

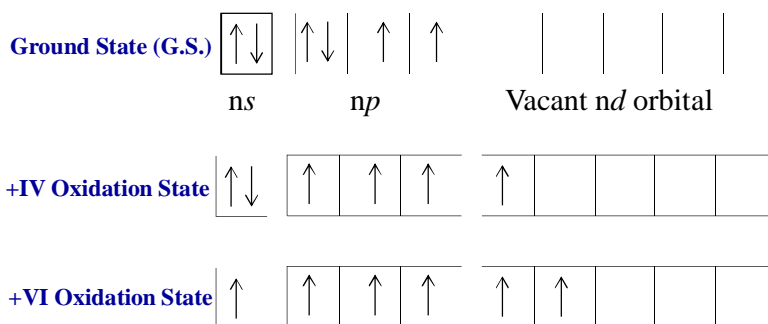
Oxygen Family (Group 16 elements)

General Description and Common Trends:

This group contains five elements with general valence shell electronic configuration $ns^2 np^4$. First four elements of this group (O, S, Se and Te) are non-metals. These elements are collectively called 'chalcogens' or 'ore forming' elements because a large number of the metal ore occur as respective oxides, sulphides etc.

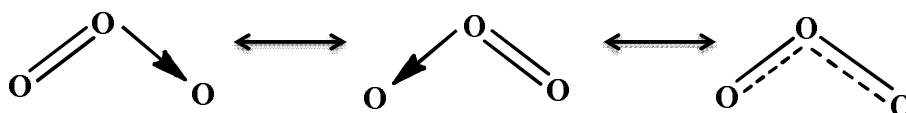
Element	Atomic Number	Electronic Configuration	Oxidation States
Oxygen, O	8	[He] $2s^2 2p^4$	-II, -I
Sulphur, S	16	[Ne] $3s^2 3p^4$	-II, II, IV, VI
Selenium, Se	34	[Ar] $3d^{10} 4s^2 4p^4$	-II, II, IV, VI
Tellurium, Te	52	[Kr] $4d^{10} 5s^2 5p^4$	II, IV, VI
Polonium, Po	84	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$	II, IV

- ❖ Metallic character increases down the group. O and S are totally non-metallic while non-metallic character is weaker in Se and Te. The last element *i.e.* Po is markedly metallic and radioactive.
- ❖ As clear from the outer shell electronic configuration mentioned in the table, these elements need two electrons to complete their octet and attain noble gas configuration. Hence, these elements tend to gain (by forming M^{2-} ions) or share two electrons. The electronegativity of O is very high and that is why it shows oxidation state of -II only and forms ionic oxides with most of the metals. However there are few exceptions where oxidation state of O is -I (H_2O_2) or +II (F_2O). The electronegativity of other elements is low and therefore the tendency to form di-negative ion (-II oxidation state) decreases down the group. Po does not show any negative oxidation state.
- ❖ S, Se and Te are able to show +IV and +VI oxidation state due to availability of vacant d orbitals. +IV oxidation state is observed when one of the p electrons gets excited to vacant d orbital. On further excitation, ns electrons also go to vacant d orbital giving +VI oxidation state.



Oxygen and Ozone

- ❖ Oxygen exists as two non-metallic forms, dioxygen (O_2) and ozone (O_3). O_2 is stable as a diatomic molecule and a gas. As explained through molecular orbital (MO) diagram of O_2 , dioxygen is paramagnetic. Liquid O_2 is pale blue while solid is blue in color.
- ❖ Ozone (O_3) is triatomic allotrope of oxygen. It is an unstable diamagnetic dark blue gas. The structure of O_3 is angular. The O–O–O bond angle is $116^\circ 48'$ and both the bond lengths are 1.278 \AA , which is intermediate between single and double bond. Valence bond approach suggests sp^2 hybridization for central oxygen atom and partial double bond character can be explained by resonance hybrids. However MO theory provides a better explanation through delocalized three-center π bonding (*for further reading*).



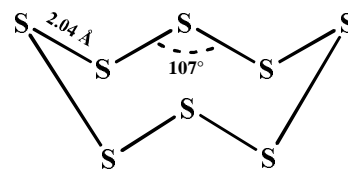
Resonance in Ozone

- ❖ Sulphur has more allotropic forms than any other element. There are two common crystalline forms of sulphur.

α or Rhombic sulphur: Stable at room temperature

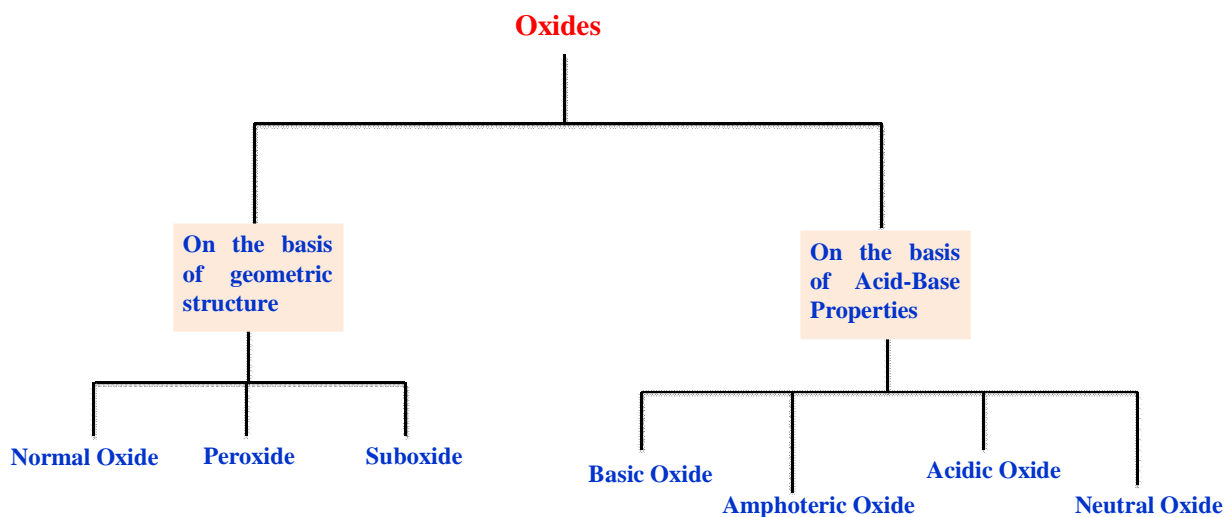
β or Monoclinic sulphur: Stable above 95.5°C

Both of them contain puckered S_8 ring.



Oxides

A. Classification

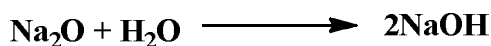


Normal Oxides: These have empirical formula M_xO_y where oxidation number of oxygen is $-II$ and accordingly oxidation number of M can be calculated. It can be understood from example of MgO , here oxidation number of O is $-II$ so oxidation number of Mg will be $+II$. Other examples are H_2O and Al_2O_3 . They contain only $M-O$ bond.

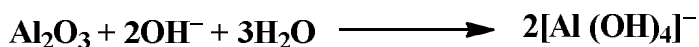
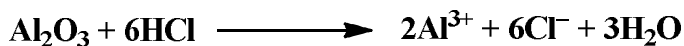
Peroxide: These contain more oxygen atom than expected from the oxidation number of M . Some are ionic and contain O_2^{2-} ion. For example, Na_2O_2 , BaO_2 ; so if we look at Na_2O_2 , $2Na^+$ ions should need one O^{2-} ion to balance two positive charges, while in Na_2O_2 , two oxygen atoms are present which is more than expected and thus it is peroxide (ionic). Covalently bonded peroxides are those who contain $-O-O-$ linkage and examples are H_2O_2 , peroxomonosulphuric acid and peroxodisulphuric acid (for structure see further).

Suboxide: As per formula, these contain less oxygen than would be expected from the oxidation number of M . These have $M-M$ bond in addition to $M-O$ bond. Example is carbon suboxide ($O=C=C=C=O$).

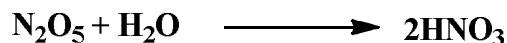
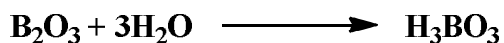
Basic Oxide: Most metallic oxides are basic. These are ionic and contain O^{2-} ions. Typical examples are oxides of Group 1, 2 and lanthanides. For formation of ionic oxides, first O_2 molecule has to be converted to O^{2-} ions which requires a large amount of energy as second electron gain enthalpy of oxygen is positive (energy required). This required energy is compensated by high lattice energy of ionic metal oxides. Thus ionic metal oxides have high lattice energy and hence high melting points. Examples are Na_2O , MgO , La_2O_3 . One important property of basic oxide is that these form base upon reaction with water or form salts upon reaction with acids.



Amphoteric Oxide: These are metal oxides which react with both strong acids and bases. Examples are BeO , Al_2O_3 , Ga_2O_3 , SnO , PbO and ZnO .



Acidic Oxide: These are non-metallic oxides and generally covalent. These may be discrete (CO_2 , NO_2 , SO_2 , Cl_2O) or polymeric (B_2O_3 , SiO_2). Some react with water to form acids.



On the other hand some do not react with water but react with bases (SiO_2).

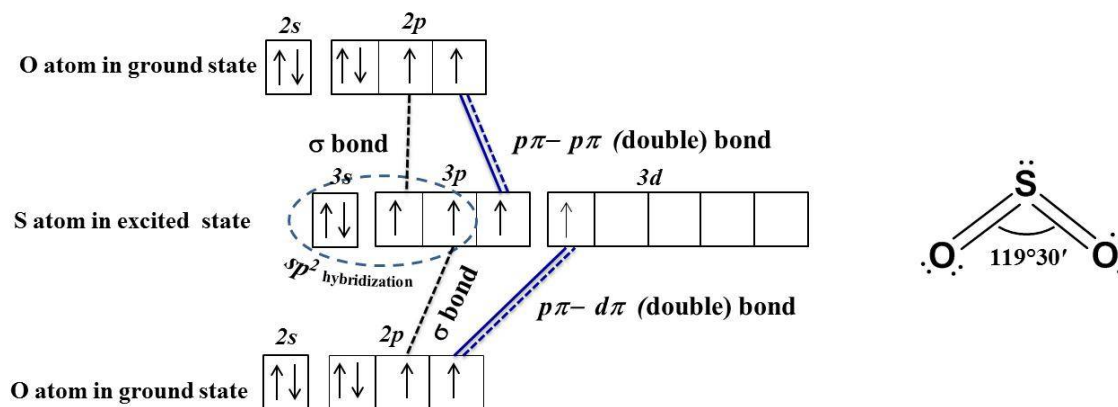
Why HNO₃ is stronger acid than HNO₂?

N₂O₅ is anhydride of HNO₃ while N₂O₃ is anhydride of HNO₂. The oxidation state of N is +V in N₂O₅ while +3 in N₂O₃. Since higher oxidation state of central N atom will tend to attract the electron density away from O–H bond this will facilitate the release of H⁺ ions. Hence HNO₃ having higher oxidation state of N atom will have easier release of H⁺ ions and it will be a stronger acid.

Oxides of Sulphur, Selenium:

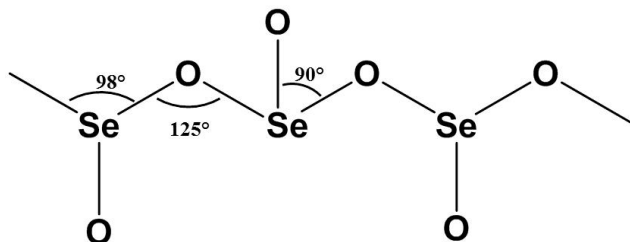
Dioxides

Sulphur dioxide (SO₂): It is a colorless gas with a choking smell and is very soluble in water. In water it is present as hydrated species such as SO₂·6H₂O with minute amount of sulphurous acid (H₂SO₃). It has a *bent / V-shaped* structure and central S-atom uses sp^2 hybridized orbitals for σ bond formation.



Central S atom has three sp^2 hybrid orbitals out of which one contains a lone pair of electron while two other half filled orbitals overlap with one of the p orbitals of each of the two oxygen atoms forming 2 σ bonds. p orbital of one of the oxygen atom overlaps with un-hybridized p orbital of S atom forming $p\pi-p\pi$ double bond while p orbital of other O atom overlaps with d orbital of S atom and forms $p\pi-d\pi$ double bond.

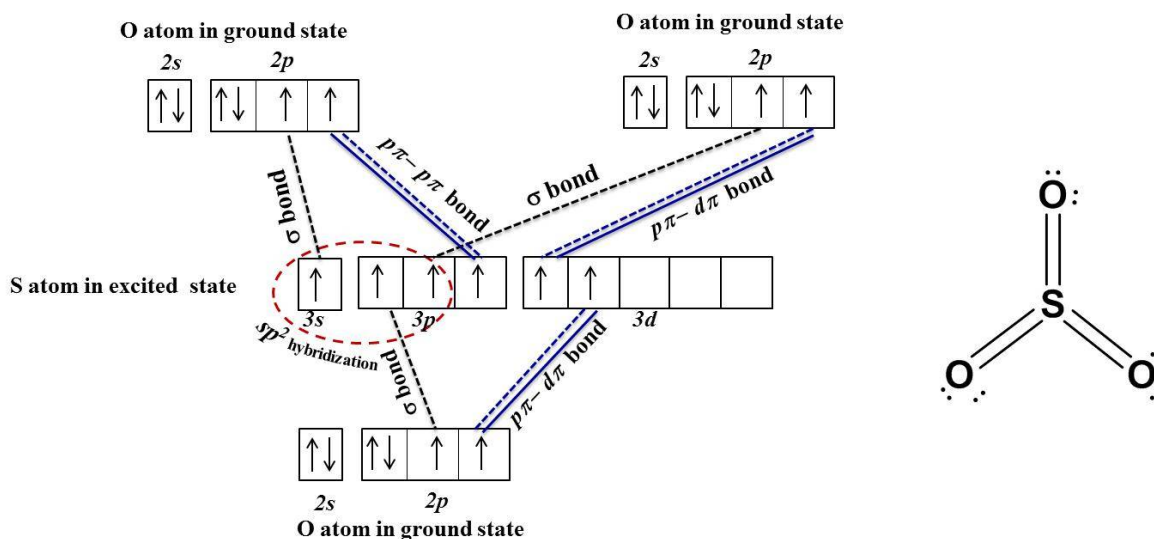
Selenium dioxide (SeO₂): It is solid at room temperature. In gaseous state it has same structure as SO₂ however in solid state it exist as infinite chains which are not planar.



Trioxides:

Sulphur trioxide (SO₃): SO₃ reacts vigorously with water and evolves a large amount of heat forming H₂SO₄.

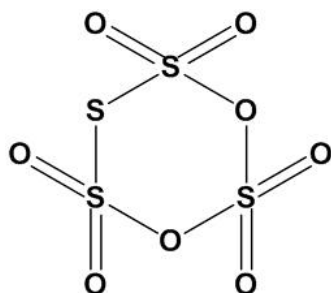
❖ In **gaseous phase** it has planar triangular structure.



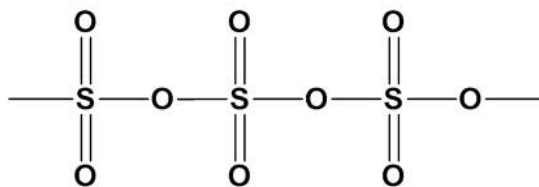
Central S atom has three sp^2 hybrid orbitals and all the three orbitals overlap with one of the p orbitals of each of the three oxygen atoms forming 3 σ bonds. p orbital of one of the oxygen atom overlaps with un-hybridized p orbital of S atom forming $p\pi-p\pi$ double bond while p orbitals of other two O atoms overlap with two d orbitals of S atom forming 2 $p\pi-d\pi$ double bonds.

❖ At room temperature SO₃ is solid and exist in three distinct forms:

1. γ -SO₃ is ice-like and is a cyclic trimer.
2. β -SO₃ is made up of infinite helical chains of tetrahedral [SO₄] units, each sharing two corner atoms.
3. α -SO₃ is most stable form and is made up of chain cross linked to sheets.

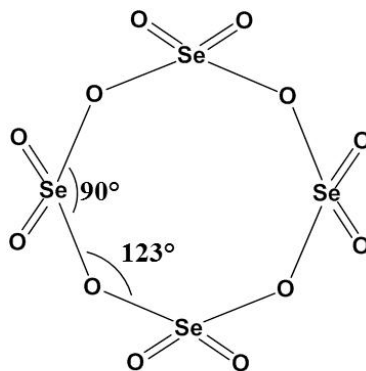


SO₃ cyclic trimer



SO₃ chains

Seleniumtrioxide (SeO₃): It exists as a monomer in vapor phase while exists as a cyclic tetramer (Se₄O₁₂) in crystalline state.



Structure of Se₄O₁₂

Oxoacids of Sulphur:

Many of the oxoacids of Sulphur exist as anions and salts. Two series can be identified on the basis of oxidation state of S atom:

1. 'ous' ending series: S has +IV oxidation state and their salts ending in 'ite'.
2. 'ic' ending series: S has +VI oxidation state and their salts ending in 'ate'.

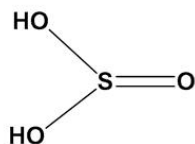
Oxoanions/Oxoacids have strong π -bonds and they have little tendency to polymerize.

On the basis of structural similarities oxoacids are classified in 4 categories:

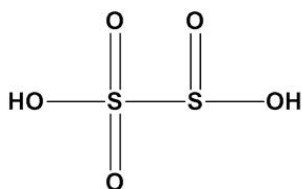
- A. Sulphurous acid series
- B. Sulphuric acid series
- C. Thionic acid series
- D. Peroxoacid series

Let's talk about them one by one.

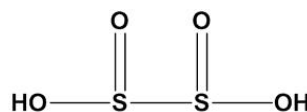
A.Sulphurous acid series:



Sulphurous Acid

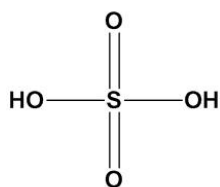


Pyrosulphurous Acid/
Disulphurous Acid

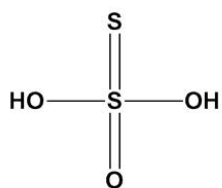


Dithionous Acid

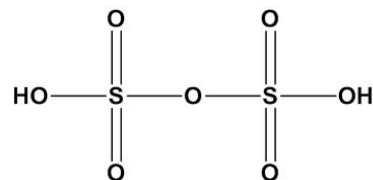
B.Sulphuric acid series:



Sulphuric Acid

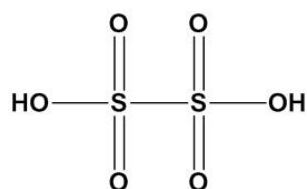


Thiosulphuric Acid

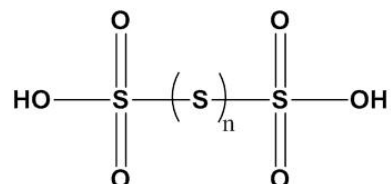


**Pyrosulphuric Acid/
Disulphuric Acid**

C.Thionic acid series:

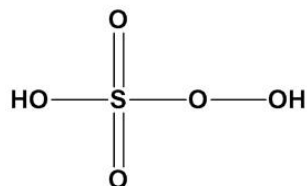


Dithionic Acid

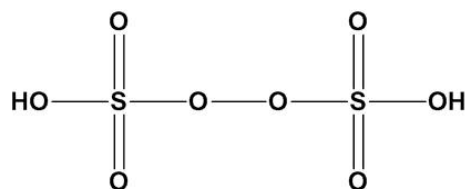


Polythionic Acid

D.Peroxoacid series:

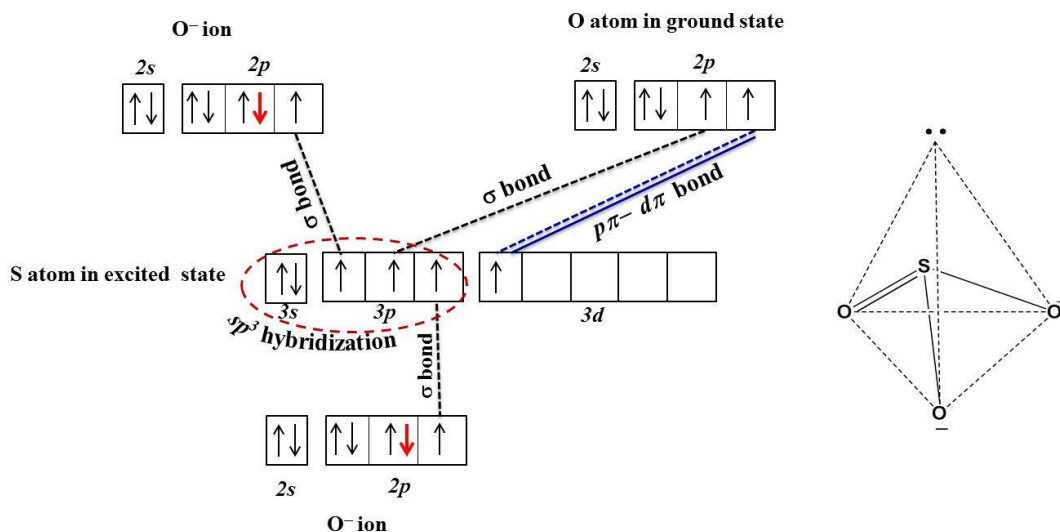


Peroxomonosulphuric Acid



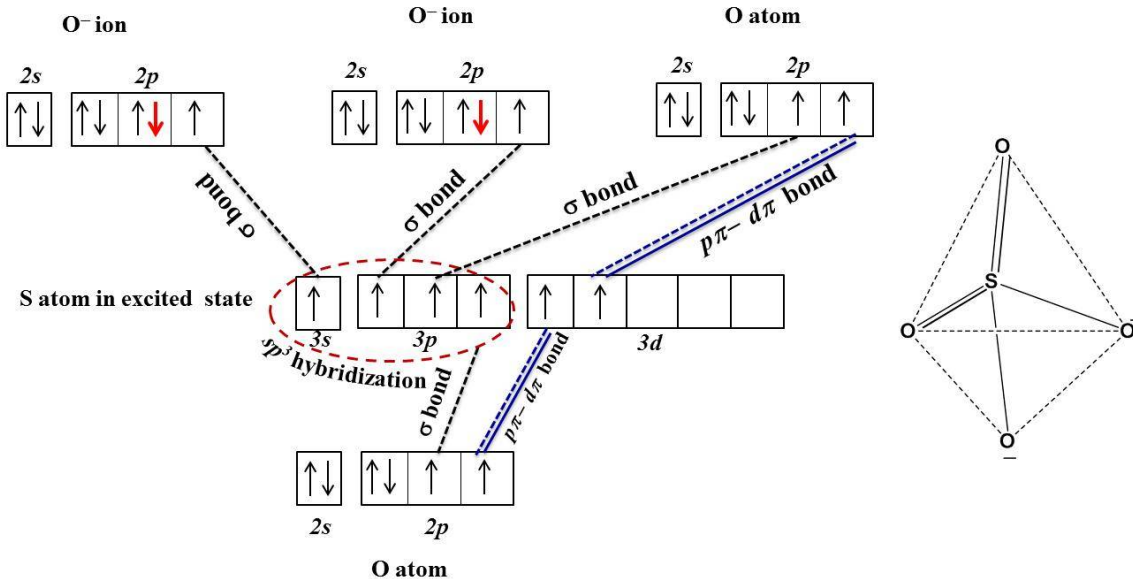
Peroxodisulphuric Acid

Structure of Sulphite (SO_3^{2-}) ions:



SO_3^{2-} ion has pyramidal shape that is tetrahedral (sp^3 hybridization) with one position occupied by lone pair and O–S–O bond angle is 106° (distortion due to lone pair). The π bond is delocalized so S–O bond order is 1.33 (in between single and double bond).

Structure of Sulphate (SO_4^{2-}) ion:



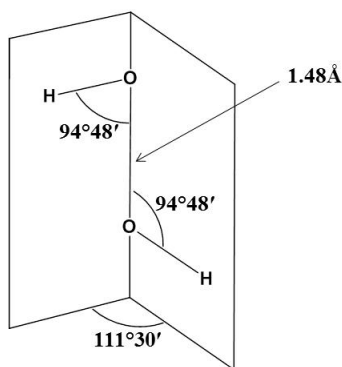
The SO_4^{2-} is tetrahedral (sp^3 hybridization) with equal bond lengths and the S–O bond order is ~ 1.5 . The bonding includes four σ bonds between S and O atoms and two π bonds delocalized over S and four O atoms.

Hydrides of Oxygen and Sulphur

H₂O₂ and H₂S₂:

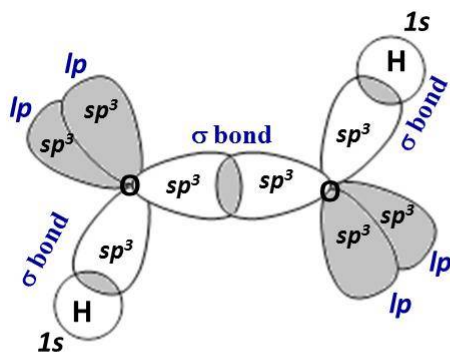
Structure of hydrogen peroxide (H₂O₂):

H₂O₂ is a colorless liquid which resembles water. Both H₂O₂ and H₂S₂ have similar non-planar 'skew' structures. The vapor phase structure has been shown below:



Structure of H₂O₂ in gas phase

Each of the two O atoms is linked with H-atoms by two σ bonds and has two lone pairs on it. Thus each of the O atoms is sp^3 hybridized with two lone pairs. The O-O σ bond results from head to head overlap of two sp^3 hybrid orbitals on both the O atoms. O-H bonds are formed by overlap of the remaining sp^3 hybrid orbital of O atom with 1s orbital of H atoms (Figure below).



Structure of H₂O₂ molecules involving sp^3 hybridization of both O atom.



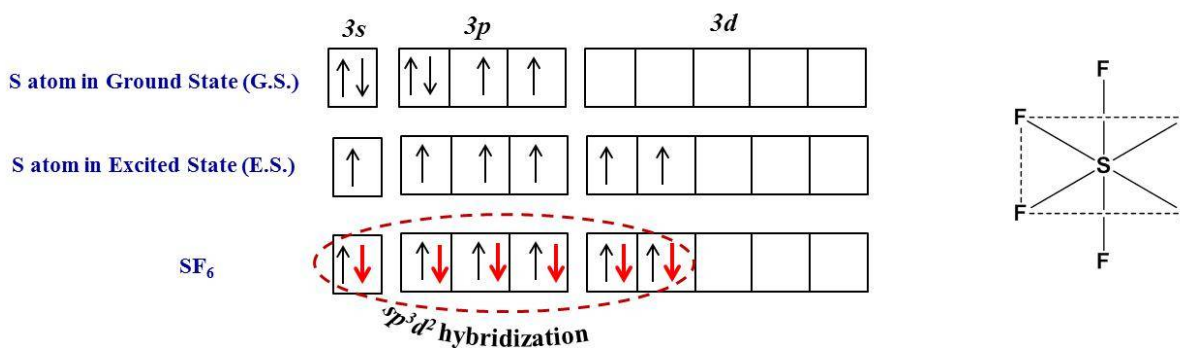
Lewis Structure of H₂O₂

Halides

General formula and structure of different type of halides with some representative examples:

A. MX_6 : SF_6 , SeF_6 , TeF_6

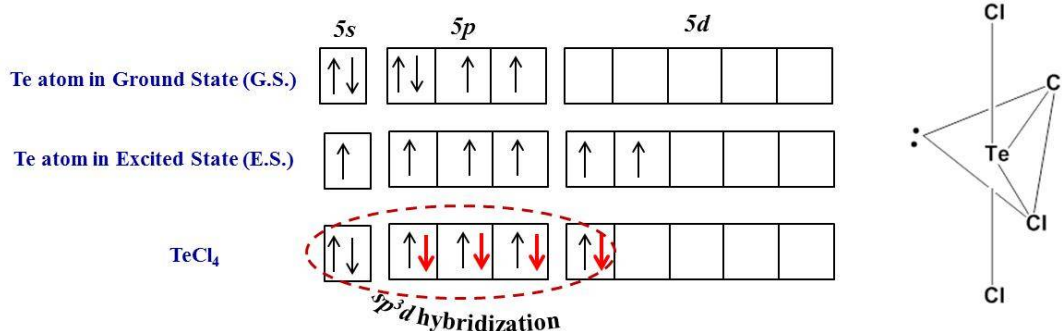
SF_6 , SeF_6 , TeF_6 all are colorless gases and have octahedral structure according to VSEPR theory. Structure of SF_6 has been given below.



Although coordination number greater than 6 are relatively rare however TeF_6 forms $[\text{TeF}_7]^-$ and $[\text{TeF}_8]^-$ by adding F^- ions.

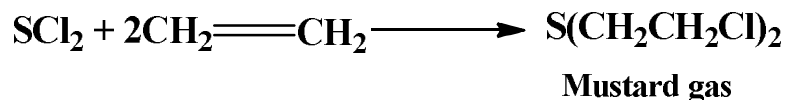
B. MX_4 : SF_4 , SCl_4 , SeF_4 , SeCl_4 , SeBr_4 , TeX_4 , PoX_4 ,

SF_4 is gaseous; SeF_4 is liquid while TeF_4 is solid. Structure of TeCl_4 is trigonal bipyramidal with one equatorial position occupied by a lone pair. All other tetrahalides probably show similar structures. Structure of TeCl_4 has been given below:

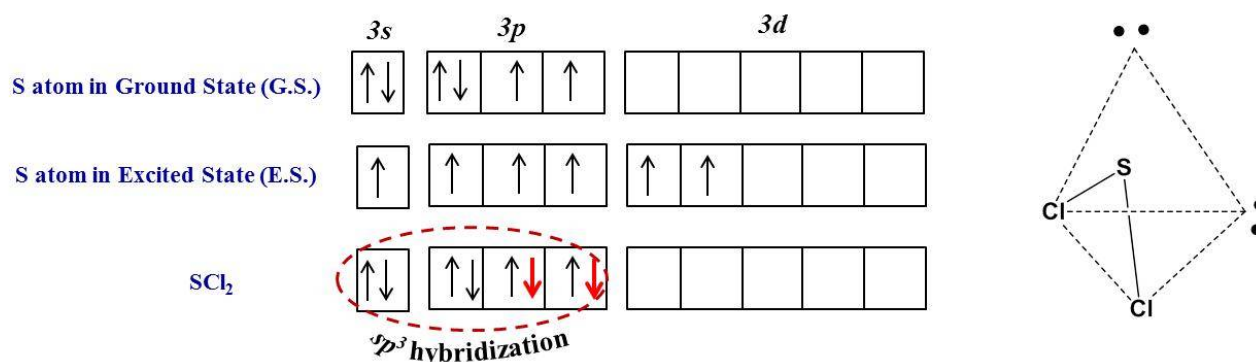


C. MX_2 : OF_2 , Cl_2O , SF_2 , SeCl_2 , TeCl_2 , PoCl_2

SCl_2 is most commonly known dihalide. It is a foul smelling liquid and produces mustard gas [di(2-chloroethyl)sulphide] upon reaction with ethylene. (*Mustard gas causes blistering of skin and death and was used in World War II*)



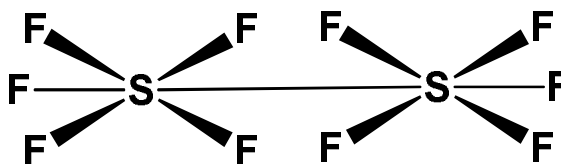
The dihalides form angular molecules, based on tetrahedron (sp^3 hybridization) with two positions occupied by lone pairs. The distortion in angle is from $109^\circ 28'$ to 103° in SCl_2 . Structure of SCl_2 has been given below.



M_2X_2 : O_2F_2 , S_2F_2 , Se_2Cl_2

These have structures similar to H_2O_2 with a bond angle of 104° .

S_2F_2 is unstable and exists in two isomeric form F-S-S-F and $\text{S}=\text{SF}_2$. S_2F_{10} has following structure:



M_2X : ClO_2 , BrO_2

Others: Cl_2O_6 , Cl_2O_7 , BrO_3

(Prepared by Dr. Roop Shikha Singh)

Further Readings:

1. Basic Inorganic Chemistry, F. A Cotton, G. Wilkinson, and Paul L. Gaus, 3rd Edition (1995), John Wiley & Sons, New York.
2. Concise Inorganic Chemistry, J. D. Lee, 5th Edition (1996), Chapman & Hall, London.