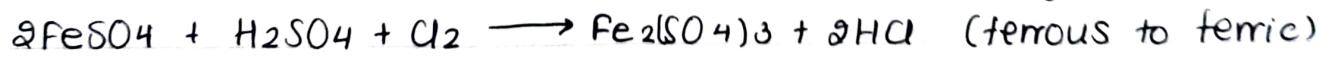
* With dry slaked lime, it gives Bleaching Powder.



* Chlorine water on standing loses its YELLOW COLOUR due to CBSE 2012
formation of HCl and HOCl.

→ HOCl formed gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

(i) Oxidation-reactions (chlorine [Cl₂] as an oxidising agent)



(ii) Chlorine is a powerful bleaching agent.



(coloured substance + O → colourless substance)

It bleaches vegetables or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.

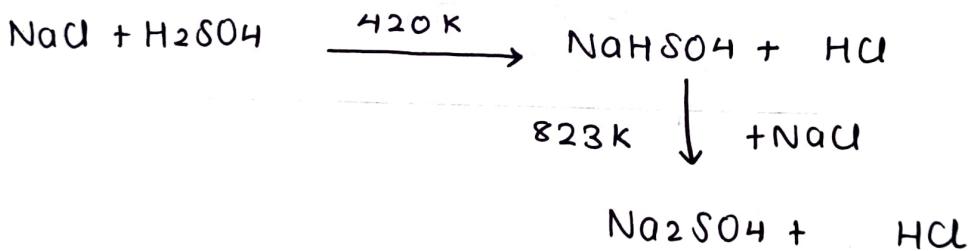
USES OF CHLORINE

- for bleaching woodpulp, textiles and cotton.
 - in the extraction of gold and platinum
 - in sterilising drinking water
 - in the manufacture of dyes, drugs and organic compds. such as CCl_4 , CHCl_3 , DDT.
 - in preparation of poisonous gases such as phosgene: COCl_2 , tear gas: Cl_3NO , mustard gas: $\text{ClCH}_2\text{CH}_2\text{S}\text{ClCH}_2\text{CH}_2\text{S}$
- CBSE 2013

HYDROGEN CHLORIDE

(A) PREPARATION

In laboratory, it is prepared by heating NaCl with conc. H_2SO_4



(B)

PROPERTIES

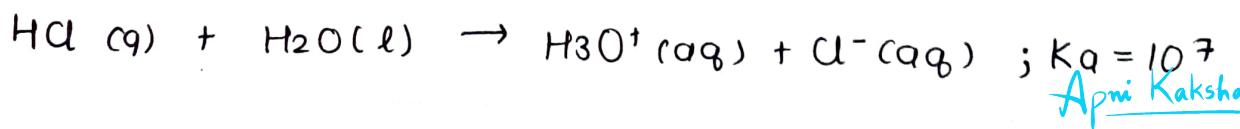
Colourless and pungent smelling gas

easily liquified to a colourless liquid

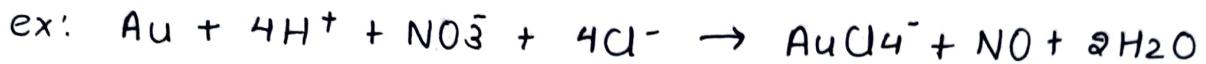
extremely soluble in water.

freezes to a white crystalline solid

→ It's aqueous solution is called hydrochloric acid. It ionises as:



- High value of dissociation constant (K_a) indicates that it is a strong acid in water.
- $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$ (white fumes)
- Aqua-regia (conc. HCl : conc. HNO_3) → for dissolving noble metals
3 : 1



(C)

USES OF HYDROGEN CHLORIDE

in the manufacture
of chlorine, NH_4Cl
and glucose

in medicine and
a laboratory
reagent.

for extracting glue
from bones and
purifying bone
black

GROUP-18 ELEMENTS

| Atomic no. | Element | Electronic Configuration |
|------------|---------------------------|----------------------------------|
| 2 | Helium (He) | $1s^2$ |
| 10 | Neon (Ne) | $[He] 2s^2 2p^6$ |
| 18 | Argon (Ar) | $[Ne] 3s^2 2p^6$ |
| 36 | Krypton (Kr) | $[Ar] 3d^10 4s^2 4p^6$ |
| 54 | Xenon (Xe) | $[Kr] 4d^{10} 5s^2 5p^6$ |
| 86 | Radon (Rn) Radioactive | $[Xe] 4f^{10} 5d^{10} 6s^2 6p^6$ |

OCCURENCE

- All noble gases except RADON occur in the atmosphere.
- Helium (He) and sometimes Neon (Ne) are formed in minerals of RADIOACTIVE ORIGIN e.g. pitchblende, monazite, clevite.
- The main commercial source of Helium (He) in natural gas.

NOTE:

The elements in Group 18 have their valence shell orbitals completely filled and therefore, react with only some elements under certain conditions. They are almost unreactive i.e. they have extremely high IE and large +ve value of EGE. Therefore, they are known as noble gases.

ELECTRONIC CONFIGURATION :

All noble gases have general electronic configuration $ns^2 np^6$ except HELIUM which has $1s^2$.

IONISATION ENTHALPY :

Due to stable electronic configuration, these gases exhibit very high Ionisation Enthalpy:

It decreases down the group, as increase in atomic size.

ATOMIC RADII:

Atomic Radii increases down the group, with increase in atomic number

ELECTRON GAIN ENTHALPY

Since, noble gases have stable electronic configuration, they have no tendency to accept the electron and therefore, have large +ve values of EGE.

PHYSICAL PROPERTIES

- All noble gases are MONOATOMIC, COLOURLESS, ODOURLESS and TASTELESS
- They are sparingly soluble in water.
- They have LOW MELTING AND BOILING POINTS
 - ↳ Why? because of weak dispersion forces between the atoms or weak vander-waal forces.

CBSE 2011

* Points To Remember:

- Helium has the lowest Boiling Point.

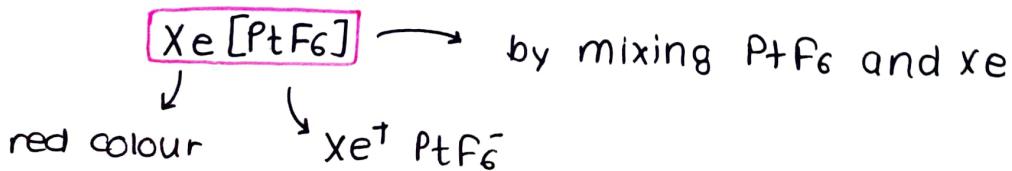
So,
→ Boiling point increases down the group with increase in VDW forces
↓
increase with increase in mass

Q. Explain how Neil Bartlett synthesized the first noble gas compound?

Delhi 2013

Ans: N. Bartlett based his synthesis on the existence of compound $O_2^{+}[PtF_6]$ in which oxygen exists as O_2^+ . (red colour)

He, then realised that energy required to convert Xe to Xe^+ was of the same order as required to convert O_2 to O_2^+ . So the first noble gas compound synthesized was $Xe^{+}[PtF_6]$



CHEMICAL PROPERTIES

- noble gases are least reactive or chemically inert
- completely filled electronic configuration in their valence shell.
- large +ve values of EGE
- high ionisation enthalpy

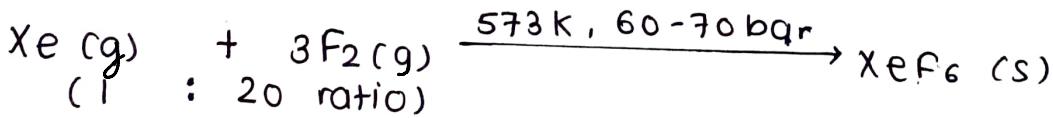
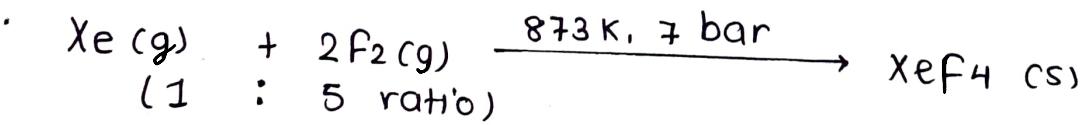
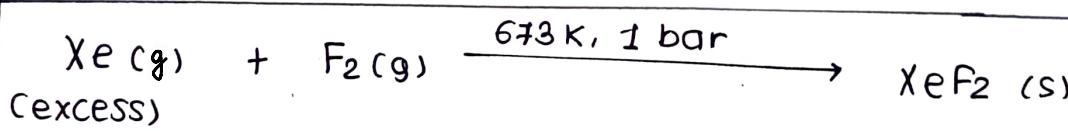
- Q. Noble gases are known to form compounds only with oxygen and fluorine. Why?
- A. Because oxygen and fluorine are the most electronegative elements of the periodic table and are able to bring about the oxidation of noble gases.
- Q. Amongst noble gases, only Kr and Xe are known to form compounds. Why?
- A. Because in grp 18, they've comparatively lesser IE as they lie at the end of the group.

CBSE 2019

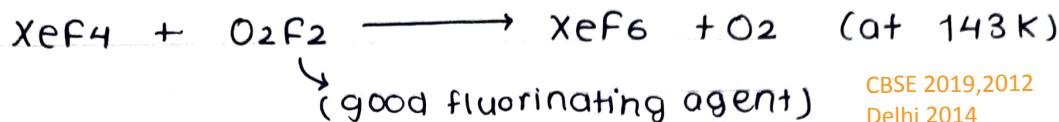
NOTE: For Krypton: \rightarrow only difluoride (KrF_2) has been studied in detail.

(A) PREPARATION :

Xenon forms three binary fluorides, XeF_2 , XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions:

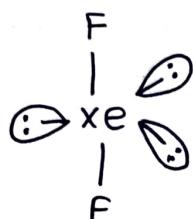


NOTE: XeF_6 can also be prepared by:



CBSE 2019, 2012
Delhi 2014

(B) STRUCTURES



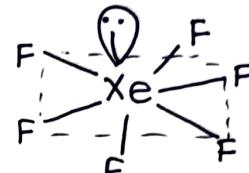
$\text{XeF}_2 \rightarrow$ linear

CBSE 2010, 2013
Delhi 2010, 2011, 2012, 2013
2014, 2015, 2017



$\text{XeF}_4 \rightarrow$ square planar

CBSE 2015, 2018, 2019
Delhi 2014, 2015, 2017



$\text{XeF}_6 \rightarrow$ distorted octahedral

CBSE 2013
Delhi 2012, 2017

(C) PROPERTIES

$\text{XeF}_2 ; \text{XeF}_4$
 XeF_6

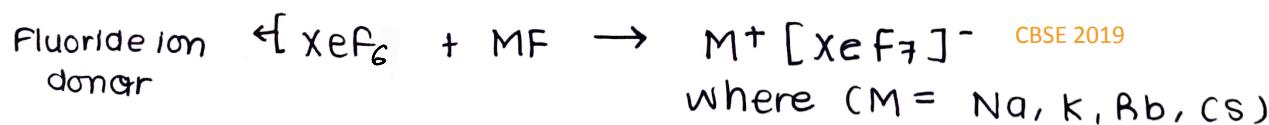
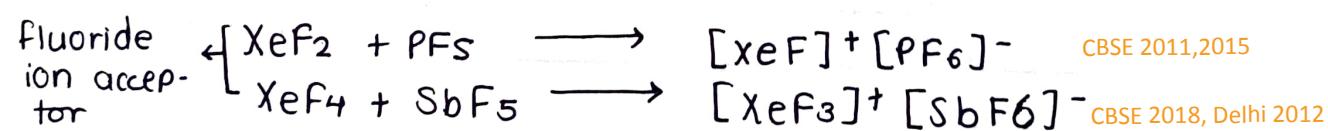
are colorless, crystalline solids

sublime readily
at 298 K

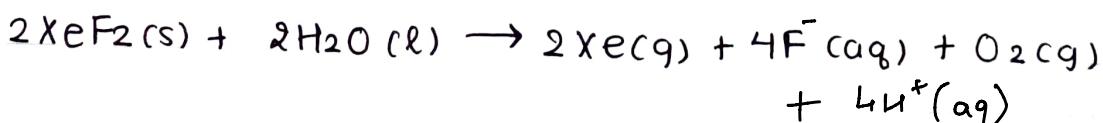
are powerful fluorinating agents

are readily hydrolysed even by traces of water

NOTE 1) Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions



2) Hydrolysis of XeF_2 give the following products:



CBSE 2019

XENON-OXYGEN COMPOUNDS

a) PREPARATION

Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3 .



CBSE 2011, 2014

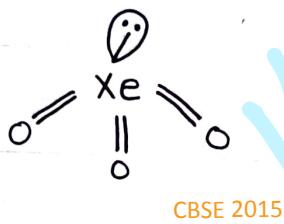
Delhi 2011



CBSE 2010, Delhi

2010, 2012, 2017

b) STRUCTURE



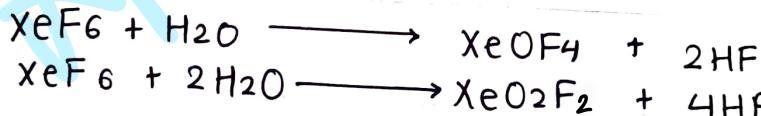
$\text{XeO}_3 \rightarrow$ pyramidal

(colorless, explosive solid)

→ (C) PROPERTY

a) PREPARATION

Partial hydrolysis of XeF_6 gives oxyfluorides, XeOF_4 and XeO_2F_2



Delhi 2010, 2017

b) STRUCTURE



$\text{XeOF}_4 \rightarrow$ square pyramidal

colourless, volatile

liquid

→ (C) PROPERTY

Q. Does the hydrolysis of XeF_6 lead to a redox reaction?

A. No, the products of hydrolysis are XeOF_4 and XeO_2F_2 where the oxidation states are the same. Thus, no redox reaction.

USES OF NOBLE GASES

• Helium:

- It is a non-inflammable and light gas. Hence, it is used to in filling balloons for meteorological observations.
It is also used in gas-cooled nuclear reactors.

Q. Why is helium used in diving apparatus?

Ans: Helium is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Delhi 2013

• Neon:

- It is used in discharge tubes and fluorescent bulbs for adv. display purposes.
Used in botanical garden and in green houses.

• Argon:

- Used mainly to provide inert atmosphere in high temp. metallurgical processes.
Used for filling electric bulb
Used in laboratory for handling substances that are air-sensitive.

• Xenon & Krypton:

- Used in light bulbs designed for special purposes.

Extra Questions:

Q. Account for following: HF is not stored in glass bottles but is kept in wax coated bottles?

Ans. HF forms fluorosilicate ion on reaction with glass. Hence, it is stored in wax coated in bottles.

CBSE 2013

Q. Why does fluorine not play the role of a central atom in interhalogen compound?

Ans. Fluorine does not have d - orbitals and can not show higher oxidation state.

Therefore, it does not play the role of a central atom in the interhalogen compounds.

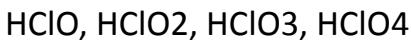
CBSE 2011

Q. F₂ is the most reactive of all the four common halogens. explain

Ans. It is due to low bond dissociation energy and high hydration energy and high electron affinity.

Delhi 2011

Q. Arrange the following in increasing order of oxidising power:



Ans. HClO > HClO₂ > HClO₃ > HClO₄

Delhi 2010

Q. Complete the following reaction:



Ans. PbS + 4 O₃ → PbSO₄ + 4 O₂

CBSE 2019

Q. Sulphur has greater tendency for catenation than Oxygen?

Ans. As, S-S bond energy is more than O-O bond energy and due to smaller size of O the lp-bp repulsion is high resulting in lower tendency for catenation.

CBSE 2012, 2009

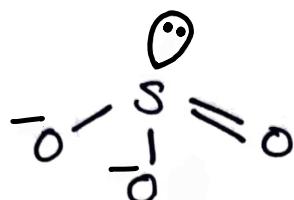
Delhi 2012, 2011

Q. Predict the shape and the asked angle (90 or more or less) in the following case:



Ans. the shape is pyramidal and the O-S-O angle is more than 90

Delhi 2012



Q. All the bonds in SF₄ are not equivalent. Explain, why?

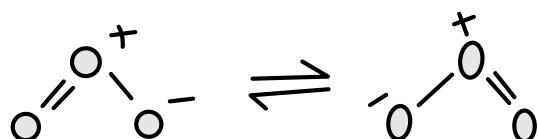
CBSE 2012

Ans. As sulphur is sp³d hybridised. It has trigonal pyramidal structure in which one of the equatorial position is occupied by an lone pair of electrons. That's why, all bonds are not identical.

Q. Draw the structure of O₃

Delhi 2010

Ans.



Q. OF₆ compound is not known. Why?

Delhi 2010

Ans. Due to the absence of d orbital in O, it limits its covalency to 4, thus OF₆ is not formed.

Q. SF₆ is less reactive than SF₄. Why ?

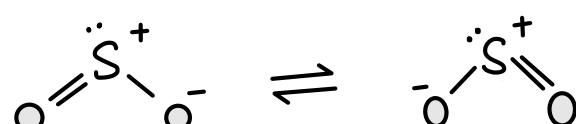
Delhi 2010

Ans. SF₆ is sterically hindered so, it is less reactive than SF₄.

Q. Why are the two S-O bonds in SO₂ molecule of equal strength?

CBSE 2010

Ans. Due to the resonance in , the two bonds equally share the double bond character and thus are identical.



Delhi 2013

Q. SO₂ is an air pollutant. Account for this statement:

Ans. As it is water soluble, when mixed with rain it causes acid rain and problems such as irritation in eyes.

Raman Shattarwal