

Chemistry of S and P block elements

Oxidation state

- Oxidation states of an element is closely related to the number of valence electrons, which means they change periodically with atomic numbers across a period.
- Positive oxidation state increases and negative oxidation state decreases across a period with increasing atomic number.

Group	1	2	13	14	15	16	17	18
Common electronic configuration	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Element	Li	Be	B	C	N	O	F	Ne
Highest Oxidation State	+1	+2	+3	+4 -4	+5 -3	-2 +2	-1	0
Element	Na	Mg	Al	Si	P	S	Cl	Ar
Highest Oxidation State	+1	+2	+3	+4 -4	+5 -3	+6 -2	+7 -1	0

- S-block elements show only one oxidation state.
- P-block elements are capable of showing more than one oxidation state.

For example,

Oxidation states of oxygen in different oxides,

Normal oxides CaO, MgO, K ₂ O, H ₂ O etc.	Superoxides KO ₂ , NaO ₂	Peroxides H ₂ O ₂ , Na ₂ O ₂	OF ₂
-2	-1/2	-1	+2

Oxidation states of nitrogen in different species in the nitrogen cycle,

NO ₃ ⁻	NO ₂	NO ₂ ⁻	NO	N ₂ O	N ₂	NH ₂ OH	NH ₃
+5	+4	+3	+2	+1	0	-1	-3

Oxidation states of chlorine in the following compounds,

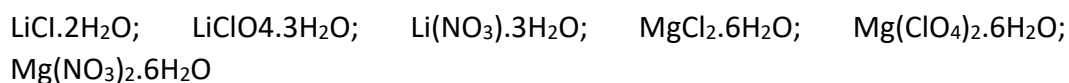
HCl	Cl ₂	ClF ₃	ClF ₅	HClO ₄
-1	0	+3	+5	+7

- Heavier elements of groups 13 and 14 shows oxidation states lower than their group oxidation states, for example: In group 13, B shows only +3 oxidation states; However, In and Tl prefer +1 oxidation state.
Similarly: In group 14, C and Si prefer +4 oxidation state, whereas +2 oxidation state is more common for Sn and Pb.
In group 15, Bi exclusively shows +3 oxidation state.

Similarities in the Pair, Li and Mg

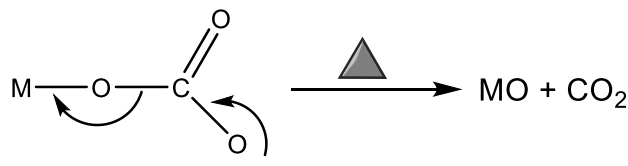
1. **High polarising power:** Compared to the other alkali metal ions (e.g. Na^+ =95 pm), Li^+ is very small in size (60 pm). Because of this fact, it is highly polarising and it has got more similarities (compared to other alkali metals) with Mg^{2+} (65 pm) though Mg^{2+} is more polarising than Li^+ (ionic potential, Z/r is more for Mg^{2+}). It may be noted that Li^+ is more polarising compared to any other alkali metal ion. This high polarising power is reflected in the following properties which are not shown by other alkali metal ions having low polarising powers.

(a) Hydration of salts: The salts having powerful polarising cations get very often hydrated; as with increasing ionic potential, ion-dipole interaction of cations towards water increases. Some of the hydrates of Li^+ and Mg^{2+} salts are given below.

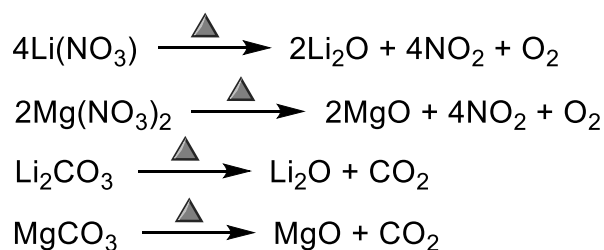


Here it is worth noting that other alkali metals do not form stable hydrates.

(b) Thermal instability of the oxy-acid salts: The thermal instability of the NO_3^- , CO_3^{2-} , SO_4^{2-} , BF_4^- salts arises due to the polarising behaviour of the cation. The metal ions having larger ionic potential values facilitate the electron movement towards the metal due to the increased electron withdrawing inductive effect.



Some examples of Li- and Mg-salts are given below.

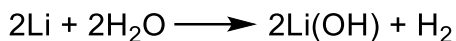


Other alkali metals give much more stable analogous salts

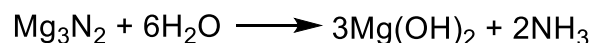
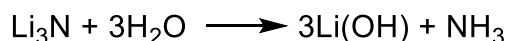
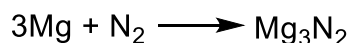
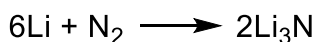
- (c) Covalence of the compounds:** According to the Fajans' rule, Li-salts are more covalent than the other alkali metal salts., In this point, it has got more similarities with the Mg-salts than with other alkali metal salts. This is why, the halides of Li and Mg are soluble in some oxygenated organic solvents.
- (d) Complexing power:** Because of the high polarising power, Li^+ has got a tendency to form complexes. In this regard, Li^+ fits better with Mg^{2+} rather than with other alkali metal ions.

(e) Hydration energy: The hydration energy of Li^+ is much greater compared to that of any other alkali metal ion and in this regard, it is comparable with Mg^{2+} .

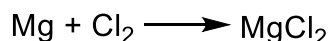
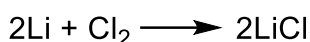
2. **Action of H_2O :** Both of them can decompose H_2O to liberate H_2 .



3. **Action of N_2 :** Both of them form nitrides when burnt in nitrogen. The nitrides are decomposed by H_2O to liberate NH_3 .

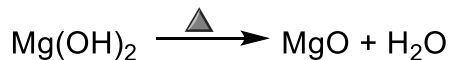
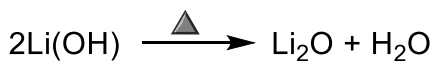


4. **Action of Cl_2 :** Both of them form chlorides which form hydrates, i.e. $\text{LiCl} \cdot 2\text{H}_2\text{O}$ and $\text{MgCl} \cdot 6\text{H}_2\text{O}$.



5. **Action of O_2 :** On burning in oxygen, Li gives its normal oxide Li_2O , and Mg gives MgO . Other alkali metals can form other types of oxides, such as superoxides (O_2^-) and peroxides (O_2^{2-}) but such oxides of lithium are unstable. This instability can be explained by considering the low r_+/r_- value. For ionic compounds having a much larger anion than cation have ineffective crystal packing and cation anion contact as a result high anion-anion repulsion. In this regard, Li fits better with Mg rather than with other alkali metals.
6. **Carbide formation:** In contrast to the other alkali metals, Li reacts with carbon to form an ionic carbide Li_2C_2 , just like MgC_2 .

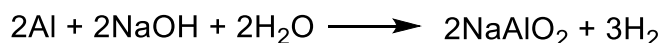
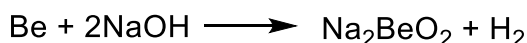
7. **Nature of hydroxides:** Both the hydroxides of lithium and magnesium are less soluble in water and these are also less basic. On heating they form their oxides.



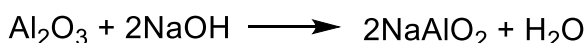
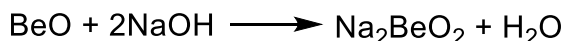
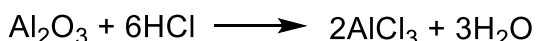
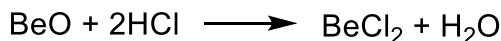
8. **Instability of the hydrosulfides:** Both LiSH and $\text{Mg}(\text{SH})_2$ are unstable compared to their respective hydroxides. Both Li^+ and Mg^{2+} being harder prefer the harder base OH^- compared to the softer one SH^- .
9. **Organometallic compounds:** Like the Grignard reagent, Li also forms many organometallic compounds
10. **Solubility:** The halides of both Li and Mg are soluble in many organic solvents. It happens so because of the covalency in such salts. Li_2CO_3 , Li_3PO_4 , LiF , and the corresponding salts of Mg are insoluble in water.

Similarities in the Pair, Be and Al

- Occurrence and extraction:** In nature they occur simultaneously in beryl, 3BeO , $\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. Both the metals are isolated by electrolysis of their fused salts in the presence of fluorides.
- High polarising power:** Because of the high polarising power of Be^{2+} and Al^{3+} as evidenced from the ionic potential value, they form covalent compounds having lower melting points and higher solubilities in organic solvents and they form hydrated salts. Because of the same ground, they yield high hydration energies in the formation of $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ species and their carbonates are thermally unstable. In these properties, Be^{2+} is more comparable with Al^{3+} rather than with other Gr 2 cations.
- Complexing power:** In contrast to other Gr 1 and Gr 2 metals, Be^{2+} has got a strong propensity to form complexes. The complexes of Be^{2+} and Al^{3+} are comparable. The examples are: $[\text{BeF}_4]^{2-}$ and $[\text{AlF}_6]^{3-}$, $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$ and $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$. $\text{Be}(\text{II})$ gives the tetrahedral complexes while $\text{Al}(\text{III})$ forms the octahedral complexes.
- Action of HNO_3 :** Both Be and Al are rendered passive by HNO_3 due to the formation of their inert oxide coatings.
- Action of alkalis:** Be forms beryllates while Al forms aluminates.

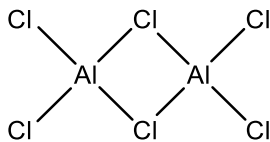
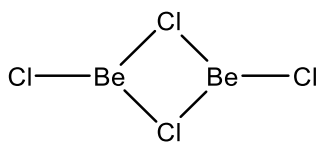


- Properties of the oxides and hydroxides:** These are amphoteric for both the metals.



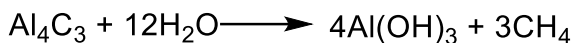
$\text{Be}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ behave similarly towards the acids and alkalis.

- Properties of the halides:** BeCl_2 actually forms the polymeric structure through the bridging by Cl. It can also attain the dimeric form $(\text{BeCl}_2)_2$ like the dimeric $(\text{AlCl}_3)_2$.



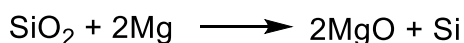
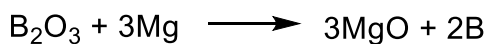
Both the halides are covalent and soluble in organic solvents. They are easily hydrolysed. They can also act as Lewis acids.

- Properties of the hydrides:** Both of them form polymerised hydrides through hydrogen bridge bonds (3c -2e) bonds.
- Properties of the carbides:** Both Be_2C and Al_4C_3 yield CH_4 on hydrolysis.

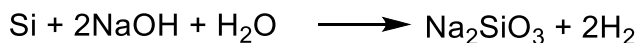
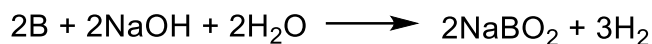


Similarities in the Pair, B and Si

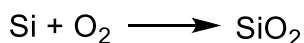
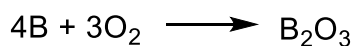
1. **Occurrence and extraction:** B exists as borates while Si exists as silicates. Both of them are isolated by reducing their respective oxides by Mg.



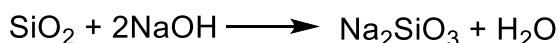
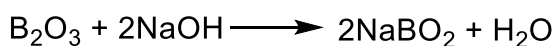
2. **Physical texture:** Both the nonmetals may have both the crystalline and amorphous allotropic forms.
3. **Covalency:** Because of the high ionic potentials, they form predominantly covalent compounds.
4. **Action of alkalis:** On fusion, B forms metaborates while Si forms metasilicates



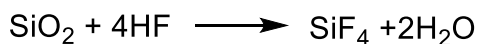
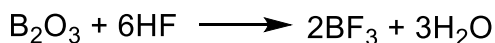
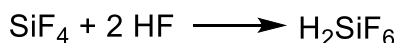
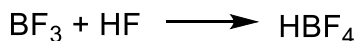
5. **Properties of the oxides:** On burning in the presence of O_2 , both B and Si form stable oxides.



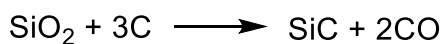
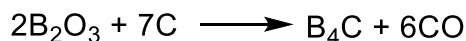
They react with strong alkalis as follows.



They also react in the same way with HF.

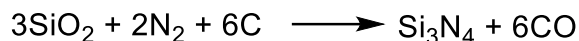
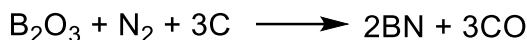


On heating with carbon in an electric furnace, they form carbides,

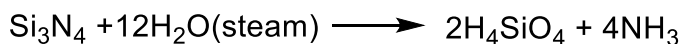
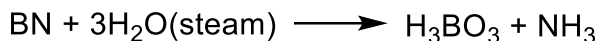


Both the carbides form the three-dimensional networks. They are inert to hydrolysis. They are very hard and used as abrasives.

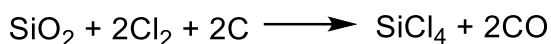
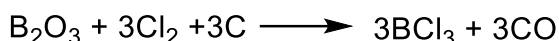
On passing N₂ over the heated mixture of the oxide and carbon, the corresponding nitrides are formed.



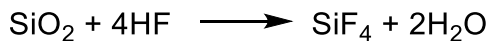
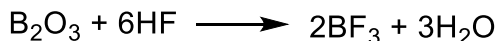
Both the nitrides can decompose steam to produce their corresponding oxyacids and NH₃.



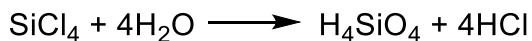
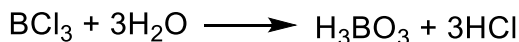
6. **Properties of the halides:** The chlorides are formed by passing Cl₂ over the heated mixture of the corresponding oxide and carbon.



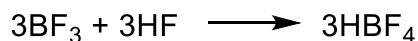
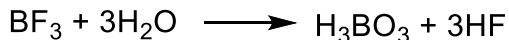
The corresponding fluorides are formed in the reaction between the respective oxides and HF.



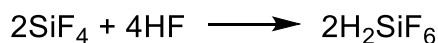
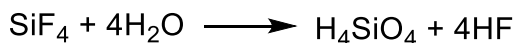
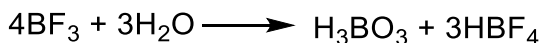
Both the chlorides, i.e. BCl₃, and SiCl₄, are liquid and are readily hydrolysed to form orthoboric acid and orthosilicic acid respectively.



Both the fluorides are colourless gases and are hydrolysed in the same way.



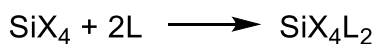
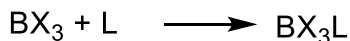
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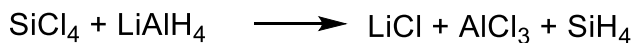
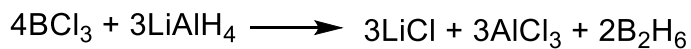
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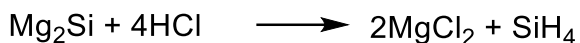
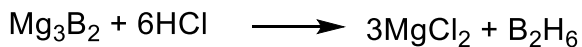
Both H₃BO₃ and H₄SiO₄ are weak acids. Both BX₃ and SiX₄ can act as Lewis acids.



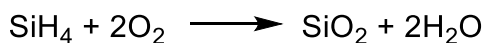
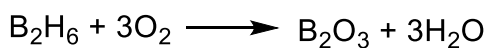
Both the halides can be reduced by LiAlH₄ to produce their corresponding hydrides.



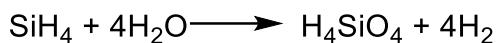
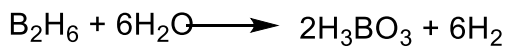
7. **Properties of the hydrides:** The hydrides can be prepared by reducing their chlorides by LiAlH_4 . They can also be prepared by using the magnesium boride and silicide respectively.



Here, some higher hydrides are also formed. The hydrides have comparable properties. They can easily burn to form their oxides.



They hydrolyse in the same way



8. **Complexing power:** Both B and Si have tendencies to form complexes, BF_4^- , SiF_6^{2-} are the halocomplexes.

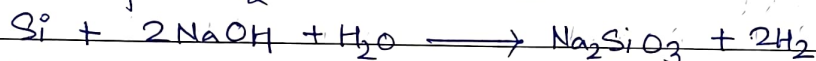
* Anomalous behaviour of C in group 14

Reasons :

- 1) Difference in sizes of C and other elements.
- 2) Non-availability of d orbitals in C atom.
- 3) C has high capacity of catenation.

Differences of C and Si

- 1) C has higher m.p. (3500°C) than Si (1410°C).
- 2) C in the form of graphite is a good conductor of electricity, while Si is poor conductor of electricity.
- 3) It has high tendency of form long chains of identical atoms (catenation). Si has lesser tendency to form such chains.
- 4) C does not react with alkalis. Si reacts with fused alkalis to form H_2 .



5. C is constituent of living organisms. Si is constituent of non-living materials: rocks, clays, soils, ores etc.

6. Hydrides : Hydrides of C are numerous and mostly stable. Only a few hydrides of Si are known and mostly unstable. This is because : Due to larger size of Si, Si-H bonds are longer and weaker. As a result they are more reactive.

7. Oxides : Two oxides of C are known: CO and CO_2 .

These are gaseous at ordinary temperature.

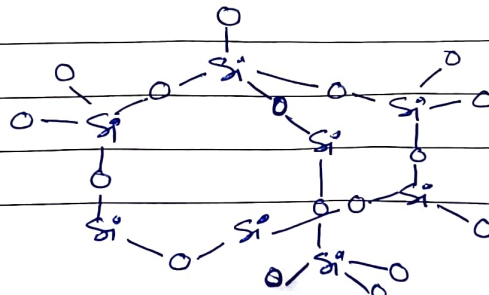
Only SiO_2 is known, lower oxide SiO is not known. also SiO_2 is solid.

Due to smaller size of C, effective p-p overlap for formation of π bond is possible. Hence, C has higher tendency to form multiple bonds (eg. $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{O}$, $\text{C}\equiv\text{N}$, $\text{C}=\text{S}$ etc.)

Structure of CO_2 : $\text{O}=\text{C}=\text{O}$

Structure of SiO_2 :

tetrahedral
3D network



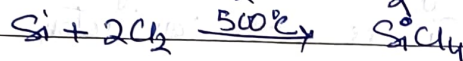
8. Halides: CCl_4 is quite stable and is not hydrolysed easily. SiCl_4 is less stable and hence hydrolysed by water.



CCl_4 cannot form the addition compounds like $\text{CCl}_4 \cdot 2\text{H}_2\text{O}$, $\text{CCl}_4 \cdot 2\text{NH}_3$ while SiCl_4 can form the addition compounds like $\text{SiCl}_4 \cdot 2\text{H}_2\text{O}$, $\text{SiCl}_4 \cdot 3\text{NH}_3$.

C does not react with Cl_2 and Br_2 directly.

Si reacts with Cl_2 or Br_2 at 500°C .



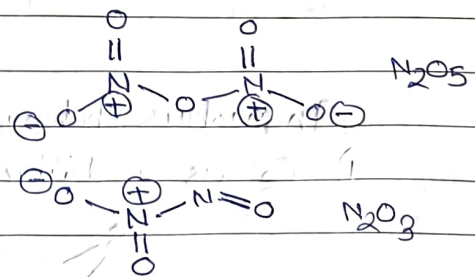
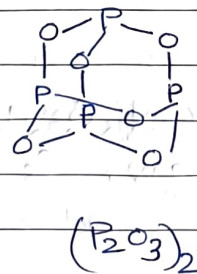
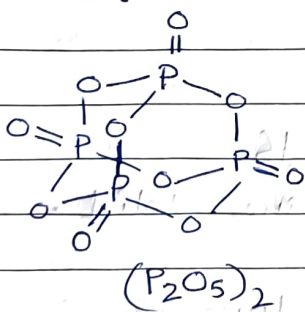
CF_4 cannot form the complex ion, CF_6^{2-} while SiF_4 can form the complex ion SiF_6^{2-} .

Differences of C and Si with other elements of Gr. 14

- 1) Both C and Si are non-metals while Ge is a metalloid and Sn and Pb are metals.
- 2) Both C and Si show tetravalency and do not give tetravalent and/or bivalent ions (M^{4+} or M^{2+}). On the otherhand Ge , Sn and Pb show tetravalency as well as form bivalent ions viz Ge^{2+} , Sn^{2+} and Pb^{2+} .
- 3) Both C and Si show an oxidation state of +4 only while Ge , Sn and Pb show two oxidation states which are +2 and +4.
- 4) CO_2 and SiO_2 are acidic while other dioxides (GeO_2 , SnO_2 and PbO_2) are amphoteric.

Anomalous behaviour of N in gr. 15.

- 1) N_2 is diatomic gaseous molecule, while S_8 , As_4 and Sb_4 are solid. Reason: Due to smaller size effective p-p overlap is possible and therefore N can form multiple bonds (σ and π).
- 2) N (and P) is non-metal. As and Sb are metalloids. Bi is metal. Reason: High electronegativity.
- 3) N exhibits large number of oxidation states \rightarrow +5, +4, +3, +2, +1, 0, -1, -3 etc. Other elements can show only a limited number of oxidation states.
- 4) Trihalides of N are explosive. eg. NCl_3 , NBr_3 , NI_3 . Exception NF_3 . Trihalides of other elements ($SbCl_3$, $AsCl_3$, SbI_3 etc.) are stable.
- 5) Hydrides of N (NH_3) is stable and non-poisonous while the hydrides of other elements are less stable and poisonous. Due to high electronegativity of N-atom, many NH_3 molecules can polymerise together by H-bonding to give associated molecule, $(NH_3)_n$. On the otherhand, due to small electronegativity of other elements, the hydride of these elements cannot be associated together to form polymer through H-bonding.
- 6) N can form various oxides N_2O , NO , NO_2 , N_2O_3 , N_2O_4 , N_2O_5 , N_2O_6 etc. Other elements can form A_2O_3 , A_2O_4 and A_2O_5 types of oxides. Exception: BiO .
- 7) Oxides of N are monomeric while others form dimeric oxides.



Reason: Due to larger size less effective p-p overlap. Hence tendency to lower the number of π bonds.

8) Since $N \equiv N$ bond energy in N_2 molecule is very high, N_2 is chemically inert under ordinary conditions. On the otherhand, due to the low

A-A bond energy in A_4 molecule ($A = P, As, Sb$) other molecules are quite reactive.

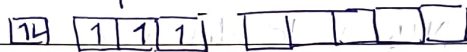
9) Due to small size and high electronegativity, N can form the nitride ion (N^{3-}). This tendency is less in phosphorus and absent in other elements.

10) Since N atom does not have d -orbitals in its valence shell, its maximum covalency is 4, while other elements can show maximum covalency of 5.

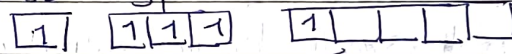
11) N can only form trihalides and not pentahalides while P, As and Sb can form both types of halides.

Reason: non-availability of d orbital in N

PCl_5 : P in $g. s^2 3s^2 3p^3 3d^0$

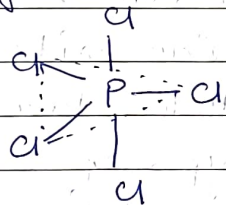


e.s.: $3s^1 \quad 3p^3 \quad 3d^1$



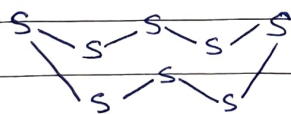
sp^3d

5 sp^3d hybrid orbitals \rightarrow t.b.p. structure



Anomalous behaviour of O in Gr 16

1) O_2 is a dimeric gas, S_8, Se_8 are solid.



structure of S_8

2) Because of high electronegativity, O atom forms O^{2-} ion readily while other elements have little tendency to form M^{2-} ions ($M = S, Se, Te$)

3) Because of high electronegativity, O atom shows negative oxidation state -2 . This element does not show any positive oxidation state except in OF_2 ($+2$). Other elements show $+2$, $+4$ and $+6$ oxidation states in addition to -2 oxidation states. P does not show -2 oxidation state.

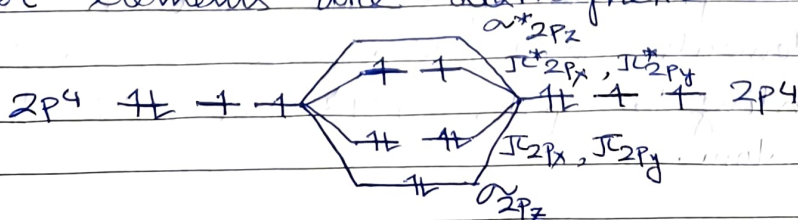
4) Maximum covalency of O atom is 2, since it has only two unpaired electrons and no d orbital in its valence shell. Due to the presence of d orbitals in the valence-shell of other elements, their np and ns paired electrons can be promoted to nd orbitals and thus more numbers of unpaired electrons may be obtained. So, other elements show covalencies of 2, 4 and 6 corresponding to 2, 4 and 6 unpaired electrons and sp^3 , sp^3d and sp^3d^2 hybridisation of the atoms.

5) On account of high electronegativity of O atom, this element forms hydrogen bond. On the other hand due to comparatively low electronegativity other elements do not form H-bond.

It is because of the H-bonding, H_2O exist as an associated molecule, $(H_2O)_n$ and hence H_2O is liquid and has high boiling point ($= 100^\circ C$). Hydrides of the other elements (eg. H_2S , H_2Se , H_2Te) are gases and have low boiling points ($H_2S \rightarrow -60.75^\circ C$, $H_2Se \rightarrow -41.5^\circ C$ and $H_2Te \rightarrow -1.8^\circ C$)

6) Oxygen forms (p-p) π bonds with itself and elements having similar size (C, N). Other elements show reluctance to form multiple bonds, i.e. other elements do not have a tendency to form (p-p) π bonds.

7) Molecular oxygen (O_2) in the gaseous, liquid and solid states is paramagnetic, while the molecules of other elements are diamagnetic in nature.



2) O_2 has high bond dissociation energy (494.6 kJ/mol) and as a result highly stable and react with other elements at a very high temperature.

Reason: double bond in O_2

Consequence: Most of the ores are sulfide and only a few are oxides.

Anomalous behaviour of F in Gr. 17.

1) F is the most electronegative element and hence shows only -1 oxidation state. Other halogens can show oxidation states $-1, +1, +3, +5, +7$ etc.

(positive oxidation states)

2) Since F shows only one oxidation state equal to -1 , this element form only one oxide F_2O . Other halogens show many oxidation states and hence form many oxides in $+1$ (Cl_2O, Br_2O), $+4$ (ClO_2, BrO_2, I_2O_4), $+5$ (I_2O_5), $+6$ (Cl_2O_6, BrO_3) and $+7$ (Cl_2O_7, I_2O_7) oxidation states. Fluorine also form F_2O_2 which is unstable.

3) Due to high electronegativity of F atom, this element gives the maximum number of interhalogen compounds. Other halogen gives less number of interhalogen compounds.

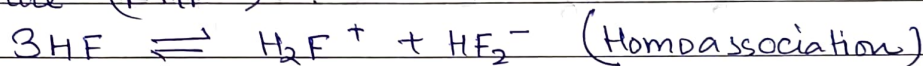
4) Since F is more electronegative than oxygen, it does not form oxyacids. On the otherhand, since the remaining halogens are less electronegative than oxygen, they give various type of oxyacids. Electronegativity values of F, Cl, Br, I and O are as $F = 4.0, O = 3.5, Cl = 3.0, Br = 2.8$ and $I = 2.5$.

5) Maximum covalency of F is 1, since it contains only one electron and no d-orbital in its valence shell. Due to the presence of valence shell 'd' orbitals, other elements show covalency of 3, 5 and 7 corresponding to sp^3d , sp^3d^2 and sp^3d^3 hybridisation of the atom.

6) Due to repulsion between non-bonding electrons in F_2 molecule, F-F bond dissociation energy is very low. Due to this weak nature of F-F bond, F_2 is the most reactive among halogens (158.8 kJ/mol). In Cl_2 , Br_2 and I_2 , the bond forms as a result of hybridised 'p' and 'd' orbitals leading to less e-e repulsion and hence the bonds are much stronger.

7) Due to high electronegativity F van form H-bond. As a result HF is liquid (b.p. = 19.5°C) while HCl, HBr and HI are gases.

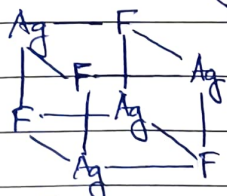
8) Due to small size and high electronegativity, an H-F bond is very strong. As a result HF is a weak acid and does not ionise completely in water. However, HF is highly corrosive due to formation of bifluoride (FHF^-).



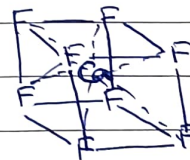
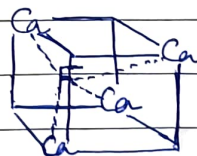
HF_2^- ions are stabilised by H-bonding. HCl_2^- and HBr_2^- are not known.

9) AgF is soluble in water, but AgCl and AgBr are not. Reason: Hydration energy is higher than lattice energy of AgF.

CaF_2 is insoluble in water while $CaCl_2$ is soluble. Reason: High lattice energy of CaF_2 , Ca^{2+} and F^- are bound very strongly due to large difference in electronegativity.



Rock salt str.

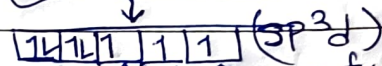
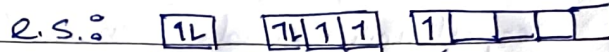


10) Due to low polarisability of F, most fluorides are ionic.

11) Because of the absence of 'd'-orbitals in the valence-shell of F atom, this element cannot accept the lone pairs of electrons donated by the halide.

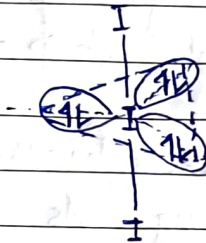
ions and hence cannot form polyhalide ions. On the other hand due to the presence of 'd' orbitals in their valence shell, other halogens can form polyhalide ions. eg. ClF_2^- , BrCl_2^- , ICl_2^- , Cl_3^- , Br_3^- , I_3^- etc.

I_3^- : I in g.s. : $s^2 p^5 d^0$



from 2 I atoms

for negative charge



ii) Since F has high electronegativity value, it can stabilise +6 oxidation state of S forming SF_6 . SCl_6 , SBr_6 etc. do not form.