

P BLOCK ELEMENTS

- ↳ The elements in which the last electron enters the p-subshell of their outermost energy level are called p-block elements.
- ↳ Since, a p-subshell has three degenerate p-orbitals, each of which can accommodate two electrons. Therefore,
- ↳ The elements belonging to groups 13 to 18 constitute p-block elements.
- ↳ The atoms of these elements, ns-orbital is completely filled and hence the general electronic configuration for the atoms of this block is $ns^2 np^{1-6}$ (where, n = number of outermost shell). Whereas the inner core electronic configuration may differ.

<u>Group</u>	<u>Elements</u>	<u>General electronic Configuration</u>
13 (III A)	B to Nh	$ns^2 np^1$
14 (IV A)	C to Fl	$ns^2 np^2$
15 (V A)	N to Mc	$ns^2 np^3$
16 (VI A)	O to Lv	$ns^2 np^4$
17 (VII A)	F to Ts	$ns^2 np^5$
18 (VIII A)	Ne to Og	$ns^2 np^6$

↳ Group 13 (III A) is called Boron family, Group 14 (IV A) is called Carbon family, Group 15 (V A) is called Nitrogen family, Group 16 (VI A) is called Oxygen family or chalcogens and Group 17 (VII A) is called Halogen family and Group 18 (VIII A) is called Noble gases.

↳ The properties of p-block elements are determined by the number of electrons present in np-orbitals.

General characteristics of p-block elements

Atomic and ionic size

↳ As we move from left to right in any period, the effective nuclear charge increases. As a result, atomic and ionic radii of the elements of p-block decrease from group (III A) to group (VIII A) in any period.

↳ Similarly, in a group, if we move from top to bottom, the last electron is filled in next shell, i.e., there is extra addition of new shells. So atomic and ionic radii of elements of p-block increase from top

to bottom in any group.

↳ The covalent radius of Al and Ga is same.

This is because, the d-electrons are absent in Al and present in Ga. d-electrons have less effective shielding effect, [i.e., $s > p > d > f$].

So, size of Ga is contracted due to the increased nuclear charge pulls the electron cloud inward.

This contraction is called d-block contraction or transition contraction.

↳ The small difference between covalent radius of In and Tl is due to Lanthanide contraction.

↳ Ionization enthalpy —

↳ The values of first ionization enthalpies of p-block elements generally increase on moving from left to right in any period due to the increase of effective nuclear charge and decrease of atomic size. Therefore, the valence electrons are more and more tightly held by the nucleus and the energy required to remove an electron keeps on increasing.

↳ Some examples of variation of ionization enthalpy in a period are —

The increase of ionization enthalpies in a

period is not uniform. There are certain elements which show irregular trends.

For example —

i) Ionization enthalpy of group IIIA is less than group IIA.

Explanation — Group IIA elements have more stable configuration (ns^2) than group IIIA elements (ns^2np^1); and p-electrons are better shielded by the intervening electrons. In case of group IIIA elements, the electron is to be removed from a p-orbital, and it is less penetrating than s-orbital from which the electron is to be removed in case of group IIA elements. As a result, the p-electrons of group IIIA elements are not firmly held by the nucleus & and lesser amount of energy is required to remove an electron.

ii) Ionization enthalpy of group VIA is less than group VA.

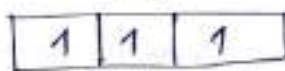
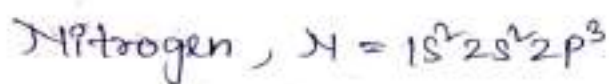
Explanation — The group VA elements have more stable electronic configuration (ns^2np^3) than the electronic configuration of group VIA elements (ns^2np^4). Also, effective

nuclear charge in case of group VA elements than the nuclear charge of group VIA elements.

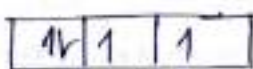
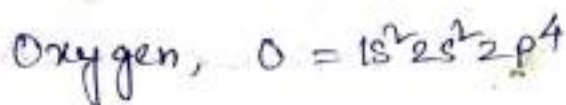
Due to the combined effect of these two factors, the valence electrons in group VA elements are firmly held and hence more energy is required to remove an electron.

Example — Ionization enthalpy of nitrogen is greater than that of oxygen.

Electronic configuration of —

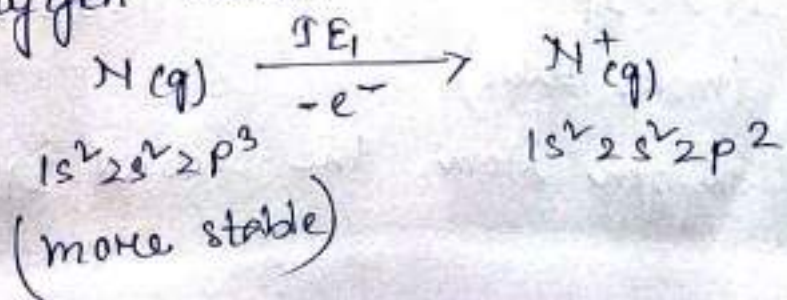


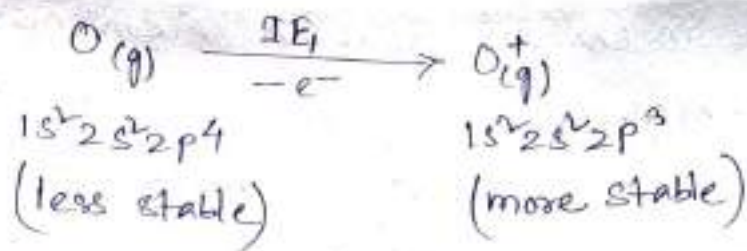
} half filled
} more stable



} partially filled
} less stable

Half-filled ^{and} ~~one~~ fully filled (i.e., symmetric) orbitals are more stable than partially filled orbitals. In case of nitrogen, the valence electrons are strongly held due to its stable configuration and require more energy to remove an electron than the less-stable partially-filled p-orbitals of oxygen atom.

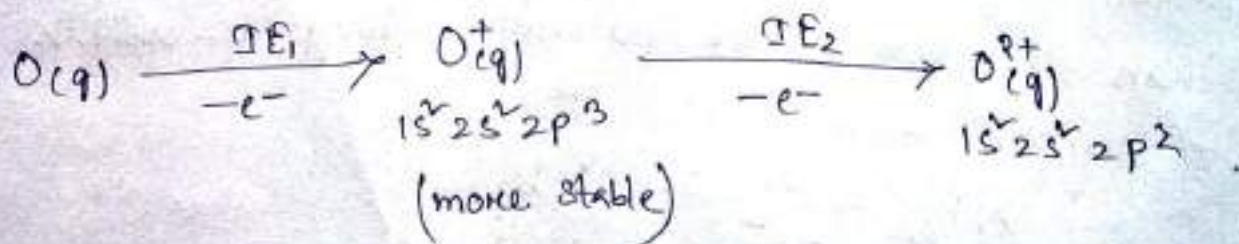
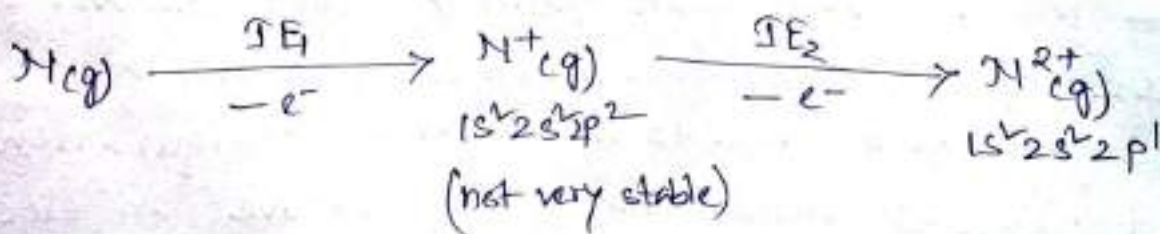
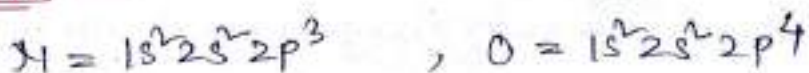




↳ The values of ionization enthalpy of p-block elements goes on decreasing as we move down a group. This is because, as we go down a group, the electrons are added in the new shells. The force of attraction between nucleus and outermost electron goes on decreasing. As a result, the ionization enthalpy goes on decreasing.

↳ The First ionization enthalpy of Nitrogen is more than oxygen but second ionization enthalpy of nitrogen is less than oxygen.

Explanation —



In case of oxygen atom, the second electron

is to be removed from monovalent ion (O^+) with stable configuration ($1s^2 2s^2 2p^3$) and this requires more energy in case of oxygen than it is to be removed required in case of N^+ ion with comparatively less stable electronic configuration ($1s^2 2s^2 2p^2$). Since, all atoms or ions have the tendency to acquire stable configuration. Therefore, the elements or ions already having the stable configuration do not want to lose electrons. Hence, second ionization enthalpy (IE_2) of oxygen with stable configuration have high values than nitrogen.

⇒ The successive ionization enthalpy values of p-block elements goes on increasing.

Explanation — This is mainly due to the fact that after removal of first electron, the atom changes into a monovalent positive ion. In the ion, the number of electron decreases but the nuclear charge remains the same. This leads to the greater attractive force between the nucleus and the remaining electrons. Hence, it becomes difficult to remove the second electron or second ionization enthalpy (IE_2) is greater than the first ionization enthalpy (IE_1).
Due to the similar reasons, the third

ionization enthalpy (IE_3) is greater than the second ionization enthalpy (IE_2) and so on.

$$IE_1 < IE_2 < IE_3 < \dots \text{ etc.}$$

3) Electronegativity —

↳ The electronegativities of p-block elements increase from left to right in the period of the periodic table due to the progressive decrease in the atomic size with the increase in the nuclear charge.

↳ Electronegativities of p-block elements decrease down a group due to the increase in atomic size and screening effect.

↳ There is some irregularities in group which is due to Lanthanide contraction. Example — electronegativity of Al is less than Ga.

4) Electropositive or metallic character —

↳ Electropositive character of an element depends on the magnitude of its ionization energy. i.e., —

$$\text{Electropositive character/metallic character} \propto \frac{1}{\text{ionization enthalpy}}$$

↳ Since the ionization enthalpy of p-block elements increases on moving from left to right in a

Period, the metallic character of the element decreases.

↳ Since the ionization enthalpy of p-block elements decreases on descending a group, the metallic character of these elements increases in same direction.

↳

- i) Electronegativity increases
- ii) Ionization enthalpy increases

	B	C	N	O	F	Ne	
	Al	Si	P	S	Cl	Ar	
	Ga	Ge	As	Se	Br	Kr	
	In	Sn	Sb	Te	I	Xe	
	Tl	Pb	Bi	Po	At	Rn	

i) Covalent radius increases
 ii) Metallic character increases
 iii) Ionic radii increases

i) electronegativity increases
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i) Covalent radius increases
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4) Metallic and non metallic character —

↳ The p-block elements contains metallic and non-metallic elements. It is interesting to note that the non-metals and metalloids exist only in the p-block of the periodic table.

↳ The non-metallic character increases along a period but decreases down a group.

↳ In between metallic and non-metallic elements, there are some elements which show characteristics of both metals and non-metals and are called metalloids. The common metalloids of p-block elements are B, Al, Si, Ge, As, Sb, Te, Po, At etc.

↳ In general, non-metals have higher ionization enthalpies and higher electronegativities than metals and therefore in contrast to metals they readily form anions.

5) Oxidation states —

↳ The oxidation states of p-block elements are closely related to the number of electrons in the valence shell of their atoms. The highest oxidation state of these elements is numerically equal to the group number minus 10. For example — the elements of group 13 show highest oxidation state of 3 ($=13-10$), while those of group 14 show highest oxidation state of 4 ($=14-10$) and so on.

↳ The lighter elements of p-block (elements of second and third) show variable oxidation states, both positive and negative.

Group	13	14	15	16	17
2 nd period	B	C	N	O	F
Oxidation States	+3	+4	+5	-	-
	-	-4	-3	-2	+1
3 rd period	Al	Si	P	S	Cl
Oxidation States	+3	+4	+5	+6	+7
	-	-4	-3	-2	-1

↳ On descending the group, a lower oxidation state which is two less than the highest oxidation state becomes more stable in groups 13 to 16. This trend is due to inert pair effect. For example, - the highest oxidation state for the elements of group 13 is +3. However, in addition to +3 oxidation state, these elements also show +1 oxidation state which becomes more stable on moving down the group.

↳ Higher oxidation state is obtained when all the ns and np electrons are lost. While

Lower oxidation state is obtained when only np electrons are lost and ns electrons are not lost due to extra stability. Such a pair of ns electrons is called inert pair electrons and the effect is caused by it is known as inert pair effect.

↳ The common oxidation states of p -block elements —

Group	13	14	15	16	17	18
Group oxidation state	+3	+4	+5	+6	+7	+8
Various oxidation states	B +3	C +4, -4	N +5 to -3	O -1, -2	F -1	
	Al +3	Si +4	P, As +3, -3, +5	S, Se, Te +4, +6, -2, +2	Cl, Br, I -1, +1, +3, +5, +7	Kr +2, +4
	Ga, In, Tl +3, +1	Ge, Sn, Pb +4, +2	Sb, Bi +3, +5	Po +2, +6		Xe +2, +4, +6, +8

Inert Pair effect —

↳ The reluctance of the valence s -electrons or ns^2 electrons of heavier elements of p -block

to take part in bond formation called inert pair effect.

↳ In general, the variable electropositivity in these elements is due to the presence of ns^2 inert pair electrons. The inertness is found only —

↳ When the ns^2 electrons are in 4th or higher principal quantum number and

↳ When their loss does not give a species with a noble gas configuration.

↳ Inert pair effect is the name given to tendency of electrons present in the outermost s-orbital of post-transition metals like Pb, Bi etc. to not undergo ionization and to remain unshared.

↳ A possible explanation of inert pair effect is that because of ineffective shielding of these valence s-electrons by inner orbital electrons like inner f or d-orbitals. Also, since the orbital is s-orbital, it is highly penetrating and these valence s-electrons are more exposed to the nucleus than p-electrons and hence held much tightly, so the electrons fail to participate in any bonding activity. Therefore, they are given the name inert pair and hence the effect is called inert pair.

↳ As a result of inert pair effect, the stability of lower oxidation state increases and the stability of higher oxidation state decreases on moving down the group or in heavier elements.

↳ Inert pair effect increases on moving down a group.

Example of same oxidation states of p-block elements —

↳ Carbides — Carbides are the compounds of carbon with less electronegative elements than itself. i.e., with elements such as Ca, Al, Be, Si etc.

eg: CaC_2 , Al_4C_3 , Mg_2C_3 etc.

These carbides are further classified as —

a) Ionic or salt like carbides —

→ These are carbides of strongly electropositive elements. eg: CaC_2 , Al_4C_3 etc. These are further classified according to the type of hydrocarbon they give on hydrolysis —

i) Methanides ⇒ Give methane on hydrolysis.



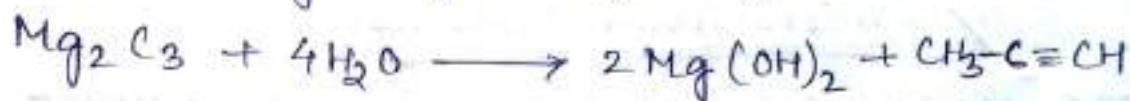
Here, carbides contain C^{4-} ion, or oxidation state of these carbon in these carbides is -4. Another example of methanides is Al_4C_3 .

ii) Acetylides \Rightarrow Give acetylene on hydrolysis.
eg:- MgC_2 , CaC_2 etc.



These carbides contain C_2^{2-} ion or $(C \equiv C)^{2-}$ ion. And oxidation state of carbon in these carbides is -1 .

iii) Alkylides \Rightarrow Give alkylene or propyne on hydrolysis. eg:- Mg_2C_3



These carbides contain C_3^{4-} ion or $[C^{2-} = C = C^{2-}]$ ion.

b) Covalent Carbides —

\rightarrow These are the compounds of carbon with elements of similar electronegativity, eg:- SiC , Be_2C etc. Here, the oxidation state of carbon is -4 .

c) Interstitial Carbides —

\rightarrow These are the compounds of carbon with transition elements. eg:- WC , TiC , ZrC , Fe_3C etc.

\hookrightarrow Therefore, carbon has negative oxidation state in carbides.

Nitrides — Nitrides are the compounds of nitrogen with less and similar electronegative elements to itself having an oxidation state of nitrogen is -3.

— These can be classified into three general categories —

i) Ionic nitrides —

→ Alkali and alkaline nitrides are called ionic nitrides. eg: Mg_3N_2 , Be_3N_2 etc.

ii) Interstitial nitrides —

→ These are largest group of nitrides that form with the transition metals. The general formulas of these nitrides are MN , M_2N and M_4N . eg: Cu_3N , Ag_3N etc.

iii) Covalent nitrides —

→ The nitrides of p-block elements are called covalent nitrides. eg: BN , P_3N_5 , S_2N etc.

Diagonal Relationship —

↳ Elements of second period resemble in certain properties with the elements of third period diagonally placed.

↳

Second period

Third period



↳ Cause of Diagonal Relationship —

As we move from left to right across a period, the electronegativity of elements increases. As we move down a group, the electronegativity of elements decreases. On moving diagonally, the two opposing tendencies almost cancel each other and their electronegativity value remains almost the same. Hence, diagonal pairs (Li-Mg, Be-Al, B-Si, etc.) show similar properties.

↳ Diagonal relationship between Boron and Silicon —

↳ Boron shows following similar properties with Silicon because of diagonal relationship —

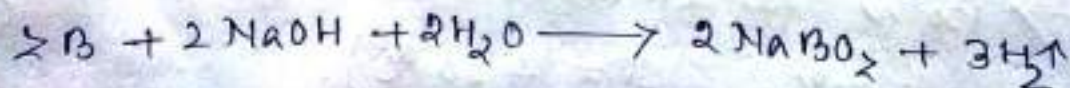
a) Preparation —

→ Both the elements can be prepared by reducing their oxides with Mg.



b) Action of alkalis —

→ Both the elements dissolve in alkalis forming metaborate (BO_2^-) and metasilicate (SiO_3^{2-}) —



c) Action of water and non-oxidising acids —
→ None of the elements is attacked by water and non-oxidising acids.

d) Occurrence —
→ None of these elements occurs in free state. Both are found as oxy-compounds, eg:- borates and silicates.

e) Non-metallic character —
→ Chemically both the elements are typical non-metals and are bad-conductors of heat and electricity.

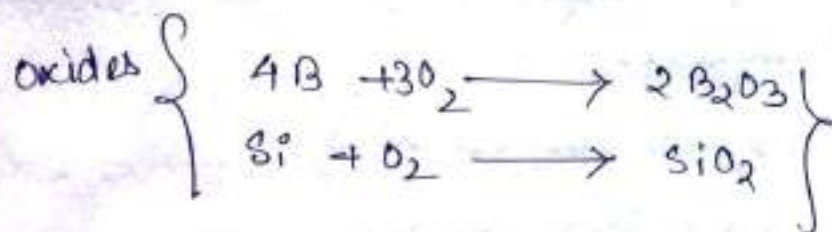
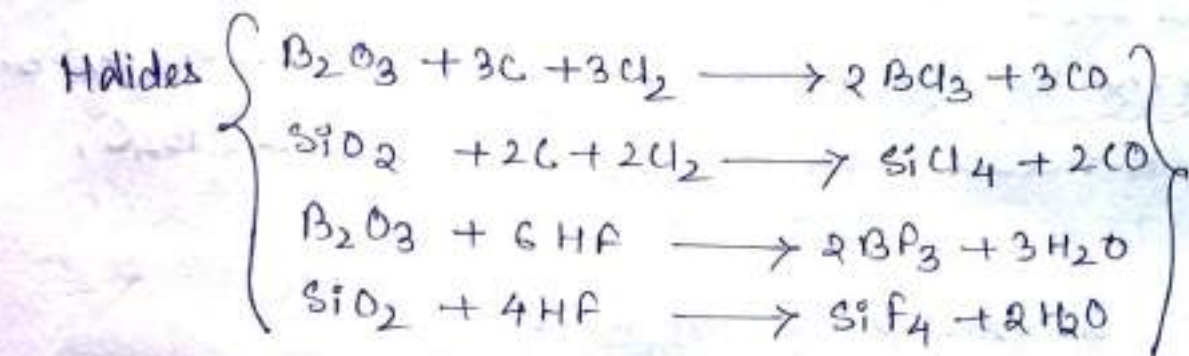
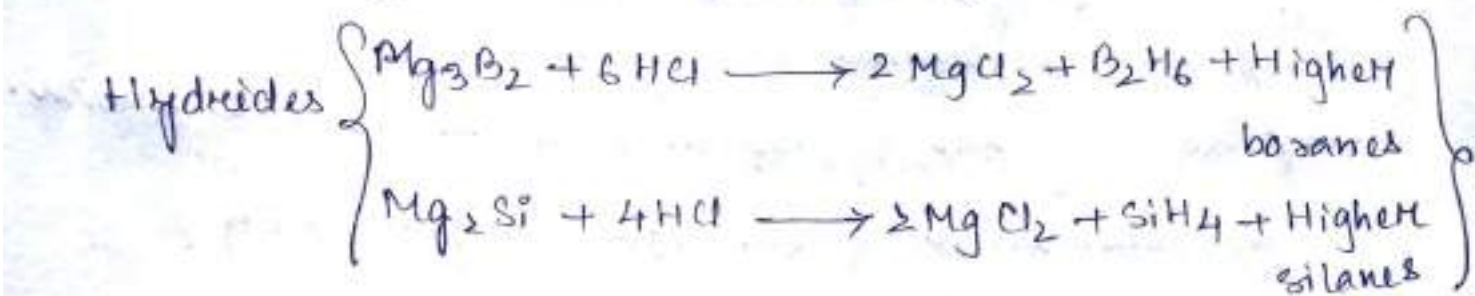
f) Allotropic forms —
→ Both the elements exist in two allotropic forms (amorphous and crystalline). The crystalline form of both elements is harder and less reactive than the amorphous form.

g) Density, electronegativity, ionization enthalpy and boiling points —
→ Both the elements have almost same these properties.

h) Melting points —
→ Both the elements have high melting points.
(B = 2300°C , Si = 1420°C).

i) Formation of covalent compounds—

→ Both the elements form mainly covalent compounds like hydrides (B_2H_6 , SiH_4), halides (BX_3 , SiX_4), oxides (B_2O_3 , SiO_2).

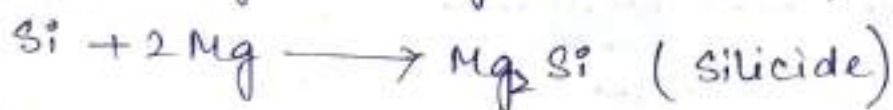
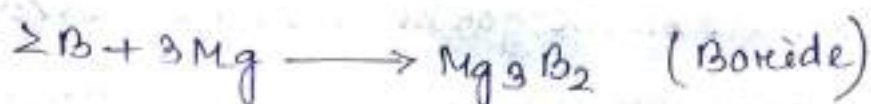


i) Reactivity—

→ Both the elements are normally inert at ordinary temperature. They are not oxidised in air and do not react with other elements or with dilute acids. However, the reactivity can be increased by increasing the temperature. At higher temperature, these elements react with a number of metals and non-metals.

↳ Combination with metals —

→



↳ Non-existence of oxy-salts —

→ No oxy-salts of Boron and Silicon are known.

m) Formation of sulphides, nitrides and carbides —

→ Both the elements can form sulphides (B_2S_3 , SiS_2), nitrides (BN , Si_3N_4) and carbides (B_4C , SiC).

n) Formation of complexes —

→ Both form complexes —

eg:- HBF_4 (Hydrofluoroboric acid)

H_4SiF_6 (fluorosilicic acid)

↳ Diagonal relationship between Carbon and Phosphorus —

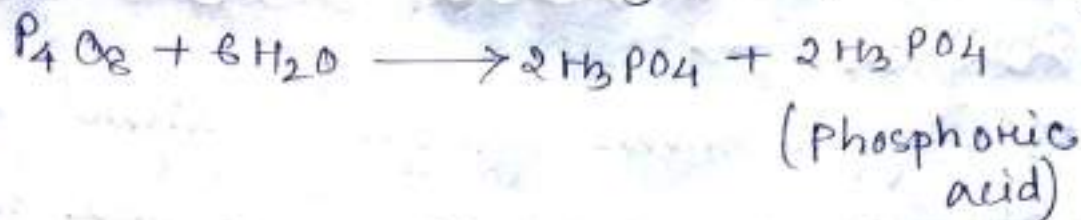
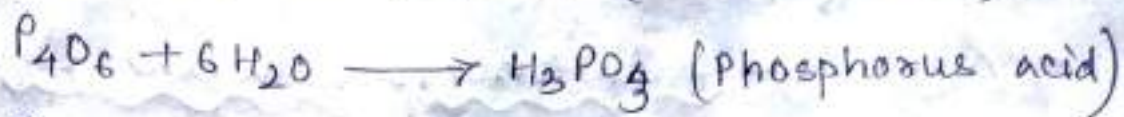
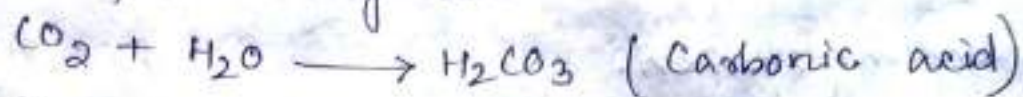
↳ Carbon shows following similar properties with Phosphorus because of diagonal relationship —

a) Both are non-metals.

b) Both form covalent hydrides. eg:- CH_4 ,

PH_3 .

c) Both form oxy-acids —



d) Both show allotropy.

e) Both react with organic radical such as alkyl and aryl.

f) Hydrides and nitrides of both are covalent in nature.

3) Diagonal relationship between Nitrogen and Sulphure —

↳ Nitrogen shows following similar properties with Sulphure because of diagonal relationship —

a) Both the elements are non-metals.

b) Both the elements have high electronegativity.

c) Both form strong oxy-acids and their salts.

d) Oxides of both the elements are acidic in nature.

⇒ Both form covalent hydrides when react with hydrogen.

4) Diagonal relationship between Oxygen and Chlorine

↳ Oxygen shows following similar properties with Chlorine because of diagonal relationship—

a) Both are gaseous.

b) Both are non-metals.

c) Both are highly reactive and strong oxidizing agents.

d) Both have high electronegativity.

⇒ Both form stable hydrides like H_2O and HCl .

Anomalous behavior of Boron — (Group 13)

↳ Boron shows different properties from other group 13 elements due to following reasons—

i) Small size,

ii) High electronegativity and

iii) Absence of d-orbitals.

↳ Boron shows following different properties from other group 13 elements—

i) Boron is non-metal while other elements are metal.

ii) Boron shows both crystalline and amorphous forms but other not.

iii) Oxides and hydroxides of Boron are acidic in nature. Al and Ga form amphoteric oxides while oxides and hydroxides of In and Tl are basic in nature.

iv) Boron has high m. pt. (2030°C) than other.

v) Boron does not form alum while other form.

vi) Boron forms borides with metals while other do not react with metals.

vii) Boron forms covalent compounds while other form both ionic and covalent compounds.

viii) Boron has less than four valence electrons and this gives it a great electron accepting power, i.e., its compounds behave as strong Lewis acid and forms a large number of complex compounds exhibiting its tendency to acquire a stable octet.

Anomalous behavior of Carbon — (Group 14)

↳ Carbon shows different properties from other group 14 elements due to following reasons —

- i) Small size,
- ii) High electronegativity and
- iii) Absence of d-orbitals.

↳ Carbon shows following different properties from other group 14 elements —

- i) Carbon is non-metal, while Ge is metalloid and Sn and Pb are metals.
- ii) Carbon has high value of ionization enthalpy than others.
- iii) CO_2 is acidic while GeO_2 , SnO_2 and PbO_2 are amphoteric
- iv) Carbon shows maximum covalency of four whereas other members can expand their covalency due to presence of d-orbitals.
- v) Carbon has a tendency for catenation while other elements do not have this property to a great extent.
- vi) Carbon also has a unique ability to form p π -p π multiple bond with itself or other atoms

of small size and high electronegativity. Heavier elements do not form p π -p π bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

Anomalous behavior of Nitrogen - (Group 15)

↳ Nitrogen shows different properties from other group 15 elements due to following reasons -

i) Small size,

ii) High electronegativity and

iii) Absence of d-orbitals.

↳ Nitrogen shows following different properties from other group 15 elements -

i) Nitrogen is gas while other elements are solids.

ii) Nitrogen is diatomic (N_2) while other elements are tetra-atomic (P_4 , As_4 , Sb_4 etc.)

iii) Nitrogen does not show allotropy while other elements (except Bi) show allotropy.

iv) NH_3 , which is hydride of nitrogen is highly stable while the hydrides of other

elements are progressively less stable. Moreover, NH_3 forms an associated $(NH_3)_x$ due to

Occurrence of hydrogen bond, while other hydrides do not show such behavior due to the absence of H-bonding.

v) Nitrogen shows a large number of oxidation states (+1, +2, +3, +4, +5, -1, -2, -3). Other elements do not show such a variety of oxidation states.

vi) NCl_3 is highly reactive and unstable while the trichlorides of other elements are more stable and less reactive.

vii) Maximum covalency for Nitrogen is 4 while other elements expand their covalency due to presence of d-orbitals. Thus, other elements can form the compounds like PF_5 , PCl_5 etc and complex like PF_6^- while Nitrogen does not form compounds like NF_5 and complexes like NF_6^- .

viii) Nitrogen is chemically inert in spite of its being the third most electronegative element. This is due to high dissociation energy of $\text{N} \equiv \text{N}$ bond. However, other elements of the group are quite reactive as they have low M-M bond dissociation energy.

Anomalous behavior of Oxygen — (Group 16)

↳ Oxygen shows different properties from other group 16 elements due to following reasons —

i) Small size,

ii) High electronegativity and

iii) Absence of d-orbitals.

↳ Oxygen shows following different properties from other group 16 elements —

i) Oxygen is gaseous while other members are solids.

ii) Oxygen does not show any positive oxidation state except in oxygen difluoride, OF_2 in which it shows +2 oxidation state, while the other members of this group show both positive and negative oxidation states.

iii) The maximum covalency of oxygen is two because of the absence of d-orbitals in its valence shell. Other elements on the other hand exhibit a maximum covalency of six due to the presence of d-orbitals.

iv) Since oxygen is highly electronegative, hydrogen bonding is found in oxygen compounds like H_2O . Other elements because of low

electronegativity; do not form compounds having H-bond. Sulphur compounds contains weak π -bonding.

vi) Hydrides of oxygen, (H_2O) is colourless, odourless and non-poisonous liquid, while the hydrides of other elements are inflammable gases with an unpleasant smell and are poisonous.

vii) Oxygen shows paramagnetic behaviour.

viii) Metals like Cu, Ag, Hg etc. show lesser tendency to react with O_2 to form oxides, than with sulphur to form sulphides. This is because of the fact that a stronger bond is formed when larger S^{2-} ion is polarized by the small Cu^{2+} , Ag^{2+} , Hg^{2+} ions.

Anomalous behavior of Fluorine :- (Group 17)

↳ Fluorine shows different properties from other group 17 elements due to following reasons —

i) Small size,

ii) High electronegativity and

iii) Absence of d -orbitals.

↳ Fluorine shows following different properties from other group-17 elements —

i) Due to maximum electronegativity, it shows a negative oxidation state of -1 . It does not show any positive oxidation state. The other members show negative as well as positive oxidation states of $+1$, $+3$, $+5$ and $+7$.

ii) Fluorine is most reactive element among halogens. This is due to the minimum value of F-F bond dissociation energy.

iii) On account of high electronegativity of fluorine atom, H-bonding occurs in HF molecule, while it is absent in HCl, HBr and HI molecules. The presence of H-bonding in HF explains why —

a) HCl, HBr and HI are gases while HF is liquid.

b) HF forms a number of compounds containing HF_2^- ion eg:- $\text{K}^+ \text{HF}_2^-$ while such compounds like $\text{K}^+ \text{HCl}_2^-$, $\text{K}^+ \text{HBr}_2^-$ etc. are not given by other HX molecules.

iv) HF ionises only slightly in aqueous solution and is therefore a weak acid. HCl, HBr and

HF on the other hand, ionise almost completely and are thus strong acids.

v) F^- ion has a great tendency to give complex ions like $[AlF_6]^{3-}$, $[FeF_6]^{3-}$ etc. The remaining halide ions show this tendency to much lesser extent.

vi) Fluoride, being the most electronegative gives SF_6 while other halogens do not form hexahalide with sulphur.

vii) Because of the absence of d-orbital in its valence shell, fluorine does not combine with F^- ions to give polyhalide ion like F_3^- while other halogens give such ions eg:- Cl_3^- , Br_3^- , I_3^- , I_5^- etc. because they contain d-orbitals.

Allotropes of Carbon, Sulphur and Phosphorus -

↳ Various forms of the same element having same chemical properties but different ^{Physical} ~~Chemical~~ properties are called allotropic forms of that element and the phenomenon is called allotropy.

Allotropy of carbon

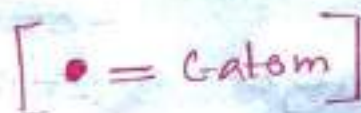
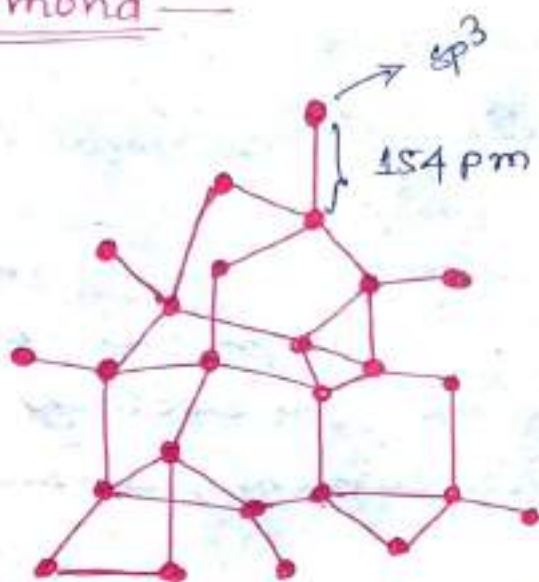
↳ There are three different forms of carbon or allotropic forms of carbon —

i) Diamond,

ii) Graphite and

iii) Fullerenes.

↳ Diamond



↳ Structure of Diamond

↳ Each carbon atom in diamond is sp^3 -hybridized. It is bonded tetrahedrally to four other carbon atoms by simple covalent bonds. Thus it has three-dimensional structure or network of strong covalent bonds in which C-C bond length is 1.54 \AA or 154 pm and each bond angle is 109.5° .

↳ On the basis of the structure of diamond, its characteristic properties can be explained as —

a) Melting point → The melting point of diamond is very high (3600°C) because it requires the breaking of strong covalent bonds.

b) Hardness → Due to strong C-C bonds, it is very hard and possess high density.

c) Bad-conductor → Since all the valence electrons are involved in bonding, leaving no free electron to conduct the electric current, diamond is a bad conductor.

↳ Varieties of diamond —

a) Bouet → It includes all impure gems which are used for cutting hard substances.

b) Barbanado → Also known as black diamond and used in

diamond drilling.

↳ Uses of diamond —

a) As a gem in jewellery because of its

ability to reflect light.

b) For cutting glass, marble stones and other hard materials

c) For grinding and polishing hard materials.

d) For drilling of rocks etc.

iii) Graphite —

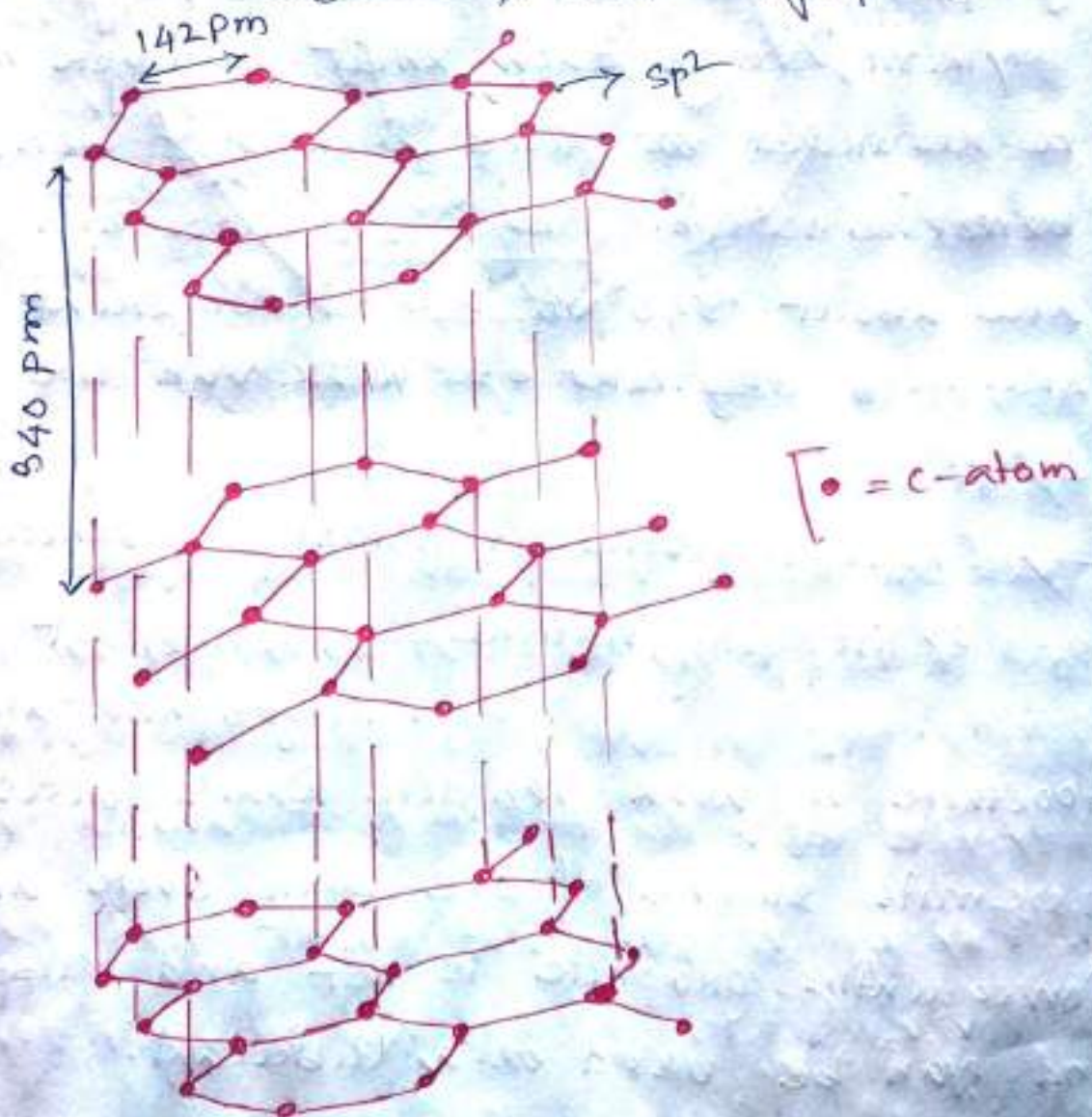
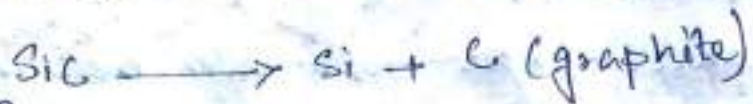


Fig: Structure of graphite

↳ Graphite, unlike diamond, has a two-dimensional sheet like structure. Each carbon atom in graphite is sp^2 -hybridized. Each carbon atom is bonded to three other carbon atoms through covalent bonds forming hexagonal planar rings. The C-C covalent bond distance in ring is 1.4 \AA or 142 pm indicating strong bonding. Thus, graphite has two-dimensional sheet like polymeric rings. Each sheet or layer may be regarded as fused system of ~~benzene~~ benzene rings. Any two successive sheets are about 340 pm apart. Different layers are held together by weak van der Waal's forces.

↳ Characteristic properties of graphite —

a) Slippery nature → Different layers in graphite are held together by weak van der Waal's forces. It permits sliding of one layer over another. Consequently, graphite is soft and slippery and can be used as a lubricant.

b) Low Density → Graphite has lower

density than diamond due to large distance between successive layers.

c) High melting point \rightarrow Within each layer, the C-atoms are firmly bonded by strong covalent bonds. Therefore melting point of graphite is high (about 3500°C).

d) Conductivity \rightarrow Since each C-atom is sp^2 -hybridized in graphite, hence one valence electron of each C-atom is free to move from one point to other. The unhybridized orbitals containing one electron each overlap laterally to form π -bonds between adjacent layers. These electrons are delocalized and are quite free to move under the influence of heat and electric field. Thus, graphite is good conductor of heat and electricity.

\rightarrow Graphite is used as —

a) In making lead pencils.

b) As a lubricant in heavy machinery

c) As a pigment in paints and in stone polish.

→ In making electrodes for the electric furnaces.

→ In nuclear reactors to slow down the high energy neutrons.

iii) Fullerenes

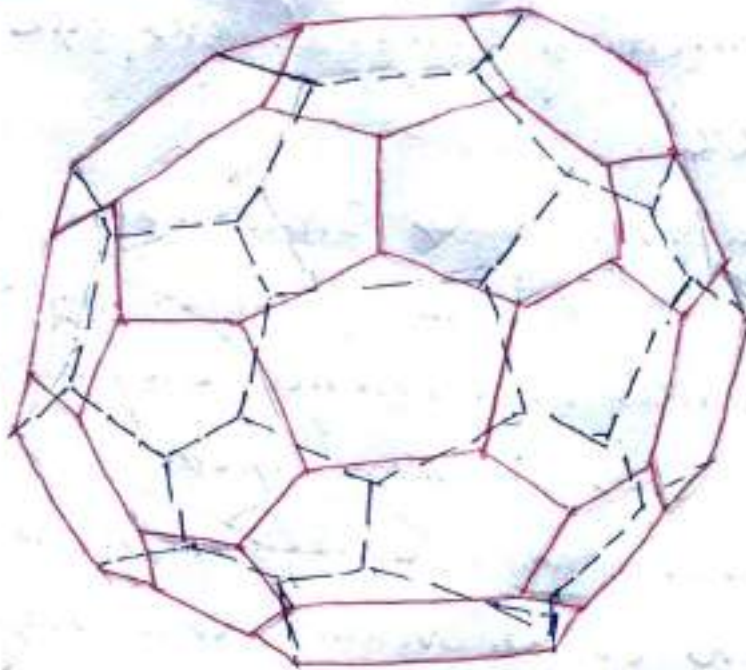


Fig. Structure of fullerene (C_{60})

↳ Molecular formula of fullerene ^{Corresponds to} is C_{60} .
This allotrope has spherical shape involving 60 vertices with a C-atom at each vertex.
Due to its similarity to the spherical domes designed and built by American architect R. Buckminster Fuller, it was named as Buckminster Fullerene or simply Fullerene.
Out of all fullerenes, (eg. C_{32} , C_{50} , C_{70} etc.)

The C_{60} isotope is most stable and it appears like a soccer ball and is also called bucky ball.

↳ The C_{60} fullerene consists of a system of (a) 20 six membered rings and (b) 12 five membered rings. As all the c-atoms are equivalent, the strain due to the distortion of the bonds from coplanarity is equally distributed among all the c-atoms. As a result, the molecule is quite stable.

↳ Properties —

a) Solubility → Fullerenes are soluble in organic solvents as they are covalent.

b) Reduction → They react with alkali metals electrochemically and the reduction products are solids such as K_3C_{60} .

c) It forms platinum complexes.

d) It reacts with OsO_4 , OsO_4 adds across one of the double bonds in a cage.

↳ Uses —

a) Used as a carrier for gene and drug delivery system.

b) Due to its antioxidant property used in many skincare products.

c) Also used as antiviral agent.

d) Used as dry lubricant.

2) Allotropy of Sulphur —

↳ There are five allotropic forms of sulphur. Two of which are in crystalline form and three are in amorphous form.

↳ Crystalline forms —

i) Rhombic or α -sulphur,

ii) Monoclinic or β -sulphur,

Amorphous forms —

iii) Plastic or γ -sulphur,

iv) Colloidal sulphur and

v) Milk of sulphur.

i) Rhombic or α -sulphur —

↳ This form is stable at ordinary temperature. All other forms change into this variety on standing.

↳ Rhombic sulphur is obtained by dissolving red sulphur in CS_2 carbon disulphide (CS_2)

and then evaporating the solution. After evaporation, octahedral crystals of rhombic sulphur are obtained.

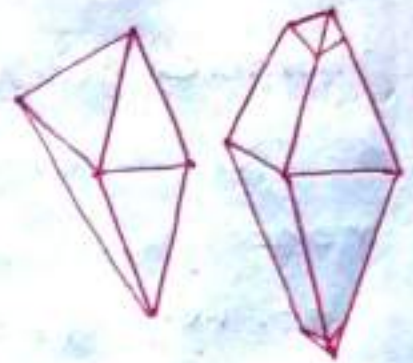
↳ Properties —

a) Melting point = 112.8°C

b) Density = 2.07 g/mL

c) Soluble in CS_2 but not in H_2O .

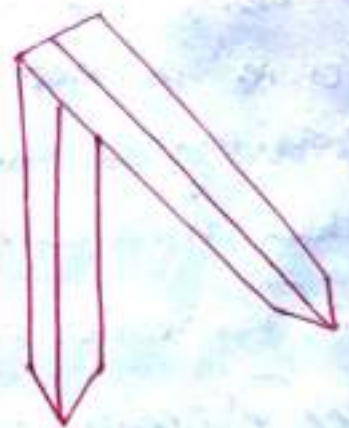
d) When slowly heated to 95.5°C it gets converted to monoclinic sulphur.



Rhombic or α -sulphur

↳ Monoclinic or β -sulphur —

↳ Some ordinary sulphur is taken in a china dish and heated to melt. On cooling, a crust is formed on the surface. A few holes are made on the crust and liquid below it is poured off. Needle



Monoclinic or β -sulphur

shaped crystals of monoclinic sulphur are formed which are seen on removing the crust.

↳ Properties —

- a) Melting point = 120°C
 - b) Density = 1.96 g/mL
 - c) Soluble in CS_2 but insoluble in H_2O .
 - d) Stable at 95.5°C and changes into rhombic sulphur below this temperature.
- 95.5°C is called transition temperature where monoclinic as well as rhombic sulphur co-exist. i.e., α -sulphur $\xrightleftharpoons{95.5^{\circ}\text{C}}$ β -sulphur

iii) Plastic or γ -sulphur —

↳ It is prepared by boiling ordinary red sulphur in a test tube and pouring the boiling mass into cold water. As a result, rubber like plastic sulphur is formed. This form is not crystalline because sudden cooling of the boiling sulphur slows down the molecular motion.

↳ Properties —

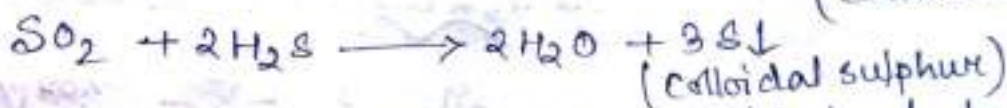
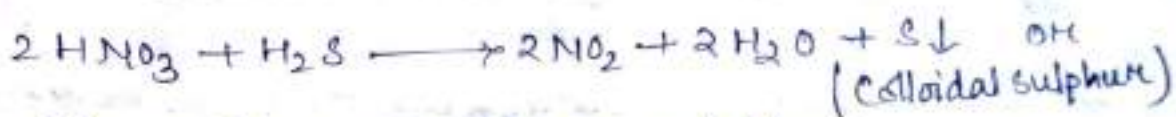
- a) Density = 1.96 g/mL , It has no sharp melting point.
- b) Insoluble in water as well as CS_2 .
- c) It changes to rhombic form on standing at ordinary temperature.

It is soft and elastic at first but solidifies afterwards.

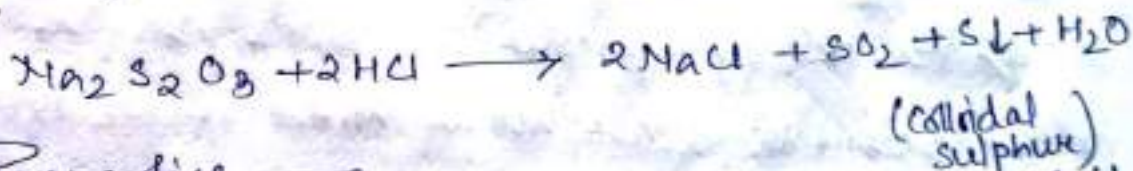
iv) Colloidal sulphur —

↳ Preparation —

a) From H_2S — It is obtained by passing H_2S gas through a solution of some oxidising agent like nitric acid, $KMnO_4$, SO_2 solution etc.



b) From $Na_2S_2O_3$ — It is obtained by treating Sodium thiosulphate with dilute HCl .



↳ Properties —

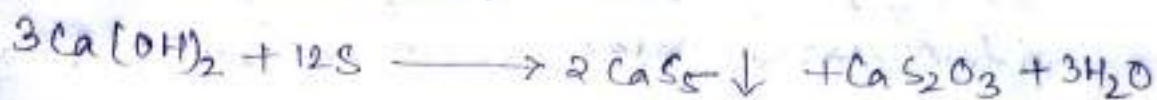
a) Some forms of this sulphur are soluble while others are insoluble in CS_2 .

b) It changes to ordinary form on heating or on long standing.

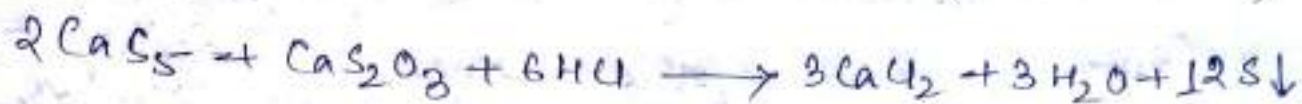
↳ Milk of sulphur —

↳ It is prepared by boiling ordinary sulphur with $Ca(OH)_2$ and treating the CaS formed

with concentrated HCl.



(Calcium penta sulphide) (Calcium thiosulphate)



↳ Properties —

(Milk of sulphur)

a) It is white, solid

b) Insoluble in H_2O as well as CS_2 .

3) Allotropes of Phosphorus —

↳ There are five allotropes of phosphorus —

i) white or yellow phosphorus.

ii) Red phosphorus

iii) Black phosphorus

iv) scarlet phosphorus and

v) violet phosphorus.

White Phosphorus —

↳ It is the most reactive form of phosphorus.

↳ Properties — (Physical)

a) It is a translucent wax like solid which attains yellow colour when exposed to light.

b) It is soft and brittle below $5-5^{\circ}\text{C}$.

c) Catches fire when exposed to air, therefore kept under water.

d) Melting point = 34°C and boiling point = 287°C

e) It is very poisonous and has garlic smell.

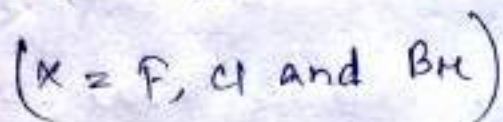
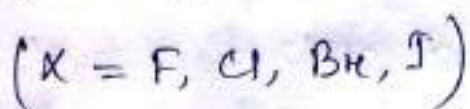
f) Its vapours decay the bones of teeth and jaw and cause a disease called phosy jaw.

g) Density = 1.8 g/mL and ignition temperature = 35°C .

h) Extremely soluble in CS_2 .

↳ Chemical Properties —

a) With halogens — (reduces halogens and lot of heat is produced)

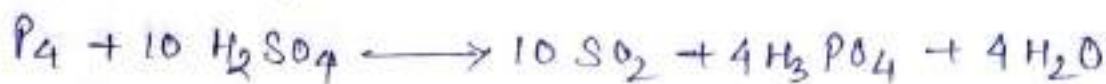
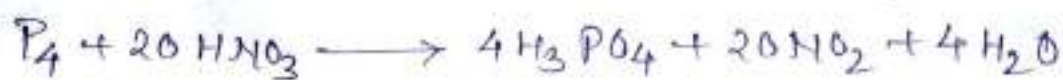


b) With sulphur — (reduces sulphur to S^{2-})

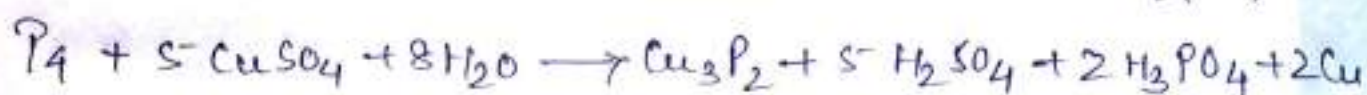


(Phosphorus trisulphide)

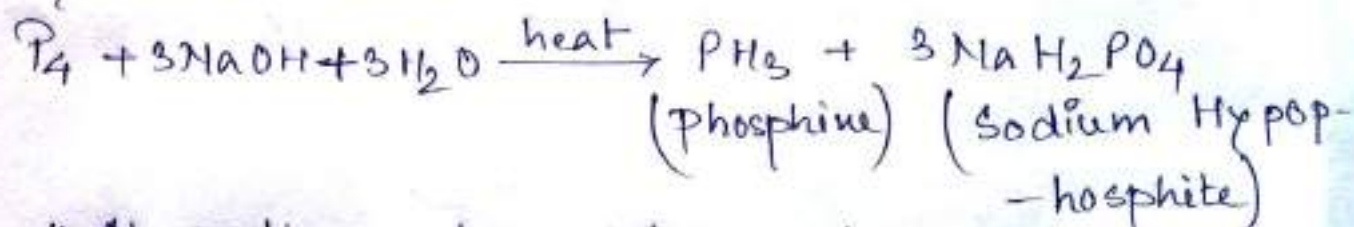
c) With conc. HNO_3 and conc. H_2SO_4 — (reduces HNO_3 to NO_2 and H_2SO_4 to SO_2)



d) With CuSO_4 — (reduces to metallic copper)



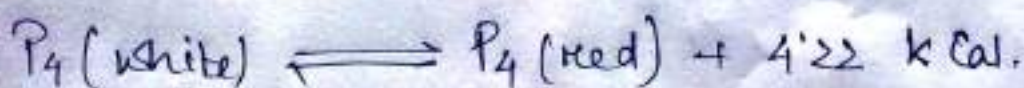
e) With NaOH —



At ordinary temperature, when phosphorus is exposed to moist air, a green glow or phosphorescence is produced.

ii) Red Phosphorus —

It is prepared by heating white phosphorus in a flask containing CO_2 and N_2 and a trace of iodine (catalyst). The conversion of white phosphorus to red phosphorus starts at 215°C . At temperature higher than 250°C , the conversion is reversible and exothermic.



↳ The main impurity in the red phosphorus is white phosphorus. The red phosphorus is ground under water and then boiled with NaOH to remove the impurity.

↳ Properties —

a) It is red-violet solid, tasteless and non-poisonous.

b) Insoluble in water as well as CS_2 .

c) Does not react with NaOH .

d) Poor conductor of electricity.

e) If heated under pressure, melts at

592.5°C .

iii) Black Phosphorus —

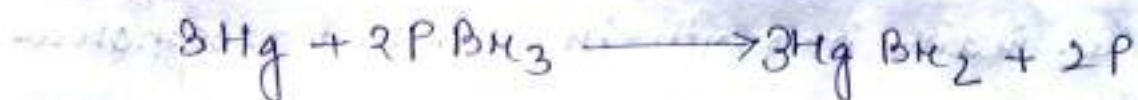
↳ It is a crystalline solid. Melts at 587.5°C and fairly good conductor of electricity.

↳ It is prepared by heating ^{white} ~~white~~ phosphorus at 200°C under a pressure of 12,000 to

$13,000 \text{ kg/cm}^2$.

iv) Scarlet Phosphorus —

↳ It is prepared by heating mercury with phosphorus tribromide at 240°C .



(Scarlet phosphorus)

↳ Also prepared by boiling 10% solution of white phosphorus in PBr_3 .

↳ It is non poisonous and when heated with an alkali, phosphine (PH_3) gas is evolved.

Violet Phosphorus -

↳ a) Obtained by heating (200°C) white phosphorus in presence of a trace of sodium under great pressure.

↳ Also obtained by heating red phosphorus at 530°C in a sealed tube.

↳ Its crystals have rhombohedral structure.

↳ It does not conduct electricity and is not oxidized by air.

_____ α _____