

Chemistry of s and p block elements

Introduction: In s-block elements the last electron enters the outermost s orbital. The general electronic configuration is ns^{1-2} . Hydrogen, Helium, Group-1 elements (Li, Na, K, Rb, Cs, Fr) and Group-2 elements (Be, Mg, Ca, Sr, Ba, Ra) are belongs to the s-block elements. Some of the general properties of s-block elements are as follows

- (i) They all are metals so good conductors of heat and electricity
- (ii) They are malleable, lustrous and soft.
- (iii) Exhibit group valency of 1 and 2 for group I and II respectively as their last shell contains 1 or 2 electrons.
- (iv) Elements are very reactive due to have low ionization enthalpies
- (v) They lose the outermost electron(s) to form cation Group 1 elements lose 1 electron while the Group 2 elements loses 2 electrons
- (vi) Metallic character increases down the group
- (vii) Because of high reactivity they are never found pure in nature
- (viii) Reactivity increases down the group
- (ix) Compounds of s-block are ionic in nature, except beryllium and lithium
- (x) They form colourless compounds except chromates, dichromates, permanganates etc.
- (xi) Their solutions in liquid ammonia are good conductor of electricity and are good reductant.
- (xii) Oxides are basic in nature.
- (xiii) The alkali metals and their salts impart characteristic colour to an oxidizing flame

s, p, d, and f blocks																																																																																																																																																																																								
	s block		d block										p block					s^2																																																																																																																																																																						
	s^1	s^2											p^1	p^2	p^3	p^4	p^5	p^6	2	He																																																																																																																																																																				
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112																																																																								
	H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																																																																								
	f block		f block														f block																																																																																																																																																																							
	f^1		f^2														f^3														f^4														f^5														f^6														f^7														f^8														f^9														f^{10}														f^{11}														f^{12}														f^{13}														f^{14}													

In p-block elements the last electron enters the outermost p orbital. The elements from Group-13 to Group-18 are referred as p-block elements. As Their valence shell electronic configuration is ns^2np^{1-6} . The difference in inner core of the elements greatly influences many physical as well as chemical properties of p-block elements. Metal, non-metal and metalloid are present in p-block elements.

- (i) They show variable valences and oxidation states.
- (ii) They are solids/liquids/gases at room temperature (Br is liquid)
- (iii) They form acidic oxides
- (iv) They impart no characteristic colour to the flame
- (v) Generally they form covalent compounds
- (vi) Halogens form salts with alkali metals
- (vii) They have comparatively high ionization potentials
- (viii) They have very large electron gain enthalpies
- (ix) The aqueous solutions their oxides are acidic in nature

Relative stability of different oxidation states:

1. **For Group-1** elements the common and stable oxidation state is +1. The first IE is lower than any other group elements and the 2nd IE is very high which is greater than IE of noble gas elements. This fact suggests the stable +1 oxidation state of Group-1 elements.

2. **For Group-2** elements the common oxidation state is +2. The third IE is very high so that M^{3+} ion is never formed. The 3rd IE is often greater than the sum of 1st and 2nd IE. Although the 2nd IE is higher than 1st IE, Group 2 metals form M^{2+} as lattice energy is higher in M^{2+} ion than M^+ form.

Group 1		Group 2	
Elements	Electron configuration	Elements	Electron configuration
Li	$[\text{He}]2s^1$	Be	$[\text{He}]2s^2$
Na	$[\text{Ne}]3s^1$	Mg	$[\text{Ne}]3s^2$
K	$[\text{Ar}]4s^1$	Ca	$[\text{Ar}]4s^2$
Rb	$[\text{Kr}]5s^1$	Sr	$[\text{Kr}]5s^2$
Cs	$[\text{Xe}]6s^1$	Ba	$[\text{Xe}]6s^2$
Fr	$[\text{Rn}]7s^1$	Ra	$[\text{Rn}]7s^2$

For Group-13 elements the common oxidation state is +3. But on descending the group stability of +3 oxidation state decreases and stability of +1 oxidation state increases. For heavier congeners Tl the stable oxidation state is +1. This occurs due to the inert pair effect which is a consequence of lanthanide contraction and relativistic effect. Sometime Ga(Gallium) shows +2 oxidation state which is very unstable.

Elements	Electronic Configuration	Oxidation state	Example
B	[He]2s ² 2p ¹	+3	B ₂ O ₃ , BF ₃ , B(OH) ₃
Al	[Ne]3s ² 2p ¹	+3	Al ₂ O ₃ , AlCl ₃ , AlF ₃
Ga	[Ar]3d ¹⁰ 4s ² 4p ¹	+3, (+2)	GaCl ₃ (+3), Ga ₂ Cl ₄ (+2) or Ga ^I [Ga ^{III} Cl ₄]
In	[Kr]4d ¹⁰ 5s ² 5p ¹	+3, (+2)	InCl ₃ (+3), InCl ₂ (+2)
Tl	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	+1	TlI ₃ (+1), Tl ₂ SO ₄

For Group-14 elements the common oxidation state is +4. On des the group stability of +4 oxidation state decreases and stability of +2 oxidation state increases. Therefore the heavier congener Pb processes stable +2 oxidation state rather +4.

Elements	Electronic configuration	Oxidation state	Example
C	[He]2s ² 2p ²	+4	CH ₄ , CF ₄ , CCl ₄
		+2	CO
Si	[Ne]3s ² 3p ²	+4	SiH ₄ , SiCl ₄
		+2	SiF ₂
Ge	[Ar]3d ¹⁰ 4s ² 4p ²	+4	GeF ₄ , GeCl ₄
		+2	GeF ₂ , GeCl ₂ , GeBr ₂
Sn	[Kr]4d ¹⁰ 5s ² 5p ²	+4	SnCl ₄
		+2	SnF ₂ , SnCl ₂ , SnBr ₂
Pb	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	+4	PbCl ₄
		+2	PbCl ₂ , PbBr ₂

For Group-15 elements the common oxidation state is +3 and +5. The elements lack of 'd' orbital processes +3 oxidation state but elements having 'd' orbital may have both +3 and +5 oxidation states. On down the group stability of +5 states decreases and stability of +3 oxidation state increases. Nitrogen exhibits a wide range of oxidation states from -III to +V.

Elements	Electronic configuration	Oxidation state	Example
N	[He]2s ² 2p ³	-3, -2, -1, 0, +1, +2, +3 +4, +5	NH ₃ (-3), NH ₂ -NH ₂ (-2) NH ₂ OH(-1), N ₂ (0), N ₂ O(+1), NO(+2), NF ₃ (+3) HNO ₂ (+4), HNO ₃ (+5)
P	[Ne]3s ² 3p ³	-3, +1, +3, +5	PH ₃ (-3), H ₃ PO ₂ (+1), H ₃ PO ₃ (+3), H ₃ PO ₄ (+5)
As	[Ar]3d ¹⁰ 4s ² 4p ³	-3, +3, +5	AsH ₃ (-3), H ₃ AsO ₃ (+3), H ₃ AsO ₄ (+5)
Sb	[Kr]4d ¹⁰ 5s ² 5p ³	-3, +3, +5	SbH ₃ (-3), H ₃ SbO ₃ (+3), Sb ₂ O ₅ (+5)
Bi	[Xe]4f ¹⁴ 6s ² 6p ³	-3, +3, +5	BiH ₃ (-3), Bi ₂ O ₃ (+3), NaBiO ₃ (+5)

For Group 16 elements common oxidation states of are -2, +4 and +6 but for oxygen common oxidation state is -2. Lower oxidation states of oxygen are -1 in peroxide, -1/2 in superoxide and -1/3 in ozonides. Sulphur shows variety of oxidation state like +2 in S₂O₃²⁻, +2.5 in S₄O₆²⁻, +5 in S₂O₆²⁻. Po exhibits a stable +2 oxidation state. All the elements exhibit +4 and +6 oxidation state except O. The stability of higher oxidation state decreases down the group i.e. oxidizing ability increases down the group in the order Se(+6) < Te(+6) < Po(+6).

Elements	Electronic configuration	Oxidation State	Oxidation state with example
O	[He] 2s ² 2p ⁴	-2, -1, +2, +1, -1/2, -1/3	OH ₂ (-2), H ₂ O ₂ (-1), OF ₂ (+2), O ₂ F ₂ (+1), KO ₂ (-1/2), NaO ₃ (-1/3)
S	[Ne] 3s ² 3p ⁴	-2, +2, +2.5 +4, +5, +6	H ₂ S(-2), Na ₂ S ₂ O ₃ (+2), Na ₂ S ₄ O ₆ (2.5), SO ₂ (+4), Na ₂ S ₂ O ₆ (+5), H ₂ SO ₄ (+6)
Se	[Ar] 3d ¹⁰ 4s ² 4p ⁴	-2, +4, +6	H ₂ Se(-2), SeO ₂ (+4), SeO ₃ (+6)
Te	[Kr] 4d ¹⁰ 5s ² 5p ⁴	-2, +4, +6	H ₂ Te(-2), TeO ₂ (+4), TeO ₃ (+6)
Po	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	-2, +4, +6	H ₂ Po(-2), PoO ₂ (+4), PoO ₃ (+6)

In Group-17, the common oxidation state is -1. Except fluorine, halogens exhibit several oxidation states in their oxide, oxoacids and interhalogens.

Elements	Electron Configuration	Oxidation state	Example
F	[He]2s ² 2p ⁵	-1	HF(-1)
Cl	[Ne]3s ² 3p ⁵	-1, +1, +3, +5, +7	HCl(-1), HOCl(+1), HClO ₂ (+3), HClO ₃ (+5), HClO ₄ (+7)
Br	[Ar]3d ¹⁰ 4s ² 4p ⁵	-1, +1, +3, +5, +7	HBr(-1), HOBr(+1), HBrO ₃ (+5), HBrO ₄ (+7)
I	[Kr]4d ¹⁰ 5s ² 5p ⁵	-1, +1, +3, +5, +7	HI(-1), HOI(+1), HIO ₃ (+5), HIO ₄ (+7)

For Group-18 elements the oxidation states are +2, +4, +6 and +8.

Elements	Oxidation state	Example
He		
Ne		
Ar		
Kr		KrF ₂
Xe	+2, +4, +6, +8	XeF ₂ , XeF ₄ , XeF ₆ , XeO ₄
Rn	+2, +4, +6	RnF ₂ , RnF ₄ , RnF ₆

2. Diagonal relationship: The element having similar chemical properties with their own group elements also have the similar chemical properties with the element lying diagonally in the next higher group is called the diagonal elements and this phenomenon is known as diagonal relationship.

Group →				
Period ↓	1	2	13	14
2	Li	Be	B	C
3	Na	Mg	Al	Si

Causes of Diagonal relationship: Chemical and physical properties depend on different parameter like atomic size, electronegativity and polarizing power. Diagonal elements have similar chemical properties because they have more or less same atomic size, electronegativity and polarizing power. Let us consider the pair Li-Mg, to reach Li to Mg there are two roots:

1) $\text{Li} \rightarrow \text{Be} \rightarrow \text{Mg}$ and 2) $\text{Li} \rightarrow \text{Na} \rightarrow \text{Mg}$, if we consider the first path then from Li to Be Z^* , electronegativity increases but atomic size decreases and from Be to Mg Z^* , electronegativity decreases but atomic size increases. As a whole Li and Mg Z^* , electronegativity and atomic size remains almost same, therefore chemical properties are similar. Similar facts are happen in path (ii) but in the reverse order.

Chemical similarities between Li and Mg

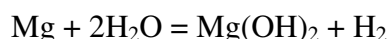
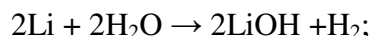
1) Both Li and Mg form hydrated salt e.g. $\text{LiCl} \cdot 3\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

2) Oxyacid salt of both Li and Mg are thermally unstable.

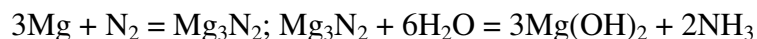
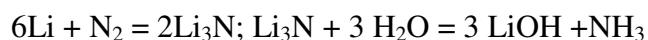


3) Hydration energy of both Li and Mg are almost comparable.

4) Both react with water to form hydroxide.



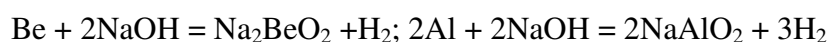
5) Both form nitride when burnt in nitrogen.



Chemical similarities between Be and Al

Ionic potential (ϕ) for Be^{2+} (~ 6.5) and Al^{3+} (~ 6.0) are similar. This is why that Be and Al have similar properties.

- 1) Both form covalent compound having lower melting point and higher solubility in organic solvent as they have high polarizing power.
- 2) They form hydrated species e.g. $\text{Be}(\text{H}_2\text{O})_4^{2+}$ and $\text{Al}(\text{H}_2\text{O})_6^{3+}$.
- 3) Both Be and Al are rendered passive by HNO_3 due to formation of their inert oxide coating. $\text{Be} + 2\text{HNO}_3 \rightarrow \text{BeO} + \text{H}_2\text{O} + 2\text{NO}_2$; $2\text{Al} + 2\text{HNO}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{NO}_2$;
- 4) Be forms beryllates while Al forms aluminates on action with alkali.



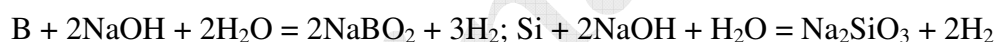
- 5) Both the metal form amphoteric oxide.



- 6) Both BeCl_2 and AlCl_3 forms dimeric structure through the bridging by Cl.

Chemical similarities between B and Si

- 1) B exists as borates while Si exists as silicates in nature.
- 2) Both form covalent compounds as sum of the ionisation energy is very high.
- 3) B forms metaborates and Si forms metasilicates on reaction with alkali.

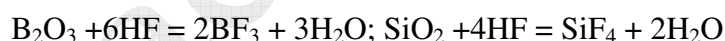


- 4) Properties of their oxide are similar.

- a) Reacts with strong alkali.



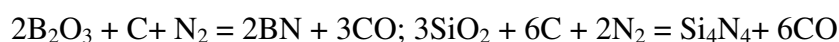
- b) Reaction with HF.



- 5) On heating with C in electric furnace they form carbides.



- 6) On heating with mixture of N_2 and C, they form nitrides.



Anomalous behaviour of first member of each group:

In Group-1, Li and its compounds differ from those of the other group elements. This is because of the smaller size and its consequence of the Li metal. Due to smaller size, it has high polarizing power, high lattice energy and high hydration energy which determine the chemical properties of Li. The anomalous behaviour of Li is as follows.

- 1) The solubility of many Li compounds in water is very low compared to other group elements. That is Li compounds are covalent while other Group-1 metal compounds are ionic.
- 2) Li_2CO_3 and LiNO_3 are thermally less stable and decompose readily to oxide on heating.
- 3) Li can form nitride on reaction with N_2 but other group elements do not form. Stability of Li_3N arises due to its very high lattice energy. The other singly charged larger alkali metal ions can't compensate the high bond energy of N_2 and the positive electron affinity to form N^{3-} ion.
- 4) Li only form monoxide Li_2O but group elements form peroxide and superoxide along with monoxide. (e.g. Na_2O_2 , KO_2). The stability of these compounds depends on the lattice energy gain from the close packing of larger anions with larger cations.
- 5) Lithium salts are normally hydrated and the anhydrous salts are extremely hygroscopic. Except Li, other Group-1 metals sulphate form alum.

In Group-2, Be differs from the rest of the group elements for three reasons

- 1) It is extremely small in size and according to Fajan's rule its ionic potential value is highest in the group. As a result it forms covalent compounds while other elements form ionic compound.
- 2) Be has high electronegativity compared to other group elements. Thus when Be reacts with other elements, the difference in electronegativity becomes small and hence compound becomes covalent.
- 3) Due to lack of d-orbital Be form only 4 bonds but other elements of the group may extend up to 6 bonds. E.g. Be form $\text{Be}(\text{H}_2\text{O})_4$ while Mg form $\text{Mg}(\text{H}_2\text{O})_6$.

In Group-13 elements, the first element B differs from other elements.

- 1) Due to small size B form interstitial metal boride on reaction with metal.
- 2) Boron compounds are covalent both in solid and solution due to high IE of B^{3+} formation.
- 3) B has high melting point due to unusual crystal structure in which unit cell contains B_{12} unit known as icosahedrons.
- 4) Due to high affinity towards oxygen, it gives rise to extensive chemistry involving boron-oxygen link, e.g. borates.
- 5) Boron only in the group forms B-B-B, B-H, B-H-B and B-B bonds.

In Group-14 elements, chemical properties of C differs from other elements due to i) small size ii) high electronegativity, iii) restriction of valence shell to octate and iv) high tendency to form p-p π bonds. The following are the anomalous behaviour of C is observed

- 1) The melting point of C is very high due to high C-C bond energy compared to other elements in the group.
- 2) C has highest catenation properties and form long chain hydrocarbon through C-C, C=C and C \equiv C bond formation. That happens due to small size and high C-C bond energy.
- 3) Chemical reactivity of the C is least in the group.
- 4) Strong tendency to form oxide and fluoride complexes.

In group-15, Nitrogen shows anomalous behaviour from the rest of the group elements, these are as follows

- 1) Nitrogen has no scope for valence expansion due to lack of d-orbital but other can expand their valence. Example, N forms only NCl₃ but P forms both PCl₃ and PCl₅.
- 2) Nitrogen forms very strong p π -p π bonds due to its small size.
- 3) Nitrogen does not form p-d π and d-d π bonds therefore does not form the higher valent oxo compound which gives important chemistry for P and other elements.
- 4) First element of the group N has high electronegativity, this results in strong hydrogen bonding in their compounds.

In group-16 the major differences between oxygen and other elements arises mainly due to the increasing size and decreasing electronegativity of the elements.

- 1) Oxygen differs from rest of the group in that it is more electronegative and form many ionic compounds.
- 2) H bonding is very important for oxygen compounds, but recently weak H-bonding in S compounds has been proven.
- 3) Co-ordination number cannot increase beyond 4 due to lack of suitable d orbital, but other can show up to 6.
- 4) In oxygen compounds p π -p π bonding is more important whereas for other elements mainly in sulphur compounds d π -p π becomes important.
- 5) Oxygen form strong π bonds in their compounds but π bond becomes weaker in heavier congeners.

In group-17, fluorine shows somehow different properties from rest of the elements due to its small size and high electronegativity.

- 1) The small bond dissociation energy of F₂ and small size of F⁻ ion, the fluoride compounds

have high lattice energy. The lattice energy if somehow greater than their hydration energy, therefore some fluoride compounds are least soluble in water (e.g. LiF, CaF₂).

2) Due to small size F⁻ ion become hard and almost non polarizable. Therefore in fluoride compounds only weak van der Waals force is operating as a consequence molecules are volatile and low melting (e.g. fluorocarbons).

3) Bond dissociation energy of F₂ is very low due to repulsion of non bonding electron pairs in F₂ molecule. Therefore bond energies of fluoride compounds are very high.

4) It has highest electronegativity in the periodic table. Therefore fluoride compounds are prone to strong H bonding.

5) High bond energy of any element-fluorine bonds its form compound with other elements.

In fluorine substituted compounds, acid-base properties greatly influenced compared to non substituted compounds (e.g. CF₃COOH is more acidic than CH₃COOH).

Relativistic effect:

In heavier elements ($Z > 80$), relativistic variation of the mass of the electron becomes so prominent it causes an effective contraction in spatial distribution of the orbitals. This phenomenon is called relativistic effect.

According to Bohr model, the radial velocity v of an electron in an orbit of principal quantum number n is given by $v = \frac{Ze^2}{2\epsilon_0nh}$. For known values of ϵ_0 , h and e , the velocity of 1s electron in H-atom ($Z = 1$, $n = 1$) will be $2.19 \times 10^6 \text{ m s}^{-1} = 0.0073c$. But, when $Z = 80$ (Hg), the velocity of 1s electron will be $0.058c$. According to the relativistic relation $m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$.

The mass of electron now becomes nearly $1.2m_0$ that means the mass of 1s electron in Hg increases about 20% relative to rest mass.

According to Bohr model, $r = \frac{Ze^2}{4\pi\epsilon_0mv^2}$, so radius of the orbit (r) will shrink, that is more closer to the nucleus.

Since, the velocity of an electron is inversely proportional to n , the relativistic effect will be most pronounced for electrons closer to the nucleus. According to wave mechanical model, this implies that the relativistic effect will be most pronounced for s-orbitals which penetrate most into inner electron core.

The relativistic effect becomes prominent in the sixth period, particularly on the 6s electrons. The contracted 6s orbital is lowered in energy and becomes largely separated from the 6p orbital. Properties of gold, mercury and last elements of p-block are largely influenced by the relativistic effect.

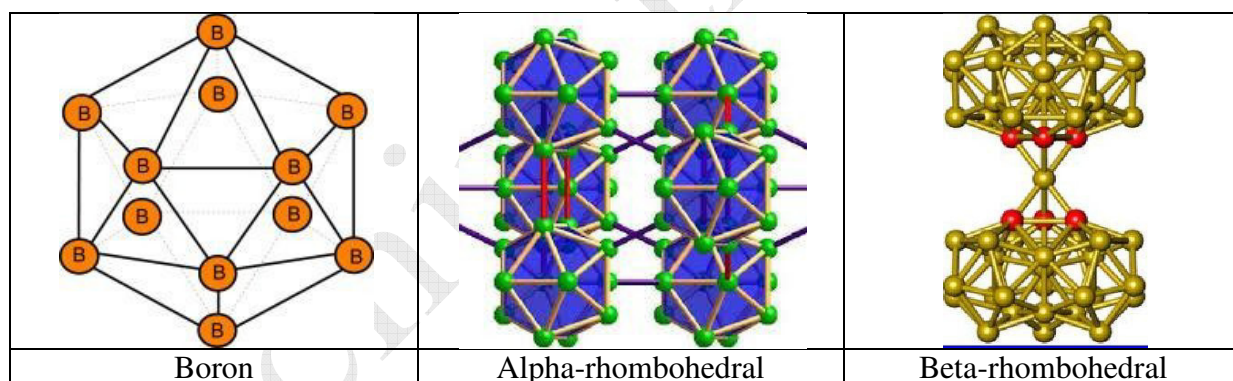
Allotropy:

Many elements occur in more than one form, which have same chemical properties but differ in physical properties is known as allotropes.

Summary of allotropes of Group 13 to Group 16

Group 13

Elemental boron has several allotropic structures. The Well known crystalline forms are α -rhombohedral, β -rhombohedral, α -tetragonal, β -tetragonal γ -boron and cubic boron etc. Due to insufficient valence electron allotropic forms of boron are complex in structure. Generally, all forms contain icosahedral units with boron atoms at all 12 corners. (An icosahedron consists with 12 corner and 20 faces). In these units 12 boron atoms form a regular shape, and each B atoms is bonded to five equivalent neighbours at a distance of 1.77 Å. The difference between the allotropic forms arises in the way the icosahedra are bonded together. The simplest form is α -rhombohedral boron. In this form, half the atoms are bonded to one atom in another icosahedron at a distance 1.71 Å and half the atoms are bonded to atoms in two different icosahedra at a distance of 2.03 Å. Only 37% of space is occupied by the atoms. The other allotropes have even more complicated structure.



Group-14

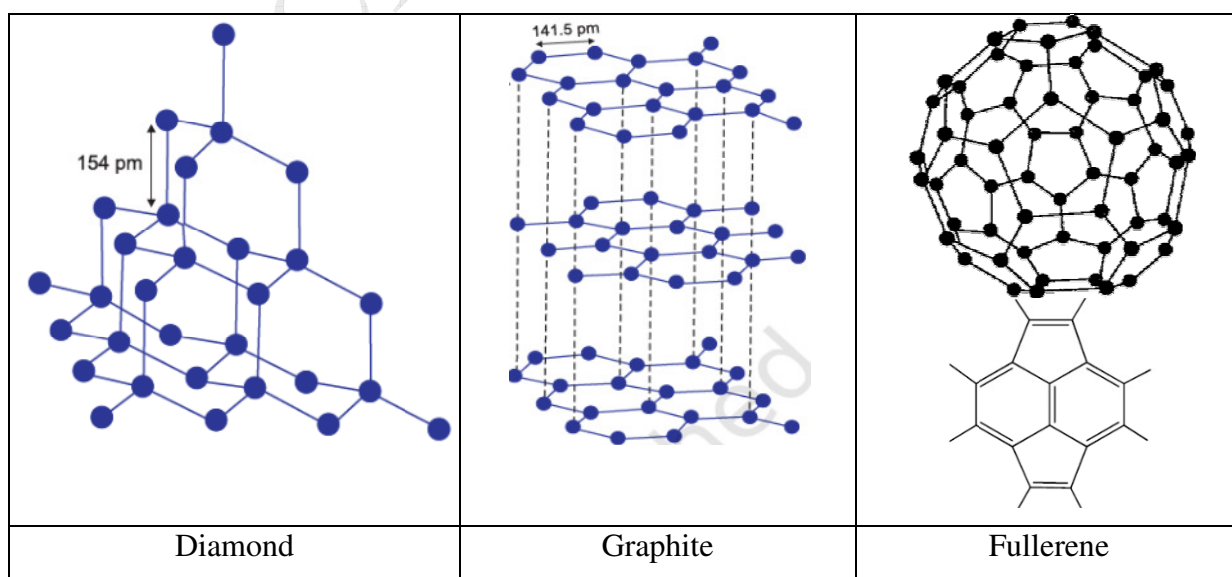
Carbon has two types of allotropic form, crystalline and amorphous. Crystalline allotropes are diamond, graphite and fullerene (C₆₀).

In diamond each carbon atom undergoes sp³ hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C–C bond length is 154 pm. The structure extends in space and produces a rigid three dimensional infinite network of carbon atoms. In this structure directional covalent bonds are present throughout the lattice.

It is very difficult to break extended covalent bonding and, therefore, diamond is one of the hardest substance. Since each C atom linked with another four C atom, there is no free labile electron in the crystal to conduct electricity. Therefore, diamond is insulator.

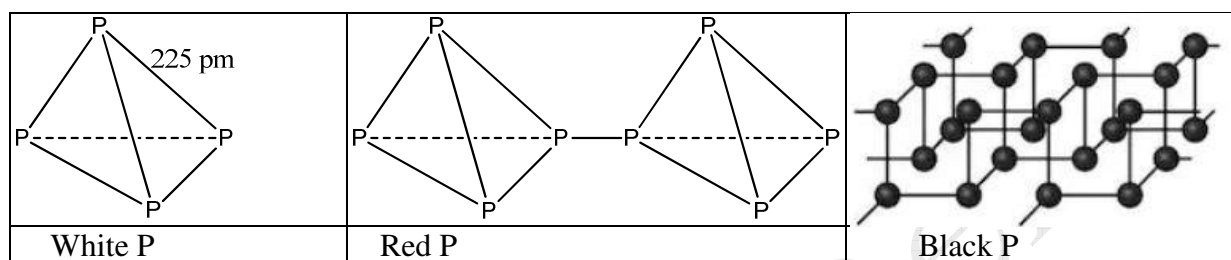
The thermodynamically more stable form of C is graphite, which has a layer structure. Layers are held by van der Waals forces and the layers are separated by 335 pm. Each layer has shared planar hexagons based on sp^2 carbon atoms. C—C bond length within the layer is 141.5 pm. Three valence electrons of C are engaged to form sigma bonds with three neighbouring carbon atoms whereas fourth electron present in p orbital perpendicular to the hexagonal plane. These p orbitals generate a delocalized band of π molecular orbitals which extend over the whole layer. Therefore graphite conducts electricity. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature.

Fullerene is another stable allotrope of carbon and has formula C_{60} but other C_{70} , C_{76} , C_{78} are also known. C_{60} was first prepared in 1985 by laser vaporization of graphite ($\sim 10,000^\circ\text{C}$) followed by sweeping of carbon atoms by a blast of high pressure helium gas and rapid cooling in vacuum. They are composed of sigma bonded hexagonal and pentagonal ring of the cage are based on sp^2 hybridized carbon atom. The remaining electron at each carbon is delocalized into a π system perpendicular to the surface of the spherical shell that imparts some aromatic character to the whole molecule. A fullerene must have exactly 12 five membered rings but number of six membered rings can vary widely ($\frac{1}{2}n-10$). C_{60} has 12 five membered and 20 six membered rings. In C_{60} each carbon is at the juncture of two six membered and one five membered ring. The six membered rings are contains three double bonds. There are two geometrically distinct C-C bonds – those at the edge shared between two fused hexagons, bond length is 139.1 ± 1.8 pm and another those at an edge between a pentagon and a hexagon are longer having length 145.5 ± 1.2 pm.



Group-15

Phosphorus has several allotropes like white phosphorus, red phosphorus and black phosphorus. White phosphorus contains the symmetrical tetrahedral P_4 unit with P-P distance 2.21 \AA and inter bond angle 60° . Red phosphorus has polymeric structure with linked P_4 tetrahedral. Black P has orthorhombic forms which consist of double layer lattice in which each P atom is bonded to three others at 2.23 \AA and bond angle are 100° .



Group-16

Oxygen has two allotropic forms, dioxygen (O_2) and ozone (O_3). O_2 is more stable than O_3 . O_3 is bent with O-O-O angle 117° and equal O-O distance 1.28 \AA .

Sulphur has several allotropic forms. Solid S contains either i) cyclic species or ii) chains species. **Cyclic species:** The most stable form of S is orthorhombic sulphur (S_α) which contain S_8 ring in crown conformation. Another form is monoclinic sulphur (S_β) which also contain S_8 rings but in a different packing. Third one is γ -monoclinic sulphur. **Chain species:** These are collectively called catena sulphur (S_∞). Examples are amorphous sulfur, Insoluble sulfur, Fibrous sulfur.

Catenation:

The ability of an element to form compounds with element-element bonds is described as catenation. The catenating abilities follow the order –

In Group 13, $B > Al > Ga > In > Tl$

In Group 14, $C > Si = Ge > Sn = Pb$

In Group 15, $N < P > As > Sb > Bi$

In Group 16, $O < S > Se > Te > Po$

Down the group size of the element increases so element-element bond strength is decreases and has less tendency to show catenation. In case of nitrogen and oxygen, there is strong $N \equiv N$ and $O = O$ bond is formed.

Hydrides and their classification as ionic, covalent and interstitial

Types of Hydrides: Hydrides are mainly divided into three major types or groups. The categories are decided based on what elements the hydrogen forms bonds with or simply on the basis of chemical bonding. The three types of hydrides are ionic, covalent, and metallic hydrides. We will learn about them in detail below.

Ionic Hydrides: They are formed when hydrogen molecule reacts with highly electropositive s-block elements (Alkali Metals and Alkaline Earth Metals). In solid-state, the ionic hydrides are crystalline, non-conducting and non-volatile.

Covalent Hydrides: Covalent hydrides are formed when hydrogen reacts with other similar electronegative elements like Si, C, etc. The most common examples are CH₄ and NH₃. In general, compounds that are formed when hydrogen is reacted with non-metals are called covalent hydrides. The compounds share a covalent bond and are either volatile or non-volatile compounds. Covalent hydrides are also either liquids or gases.

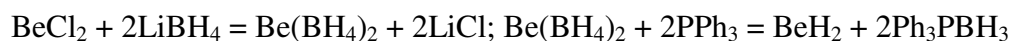
Metallic Hydrides: A hydrogen compound that forms a bond with another metal element is classified as a metal hydride. The bond is mostly covalent type but sometimes the hydrides are formed with ionic bonds. These are usually formed by transition metals and are mostly non-stoichiometric, hard, high melting and boiling points.

Li	Be	← Multicentre bonding →										B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
Ionic Hydride		Metallic hydride			Poorly Characterized						Covalent Hydride						

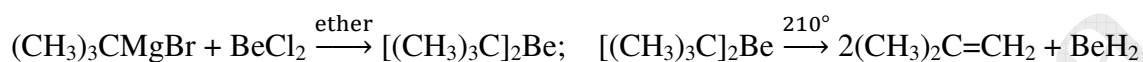
Study of the following compounds with emphasis on structure, bonding, preparation, properties and uses

Beryllium hydride

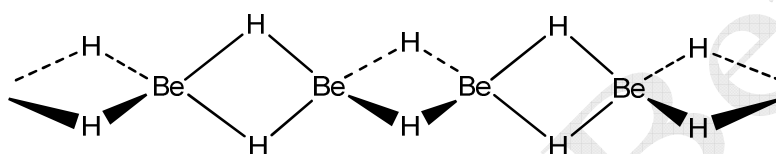
Preparation: i) Pure BeH_2 can be prepared by reducing BeCl_2 with lithium borohydride (LiBH_4) to give BeB_2H_8 , then it heated in a sealed tube with triphenylphosphine (PPh_3).



ii) From pyrolysis of di-tert-butylberyllium.



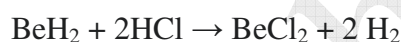
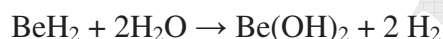
Structure: Beryllium hydride is covalent and polymeric and remains as $(\text{BeH}_2)_n$.



Bonding: Be is bonded to four H atoms. Be has two valence electrons and each H has one electron. Therefore, Be has insufficient electrons to make normal two centre two electrons covalent bond with four H atoms. That is why Be makes three centre two electrons ($3c-2e$) covalent bond to solve the problem. Therefore, each Be atom bonded with four H atoms with $3c-2e$ bridge bond (which also called a $3c-2e$ banana bond).

Reactions:

BeH_2 reacts with diborane to form the volatile beryllium borohydride, $\text{Be}(\text{BH}_4)_2$

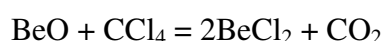
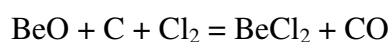


Uses: Beryllium hydride of high bulk density, suitable for use as a component of high-energy fuels, is prepared by the pyrolysis, in solution in an inert solvent, of a ditertiary-alkyl beryllium.

Beryllium halides

Be forms BeX_2 type halides where $X = \text{F}, \text{Cl}, \text{Br}$ and I . Beryllium halides are covalent, hygroscopic, do not conduct electricity and fume in air due to hydrolysis. Anhydrous halides cannot be obtained from materials made in aq. solution because hydrated ion $[\text{Be}(\text{H}_2\text{O})_4]\text{X}_2$ converted to oxide of Be.

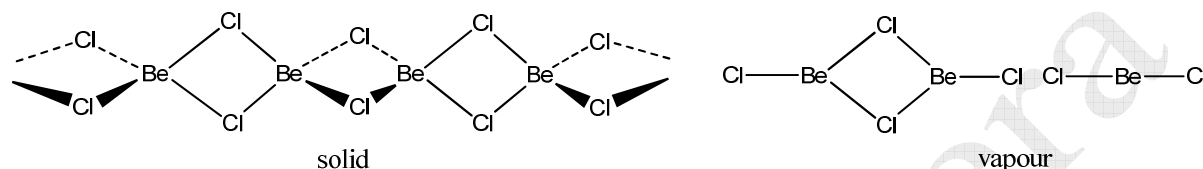
Preparation: Reaction of halogen on a mixture of the metal oxide and carbon at $600-800^\circ\text{C}$ makes the corresponding halides.



Structure: BeF_2 is a glassy solid containing randomly oriented chain like $\dots\text{F}_2\text{BeF}_2\text{Be}\dots$

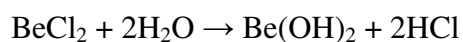
Each Be is coordinated by four F atom making bridge bond similar to BeH_2 .

BeCl_2 has a polymeric structure at solid state making Cl bridging. Be atoms are sp^3 hybridized with bridging Cl atoms. The Cl-Be-Cl bond angle is 109° and increase the bond length of Be-Be around 263 pm and hence minimizes the repulsion between Be atoms. In the gaseous state BeCl_2 form a mixture of dimer and monomer. In dimer Be is sp^2 hybridized whereas in monomer it is sp hybridized.



BeBr_2 and BeI_2 are similar to the chloride but with lower stability.

Properties: Beryllium chloride is stable in dry air. Beryllium chloride is a Lewis acid and has been used as a catalyst in some organic reactions. It hydrolyzes, evolving hydrogen chloride:



It forms a tetrahydrate, $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ ($[\text{Be}(\text{H}_2\text{O})_4]\text{Cl}_2$). BeCl_2 is also soluble in oxygenated solvents such as ethers.

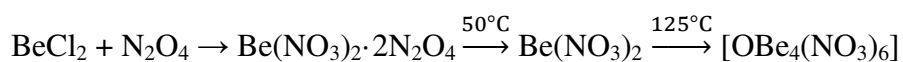
Uses: Beryllium chloride is used as a raw material for the electrolysis of beryllium, and as a catalyst for Friedel-Crafts reactions.

Basic beryllium nitrate and acetate:

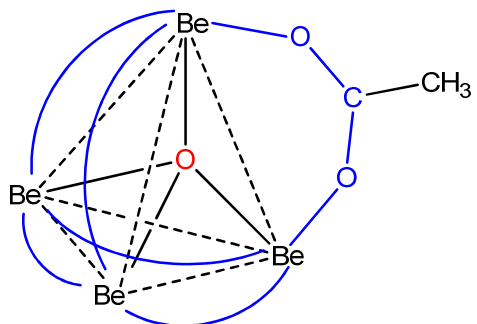
Basic beryllium nitrate:

Basic beryllium nitrate is covalent and has an unusual structure as shown in the figure below. In which four Be atoms located at the corner of the tetrahedron with six NO_3^- groups along the six edges of the tetrahedron and a oxygen (basic) at the centre. The chemical formula is $[\text{Be}_4\text{O}(\text{NO}_3)_6]$. Be form similar structure with formula $[\text{Be}_4\text{O}(\text{R}_6)]$, where $\text{R} = \text{NO}_3^-, \text{HCOO}^-, \text{CH}_3\text{COO}^-, \text{C}_2\text{H}_5\text{COO}^-$ etc.

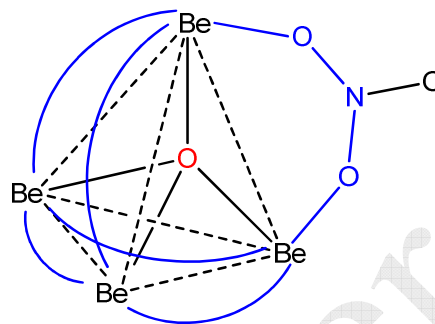
Synthesis: Nitrates of the metals can be prepared in solution and can be crystallized as hydrated salts by the reaction of HNO_3 with carbonates, oxides or hydroxides. Anhydrous beryllium nitrate can be prepared by dissolving BeCl_2 in liquid dinitrogen tetroxide and ethyl acetate. When heated to 50°C this gives $\text{Be}(\text{NO}_3)_2$, which decomposes suddenly at 125°C into N_2O_4 and $[\text{OBe}_4(\text{NO}_3)_6]$.



Basic beryllium acetate: Basic beryllium acetate is formed when $\text{Be}(\text{OH})_2$ is evaporated with acetic acid. The structure is similar to basic beryllium nitrate. It is a covalent molecule and soluble in organic solvents. It has low melting point ($285\text{ }^\circ\text{C}$) and boiling point ($330\text{ }^\circ\text{C}$).



Basic beryllium acetate



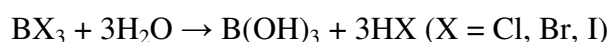
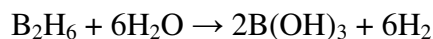
Basic beryllium nitrate

Boric acid

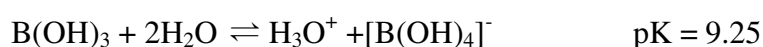
Preparation: i) Boric acid may be prepared by reacting borax (sodium tetraborate decahydrate) with a mineral acid, such as hydrochloric acid:



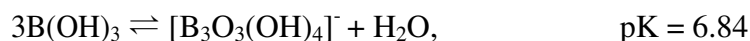
ii) It is also formed as a byproduct of hydrolysis of boron trihalides and diborane:



Properties: i) Orthoboric acid H_3BO_3 is soluble in water and behaves as a weak acid. It does not donate protons like other acids but rather it accepts OH^- . It is therefore a Lewis acid and may be written as $\text{B}(\text{OH})_3$.



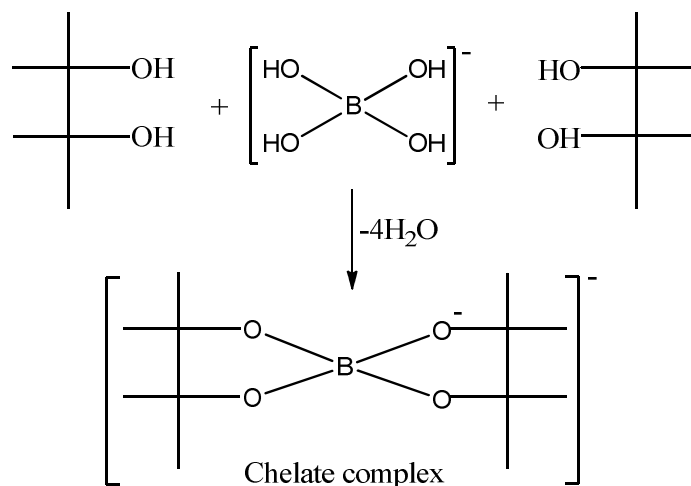
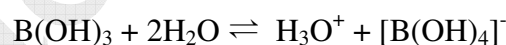
ii) Polymeric metaborate species are formed at higher concentration ‘



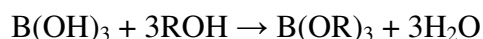
iii) Boric acid when heated above 170°C , it dehydrates, forming metaboric acid (HBO_2):



iv) Boric acid is a weak acid and hence cannot be titrated against strong base NaOH using phenolphthalein indicator. During titration no sharp end point is obtained. But in presence of glycerol, mannitol or sugar (Cis-diol) it behaves as strong acid. Because H_3BO_3 first reacts with water to form $[\text{B}(\text{OH})_4]^-$ and liberate H^+ which is a reversible reaction. Now glycerol is a complexing agent form a stable chelate complex with $[\text{B}(\text{OH})_4]^-$ ion, as a result rate of formation of H^+ will increase and H_3BO_3 becomes a strong acid. Therefore, H_3BO_3 can be titrated with NaOH in presence of phenolphthalein indicator.

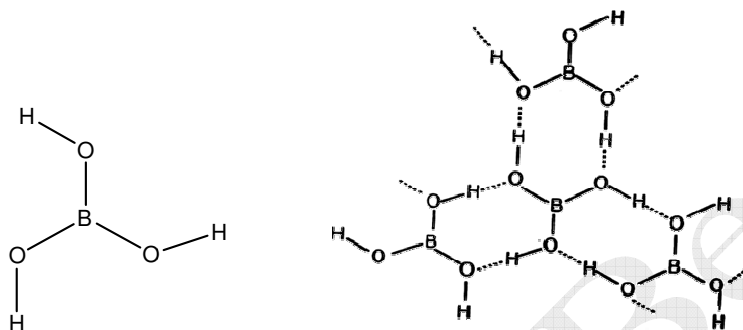


v) Boric acid reacts with alcohols to form borate esters, $B(OR)_3$ where R is alkyl or aryl. A dehydrating agent, such as concentrated sulfuric acid is typically added:



A variety of salts are also known, involving the planar trigonal BO_3^{3-} borate anion.

Structure: White crystal of boric acid contains $B(OH)_3$ units linked by H-bonds in infinite layers of nearly hexagonal symmetry.



Uses: i) Boric acid can be used as an antiseptic for minor burns or cuts.

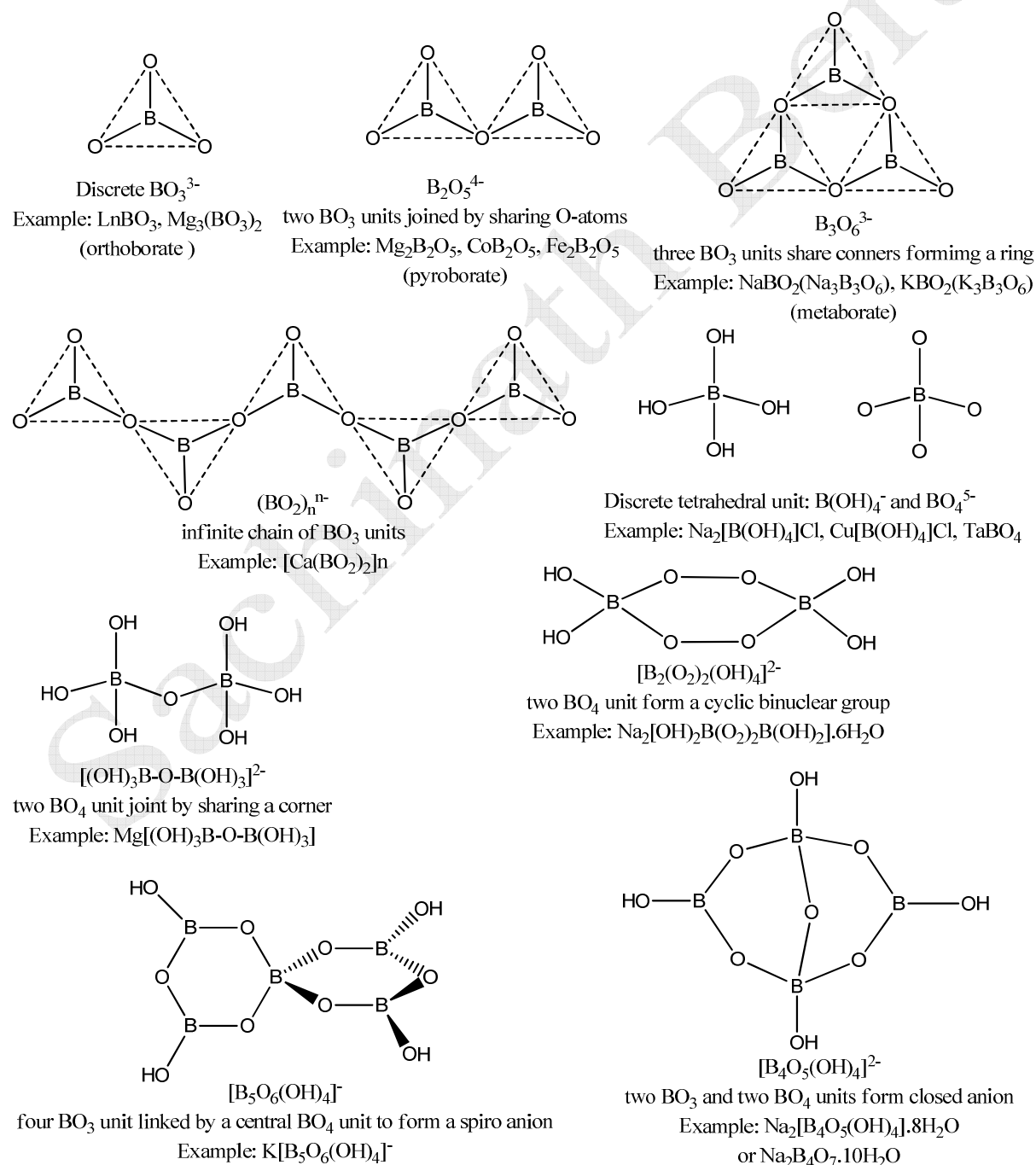
ii) Boric acid also used as an insecticide to control of cockroaches, termites.

iii) The solution containing boric acid and borax used for fire retarding agent of wood by impregnation.

Borates: Borates are boron-oxygen compounds which forms boron oxyanions. Fusion of boric acid with metal oxides produces the anhydrous borates. Crystallization from aqueous solution produces the hydrate form. The structures of borates are based on triangular BO_3 units, tetrahedral BO_4 units or combination of both. Polynuclear anions are formed by sharing of O-atoms. The overall charge of a borate will be total number of terminal O-atoms and tetrahedral B-atoms, each contributing one unit -ve charge.

The B-O bond lengths in borates (BO_3^{3-}) is 137 pm, slightly shorter than the B-O bond length (148 pm) in BO_4^{4-} . This is because of p-p π -bonding in BO_3^{3-} .

Different types of borates:



Borax:

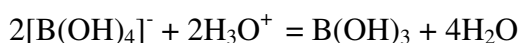
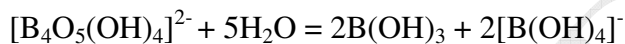
Preparation: It is prepared by boiling mineral colemanite with sodium carbonate solution.



The product solution containing NaBO_2 is again converted to borax by passing CO_2 .



Use: Borax is used to manufacture of optical and hard glasses and enamels. It is also used in giving glaze to pottery, stiffening candle-wicks and in laundering. It is a useful primary standard for titrating against acids. One mole borax reacts with two moles of acids. This is because, on hydration borax gives two moles $[\text{B}(\text{OH})_4]^-$ and two moles of $\text{B}(\text{OH})_3$. Only $[\text{B}(\text{OH})_4]^-$ can react with acids.



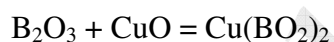
The overall reaction becomes



One of the reaction product boric acid is itself a weak acid. Therefore Methyl orange indicator is normally used as it changes colour in the pH range 3.1 – 4.4.

Borax bead test:

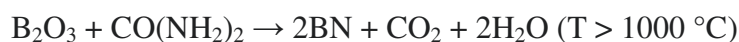
Fusion of borax with metal oxide forms metal borates having characteristic colours.



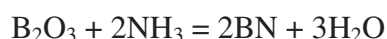
These are green at hot and blue at cold condition.

Boron nitride:

Preparation: Boron nitride is prepared by the reacting boron trioxide (B_2O_3) or boric acid (H_3BO_3) with ammonia (NH_3) or urea ($CO(NH_2)_2$) in a nitrogen atmosphere.

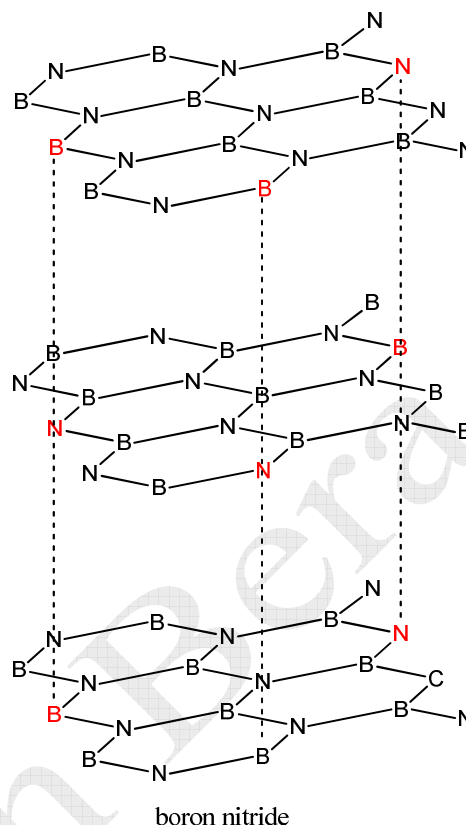
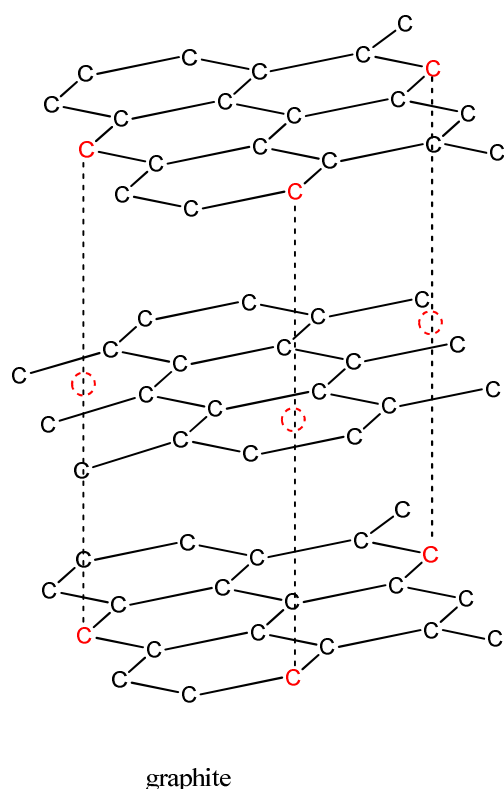


In small scale it may be prepared by fusing borax with ammonium chloride.



Structure: Boron nitride is a white slippery solid. Boron nitride has layer structure like graphite. In each layer alternate B and N form planar hexagons. The layers are stacked over one another so that the N atom of one layer is directly over the B atom of another layer. The distance between two successive layer is 333 pm.

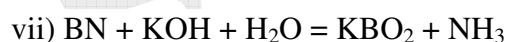
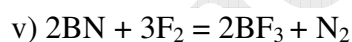
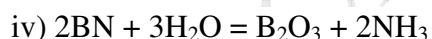
Bonding: The planner hexagon rings are formed by the alternate B and N atoms. One B atom and one N atom together have total 8 electrons isoelectronic with C-C of graphite. Each B and N atoms are sp^2 hybridized. The B-N bond distance is 145 pm, lesser than the sum of the covalent radii of B and N ($88 + 70 = 158$ pm), indicating the substantial π -bonding in the layer. This is actually N to B π delocalization involving 2p orbital of both atom. However, the B-N bond is more polar than C-C bond, leading to different reactivities. In graphite the C-C bond length is 142 pm close to B-N bond length. The distance between the successive layers in BN are 333 pm, very close to the layers distance in graphite (335 pm). Therefore boron nitride is sometime called 'inorganic graphite'.



Properties: i) The partly ionic nature of BN layers reduces covalency and electrical conductivity, whereas the interlayer interaction increases resulting higher hardness of BN relative to graphite.

ii) The electron-delocalization is reduced in hexagonal BN which indicates its colourless appearance and a large band gap.

iii) Boron nitride is insoluble in the usual acids, but is soluble in alkaline molten salts and nitrides, such as LiOH, KOH, NaOH-Na₂CO₃, NaNO₃, Li₃N, Mg₃N₂.



Uses: i) It is used as lubricant both in high and low temperature. It is used in cosmetics, paints and dental cements.

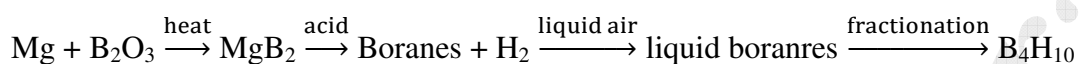
ii) Boron nitride ceramics are traditionally used as parts of high-temperature equipment.

Boron hydride:

Hydrides of the boron are generally called boron hydride or boranes. Boron hydride first prepared by Alfred Stock and latter their bonding was illustrated by W. N. Lipscomb and got his Nobel Prize in 1976. Boranes are classified as closoboranes (B_nH_{n+2}), nidoboranes (B_nH_{n+4}) and arachnoboranes (B_nH_{n+6}).

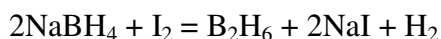
Diborane:

General Syntheses: Reaction of magnesium boride with acids (HCl or H_3PO_4) gives mixture of boranes. Then fractional distillation gives required borane.



Laboratory synthesis of diborane (B_2H_6):

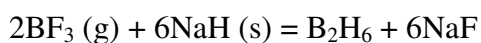
1. Action of I_2 on $NaBH_4$ in diglyme [(dimethyl ether of diethylene glycol), $(MeOCH_2CH_2)_2O$] gives diborane with 98% yield.



2. Reaction of $NaBH_4$ with 85% phosphoric acid or anhydrous sulphuric acid gives diborane.



3. Industrially, BF_3 gas is directly reduced with solid sodium hydride at $180^\circ C$



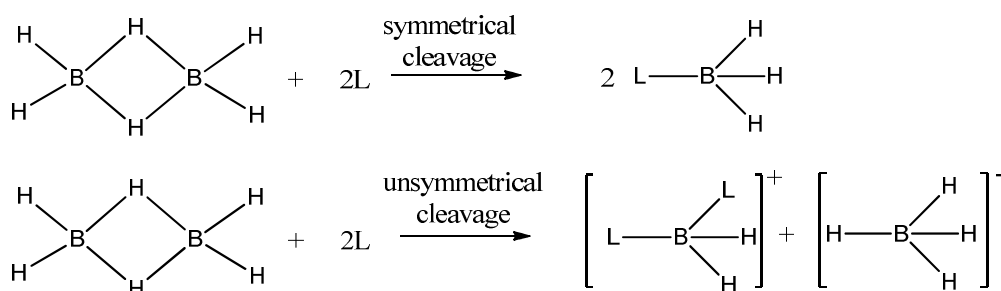
Properties:

1. Oxidation: Diborane reacts spontaneously with air to form boric oxide and hydrolyzed by water to form boric acid.

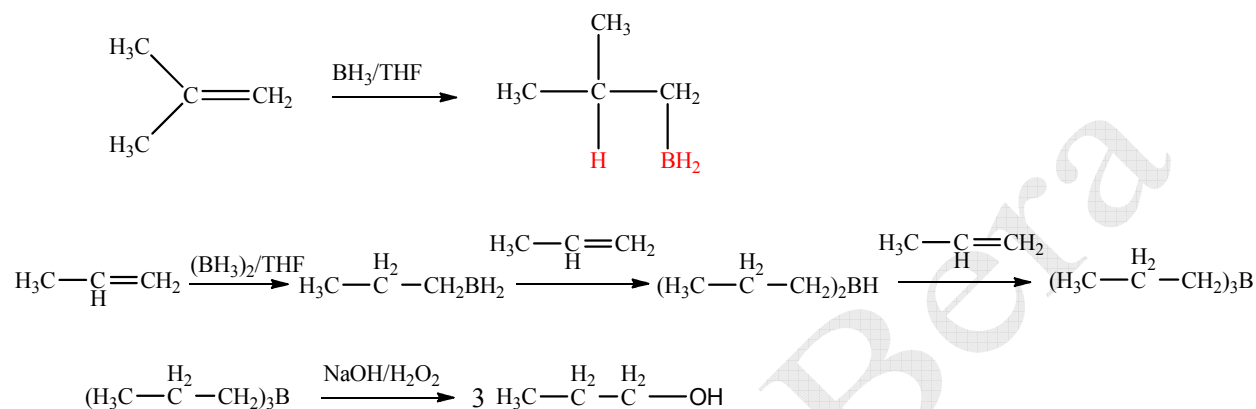


2. Lewis acidity: Borane (BH_3) is an electron deficient species and undergoes dimerization to form diborane. The hydrolysis of diborane illustrates its Lewis acid character. Diborane undergoes symmetrical and unsymmetrical cleavage of B-H-B bond depending on the nature of Lewis base. Lewis base forms stable adduct with borane and the stability of the adducts follow the sequences: $PF_3 < CO < Et_2O < Me_2O < Et_2S < Me_2S < Py < Me_2N < H^-$

If the Lewis base is sufficiently large in size then symmetrical product results, but for smaller Lewis base unsymmetrical product results.

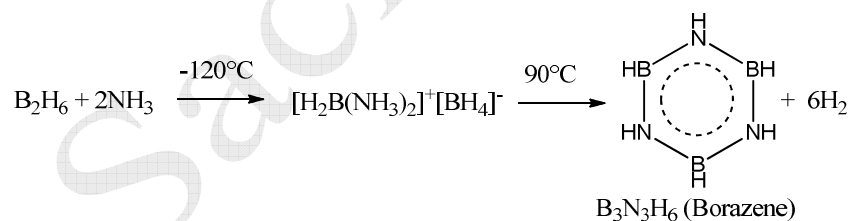
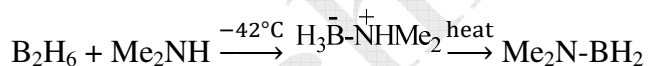
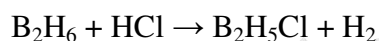
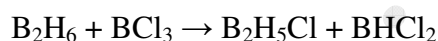
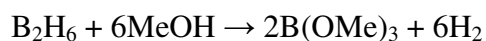


Hydroboration: In hydroboration reaction, BH_3 unit added to the alkene or alkyne in ether/THF solvent at room temperature in N_2 atmosphere. The $\text{BH}_3(\text{BH}_2\text{-H})$ unit added to the alkene or alkyne in the anti-Markownikov way i.e. BH_2 unit added to the alkene carbon containing higher number of H^\ominus atom whereas H added to the carbon containing lesser number of H -atom.

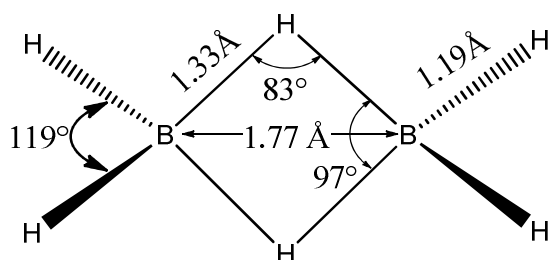


Reducing character:

Diborane is an electrophilic reagent can be reduced with the reaction of electron rich species. It is preferentially attack a molecule at a position of high electron density for example O in $\text{C}=\text{O}$ and N in $\text{C}\equiv\text{N}$ or $\text{C}=\text{N}$.



Structure of Diborane:

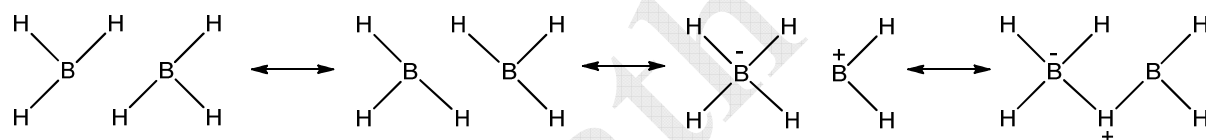


Electron diffraction and other physical measurements established that in diborane the two B atoms are joined by two B-H-B bridges in a plane nearly perpendicular to the plane of terminal B-H bonds. The bridge B-H bond lengths are to some extent greater (133 pm) than the terminal B-H bond lengths (119 pm). Here the terminal B-H bonds are considered as 2c-2e, normal covalent bond whereas bridge B-H bonds are considered as 3c-2e covalent bonds. The different chemical environments were confirmed by i) Raman spectra and ii) methylation reaction.

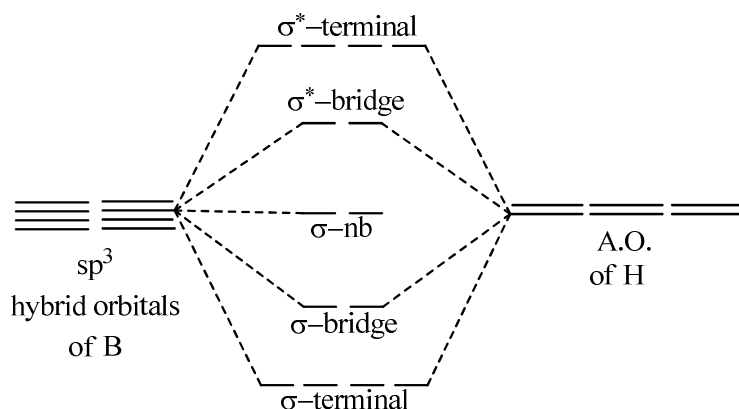
Methylation of diborane gives $\text{Me}_4\text{B}_2\text{H}_2$ and further methylation gives BMe_3 i.e. diborane broke into two equivalent fragments. This reaction indicates that four terminal H atoms replaced by -Me group but bridge H atom remain silent. Further methylation broke the molecule into BMe_3 .

Bonding:

There are 12 valence electrons in B_2H_6 , considering 2c-2e bond it is electron deficient. According to VBT it may be represented by resonance of several canonical forms.



From MOT point of view, consider four sp^3 hybrid orbital on each boron and 1s orbital on H-atoms. Two sp^3 orbital on each B-atom overlap with 1s orbital of H-atoms formed two terminal B-H bond (2c-2e). Therefore, total four terminal bond and eight electrons, four electrons from two boron and four electrons from four H-atoms, are placed in bonding molecular orbital. The remaining two hybrid orbital having 1 valence electron of each B-atom will point approximately perpendicular of BH_2 unit. Now, these orbitals forming two sets of B-H-B bridge 3c-2e bond overlapping with 1s orbital of H-atoms. Each B-H-B unit have three orbital, two from B-atoms and one 1s orbital of H-atoms forming three molecular orbital – one bonding containing two electrons, one vacant non bonding and anti bonding.



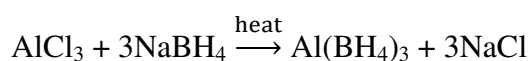
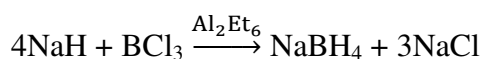
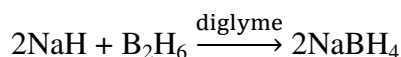
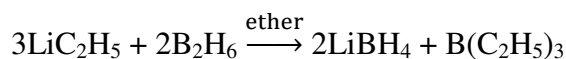
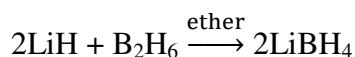
Hydrido complex and Borohydride:

The boron group elements form tetrahydrido complex MH_4^- having tetrahedral geometry. These are called as borohydride (BH_4^-), aluminohydride (AlH_4^-) etc. The thermal stability of these hydrides decreases down the group which can be explained by the ability of MH_3 to function as a Lewis acid towards H^- . Down the group the size of the element increases and effective nuclear charge decreases. Therefore, the binding affinity and M-H bond energy both decreases from boron to thallium. So, expected thermal stability order will be as follows:

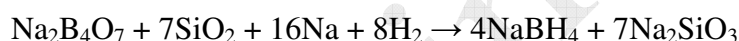


Preparation:

The borohydrides are prepared directly from diborane or boron halide and the metal hydride in a suitable solvent at room temperature.

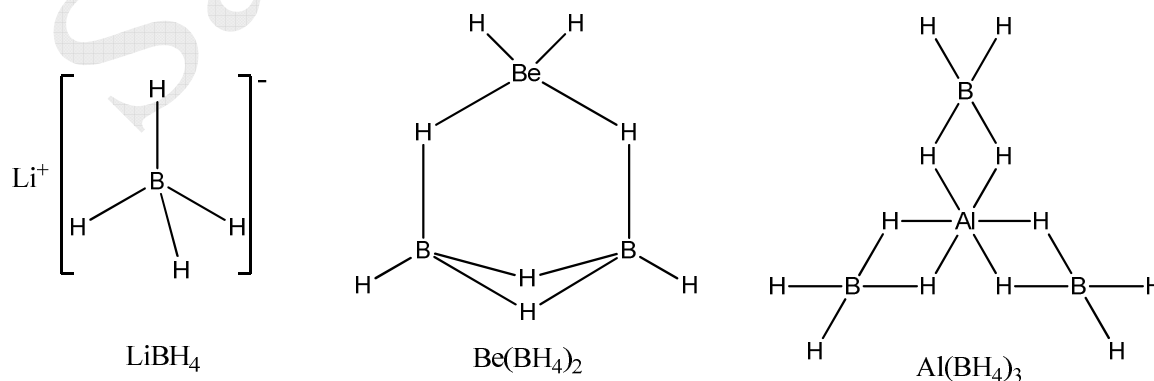


Industrially, sodium borohydride is prepared from borax and hydrogen gas at $500^\circ C$.



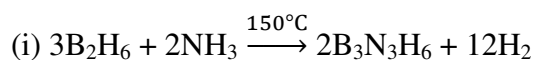
Structure:

The BH_4^- ion is tetrahedral with sp^3 hybridized boron atom. Tetrahydroborates are known for various metal ion and cations e.g. Li, Na, K, Rb, Be, Mg, Ca, Zn, Al, Ti, Zr, Hf, Th, U, Me_4N , Et_4N etc. The borohydrides of alkali metals, thorium and nitrogen base cations are nonvolatile crystalline solids. Other borohydrides are mostly covalent.

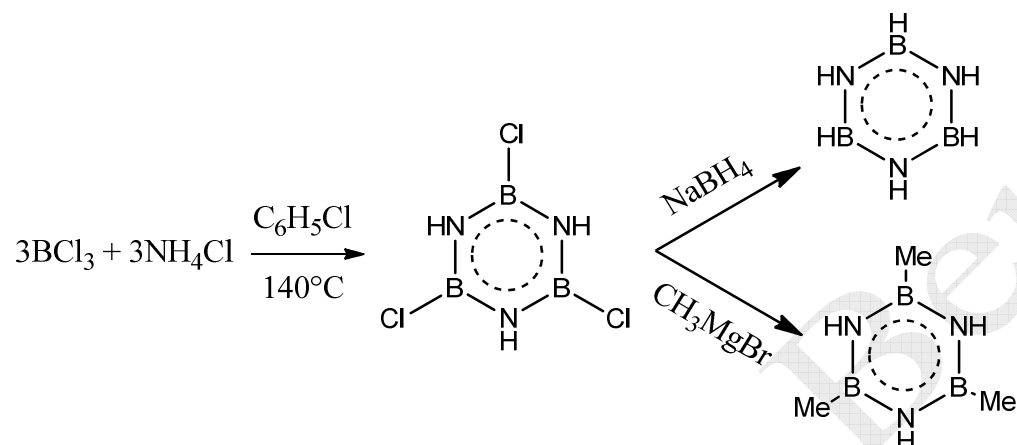


Borazine:

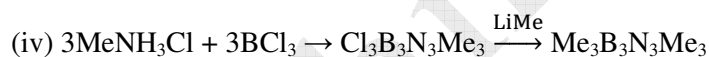
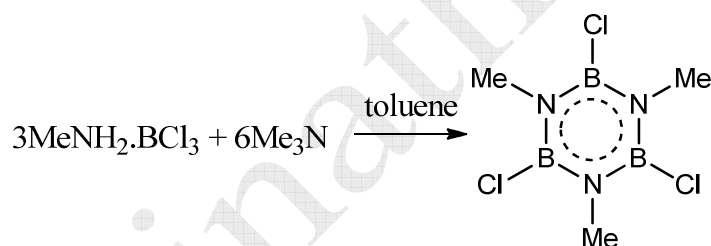
Borazine a colourless liquid having a hexagonal planar cyclic skeleton of B and N was isolated as a intermediate products of heating B_2H_6 with NH_3 .



(ii) Borazine and substituted borazines are prepared by the following way.

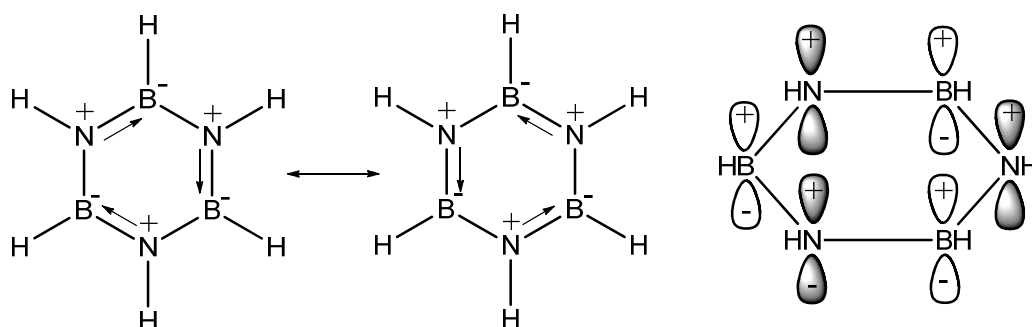


(iii) A primary ammonium chloride would yield N-alkyl substituted B-trichloro borazines.



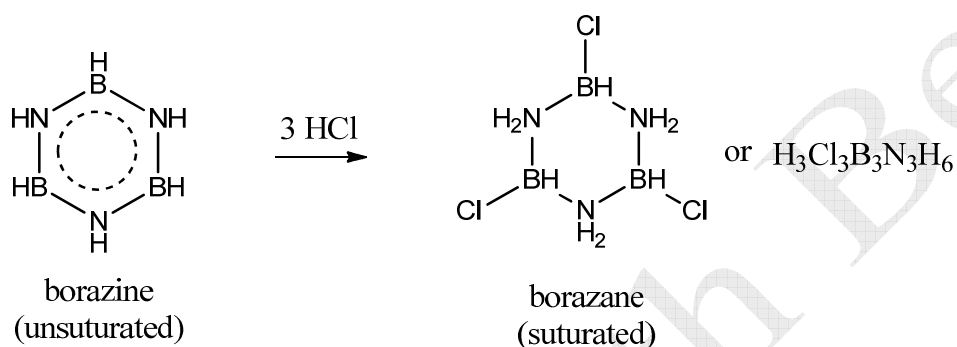
Structure and bonding:

Borazine is isoelectronic with benzene possesses a planar cyclic structure with all equal B-N distance, 144 pm. This bond length are shorter than the B-N distance in H_3B-NH_3 (156 pm) but similar to that in boron nitride (145 pm) and also C-C bond in benzene (140 pm). Thus substantial delocalization of the lone pair electron to vacant p-orbital of boron where both N and B is sp^2 hybridized. Electron delocalization can be represented by resonance among valence bond structures.



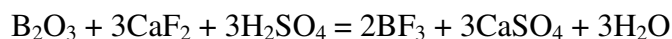
The similarity in structure and other physical properties as in M.P. ($-57 - 6^{\circ}\text{C}$), B.P. ($55 - 80^{\circ}\text{C}$), critical temperature ($252 - 288^{\circ}\text{C}$), density in liquid ($0.81 - 0.81 \text{ g cm}^{-3}$), surface tension ($31 - 31 \text{ dyne cm}^{-1}$) borazine is called inorganic benzene. But, in borazine perfect delocalization of π -electron cloud is not occur since the nitrogen π -orbitals are much lower in energy than the π -orbitals of boron because N has higher effective nuclear charge than B.

In fact, boron to nitrogen σ -electron drift is more effective than nitrogen to boron π -electron drift, leaving the nitrogen atom relatively more negative. This is exemplified by simple addition reaction with polar reagent like H_2O , MeOH , HX etc. across the B-N bond. It is observed that negative parts always attached with boron through the nucleophilic attack.

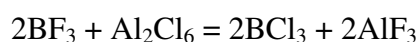
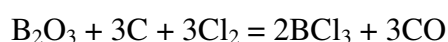


Boron halide:

All four halides of boron are known. BF_3 is prepared by heating a mixture of calcium fluoride and boric oxide with concentrated sulphuric acid. Thermal decomposition of benzene Diazonium fluoroborate produces very pure BF_3 .



BCl_3 and BBr_3 are obtained by heating B_2O_3 with Cl_2 or Br_2 in presence of coke. Halogen exchange reaction between BF_3 and $\text{Al}_2\text{Cl}_6/\text{Al}_2\text{Br}_6$ also leads to BCl_3 or BBr_3 .

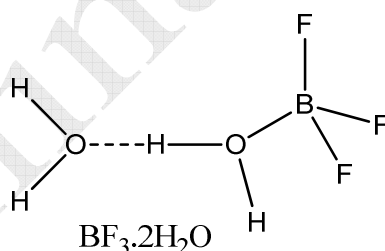
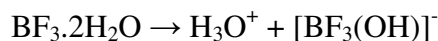


Reaction:

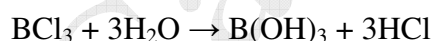
BF_3 is partially hydrolyzed by water into fluoroboric acid and boric acid with excess water.



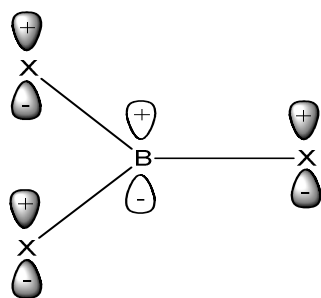
With small amount of water at low temperature BF_3 forms two adducts, $\text{BF}_3 \cdot \text{H}_2\text{O}$ and $\text{BF}_3 \cdot 2\text{H}_2\text{O}$. In 1:1 adduct the B-atom is tetrahedrally surrounded by 3F and an O-atom from H_2O . In 1:2 adduct, a second molecule of H_2O is associated through strong H-bonding. On melting, ionisation reaction takes place.



BCl_3 and BBr_3 are rapidly and completely hydrolyzed by water, BI_3 even more vigorously.

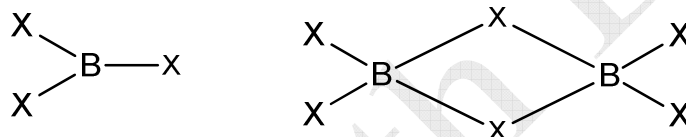


Electron deficient boron halides are expected to be good Lewis acid. They react with Lewis bases like halide ions, ethers, nitriles, amines etc. The order of Lewis acidity among the trihalides depends on the stability of such adduct, $\text{L} \rightarrow \text{BX}_3$. The trend appears as $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$. Though the trend is contrary from the electronegativity considerations but can be explained by π overlap between the vacant p-orbital of boron with filled π -orbital of halogens. This interaction is strongest in BF_3 because of best match of size and energy of the overlapping orbitals and it decreases from F to I. Therefore, the energy required for reorganization during adduct formation ($\text{BX}_3, \text{sp}^2 \rightarrow \text{L-BX}_3, \text{sp}^3$) is greatest at BF_3 and smallest at BI_3 . So, the B-atom in BF_3 is less electron deficient and the poorest acceptor.



Monomeric nature of boron trihalides:

In boron trihalides there is appreciable π -overlap between the vacant p-orbital of boron with filled π -orbital of halogens. This π -bonding has to be disrupted on forming the halogen bridged dimer. In such bridged structure, boron atom will not have any vacant orbital left for π -bonding. This makes the monomer comparatively more stable. It is also unlikely that the boron atom is too small to form the stable 4-membered ring system in such dimer. Whereas, AlX_3 are generally exist as Al_2X_6 dimer.

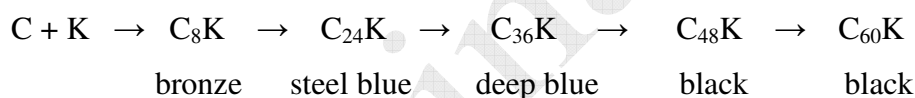


Graphitic compounds:

As the successive layers are held by weak van der Waals force at a comparatively large distance a wide variety of reactants are penetrated into graphite lattice producing two principal types of compounds.

a) Due to intercalation the interlayer separation increases (10 \AA) in new compounds but graphite sheet remain flat and retained graphite like character that is the π -electron system of graphite is delocalized with consequent retention of electrical conductivity.

- ❖ If the intercalated atoms add electrons to the π -system, the conductivity is increased.
- ❖ Such intercalation reactions are often reversible. Such compounds are also called lamellar compound of graphite.
- ❖ These types of compound are formed by insertion of various atoms particularly the alkali metal atoms, molecules or ions between the graphite layers.
- ❖ These alkali metal compounds are highly reactive. They may explode in water, and react vigorously in air.
- ❖ When graphite is heated to about $300 \text{ }^\circ\text{C}$ with vapour of alkali metal (K, Rb, Cs) it absorbs metal, forming bronze coloured compound C_8M . If C_8M is heated to $350 \text{ }^\circ\text{C}$ under reduced pressure, metal is lost and a series of intercalated compounds are formed depending on the number of layers invaded by the metal.



(The bronze colour is due to the formation of metal atom clusters at these relatively high metal concentrations, in the same way as clusters are formed in solutions of these metals in liquid ammonia.)

- ❖ Different types of intercalation compounds are formed by the reaction of graphite with Cl_2 , Br_2 , HF, halides including CdCl_2 , CuBr_2 , FeCl_3 , AlCl_3 , ClF_3 , TiF_4 , MoCl_5 , SbF_5 , UCl_6 , XeF_6 , oxides including CrO_3 , MoO_3 , SO_3 , N_2O_5 , Cl_2O_7 and sulphides like FeS_2 , PdS , V_2S_3 .

b) Compounds in which the π -bonding is destroyed and graphite becomes non-conducting. The carbon layers lose planarity and get buckled.

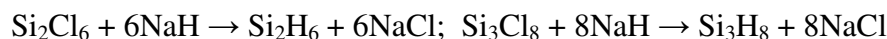
- ❖ Two principal types of compounds are known: graphite oxide and graphite fluoride.
- ❖ Graphite oxide is formed when graphite is reacting with strong oxidizing agent such as concentrated HNO_3 , HClO_4 or KMnO_4 .
- ❖ Graphite oxide is unstable, pale lemon coloured and non-stoichiometric.
- ❖ It decomposes slowly at 70°C and catches fire at 200°C , forming H_2O , CO_2 , CO and C .
- ❖ The $\text{O} : \text{C}$ ratio approaches $1 : 2$, but is often short of oxygen and frequently contains hydrogen.
- ❖ The oxide absorbs water, alcohols, acetone and variety of molecules. This may increase the interlayer spacing upto 19 \AA .
- ❖ X-ray diffraction shows a layer structure with puckered sheets made up of a hexagonal network of atoms. The C_6 units are mostly in chair conformation, but a few $\text{C}=\text{C}$ bonds remain. The oxygen forms bridging linkages $\text{C}-\text{O}-\text{C}$ and $\text{C}-\text{OH}$ groups which may undergo keto-enol tautomerism $\equiv\text{C}-\text{OH}$ to $>\text{C}=\text{O}$. The sheets are buckled because all four electrons on a C atom are now involved in σ -bonding. This destroys the delocalized system of mobile π -electrons and this explains the loss of electrical conductivity.

Graphite fluoride is formed by heating graphite in F_2 at 450°C .

- ❖ The product CF_n is nonstoichiometric and n varies 0.7 to 0.98 .
- ❖ The colour varies from black through grey to silver and white with increasing fluorine content.
- ❖ The interlayer spacing is about 8 \AA .
- ❖ Carbon atoms in the layer change to sp^3 hybridization adopting the boat or chair conformation and fluorine atoms are covalently bonded to carbon atoms.
- ❖ Destruction of the π -system makes the compound non-conducting and unreactive.

Silanes: Silicon forms saturated hydride, $\text{Si}_n\text{H}_{2n+2}$, called silanes. e.g., SiH_4 , Si_2H_6 , Si_3H_8 , Si_4H_{10} . They may exist as straight chains or branched chains containing upto eight Si atoms.

Preparation: i) Reduction of Si-Cl bonds with LiAlH_4 , LiH or NaH in ether solution at low temperatures. $\text{SiCl}_4 + \text{LiAlH}_4 \rightarrow \text{SiH}_4 + \text{LiCl} + \text{AlCl}_3$

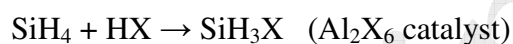
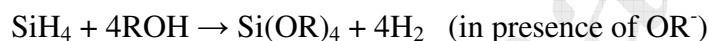
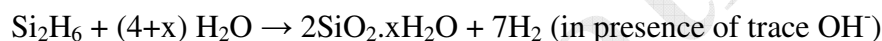
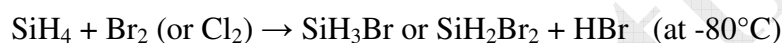
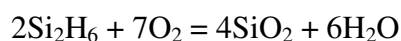


ii) Reaction of silicon with anhydrous HX or RX to form chlorosilanes which form silane on heating. $\text{Si} + 3\text{HCl} \rightarrow \text{SiHCl}_3$; $4\text{SiHCl}_3 \rightarrow \text{SiH}_4 + 3\text{SiCl}_4$

Properties:

Silanes are all colourless gases. Silanes spontaneously ignite or explode in air. Thermal stability of the silanes decreases with increasing chain length. The silanes violently react with Cl_2 and hydrolyzed in contact with traces of aqueous alkali, even that which dissolves from the glass apparatus. Pure silanes do not react with dilute acids or pure water in silica apparatus. Silanes are also good reducing agents.

Reactions:



The reactions are consistent with hydridic nature of hydrogen in Si-H bond. An Si-H bond can add across $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ bonds in alkenes or alkynes at 300°C or under UV radiation or in presence of platinum complex as catalyst. The reaction is called hydrosilylation similar to hydroboration.



Difference between silanes and alkanes:

The difference in reactivity between silanes and alkanes may be due to the factors:

i) Larger size of the Si atom facilitates nucleophilic attack at Si.

ii) Polarity of the Si-H bond is opposite to that of the C-H bond. $\overset{\delta-}{\text{C}}-\overset{\delta+}{\text{H}} \quad \overset{\delta+}{\text{Si}}-\overset{\delta-}{\text{H}}$

iii) Si has energetically accessible vacant 3d orbitals which favours to form adduct formation through expansion of valence shell demanding lower energy of activation.

iv) Si-H bond energy (393 kJ mol^{-1}) is significantly lower than that of either C-H (435 kJ mol^{-1}) or Si-O bond (452 kJ mol^{-1}). The Si-Si bond (340 kJ mol^{-1}) is also weaker than the C-C bond (386 kJ mol^{-1}).

Oxides of nitrogen:

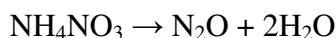
The oxides and oxoacids of nitrogen all exhibit $p\pi-p\pi$ multiple bonding between the nitrogen and oxygen atoms. This does not occur with the heavier elements in the group, and consequently nitrogen forms a numbers of compounds which have no P, As, Sb or Bi analogues. Nitrogen forms a very wide range of oxides, exhibiting all the oxidation states from +I to +V. The lower oxides are neutral, and the higher ones are acidic.

❖ High values of electronegativity, $N\equiv N$ bond energy and ionisation enthalpy make it difficult to oxidize nitrogen directly. Only NO is formed from N_2 and O_2 under electric spark. N_2O_5 may be made by dehydrating HNO_3 or by the action of FNO_2 with excess $LiNO_3$.

Formula	Nature	Structure
N_2O (dinitrogen monoxide)	Colourless gas not very reactive.	$N \equiv N - O$
NO (nitrogen monoxide)	Colourless gas and paramagnetic. Moderately reactive.	$N = O$
N_2O_3 (dinitrogen trioxide)	Blue solid. Dissociate into NO and NO_2 in gas phase.	
NO_2 (nitrogen dioxide)	Brown gas, paramagnetic, reactive.	
N_2O_4 (dinitrogen tetroxide)	Colourless liquid. Dissociate into NO_2 in gas phase.	
N_2O_5 (dinitrogen pentoxide)	Colourless solid exists as $NO_2^+NO_3^-$. Unstable in gas phase.	
NO_3, N_2O_6	Not isolated as pure. Indicated by absorption spectrum. Paramagnetic	

Dinitrogen monoxide or nitrous oxide (N₂O)

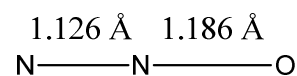
Synthesis: It is prepared by careful thermal decomposition of molten ammonium nitrate at about 280 °C. N₂O can also be made by heating a solution of NH₄NO₃ acidified with HCl.



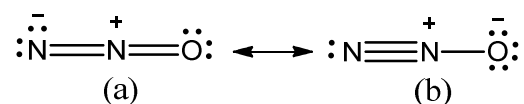
Properties: N₂O is a neutral oxide and does not form hyponitrous acid, H₂N₂O₂ with water nor hyponitrites with alkali. The reaction of molten sodamide with N₂O produces azides.



N₂O molecule has unsymmetrical linear structure having N-N-O skeleton rather than N-O-N. Bond lengths are short and bond orders have been calculated as N-N (2.73) and N-O (1.61).



The Lewis dot structures consistent with its low dipole moment ($\mu = 0.166 \text{ D}$) are

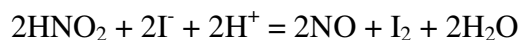
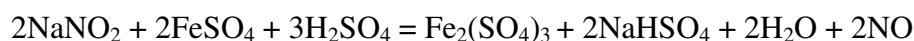


The central N-atom uses sp hybrid orbitals to form two σ -bonds N and O-atom on two sides. The two p-orbitals excluded from hybridization form two π -bonds with N and O-atoms in structure (a) and to N only in structure (b).

Use: N₂O is known as laughing gas. It has been used as an anaesthetic but has now been discontinued due to undesirable side effects. Its principal use is as aerosol propellants and as aerating agent for whipping cream because it has no taste and is non toxic.

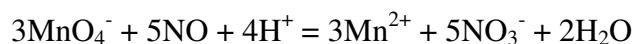
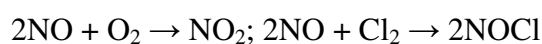
Nitrogen monoxide or nitric oxide (NO):

Preparation: It is formed in several reactions involving nitrous and nitric acids or their salts.



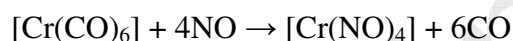
Properties:

NO is a neutral oxide and is not an acid anhydride. It is colourless paramagnetic gas as it has 11 electrons so it must contain an odd electron. It is diamagnetic in liquid and solid states because the molecule dimerizes. It reacts instantly with O_2 to give NO_2 and with halogens it gives nitrosyl halides, NOX . Strong oxidizing agents like KMnO_4 or I_2 oxidize it to HNO_3 .



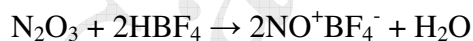
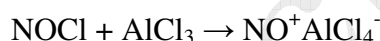
NO readily forms coordination complexes with transition metal ions. These complexes are called nitrosyls. A cold solution of iron(II) sulphate absorbs NO and turns brown due to formation of complex, $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$ which is responsible for brown ring test for nitrates. Another example is sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}].2\text{H}_2\text{O}$.

NO acts as a three electron donor, in contrast to most ligands which donate two electrons.



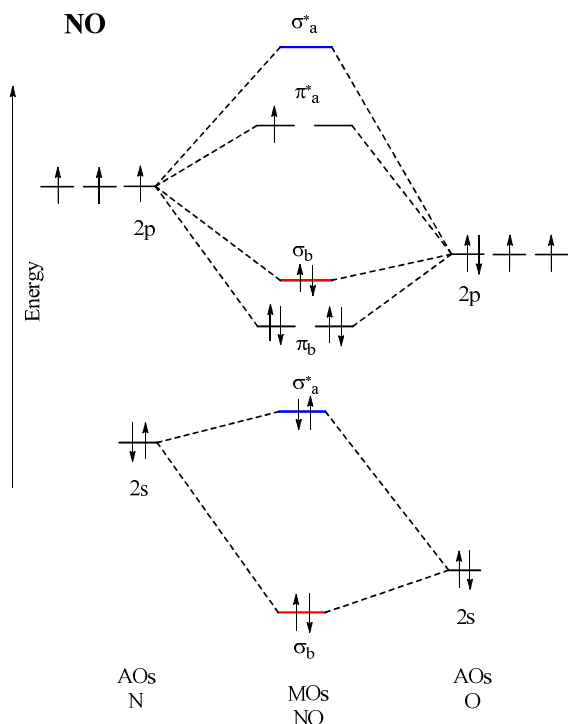
Salts of nitrosonium ion:

Removal of odd electron from π^* orbital requires 900 kJ mol^{-1} . The NO^+ ion is readily formed in several reactions in anhydrous conditions.

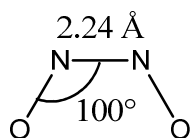


Structure:

The NO molecule is best described by M.O. approach. The M.O. description is similar to N_2 or CO with an additional electron in the antibonding level, $\text{KK}1\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 2\pi_g^1$. The bond order is 2.5. The bond length is 1.15 \AA , which is intermediate between double bond and triple bond. If odd electron removed NO^+ is formed and bond length is decreases to 1.06 \AA . The N-O stretching frequency increases from 1877 cm^{-1} in NO to about 2320 cm^{-1} in NO^+ .



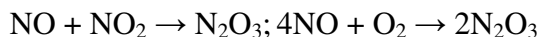
Though gaseous NO shows reluctance of dimerization, partial dimerization occurs in liquid state. Weak association in solid is revealed by the relatively long N-N distance and the low heat of dimerization, 15.5 kJ mol^{-1} . The notable reluctance of gaseous NO to dimerize in comparison to NO_2 shows that the odd electron in the π^* M.O. of NO has greater delocalization. Also, due to dimerization of NO to $\text{O}=\text{N}-\text{N}=\text{O}$ no change of total bond order is observed. ($2 \times 2.5 = 5$)



Use: NO is important intermediate in the manufacture of nitric acid by catalytic oxidation of ammonia in Oswald process. $\text{NO}^+\text{HSO}_4^-$ was also an important intermediate of manufacture of H_2SO_4 . Apart that nitrosonium ion has extensive use in syntheses of many compounds.

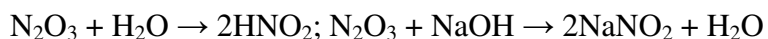
Dinitrogen trioxide (N₂O₃):

N₂O₃ can only be obtained by condensing equimolar amounts of NO and NO₂ or by reacting NO with the appropriate amount of O₂. The reaction gives a blue solid or liquid which is unstable and dissociates into NO and NO₂ at 30°C.

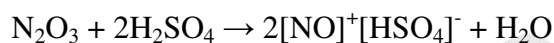
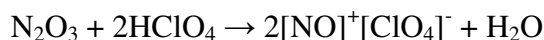


Properties:

It is an acidic oxide and the anhydride of HNO₂. It forms nitrite with reaction of alkali.

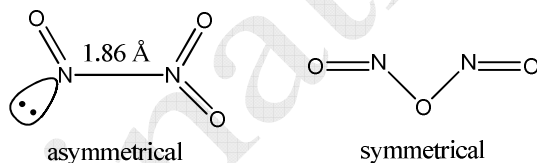


N₂O₃ reacts with concentrated acids, forming nitrosyl salts.



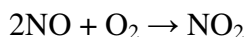
Structure:

The oxide exists in two different forms. These may be inter converted by irradiation with light of appropriate wave length. Asymmetrical form has planar structure with unusually long N-N bond length of 1.86 Å in comparison to the N-N single bond length in H₂N-NH₂, 1.47 Å. The compound is diamagnetic hence contains no unpaired electron.

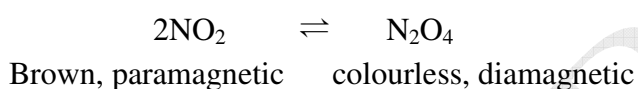


Nitrogen dioxide (NO₂) and dinitrogen tetroxide (N₂O₄):

Preparation: In small scale, it is prepared by heating heavy metal nitrates and on a large scale, oxidizing NO by O₂ in the Ostwald process for the manufacture of nitric acid.



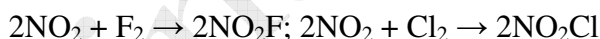
Properties: NO₂ is a red brown poisonous gas, dimerize to colourless N₂O₄. These two oxides co-exist in equilibrium at the liquid and gaseous state. Solid is entirely N₂O₄ and brown liquid contains 0.1% NO₂ while deep brown vapour contains 15% NO₂ and high temperature vapour (100 °C) contains ~ 90% NO₂.



NO₂ is acidic and is a mixed anhydride because it gives a mixture of nitric and nitrous acid with reaction of water. $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2$

On warming HNO₂ decomposes to give NO. $2\text{HNO}_2 = \text{NO}_2 + \text{NO} + \text{H}_2\text{O}$

The gases are highly reactive and oxidizing. NO₂ reacts with fluorine and chlorine, forming nitryl fluoride and nitryl chloride. It also oxidizes HCl to Cl₂, CO to CO₂ etc.

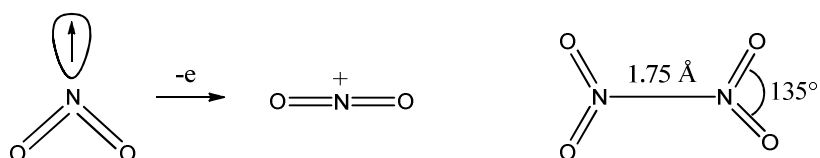


Liquid N₂O₄ is used as a non-aqueous solvent. It self ionizes as: $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}^+ + \text{NO}_3^-$

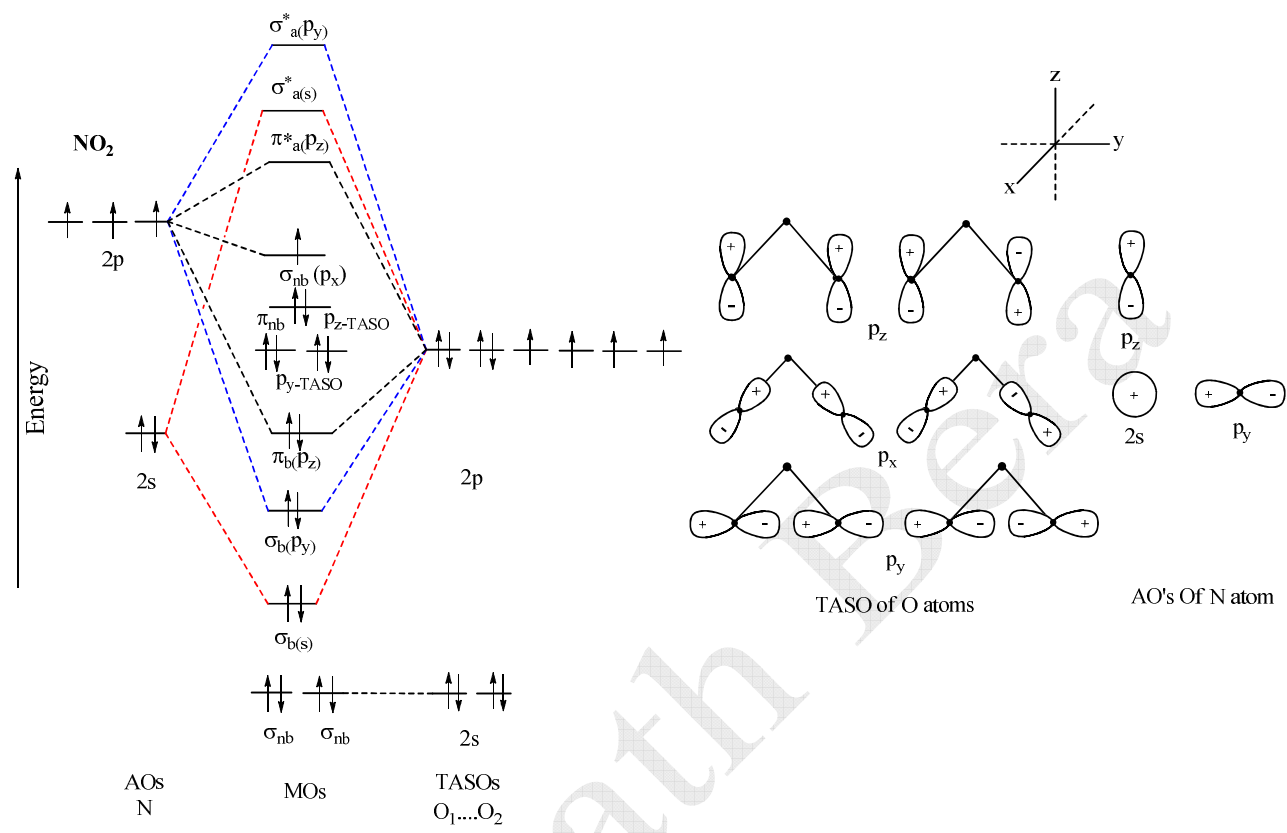
A typical acid base reaction is $\text{NOCl} + \text{NH}_4\text{NO}_3 \rightarrow \text{NH}_4\text{Cl} + \text{N}_2\text{O}_4$

Structure:

NO₂ is a radical with one unpaired electron. The molecule is angular with O-N-O angle is 134°. The central N-atom is sp² hybridized; one hybrid orbital contains the odd electron and other two make σ bond with O-atoms. The remaining unhybridized p-orbital on N combined with O-atoms to produce a delocalized π-bond extending over the skeleton. The N-O bond length is 1.20 Å, intermediate between single and double bond. It can lose its odd electron to give the nitronium ion, NO₂⁺ which is linear. N₂O₄ is a planar molecule with a long N-N bond, 1.75 Å.

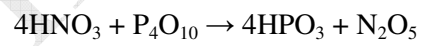


Unpaired electron appears to be more localized on the N-atoms leading to ready dimerization. It can be explain from MO diagram as shown below.



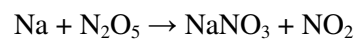
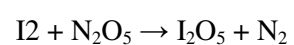
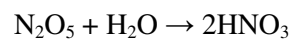
Dinitrogen Pentoxide (N₂O₅)

N₂O₅ is obtained by dehydration of concentrated nitric acid by P₄O₁₀ at low temperature.



Properties:

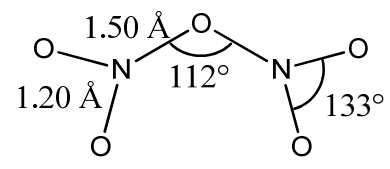
It is a colourless deliquescent solid which is highly reactive. It is a strong oxidizing agent and is light sensitive. It is anhydride of HNO₃.



With H₂O₂, N₂O₅ produces nitric and per-nitric acid.

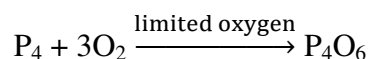


In solid state, it exists as NO₂⁺NO₃⁻ called as nitronium nitrate. In solution or gas phase probably has the structure as shown below.



Phosphorous trioxide (P₄O₆)

It is prepared by burning white phosphorous in an oxygen deficient atmosphere.



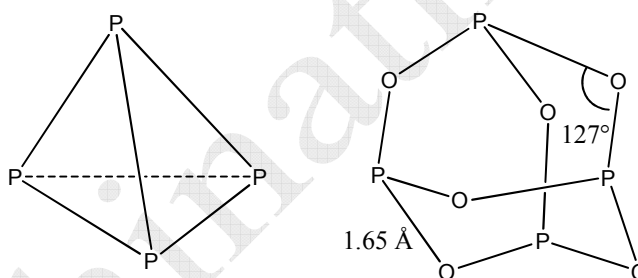
Properties:

It is a soft white solid. It forms low melting white crystals, which are stable to oxygen at room temperature but should be free from even traces of white phosphorous. It burns in air forming P₄O₁₀.

P₄O₆ is an acidic oxide and gets hydrolyzed by excess of cold water to H₃PO₃. With hot water, PH₃, H₃PO₄ and elemental P are formed presumably due to disproportionation of H₃PO₃. $\text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_3$

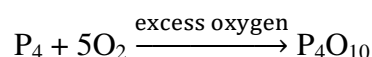
Structure:

Phosphorous trioxide is dimeric. P₄O₆ has four P atoms at the corner of a tetrahedron, with six O atoms along the edges, each O being bonded to two P atoms. The P-O-P bond angle is 127°. That means, O-atoms is inserted between the each P-P bond of P₄ unit of elemental white phosphorous.



Phosphorous pentoxide (P₄O₁₀):

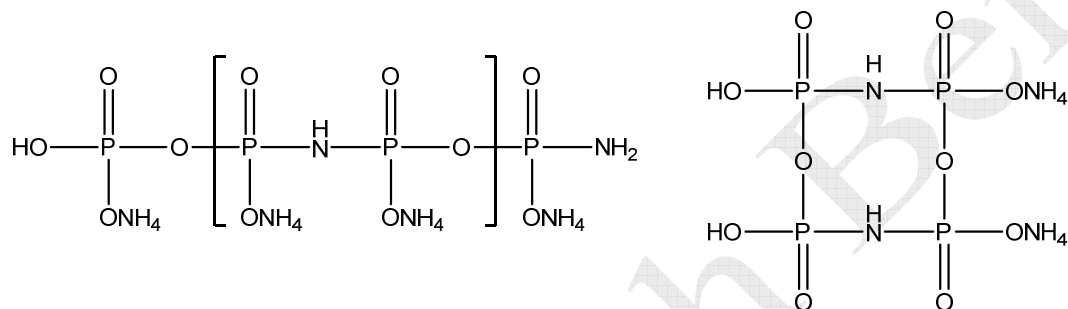
It is obtained by burning phosphorous in excess air and also by burning P₄O₆ in air.



Properties:

It forms white crystalline solid. It has strong affinity for water with which it forms phosphoric acid. It can extract water even from concentrated H₂SO₄ which is also a dehydrating agent. It dehydrates H₂SO₄ to SO₃, HNO₃ to N₂O₅, and RCONH₂ to RCN etc.

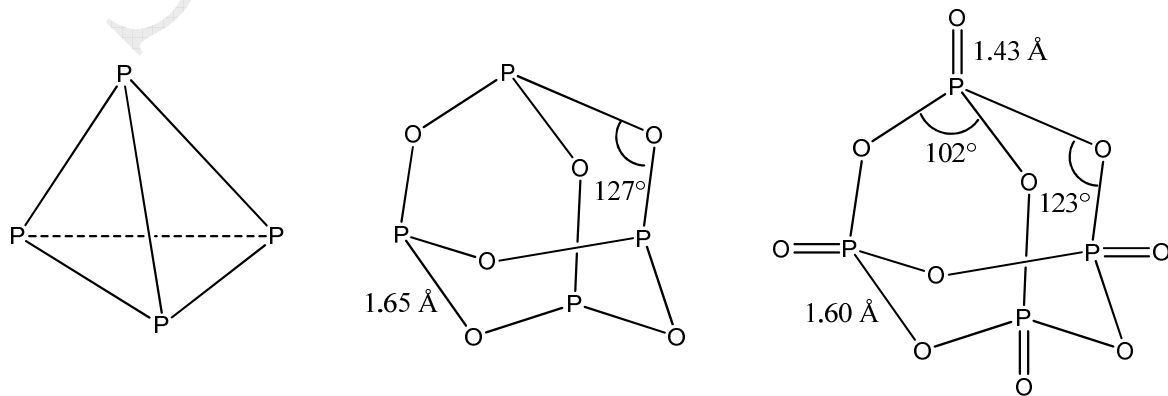
P₄O₁₀ reacts vigorously with NH₃ to form condensed linear or cyclic amidopolyphosphates of wide composition.



Structure:

It exists as a dimer. Its basic structural pattern is similar to P₄O₆. Each P atom in P₄O₆ forms three bonds to O atoms. Out of five valence electrons, three electrons are involved bond with oxygen and another two comprise a lone pair which is situated on the outside of the tetrahedral unit. In P₄O₁₀, the lone pair on each of four P atoms forms a coordinate bond to an oxygen atom.

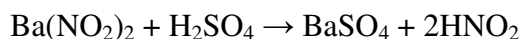
The bridging P-O bonds are evidently longer (1.60 Å) than the terminal P-O bond (1.43 Å) having considerable double bond character. These terminal P=O bond is formed by overlapping the filled p-orbital of oxygen with the vacant π-symmetric d-orbital of phosphorous i.e., pπ-dπ back bonding is occur. Since, one atom provides two electrons to form a bond, the bond is called dative bond.



Oxoacids of Nitrogen

Nitrous acid (HNO₂)

The free acid is very unstable except in dilute solution. A dilute aqueous solution may be obtained by adding dilute H₂SO₄ to an ice cold solution of barium nitrite.

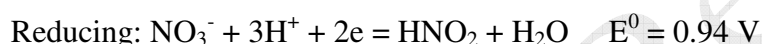
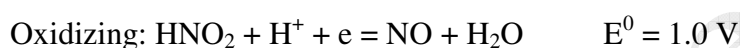


Properties:

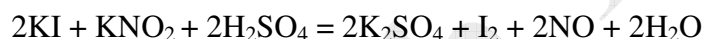
Nitrous acid is a weak acid. Its aqueous solution is unstable, decomposes rapidly on heating.



Nitrous acid and nitrites can behave both as an oxidizing and reducing agent.



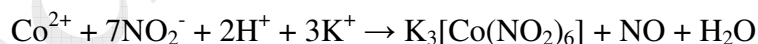
HNO₂ oxidizes Fe²⁺, I⁻ and itself gets reduced to NO. HNO₂ is oxidized by H₂O₂, Br₂, and KMnO₄ to nitrates.



Urea, sulphamic acid, ammonium chloride, azides reduces HNO₂ to N₂. These reaction are used in detect nitrates in presence of nitrites.



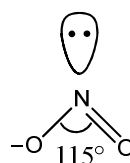
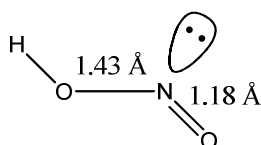
In presence of excess NO₂⁻, solution of Co²⁺ ions is oxidized to Co³⁺ by NO₂⁻ ions and form a complex, [Co(NO₂)₆]³⁻. With K⁺ ion, it forms yellow a precipitated due to formation of K₃[Co(NO₂)₆]. The reaction is used to detect K⁺ in solution.



The NO₂⁻ ion can coordinate to metals either through N (nitro complex) or through O (nitrito complex) e.g., [Co(NH₃)₅NO₂]Cl₂ (yellow) and [Co(NH₃)₅(ONO)]Cl₂ (red)

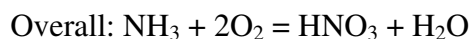
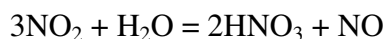
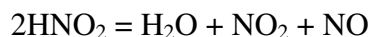
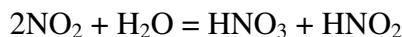
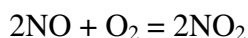
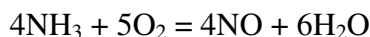
Structure:

HNO₂ has planar structure with OH and N=O in trans position. The nitrite, NO₂⁻ has a planar triangular structure. Two corners occupied by O-atoms and third corner occupied by the lone pair. The central N atom is sp² hybridized. N-O bond order is 1.5 and bond length is in between single and double bond.



Nitric acid (HNO₃)

It is manufactured by oxidation of NH₃ in presence of Pt catalyst known as Ostwald process.



Properties:

When nitric acid is mixed with concentrated sulfuric acid, nitronium ion, NO₂⁺ is formed, which acts a reactive electrophile for nitration of aromatic hydrocarbon. Mixed acid is called nitrating agent. $\text{HNO}_3 \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}$

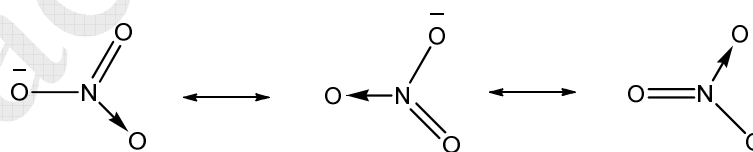
A mixture of concentrated HNO₃ and concentrated HCl in a volume ratio 1:3 is known as aqua regia. It is used to dissolve gold, platinum.

Structure:

The gaseous HNO₃ molecule has planar structure. The N-O distance in -NO₂ group are equal. The third N-O bond is longer and it is a single bond. The structure is consistent with roughly sp² hybridization of the N atom involving the VB structure:



The nitrate ion is symmetrical planar with all ONO bond angle 120° and N-O distance equal to 1.22 Å, consistent with bond order 1.33. The central N-atom is sp² hybridized.



Oxo-acids of Phosphorous

Phosphorous forms a vast number of oxo-acids and anions are listed below.

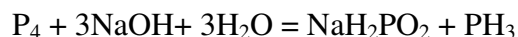
H_3PO_2 Hypophosphorus acid		Monobasic, strong reducing Synthesis: White P + alkali
H_3PO_3 Phosphorus acid		Dibasic, reducing Synthesis: P_4O_6 or $\text{PCl}_3 + \text{H}_2\text{O}$
H_3PO_4 Phosphoric acid		Tribasic Synthesis: P_4O_{10} or $\text{PCl}_5 + \text{H}_2\text{O}$
$\text{H}_4\text{P}_2\text{O}_5$ Pyrophosphorus acid		Dibasic, reducing Synthesis: Heating phosphite
$\text{H}_4\text{P}_2\text{O}_6$ Hypophosphoric acid		Tetrabasic, resistant to oxidation Synthesis: Oxidation of red P in alkali
$\text{H}_4\text{P}_2\text{O}_7$ Pyrophosphoric acid		Tetrabasic Synthesis: Heating H_3PO_4

Characteristics:

- (i) In all oxoacids and anions, P-atoms are 4-coordinate with at least one P=O unit.
- (ii) All oxo acids have at least one P-OH group in which the hydrogen atom is ionizable. The number of P-OH groups determines the basicity of the acids.
- (iii) Some oxoacids or ions may have one or more P-H groups. Such hydrogen atoms are not ionizable.
- (iv) Catenation may occur by direct P-P bonds or P-O-P links. The linear and cyclic polyphosphoric acids contain P-O-P links through corner sharing of tetrahedral units.
- (v) The oxo-acids with phosphorus in +V oxidation state have oxidizing properties.
- (vi) The oxo acids with phosphorus in +III oxidation state have reducing properties.

Hypophosphorus acid (H₃PO₂)

The hypophosphite ion is prepared by alkaline hydrolysis of phosphorus.



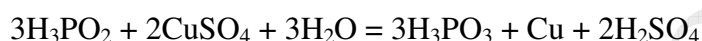
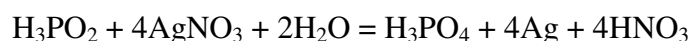
Properties:

Aqueous solution of H₃PO₂ undergoes disproportionation to PH₃ and H₃PO₃ on heating.



It is monobasic. $H_3PO_2 \rightleftharpoons H_2PO_2^- + H^+$

H₃PO₂ and H₂PO₂⁻ are strongly reducing.



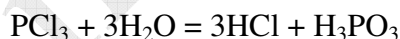
Structure:

The acid and hypophosphite ion are tetrahedral involving sp³ hybridization of the P-atom after unpairing the s-pair and promotion to 3d orbital. This 3d orbital involved in dπ-pπ bond with oxygen.

Use: The solution of NaH₂PO₂·H₂O is used in deposition of Ni on both metal and non-metals by electrode less plating.

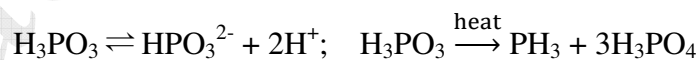
Phosphorus acid (H₃PO₃)

The acid is readily obtained by hydrolysis of PCl₃ or P₄O₆ in cold CCl₄ solution.

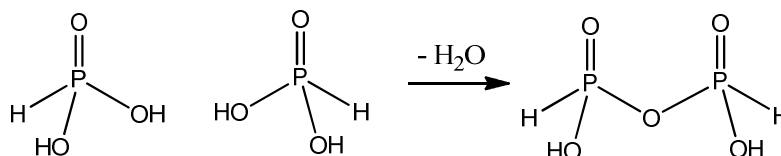


Properties:

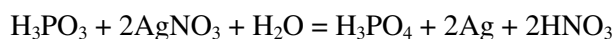
The acid forms colourless deliquescent crystal with H-bonded network. The acid is dibasic and disproportionate on heating.



The acid phosphites on dehydration under reduced pressure converted into pyrophosphites with P-O-P bridge.

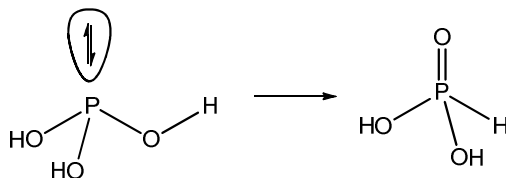


The acid is reducing in nature, reducing SO₂, CuSO₄, AgNO₃ etc.



Structure

It is tetrahedral with sp^3 hybridized P-atom. A structural rearrangement is occurring involving replacement of a P-OH bond (P-O and O-H) by a P-H and a P=O involves better utilization of the valence of P and is energetically favourable.



Phosphoric acid (H_3PO_4)

It is prepared by burning phosphorus in a mixture air and steam in a stainless steel chamber.



Properties

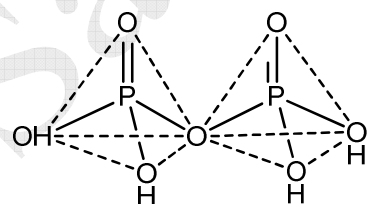
Pure H_3PO_4 forms colourless crystal. In aqueous solution it has extensive H-bonding make it syrupy and viscous. The acid is tribasic. Phosphoric acid has ordinarily no oxidizing property consistent with the stability of P(V). It loses water steadily on heating forms pyrophosphoric acid and metaphosphoric acid.



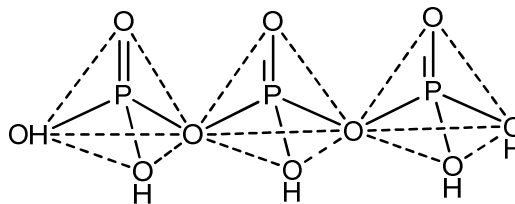
Phosphate (PO_4^{3-}) is detected in solution by mixing a solution of the salt with dilute HNO_3 and ammonium molybdate solution. A yellow precipitate of complex ammonium 12-molybdophosphate forms slowly, confirming the presence of phosphate.



A very large number of polyphosphoric acids and their salts, polyphosphates, arises by polymerizing acidic PO_4 units forming isopolyacids. These consist of chains of tetrahedra, each sharing the O atoms at one or two corners of the PO_4 tetrahedron.



$H_4P_2O_7$ (pyrophosphoric acid)



$H_5P_3O_{10}$ (triphosphoric acid)

Structure: Crystalline phosphoric acid has a H-bonded layer structure of tetrahedral PO_4 units, P=O length is 1.52 \AA and P-OH length is 1.57 \AA .

Use: Phosphate used as fertilizer as superphosphate, triple superphosphate and ammonium phosphate. Na_2HPO_4 is used as buffer, emulsifier in cheese manufacture.

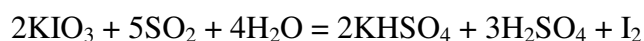
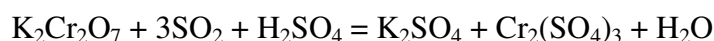
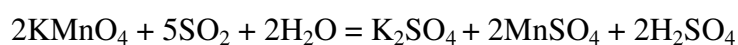
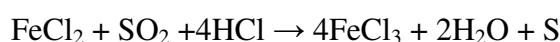
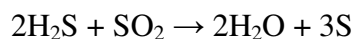
Oxide of sulphur

Sulphur dioxide (SO₂)

It is prepared by burning sulphur in air, roasting of sulphide mineral and burning sulphur containing fuel etc.

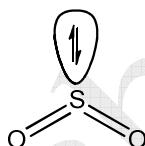
Properties:

SO₂ is a colourless gas with a choking smell. It is highly soluble in water. It can act as both oxidizing and reducing agent.



Structure

The angular structure of SO₂ is consistent with sp² hybridization on S atom with two unpaired electrons in one p and one d orbital. Thy hybrid orbital involve in two σ-bonds and a lone pair. The bond angle is 119°30'. It exists as discrete molecule because of strong π-bonding with oxygen atoms. But, SeO₂ solid contains Se-O-Se chain.



Sulphur trioxide (SO₃)

It is manufacture by aerial oxidation of SO₂ in presence of V₂O₅ catalyst. The SO₃ is not usually isolated, it is converted to H₂SO₄.

Properties

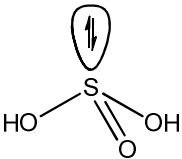
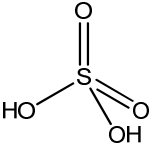
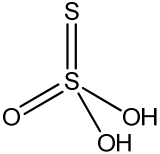
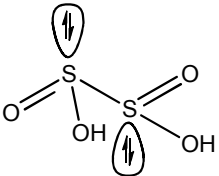
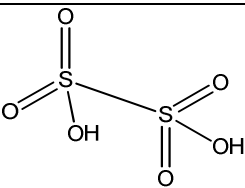
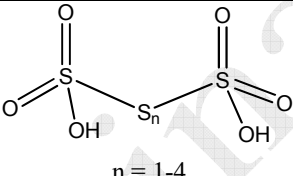
SO₃ is a colourless solid (m.p. 17°C) which reacts vigorously with water to form H₂SO₄. Since this gives rise to thick mist, the gas is absorbed in concentrated H₂SO₄ to obtain oleum.

SO₃ is a strong acidic oxide. It is also a powerful oxidizing agent.

Structure

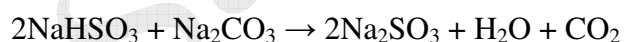
In gas phase, it has a symmetrical planar triangular structure with short S-O bond, 1.43 Å. The bonding is best described as S forming three σ-bonds and three delocalized π-bonds. In solid state it exists in three forms, γ form of cyclic trimer, (SO₃)₃, β form of infinite helical chains of tetrahedral SO₄ unit and α form of cross linked chain structure.

Oxoacids of sulphur

Sulphurous acid H_2SO_3		$\text{SO}_2 + \text{H}_2\text{O}$. Unstable, weak, reducing and dibasic
Sulphuric acid H_2SO_4		$\text{SO}_3 + \text{H}_2\text{O}$ Stable, strong, dibasic and oxidizing
Thiosulphuric acid $\text{H}_2\text{S}_2\text{O}_3$		$\text{S} + \text{SO}_3^{2-}$ in alkaline medium. Decomposes to S in acid medium. Mild reducing
Dithionous acid $\text{H}_2\text{S}_2\text{O}_4$		Reduction of H_2SO_3 or sulphites by zinc. Salt stable in solid or alkaline medium. Powerful reducing agent.
Dithionic acid $\text{H}_2\text{S}_2\text{O}_6$		Oxidation of sulphites, stable only in dilute solution, strong, dibasic acid
Polythionic acids $\text{H}_2\text{S}_n\text{O}_6$ (n = 3-6)		Various anions formed by reaction of SO_2 and H_2S or arsenates, unstable, reducing

Sulphurous acid (H_2SO_3)

The free acid has not been isolated. But, salts of sulphite (SO_3^{2-}) and bisulphites (HSO_3^-) are well known. It is made by passing SO_2 into an aqueous solution of Na_2CO_3 .

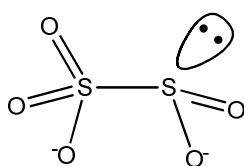


Properties

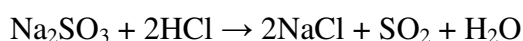
The sulphites of smaller ions converted to disulphites on evaporation its solution.



The $\text{S}_2\text{O}_5^{2-}$ ion contains S-S bond but not has any S-O-S linkage.

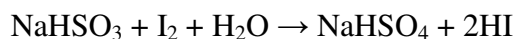


Sulphites and bisulphites liberate SO₂ on treatment with dilute acids.

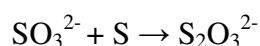
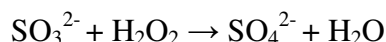


Sulphites and bisulphites contain S in +IV oxidation state and are moderate reducing agent.

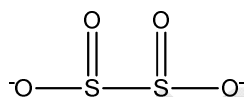
Sulphites are determined by reaction with I₂ and excess I₂ is determined with thiosulphate.



On oxidation sulphite forms sulphates and with sulphur they form thiosulphates.



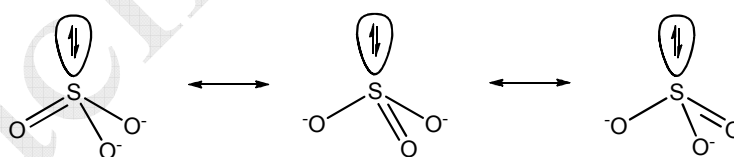
The reduction of sulphite solution in presence of SO₂ with Zn dust, or electrolytically, yields dithionates that contains S in +III oxidation state.



The dithionate ion has eclipsed conformation, with very long S-S bond (2.39 Å) and S-O bond lengths of 1.51 Å. Na₂S₂O₄ is a powerful reducing agent, which has variety of industrial use. These include bleaching paper pulp and making dye stuffs.

Structure:

The sulphite ion has a pyramidal structure that is a tetrahedral with one position occupied by lone pair. The bond angles O-S-O are slightly distorted (106°) due to lone pair and S-O length is 1.51 Å. The π-bond is delocalized giving the S-O bond order 1.33.



Sulphuric acid (H₂SO₄)

H₂SO₄ is the most important acid used in chemical industry. It is manufactured by Contact process, in which SO₂ is oxidized by air to SO₃ using V₂O₅ catalyst. The produced SO₃ is now passed into 98% H₂SO₄, forming pyrosulphuric acid, H₂S₂O₇. It is also called oleum or fuming H₂SO₄. H₂SO₄ is prepared from oleum by dissolution in water.



Properties

Sulphuric acid is viscous liquid because of strong H-bonding between the molecules. It is

dibasic acid. In aqueous solution it dissociates very rapidly and produces HSO_4^- and SO_4^{2-} . Concentrated H_2SO_4 has quite strong oxidizing properties. Thus when NaBr is dissolved in concentrated H_2SO_4 , HBr is formed and at the same time Br^- ion is oxidized to Br_2 . Concentrated H_2SO_4 absorbs water and is an effective drying agent for gases. It is sometimes used as a drying agent in desiccators. It dehydrates HNO_3 , forming NO_2^+ , which is very important in the nitration of organic compounds.

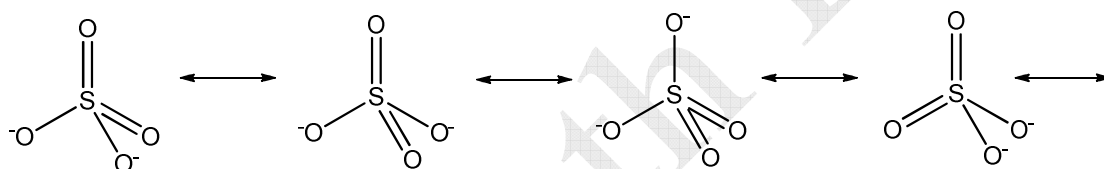


H_2SO_4 can also remove water from alcohol to produce ether or alkene.



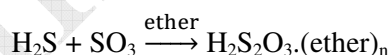
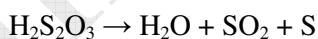
Structure:

The SO_4^{2-} ion is tetrahedral. The bond lengths are equal, 1.49 Å and bond order is approximately 1.5. The bonding is best described as four σ -bonds between S and O atoms with two π -bonds delocalized over the S and four O atoms.

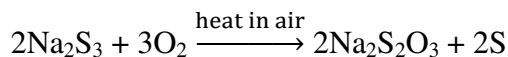
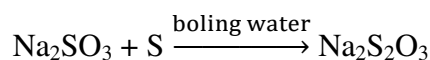


Thiosulphuric acid ($\text{H}_2\text{S}_2\text{O}_3$)

Thiosulphuric acid cannot be formed by adding acid to a thiosulphate salt because the free acid decomposes to SO_2 and S. It can be made in absence of water at low temperature (-78°C).

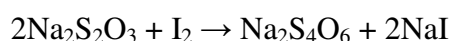


In contrast, the salt called thiosulphates are stable. It is made by boiling alkaline or neutral sulphite solution with S and oxidizing polysulphides with air.



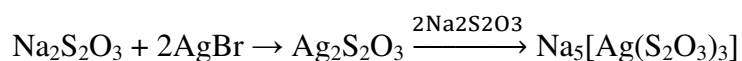
Properties:

The hydrated sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is called hypo. It is readily soluble in water and solution is used for iodine titration in volumetric analysis. Iodine very rapidly oxidizes thiosulphate ions to tetrathionate ions $\text{S}_4\text{O}_6^{2-}$ and I_2 is reduced to I^- .

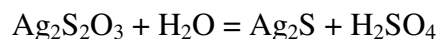
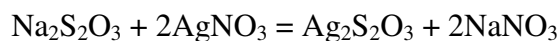


Hypo is used in photography for fixing films and prints. Photographic emulsions are made of AgNO_3 , AgCl and AgBr . Parts of the film exposed to light begin to decompose to Ag, forming a negative image. The process is enhanced by the developer solution. After

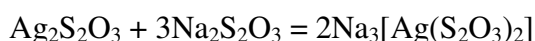
developing, the film is put in hypo to dissolving out the unchanged silver salt.



Silver nitrate first gives white precipitate of silver thiosulphate which undergoes rapid hydrolysis, the colour changing to yellow, brown and finally black.

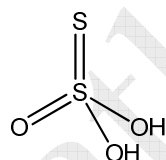


When excess thiosulphate is added, silver thiosulphate dissolves to form a colourless thiosulphate complex.



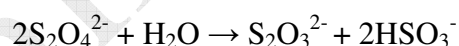
Structure:

The thiosulphate ion is tetrahedral, consistent with sp^3 hybridized S atom. The difference oxidation state of two S-atoms has been established by radioactive tracer study.



Dithionous acid ($\text{H}_2\text{S}_2\text{O}_4$)

Acid is not known but salt containing $\text{S}_2\text{O}_4^{2-}$ ion (dithionite) is stable under anhydrous condition and in aqueous solution readily disproportionate.



Dithionites are prepared by reduction of aqueous sulphite solution containing excess of SO_2 by zinc dust, sodium amalgam or electronically.

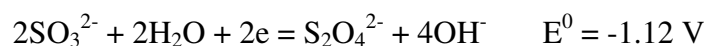


Properties:

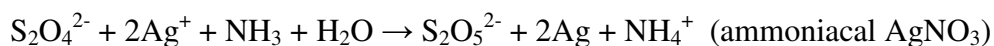
Sodium dithionite is white crystalline solid. The anhydrous compound is stable but the hydrate is rapidly oxidized. $\text{Na}_2\text{S}_2\text{O}_4$ also decomposes on heating above 150°C .



Dithionites are powerful reducing agent.



They reduce the solution containing Cu(II), Ag(I), Hg(II), Pb(II) etc. heavy metal ions to metals. Cr(VI) is reduced to Cr(III), I_2 to I^- and $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$.

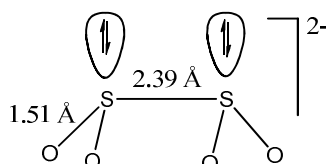


Use:

Sodium dithionite is extensively used as a powerful reducing and bleaching agent in dyeing and also used in removing O_2 from gases-catalyzed by 2-anthraquinonesulphonate.

Structure:

The structure of the dithionite ion has a rather long S-S bond and an eclipsed conformation. The bonding is formally consistent with sp^3 hybridization at the both S atoms with strong lone pair-lone pair repulsion.

**Dithionic acid ($H_2S_2O_6$)**

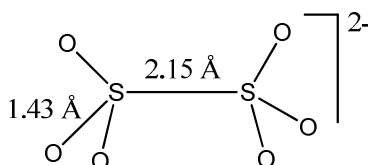
$H_2S_2O_6$ is known only in solution. It can be made by oxidizing a cooled aqueous solution of SO_2 with MnO_2 or Fe_2O_3 . $2MnO_2 + 3SO_2 \rightarrow MnSO_4 + MnS_2O_6$

Properties:

The acid is dibasic and salts are called dithionates. Dithionates are stable to mild oxidizing agents though strong oxidizing agents such as $KMnO_4$ or the halogens, oxidize them to sulphate and similarly, strong reducing agent reduce dithionates to dithionites and sulphites.

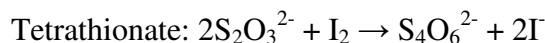
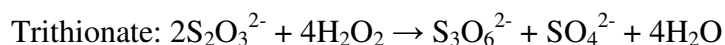
**Structure:**

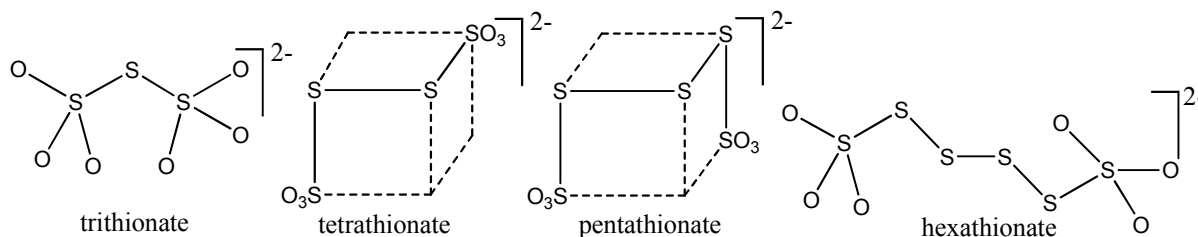
The dithionate ion has two approximately tetrahedral SO_3 unit adopt eclipsed conformation is linked by S-S bond. The S-S length is 2.15 Å and shorter S-O bond lengths are 1.43 Å. The S-S-O angles are 103° .

**Polythionic acids ($H_2S_nO_6$)**

The free acids are unstable but polythionate salts are known. Polythionates are known as tri-, tetra-, penta- etc. depending on the number of sulphur atoms present in $S_nO_6^{2-}$ ion.

Polythionates are prepared by selective reactions.



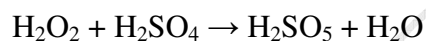


Peroxo acids of sulphur

Peroxomonosulphuric acid (H_2SO_5)

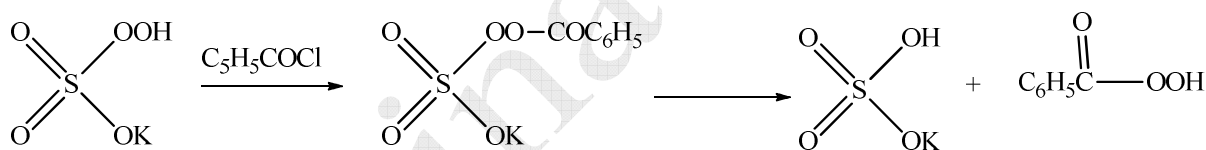
Replacement of one $-\text{OH}$ group in H_2SO_4 by $-\text{OOH}$ group results H_2SO_5 called Caro's acid.

It can be prepared by the action of concentrated H_2O_2 on sulphuric acid or chlorosulphuric acid.



Properties:

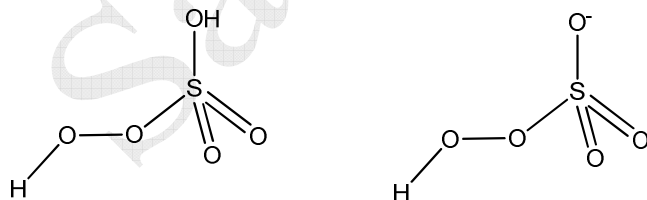
H_2SO_5 is colourless, crystalline solid. The acid has specific oxidizing properties. It oxidizes aniline to nitroso benzene and rapidly liberates iodine from KI. The hydroperoxide group is too weakly acidic to form salt. The benzoyl derivative gives benzoyl peroxide on acid hydrolysis in ether solvent.



An aqueous solution of KHSO_5 evolves O_2 on boiling. $2\text{KHSO}_5 = 2\text{KHSO}_4 + \text{O}_2$

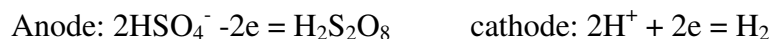
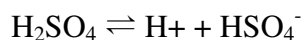
Structure:

The S-atom is sp^3 hybridized. HSO_5^- has three shorter S-O distances of 1.44 Å and the S-O distance to $-\text{OOH}$ is longer, 1.63 Å.



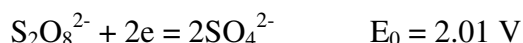
Peroxodisulphuric acid (H₂S₂O₈) (Marshall's acid)

It is prepared by anodic oxidation in the electrolysis of ice-cold 50% sulphuric acid with platinum electrodes.

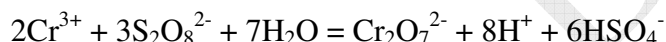
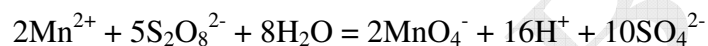


Properties:

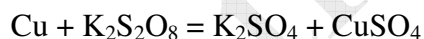
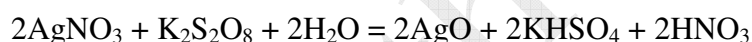
It is colourless solid. The acid and its salt are powerful oxidizing agent.



Mn(II) and Cr(III) are quantitatively oxidized to MnO₄⁻ and Cr₂O₇²⁻ respectively under boiling condition in presence of AgNO₃ catalyst.

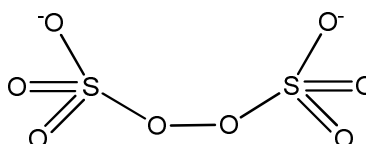
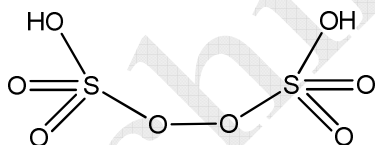


AgNO₃ is oxidized to AgO by K₂S₂O₈. Cu, Zn metals are dissolving in persulphate solution.



Structure:

Each S-atom is sp³ hybridized and linked through a -O-O- peroxy bond. O-O bond distance is 1.31 Å whereas S-O length is 1.50 Å.



Sulphur-nitrogen compounds:

There are no binary sulphur-nitrogen compounds corresponding to the nitrogen oxides. But, a large number of sulphur-nitrogen compounds are known having interesting properties. The electronegativity of S and N are similar that leading to covalent bonding along with extensive π -delocalization. The most important compound is tetrasulphur tetranitride, S_4N_4 and this is starting point for many other S-N compounds.

Tetrasulphur tetranitride (S_4N_4):

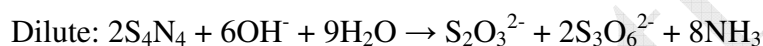
It is prepared by passing ammonia gas into solution of S_2Cl_2 or SCl_2 in dry CCl_4 .



It is also formed by heating NH_4Cl with S_2Cl_2 . $6S_2Cl_2 + 4NH_4Cl = S_4N_4 + 8S + 16HCl$

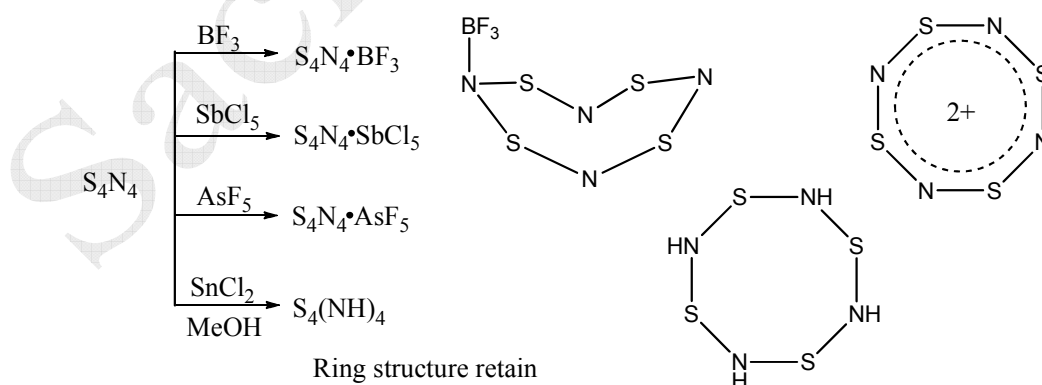
Properties:

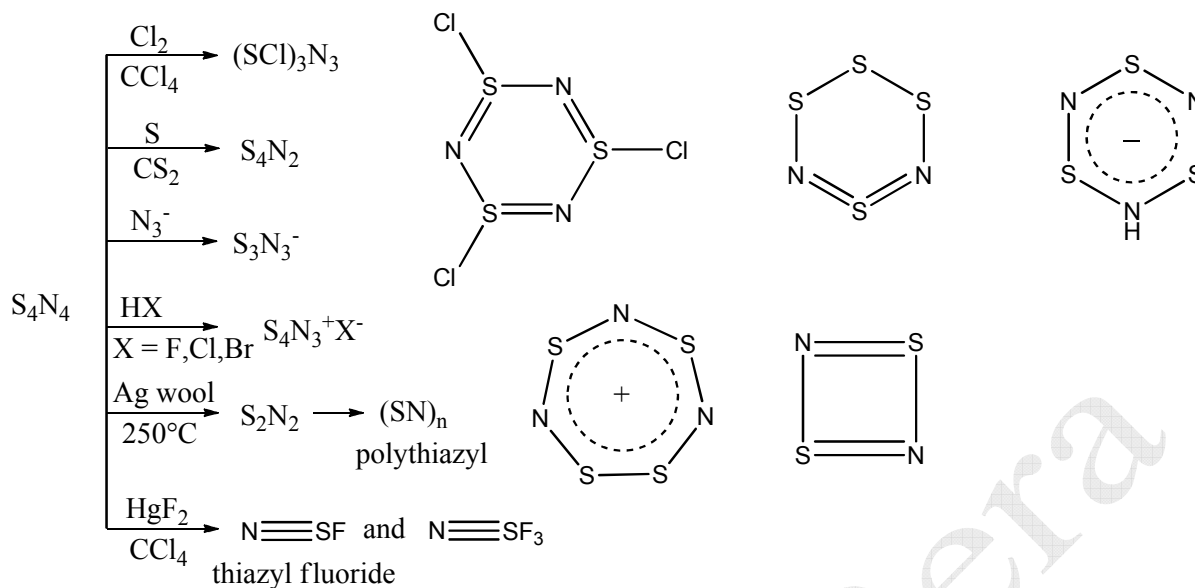
S_4N_4 is solid. It is thermochromic that is changes colour with temperature. At low temperature ($-180^\circ C$) it is colourless, but at room temperature it is orange-yellow and $100^\circ C$ it is red. S_4N_4 is very slowly hydrolyzed in water but rapidly in alkali at warm condition.



S_4N_4 may undergo two main type of reaction (a) reaction with retention of ring (b) reaction in which ring is cleaved.

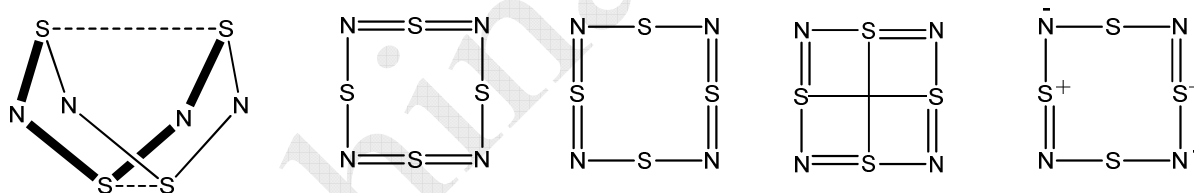
S_4N_4 form N-donor adducts with BF_3 , $SbCl_5$, SO_3 of type $S_4N_4 \cdot BF_3$, $S_4N_4 \cdot SbCl_5$ and $S_4N_4 \cdot SO_3$. It produces $S_4(NH)_4$ with reaction $SnCl_2$ in MeOH.





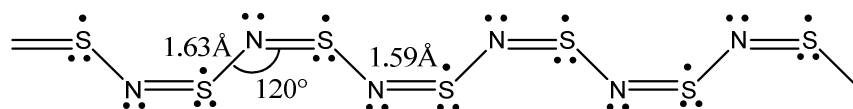
Structure:

S_4N_4 has an 8-membered heterocyclic cradle shape structure differ from S_8 (crown shape). The S-N distances are equal (1.62 Å) and shorter than the sum of covalent radii (1.78 Å) that indicates bonds have some double bond character. The S...S distances at the top and bottom cradle are 2.58 Å are well less than the non-bonding van der Waals distance (3.30 Å) suggesting significant bonding interaction. No valence bond structure appears to fit the bonding of S_4N_4 . Numerous resonance hybrids may be considered, e.g.,



Disulphur dinitride (S_2N_2): It is formed as an extremely unstable cyclic dimer when the vapour of S_4N_4 is passed over the heated silver wool (300°C) at low pressure (0.1 -1.0 mm Hg). The compound undergoes slow but spontaneous polymerization at ordinary temperature forms $(SN)_n$.

Polythiazyl, $(SN)_n$ is a bronze coloured solid with metallic luster. It has electrical conductivity. It becomes semiconductor below 0.26K. It's conductance is much higher in one direction than perpendicular direction. It consists of zig-zag nearly planar chains of S-N-S- over which π -electrons are extensively delocalized.



Oxides of halogens:

F	OF ₂ , O ₂ F ₂
Cl	Cl ₂ O, Cl ₂ O ₃ , ClO ₂ , Cl ₂ O ₄ , Cl ₂ O ₆ , Cl ₂ O ₇
Br	Br ₂ O, BrO ₂
I	I ₂ O ₄ , I ₄ O ₉ , I ₂ O ₅

Fluorides of oxygen:

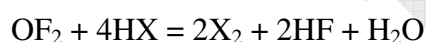
Oxygen difluoride (OF₂):

It is formed when fluorine is passed rapidly through 2% sodium hydroxide solution.



Properties:

It is pale yellow poisonous gas. It reacts slowly with water, explosively with steam. It hydrolyzed readily in base. OF₂ is strong fluorinating and oxidizing agent liberating other halogens from halides. $OF_2 + H_2O = O_2 + 2HF$; $OF_2 + 2OH^- = O_2 + 2F^- + H_2O$



Structure:

OF₂ molecule is angular with sp³ hybridized central oxygen. The F-O-F angle is slightly smaller than that in H₂O (104.5°).

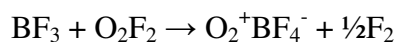
Dioxygen difluoride (O₂F₂)

It is formed by subjecting liquid O₂-F₂ mixture to high voltage electric discharge at low temperature and pressure (-196°C, 10-20 mm Hg).

Properties:

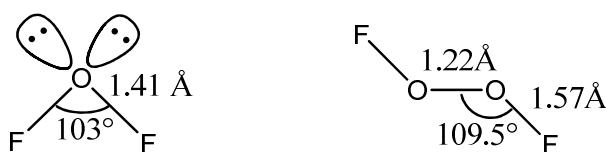
It is yellow orange solid below -154°C which decomposes rapidly above -100°C. It is strong oxidizing and fluorinating agent. $H_2S + 4O_2F_2 = SF_6 + 2HF + 4O_2$

It can form dioxygenyl salts by transferring a F⁻ ion to suitable acceptor.



Structure:

The structure of O₂F₂ is comparable with H₂O₂. The O-O distance is remarkably smaller than H₂O₂. Conversely, the O-F distance is somewhat longer than OF₂. The bonding might be rationalized by the formation of two 3c-2e bond (O-O-F) between two singly occupied π* of O₂ with singly occupied σ-AO's of two F approximately perpendicular direction. The O-O bond thus retains double bond character as in O₂ while the O-F bonds become weaker.



Oxides of chlorine

Chlorine monoxide (Cl₂O)

It is formed when dry chlorine gas is passed through a cold tube containing yellow precipitated mercuric oxide. Basic mercuric oxide remains in tube.



Properties

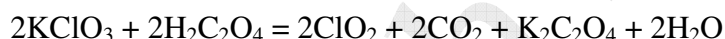
It is brownish yellow gas. The gas readily dissolves in water to form hypochlorous acid (HOCl). It is powerful and selective chlorinating agent for organic compounds. The gas is mainly used to produce hypochlorites, NaClO₂, Ca(OCl)Cl which are useful bleaching agent.

Structure

The molecule is bent (111°) with sp³ hybridized central oxygen atom. The Cl-O bond distance is 1.71 Å.

Chlorine dioxide (ClO₂)

It is prepared by heating potassium chlorate with moist oxalic acid.

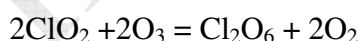


Properties:

It is yellowish gas, condenses to deep red liquid which explodes above -40°. It is a mixed anhydride, dissolves in alkali to form chlorite and chlorate.



It is powerful oxidizing and chlorinating agent. Ozone oxidizes ClO₂ to Cl₂O₆.



Structure:

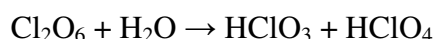
The ClO₂ is bent with O-Cl-O angle 118°. Bond lengths, 1.47 Å, are equal and shorter than single bond. The molecule contains odd electron but shows little tendency to dimerization because the odd electron is more extensively delocalized over the entire skeleton like NO₂.

Dichlorine hexoxide (Cl₂O₆)

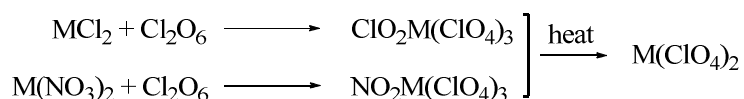
It can be made by ozonolysis of ClO₂. $2\text{ClO}_2 + 2\text{O}_3 = \text{Cl}_2\text{O}_6 + 2\text{O}_2$

Properties:

It is unstable red oil. It reacts with water and alkali to form chlorates and perchlorates.

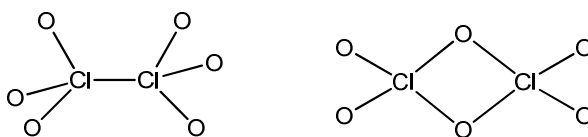


Cl₂O₆ may be used to prepare anhydrous metal perchlorates according the reaction below:



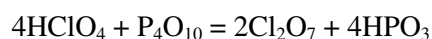
Structure

The solid has the ionic composition $[\text{ClO}_2]^+[\text{ClO}_4]^-$. The liquid may have either of two possible structures given below:



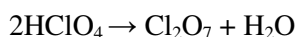
Dichlorine heptoxide (Cl_2O_7)

It is most stable oxide of chlorine. It is made by careful dehydration of perchloric acid with phosphorous pentoxide at -10°C followed by cautious vacuum distillation at -35°C and 1 mm Hg.

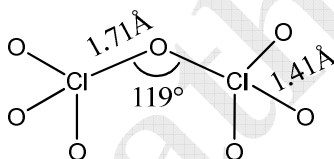


Properties:

It is anhydride of perchloric acid. It reacts with alkali produces perchlorates.



Structure: Cl_2O_7 has bent structure with a bridging O-atom. The terminal Cl-O bonds are substantially shorter than the bridge Cl-O bonds, showing appreciable double bond character.

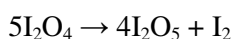


Oxides of Iodine

I_2O_4 and I_4O_9

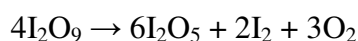
It is obtained as lemon-yellow diamagnetic solid by partial hydrolysis of iodosyl sulphate, $(\text{IO})_2\text{SO}_4$.

It is decomposed to I_2O_5 above 135°C .



It has polymeric I-O chains cross-linked by IO_3 groups. It is thus formulated as $[\text{IO}]^+[\text{IO}_3]^-$

I_4O_9 may be prepared by oxidizing I_2 with O_3 . The yellow hygroscopic solid decomposes above 75°C into I_2O_5 and I_2 . It is formulated as $\text{I}^{\text{III}}(\text{I}^{\text{V}}\text{O}_3)_3$.



Diiodine pentoxide(I_2O_5)

It is obtained by dehydrating iodic acid at 200°C in dry air.

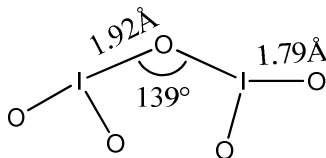


Properties:

It is white hygroscopic solid. It dissolves in water forming HIO_3 . It is strong oxidizing agent. CO is oxidized to CO_2 at room temperature. This reaction is quantitative and very sensitive. It may be used to detect and estimate carbon monoxide, carbon exhaust etc.



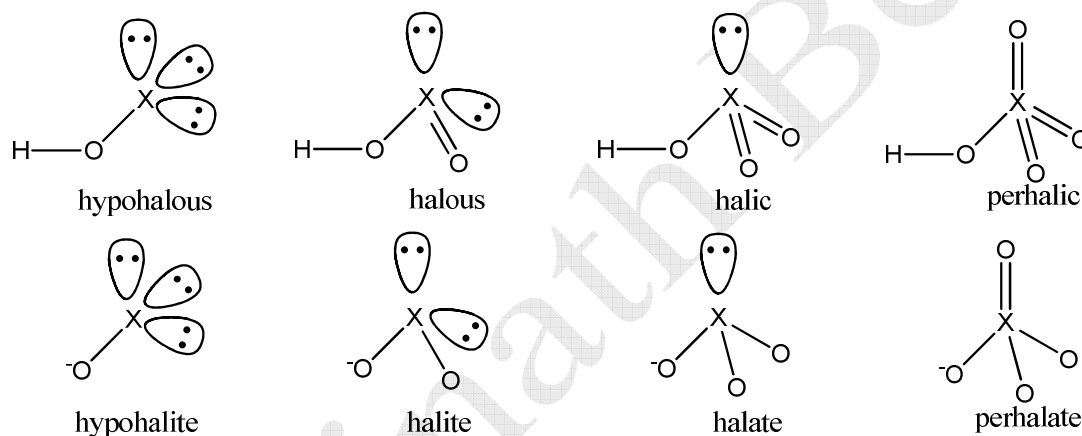
Structure: I_2O_5 consists of cross linked chains of $O_2I-O-IO_2$ units. The unit may be supposed to consist of two pyramidal IO_3 units joined by sharing an oxygen at an apex. The bridge I-O bond lengths is 192 pm corresponding to usual single bonds while the terminal I-O bonds are somehow shorter, 177-183 pm.



Oxoacids and salts

HOX	HOXO (HXO ₂)	HOXO ₂ (HXO ₃)	HOXO ₃ (HXO ₄)
HOF			
HOCl	HClO ₂	HClO ₃	HClO ₄
HOBr	HBrO ₂	HBrO ₃	HBrO ₄
HOI	HIO ₂	HIO ₃	HIO ₄

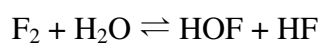
The oxoacids and anions may be supposed to be derived through sp^3 hybrid orbitals on the halogens linking one or more oxygen atoms. The remaining orbitals are occupied by unshared pairs of electrons of the halogen. The anions are stabilized by strong $p\pi-d\pi$ bonding between filled 2p orbital of oxygen with empty d-orbitals on halogen atoms. The skeleton arrangement of the oxoacids and corresponding anions are given below.



Hypohalous acid (HOX)

The Hypohalous acids HOF, HOCl, HOBr, HOI are known and halogen is in +I oxidation state.

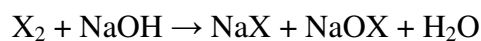
HOF has been prepared by passing F_2 over ice below $0^\circ C$ and at low pressure (~ 100 mm Hg).



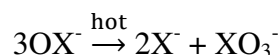
HOF is colourless unstable gas decomposes to HF and O_2 . It is strong oxidizing agent and oxidizes H_2O to H_2O_2 .

HOCl, HOBr, HOI can be prepared by shaking the halogen with freshly precipitated HgO in water. $2HgO + HO + 2Cl_2 \rightarrow HgO.HgCl_2 + 2HOCl$

HOCl acid is the most stable and NaOCl is well known. Hypohalites are made by dissolving the halogens in NaOH.

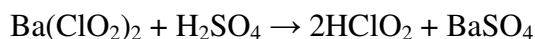
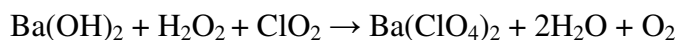


Hypohalites are disproportionate in hot condition or in concentrate NaOH.

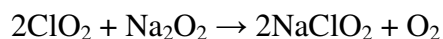


Halous acids (HXO₂)

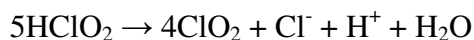
The only halous acid known is chlorous acid. It is weak acid but stronger than HOCl. It is made by treating barium chlorate with H₂SO₄.



Salts of HClO₂ are called chlorites and are made from ClO₂ and NaOH or Na₂O₂.

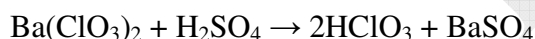


Chlorites are stable in alkaline solution but in acid solution they disproportionate on heating.



Hallic acid (HXO₃)

HClO₃ and HBrO₃ are made by treating the barium halates with H₂SO₄. HIO₃ can be made by oxidizing I₂ with concentrated HNO₃ or O₃.



HClO₃ and HBrO₃ are not very stable but known in solution and as salts. But, HIO₃ is stable and exists as a white solid. The Halic acids are strong oxidizing agent and strong acids.

Halates are made by passing halogens into hot NaOH solution.

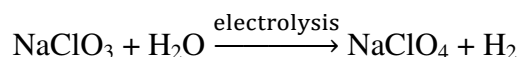


Chlorates are used to make fireworks and matches. Sodium chlorate is widely used as a powerful weed killer.

Perhalic acids and perhalates:

Perchloric acid (HClO₄) and Perchlorates

HClO₄ and different perchlorate are prepared from reacting sodium perchlorate. NaClO₄ is made by electrolyzing aqueous NaClO₃. HClO₄ is made from NaClO₄ reacting with concentrate HCl.

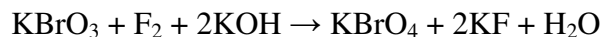
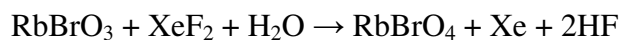


It is a very strong acid. It dissolves electropositive metals like Mg, Zn, Fe evolving H₂. Aqueous solutions of perchloric acid and perchlorates are not good oxidizing agents at room temperature. But, anhydrous or hot concentrated solution is powerful oxidizing.

A large number of perchlorates are known as perchlorates of group-I metals, NH₄ClO₄, Mg(ClO₄)₂ etc.

Perbromic acid (HBrO₄) and Perbromates:

Perbromates can be prepared by oxidation of BrO₃⁻ by F₂ or XeF₂.

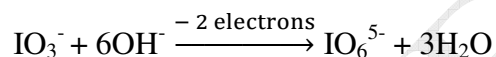
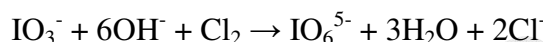


A dilute solution of HBrO₄ may be prepared by passing the solution of solution of KBrO₄ through cation exchange resin.

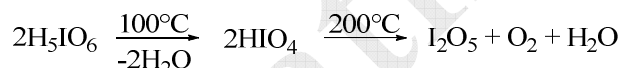
Dilute solution of BrO₄⁻ are weakly oxidizing, oxidize Br⁻ and I⁻ only not Cl⁻.

Periodic acid (HIO₄) and periodates:

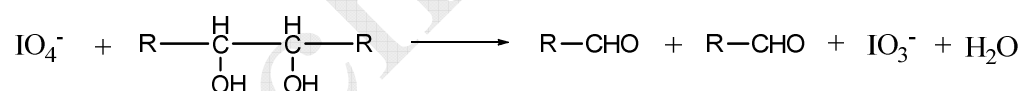
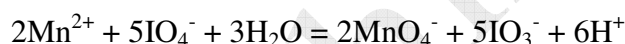
Periodates are made by oxidizing iodates in alkali medium either with Cl₂ or electrolytically.



The common form of periodic acid is HIO₄·2H₂O or H₅IO₆. This is called paraperiodic acid and exists as white crystals. Water is lost on heating to 100°C under reduced pressure. On strong heating it decomposes to I₂O₅ by losing O₂.

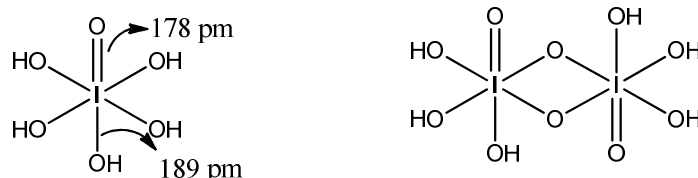


Periodates are important as oxidant, oxidize Mn²⁺ to MnO₄⁻ and also oxidize organic compound. Solutions of periodic acid are used to determine the structure of organic compounds by degradative method.



Structure:

Periodates are of two structural types: tetrahedral IO₄⁻ and Octahedral H₅IO₆ and IO₆⁵⁻. Octahedral geometry is consistent with sp³d² hybridization of the central I atom. A wide range of isopolyacids exists with octahedral unit, linked together by sharing the O-atom.

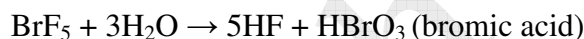


Interhalogen compound:

The halogens react with other to form interhalogen compounds. These are divided into four types AX, AX₃, AX₅ and AX₇. They can be prepared by direct reaction between halogen or by the action of halogen on interhalogen. The product formed depends on the condition.

There are never more than two different halogens in a molecule. The bonds are essentially covalent because of small electronegativity difference. The melting and boiling point increases as the difference in electronegativity increases. The higher valencies AX₅ and AX₇ are shown by large atom such as Br and I associated with small atom F.

The interhalogens are generally more reactive than the halogens (except F₂). This is because A-X bond is weaker than the X-X bond in halogens. Hydrolysis of interhalogens gives halide and oxohalides ions. It is seen that the oxohalides ion is always formed from the larger halogen.



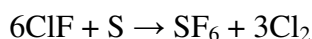
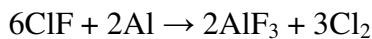
AX compounds:

All six compounds (ClF, BrF, IF, BrCl, ICl, IBr) can be made by controlled reaction of the elements.

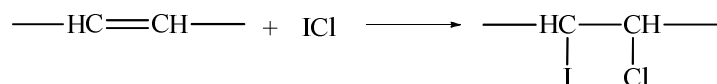


Properties:

ClF is very reactive. ICl and IBr are the most stable. ClF can fluorinate metal and nonmetal.



ICl is used as Wj's reagent to estimate iodine number of fats and oils. The iodine number is a measure of the number of double bonds, i.e., the degree unsaturation in fat.

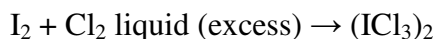
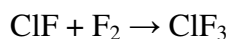
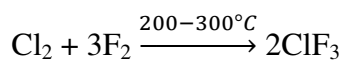


ICl undergoes ionization to the extent of 1%, do not form I⁺ and Cl⁻ but, the ions are solvated.



AX₃ compounds:

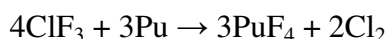
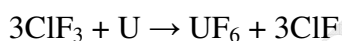
The compounds ClF₃, BrF₃, IF₃ and (ICl₃)₂ can be made by direct combination of the elements depending on the condition.



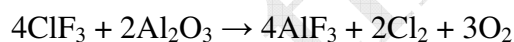
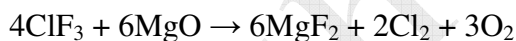
IF₃ is stable only below -30°C and tends to form the more stable IF₅. It is made using XeF₂ to fluorinate I₂. $3\text{XeF}_2 + \text{I}_2 \rightarrow 2\text{IF}_3 + 3\text{Xe}$

Properties:

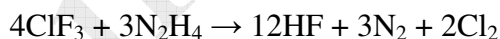
Both ClF₃ and BrF₃ are covalent liquids. ClF₃ is most reactive compound. It is used to make UF₆ which is useful in making enriched ²³⁵U fuel.



ClF₃ is a powerful fluorinating agent for inorganic compounds.



ClF₃ has been used as fuel in short range rocket reacting with hydrazine.

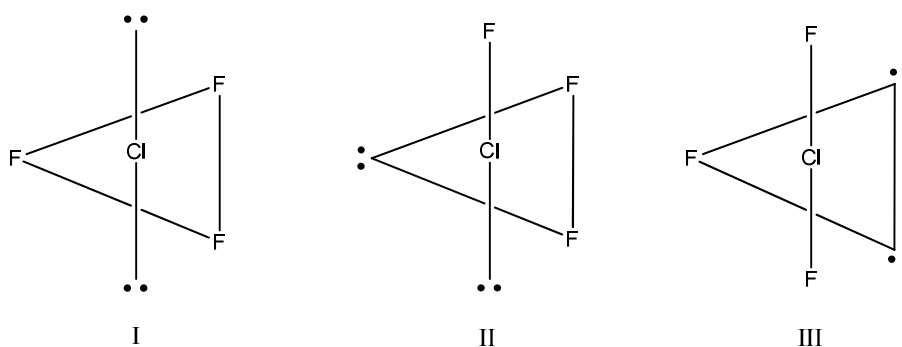


BrF₃ has been more widely used as solvent because it has a convenient liquid range (m.p. 8.8°C, b.p. 126°C), it is not too violent fluorinating agent and it self-ionizes considerably and much more than ClF₃.



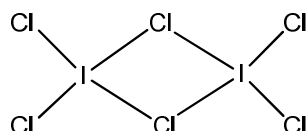
Thus, the substance producing BrF₂⁺ ions are acids and BrF₄⁻ ions are bases in BrF₃ solvent.

Structure:



ClF_3 molecule is T-shaped, with bond angle 87° and distorted from 90° due to lone pair-lone pair repulsion. Two types of Cl-F bond having bond lengths are 1.621 and 1.716 Å because shorter bond is equatorial and longer is axial. The structural parameter suggests structure III.

ICl_3 does not exist, but the dimer I_2Cl_6 is a bright yellow solid. Its structure is planar. The terminal bonds are common single bond of length 2.38 and 2.39 Å. The bridging I-Cl bonds are appreciably longer 2.68 and 2.72 Å, suggesting delocalized bonding rather than simple halogen bridges formed by coordinate bonds from Cl to I.

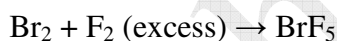


The liquid I_2Cl_6 has an appreciable electrical conductivity due to self ionization.



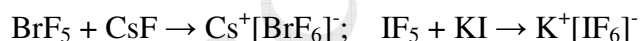
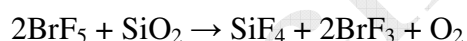
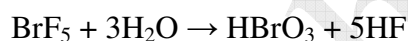
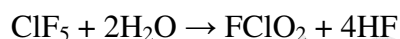
AX_5 compounds:

Three compounds are known ClF_5 , BrF_5 and IF_5 .



Properties:

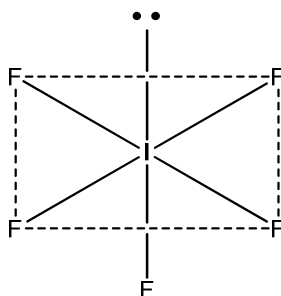
ClF_5 and BrF_5 are extremely reactive but IF_5 is comparatively less reactive. They fluorinate many compounds, reacts explosively with water, attack silicates and also form polyhalides.



Liquid IF_5 self-ionizes and therefore conducts electricity.

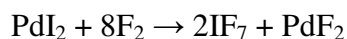
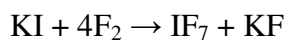


Structure: The central atom is sp^3d^2 hybridized containing one lone pair of electron. The shape is square pyramidal that is octahedral with one lone pair.



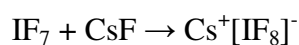
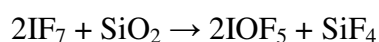
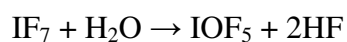
AX₇ compounds:

IF₇ is formed by direct combination of the elements at 250-300°C by heating IF₅ with F₂ or by treating iodides with F₂.



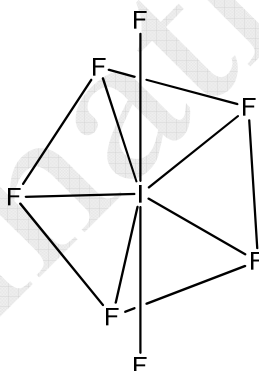
Properties:

IF₇ is a violent fluorinating agent and reacts with most elements. It also reacts with water, SiO₂ and CsF.



Structure:

In IF₇, central iodine is sp³d³ hybridized and geometry is pentagonal bipyramidal. It is probably the only known example of a non-transition element using three d-orbital for bonding.

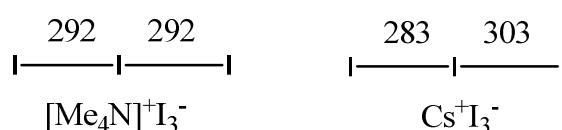


Polyhalides:

The dihalogens and several interhalogens may act as a Lewis acid by accepting electron pair into LUMO. When the donor is halide ion, adducts are called polyhalides.

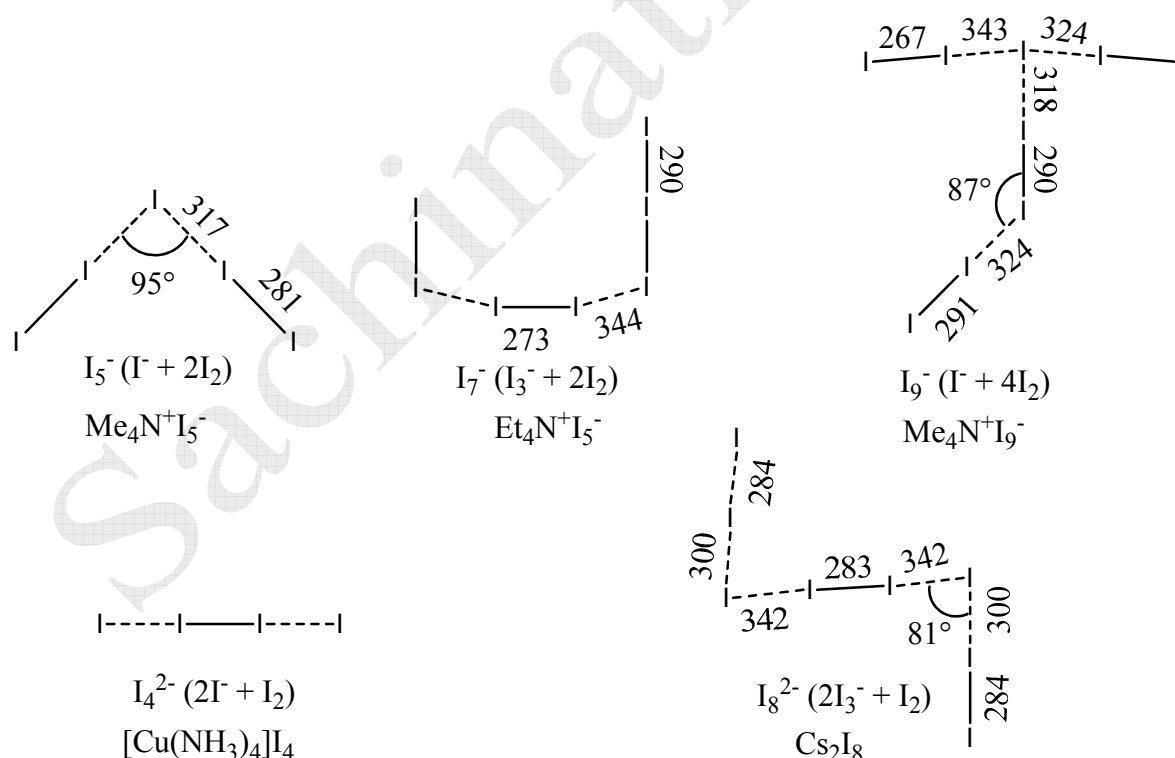
Polyiodides $[(I_2)_n I^-]$ formed by I_2 as a Lewis acid and I^- or I_3^- as the Lewis base. Other polyhalides like Br_3^- , Cl_3^- and polyhalides of interhalogen have also known.

The most stable polyhalides is I_3^- . It is obtained with larger cations like K^+ , Rb^+ , Cs^+ , $[Me_4N]^+$, Ph_4As^+ etc. I_3^- ion is linear with both symmetrical and unsymmetrical I-I bond depending on crystal environment.



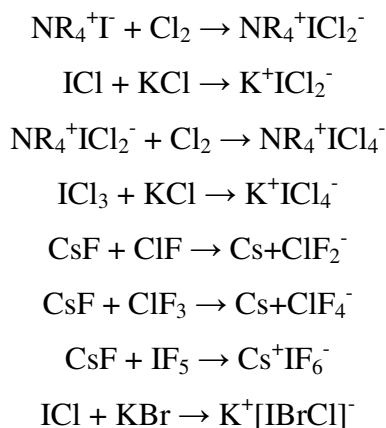
The solubility of I_2 in water is greatly increased in presence of I^- due to formation of polyhalides I_3^- ion.

The more complex polyhalides I_5^- , I_7^- and I_9^- are also known with larger cations. This is because a larger anion with larger cations gives a high coordination number and hence high lattice energy. The structural motif of these polyhalides is given below.



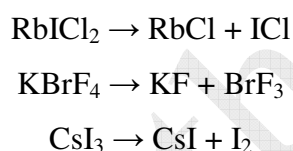
Cl_3^- and Br_3^- are known in solution and also as solid with large cations, for example, Me_4NCl_3 , Me_4NBr_3 , $CsBr_3$ but, F_3^- compounds are unknown.

Many polyhalides are known which contain two or three different halogens, for example, $K[ICl_2]$, $K[ICl_4]$, $Cs[IBrF]$, $K[IBrCl]$. These are formed from interhalogens and metal halides.



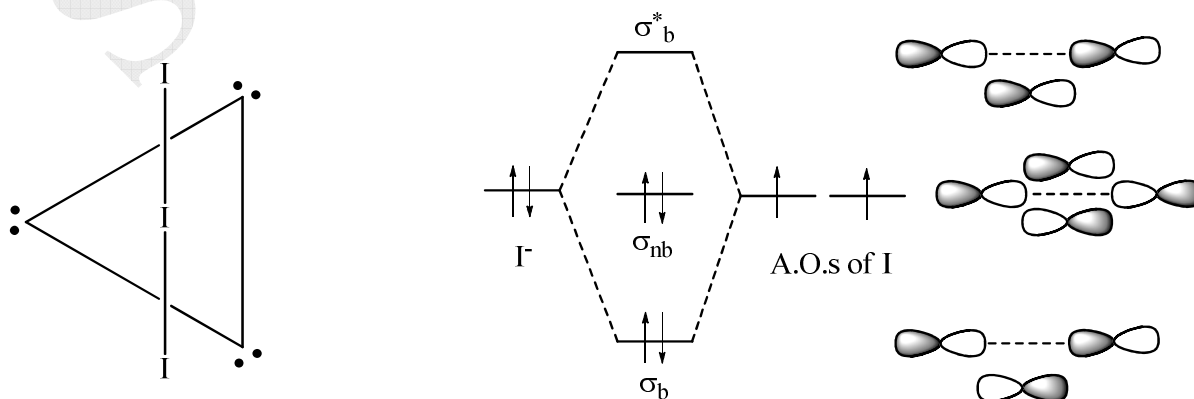
For a given cation, the stability of a polyhalides is found to increase with (i) the size of the central atom and (ii) symmetrical disposal of the adjacent halogen atoms. The approximate sequence of symmetry decreasing as: $\text{I}_3^- > \text{IBr}_2^- > \text{ICl}_2^- > \text{I}_2\text{Br}^- > \text{Br}_3^- > \text{BrCl}_2^- > \text{Br}_2\text{Cl}^-$

Polyhalides containing two different halogens decompose thermally to form the halide having the highest lattice energy, for example:

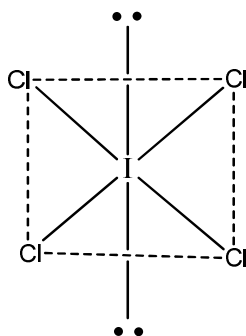


Structure

Trihalide ions (I_3^- , ICl_2^- etc.) are linear with 10 valence electron of the central atom which is sp^3d hybridized. The geometry is trigonal bipyramid with three lone pairs in equatorial plane. But, I-I distance is longer than in I_2 suggests it is not the normal 2c-2e bond. MO theory approach is more meaningful. Assuming, singly occupied 5p_z orbitals on two I atoms and a fully occupied 5p_z orbital of I^- are involved in bonding. These three orbital formed three M.O., one bonding, one non-bonding and one anti-bonding. Out of 4 electrons, 2 electrons occupy bonding MO and another two occupy non-bonding MO i.e., 3c-4e bonding where, one bond is spreading over two position giving bond order 0.5.



The structure of penta-atomic polyhalides (IF_4^- , ICl_4^- , BrF_4^- etc) is all planar with 12 valence electrons and central atom is sp^3d^2 hybridized. The geometry is octahedral with two lone pairs.



Pseudohalogens and pseudohalides:

A few uninegative ions that contains two or three atoms of which at least one is N, that have properties similar to those of the halide ions are called pseudohalides.

Pseudohalides	Pseudohalogens	Hydracids
CN ⁻ (cyanide)	(CN) ₂ (cyanogens)	HCN
SCN ⁻ (thiocyanate)	(SCN) ₂ (thiocyanogen)	HSCN
SeCN ⁻ (selenocyanate)	Se(CN) ₂ (selenocyanogen)	
OCN ⁻ (cyanate) ⁻ O-C≡N		HOCN
NCO ⁻ (isocyanate) ⁻ N=C=O		HNCO
CNO ⁻ (fulminate) ⁻ C-N=O		HCNO
N ₃ ⁻ (azide)		HN ₃

Similarities in properties:

(i) Pseudohalides are oxidized to dimeric molecule like halogens.

(CN)₂, (SCN)₂ etc.

(ii) Like halogen molecule, Pseudohalogens undergoes thermal and photochemical dissociation. (CN)₂ → 2CN[•]

(iii) Pseudohalogen reacts with aqueous alkali similar to halogen.

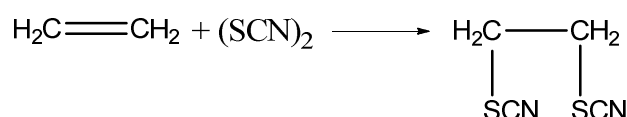


(iv) Solubility of silver salts of pseudohalides in water resembles those of silver halides, e.g., AgCN is insoluble in water but dissolves in aqueous ammonia like AgCl.

(v) Pseudohalogens can also form interpseudohalogens, e.g., BrCN, ClCN, CNN₃, SCNCl.

(vi) Pseudohalides may form stable complexes similar to halocomplexes, e.g., [Cu(CN)₄]⁻, K₂[Hg(SCN)₄]⁻

(vii) Pseudohalogens can add to C=C double bond like halogens.



(viii) Similar to halides, pseudohalides forms hydracids, e.g., HCN, HSCN, HN₃ etc.

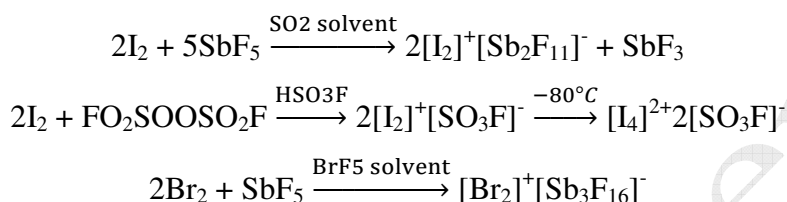
(ix) Pseudohalides forms insoluble salts with Ag⁺, Hg⁺, Pb²⁺ similar to halides.

In spite of similarities with halogens, there are some inherent differences between halides and pseudohalides.

- (i) most pseudohalides are strong coordinating agents but halides are weak ligands.
- (ii) many of pseudohalides are ambidentate, having two alternate sites for coordination. For example, CN^- can coordinate through either C or N atoms. SCN^- can coordinate through either S or N atom.
- (iii) Pseudohalides are good π -acids and occupy higher positions than the halides in spectrochemical series. $\text{CN}^- > \text{N}_3^- > \text{-NCS}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- \sim \text{SCN}^- > \text{I}^-$.
- (iv) Hydracids formed by pseudohalides are extremely weak, e.g., HCN (pK = 9.2), HN_3 (pK = 4.9), HNCO (pK = 3.5).

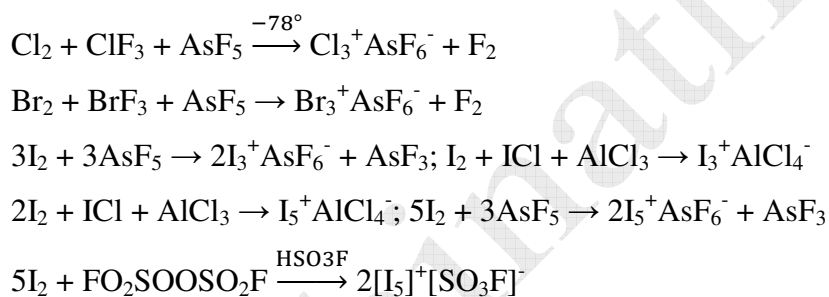
Basic Properties of halogens:

The increasing stability of positive ions indicates an increasing tendency to show basic character. Generally, down the group basicity of the elements increases. In case of halogens, iodine has more basic property and the basicity order will be $F_2 < Cl_2 < Br_2 < I_2$. Halogens show basicity through forming X_2^+ cation by removal of an electron from π^* M.O. Various salts of I_2^+ and Br_2^+ are known while Cl_2^+ has been observed in gas phase only. Few other cation X_n^+ ($n = 3,5$) and I_4^{2+} are also known.

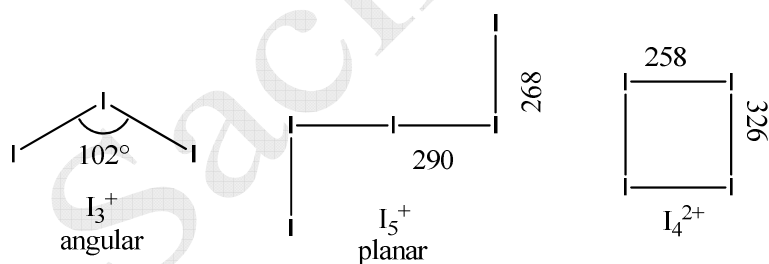


HSO_3F = fluorosulphonic acid and FO_2SOOSO_2F = bis(fluorosulphuryl)peroxide, an oxidizing agent. The salt containing Br_2^+ have bright red colour while those of I_2^+ are bright blue. Cl_3^+ is yellow, Br_3^+ is brown and I_3^+ is dark brown.

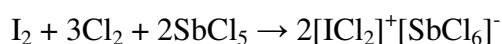
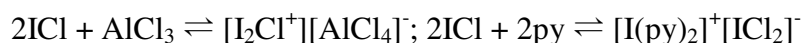
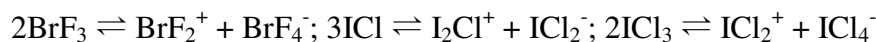
The compounds containing cations such as $[Cl_3]^+$, $[Br_3]^+$, $[I_3]^+$, $[Br_5]^+$, $[I_5]^+$ have prepared.



The structures of few cations are established from X-ray crystallography study.

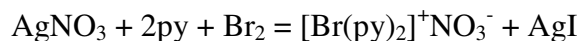
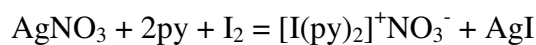


Not only that, different interhalogen cation also known, for example,



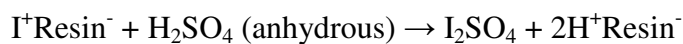
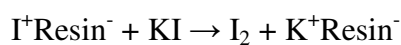
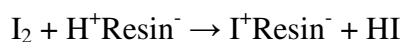
Compounds containing I(I)

Compounds containing I(I) may be generally prepared by reacting stoichiometric quantities of iodine with excess of pyridine and a silver salt in chloroform.



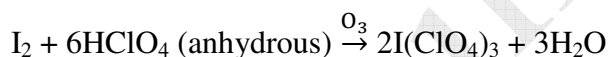
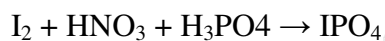
Similarly, $[\text{I}(\text{py})_2]^+\text{ClO}_4^-$, $[\text{I}(\text{py})]^+\text{CH}_3\text{COO}^-$, $[\text{I}(\text{py})]^+\text{PhCOO}^-$ are known.

I^+ cation may be retained on cation exchange resin by passing a solution of iodine in an inert solvent. The bound I^+ may be eluted with KI, to estimate the amount of I^+ or eluted with other reagent.

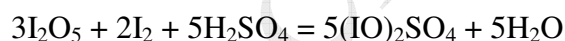


Compounds of I(III)

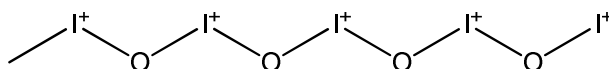
Though there is no structural evidence for I^{3+} , it is formally present in compounds like $\text{I}(\text{CH}_3\text{COO})_3$, $\text{I}(\text{ClO}_4)_3$, IPO_4 , $\text{I}(\text{SO}_3\text{F})_3$. $\text{I}(\text{CH}_3\text{COO})_3$ is obtained from the treatment of I_2 with fuming HNO_3 and acetic anhydride.



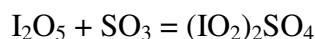
Iodosyl compounds: These compounds contain IO^+ group, are obtained by reaction I_2O_5 and I_2 in concentrated acids. For example, $[\text{IO}^+]_2\text{SO}_4$, $[\text{IO}^+]_2\text{S}_2\text{O}_7$, $[\text{IO}^+]\text{SeO}_4$.



Iodosyl sulphate, $(\text{IO})_2\text{SO}_4$ is a yellow solid which may have a zig-zag chain of I-O-I cross-linked by the anion.



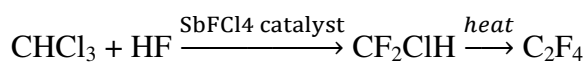
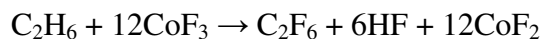
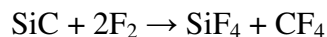
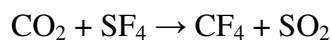
Iodyl salts: These compounds contain IO_2^+ ion. Iodyl sulphate is prepared by reacting I_2O_5 with SO_3 .



Peroxodisulphuryl difluoride, $\text{FO}_2\text{SOOSO}_2\text{F}$ yields $[\text{IO}_2]^+[\text{SO}_3\text{F}]^-$ with I_2O_5 .

Fluorocarbons and Chlorofluorocarbons:

These are fluorides or mixed halides of carbon corresponding to different hydrocarbons. For example, CF_4 , C_2F_6 , CF_2Cl_2 , CFCl_3 etc. CF_4 and C_2F_6 can be made as follows:

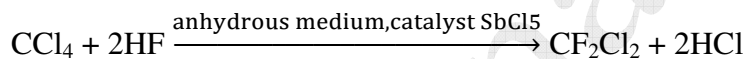


Fluorocarbons may be liquid, gas or solid. These are useful lubricants, solvent and insulator.

The fluorocarbons are chemically inert and unaffected by concentrated acids or alkalis. They dissolve only in nonpolar solvent. The inertness and stability of fluorocarbons due to:

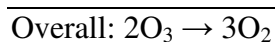
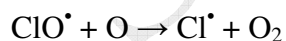
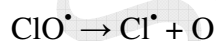
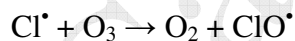
(i) high C-F bond energy (ii) absence of any suitable acceptor orbital at F or C atom to initiate hydrolytic attack (iii) due to higher electronegativity of F atom than C, F acquire δ^- charge while C atom acquire δ^+ charge. (iv) size of F atom is large than H atom, so F atoms shields the C skeleton.

Freons (CFCs): Chlorofluoro carbon, CFCl_3 , CF_2Cl_2 , CF_3Cl is called freons. These may be prepared by fluorination of the chloro compound with SbF_3 in presence of SbCl_5 or by HF in presence of SbF_3 - SbCl_5 .



Freons are unreactive and non toxic widely used as refrigeration fluids, as the propellant in aerosols for washing computer boards.

Freons are air pollutant as it acts as greenhouse gas and damage ozone layer in upper atmosphere through the formation of free radical.



Group 18

Group 18 elements are the noble gas, He, Ne, Ar, Kr, Xe, Rn, having general outermost configuration $ns^2 np^6$. The noble gases are present in the earth atmosphere about 1%. Ar is highest abundant and He is 2nd highest abundant. Ar is obtained by fractional distillation of liquid air while He is obtained from liquefaction of natural gas.

Liquid helium is used in the laboratory as a refrigerant and used to provide an inert atmosphere in welding metals. Helium is also used as a substituent for nitrogen in breathing gas for deep sea diver. It is also used sea coolant in high temperature nuclear reactors.

Argon is largely preferred over helium in metallurgy and systems of inert atmosphere as in arc welding of aluminium. It is also used in fluorescent tube, discharge tubes, ionisation counters. Neon is widely used in electronics for filling photoelectric cells, voltage stabilizers and neon lights.

The valence shell of the noble gas element is fully filled make is stable configuration. Therefore, the energy required for promotion of an electron to next vacant orbital or to accommodate an extra electron to vacant orbital demands high energy. For this reason noble gas are chemically inert.

Clathrate:

Clathrates or cage compounds are the compounds in which some molecules or atoms (inert gas) of appropriate size are trapped in the cavities of crystal lattice of other compounds. The trapped molecule does not form any chemical bond, only weak van der Waals force exists. The trapped molecule are called guest and the molecule which trap the guest molecule in its cavity is called host. **Example:**

(i) Trapping in the H-bonded crystalline structure of quinol: During crystallization of quinol(1,4-dihydroxybenzene) in water or methanol under an inert gas of high pressure, the inert gases are trapped in the cavities of diameter 4 Å. Hydroquinone molecule produce hexagonal prism of O-atoms surrounded by benzene rings. Within the hexagonal prisms the guest species are trapped. Three host molecules collectively provide one cavity. Noble gases escape on dissolution of quinol in suitable solvent when the H-bonded crystal structure breaks down. Generally, Ar, Kr, Xe are known to form such compounds.

(ii) Trapping in H-bonded structure of ice: Ar, Kr, Xe are also trapped in cavities when water is frozen under a high pressure of gas. These clathrates are commonly called 'the noble gas hydrates'. They have formula approximating to $6H_2O : 1$ gas atom. The heavier noble gases can also be trapped in cavities in synthetic zeolites. Clathrates provide a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.

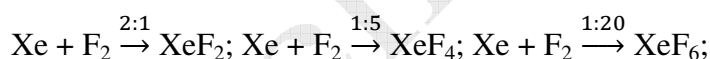
Compounds of noble gases:

But, Bartlett first observed that PtF_6 changes colour on exposure to air. Very strong oxidizing agent PtF_6 is oxidizing O_2 to form a compound, $\text{O}_2^+\text{PtF}_6^-$. Since, the ionisation energy of Xe and O_2 is very similar, it was expecting PtF_6 would also oxidize Xe. Experimentally it was found that the reaction of Xe with PtF_6 vapour produces an orange solid, $[\text{XeF}]^+[\text{Pt}_2\text{F}_{11}]^-$.

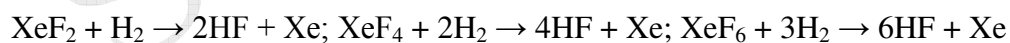


compounds	Oxidation state			
	+2	+4	+6	+8
Halides	KrF_2 , XeF_2 , XeCl_2 , (RnF_2)	XeF_4 (RnF_4)	XeF_6 (RnF_6)	
Oxides			XeO_3	XeO_4
Oxofluorides			XeOF_4 , XeO_2F_2	XeO_3F_2
Fluoro complexes	$[\text{KrF}][\text{MF}_6]$ $[\text{XeF}][\text{MF}_6]$	$[\text{XeF}_3][\text{MF}_6]$	$[\text{XeF}_5][\text{MF}_6]$ $[\text{XeOF}_3][\text{MF}_6]$ $\text{Cs}_2[\text{XeF}_8]$	$[\text{XeOF}_5][\text{MF}_6]$
Salts of oxoacids	$\text{Xe}[\text{ClO}_4]_2$ $[\text{XeF}][\text{NO}_3]$			
acids			H_2XeO_4	H_4XeO_6

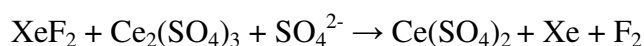
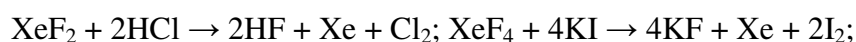
Xenon fluorides are obtained from direct reaction of Xe with fluorine at 400°C in a sealed nickel vessel. The products depend on the F_2 and Xe ratio.



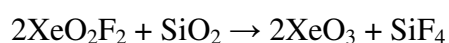
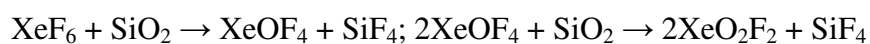
These compounds are white solid. The lower fluoride can form higher fluorides when heated with F_2 under pressure. The fluorides are all extremely strong oxidizing and fluorinating agents. They react quantitatively with hydrogen as follows:



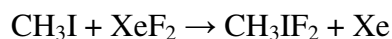
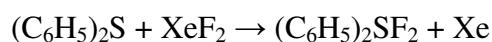
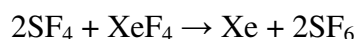
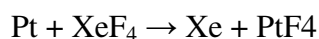
They oxidizes Cl^- to Cl_2 , I^- to I_2 and cerium(III) to cerium(IV):



XeF_6 attacks glass at ordinary temperature while other fluorides react on heating. For this reason XeF_6 cannot be handled in glass or quartz apparatus.

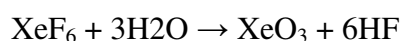
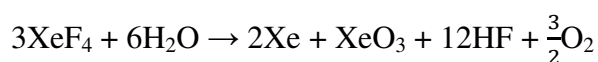
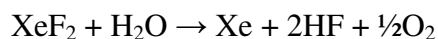


Fluorinating agents:



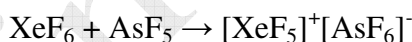
Hydrolysis:

All the xenon fluorides are readily hydrolyzed, the reaction of XeF_6 being most vigorous.



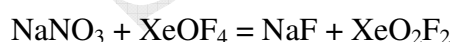
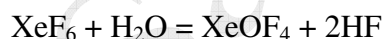
Complex:

Xenon fluorides react with fluoride ion acceptors like MF_5 ($\text{M} = \text{As, Sb, Bi, Nb, Ta, Ru, Os, Ir, Pt}$) forming complexes with stoichiometries $(\text{XeF}_n)_2\text{MF}_5$, $(\text{XeF}_n)\text{MF}_5$ and $\text{XeF}_n(\text{MF}_5)_2$. For example, XeF_2 gives three products: (i) $2\text{XeF}_2 \cdot \text{MF}_5$ or $[\text{Xe}_2\text{F}_3]^+[\text{MF}_6]^-$ (ii) $\text{XeF}_2 \cdot \text{MF}_5$ or $[\text{XeF}]^+[\text{MF}_6]^-$ (iii) $\text{XeF}_2 \cdot 2\text{MF}_5$ or $[\text{XeF}]^+[\text{M}_2\text{F}_{11}]^-$

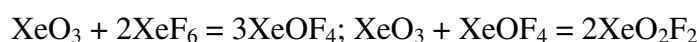


Xenon Oxofluorides

XeOF_4 is stable colourless liquid, which is obtained by the controlled hydrolysis of XeF_6 . It is also prepared by treating sodium nitrate with a slight excess of XeF_6 at 70°C . Excess NaNO_3 leads to XeO_2F_2

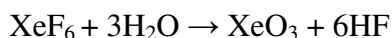


Oxofluorides are also produced when XeO_3 reacts with XeF_6 and XeOF_4 .

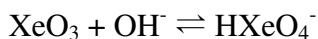


Xenon oxides, Xanates and Perxenates:

Xenon trioxide is obtained from hydrolysis of XeF_6 or XeF_4 . The violence of the reaction is controlled by sweeping XeF_6 vapour with dry N_2 into water.



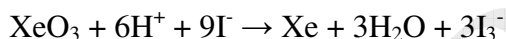
XeO_3 is a white deliquescent solid. In strongly alkaline solution, the xenate ion is formed.



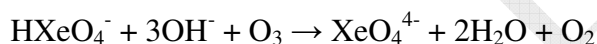
However, in solution HXeO_4^- undergoes slow disproportionation to perxenate and xenon gas.



XeO_3 is strong oxidizing agent in aqueous medium. It oxidizes KI quantitatively and can be used to estimate the oxide content in any sample.



Perxenates is also obtained by passing ozone into dilute solution of XeO_3 in aqueous NaOH.



Structure and Bonding in Xenon compound

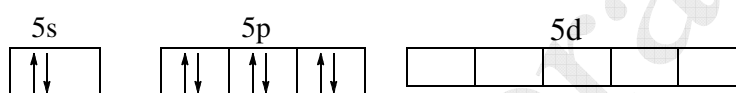
Formula	Structure	No. of electron pair	No. of lone pair	VSEPR explanation
XeF_2	linear	5	3	Five electron pair form TBP with three lone pair in equatorial position
XeF_4	Sq. planar	6	2	Six electron pairs form an octahedron with two position occupied by lone pair
XeF_6	Distorted octahedron	7	1	Pentagonal bipyramid or, capped octahedron with one lone pair
XeO_3	Pyramidal	7	1	Three π bond. The remaining four pairs form tetrahedron with one corner occupied by a lone pair
XeO_2F_2	Trigonal bipyramid	7	1	Two π bond. Remaining five pairs form TBP with a lone pair in equatorial position
XeOF_4	Sq. pyramid	7	1	One π bond. Remaining 6 pairs form an octahedron with one lone pair
XeO_4	Tetrahedral	8	0	Four π bond. Remaining four pairs form tetrahedron
XeO_6^{4-}	octahedral	8	0	Two π bond. Remaining six pairs form octahedron

XeF₂

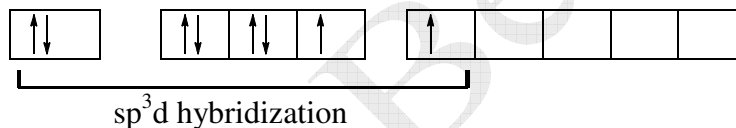
XeF₂ is linear molecule with both X-F distances 2.00 Å. Xe undergoes sp³d hybridization by promoting an electron from the 5p level to the 5d level. The two unpaired two electrons forms bond with fluorine atom occupies axial position and remaining three paired electrons occupy the equatorial positions generating a trigonal bipyramid geometry.

(Note: The validity of effective overlap of large 5d orbital of Xe with 2p orbital of F and mixing of the Xe orbitals for hybridization as energy difference of 5p and 5d orbital is about 960 kJ mol⁻¹ is a serious issue for VBT.)

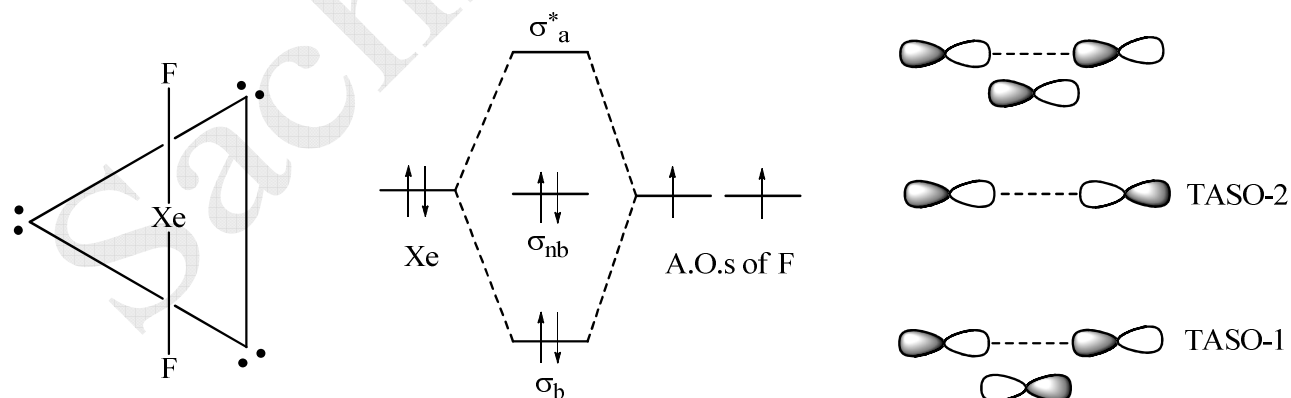
Ground state of Xe



Excited state of Xe

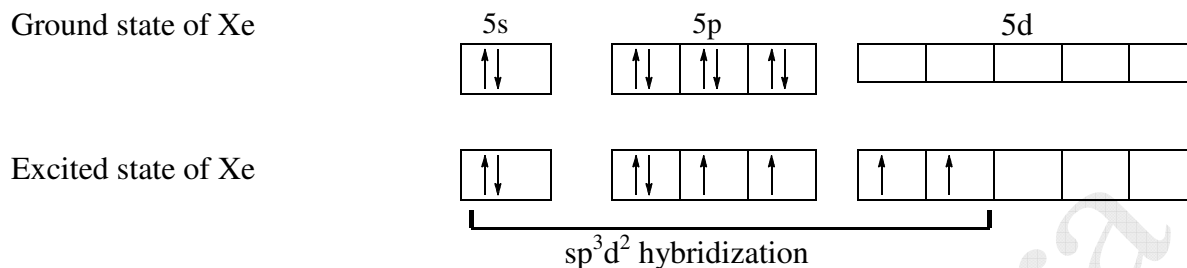


According to MOT 3c-4e bond is formed. The singly occupied 2p_z orbitals on two F atoms and a fully occupied 5p_z orbital of Xe are involved in bonding. These three orbitals form three M.O., one bonding, one non-bonding and one anti-bonding. Out of 4 electrons, 2 electrons occupy bonding MO and another two occupy non-bonding MO resulting in the single bonding electron pair spreading over all three atoms and the non-bonding electrons are basically localized on the F-orbitals, imparting some ionic character. This is equivalent to valence bond resonance among the structures F—Xe⁺F⁻ ↔ F⁻Xe⁺—F.



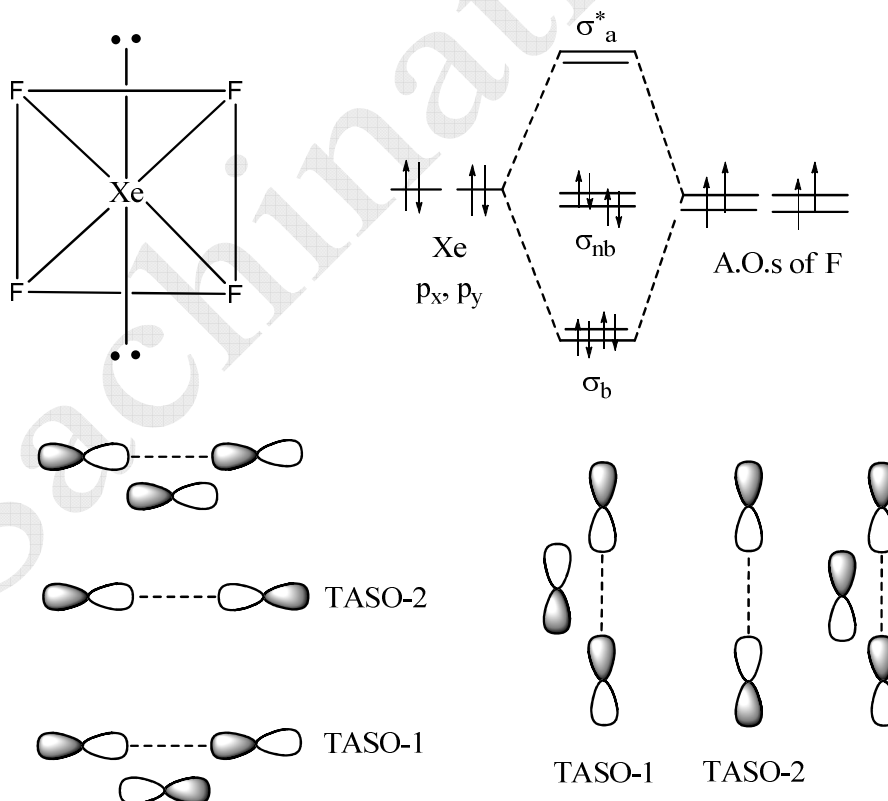
XeF₄

The structure of XeF₄ is square planar with Xe-F distances of 1.95 Å. The VBT explains the bonding by promoting two electrons from 5p to 5d level as shown below:



Four unpaired electrons form bonds to four F atoms. Total six paired electrons forms an octahedral geometry with two position occupied by lone pairs.

According to MOT, Xe atom forms two 3c-4e bonds with four F-atoms. The 5p_x orbital of Xe forms a three-centre MO with 2p_x orbitals of two F atoms just as in XeF₂. Similarly, 5p_y orbital forms another three-centre MO involving two another F-atoms. These two 3c MO are at right angle to each other giving a square planar molecule.



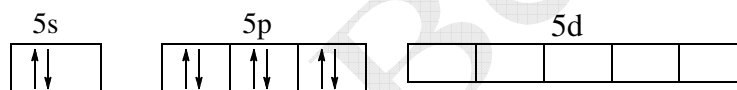
XeF₆

The structure of XeF₆ is a distorted octahedron. According to VBT, promotion of three 5p electrons of Xe to 5d level giving six unpaired electrons which form bonds with fluorine atoms and one lone pair. The lone pair continuously interchanges its position between various triangular faces and centre of edges and it is stereochemically active.

The MOT fails to explain the structure of XeF₆, since three 3c-4e molecular orbital mutually perpendicular would give a regular octahedral shape.

Solid XeF₆ is polymeric consisting XeF₅⁺F⁻ units. Generally, it contains tetramers, where four square pyramidal XeF₅⁺ ions are joined to two similar ions by means of two bridging F⁻ ions. The Xe-F distances are 1.84 Å on the square pyramidal units and 2.23 and 2.60 Å in the bridging groups.

Ground state of Xe



Excited state of Xe

