

Group VIB (Group 16)*

Oxygen, Sulphur, Selenium, Tellurium and Polonium

This group has as its members oxygen, sulphur, selenium, tellurium and polonium. Oxygen is the most abundant of elements and makes up ~ 47% of the earth's crust in the form of oxides and oxosalts. It occurs to ~ 21% by volume in air, and to ~ 86% by weight in oceans. Natural oxygen is an isotopic mixture of O-16, O-17 and O-18. Oxygen supports respiration and is essential for life. A grown-up person consumes ~ 20 litres of oxygen per hour. Sulphur occurs in the native state in considerable amount and also in the form of metal sulphides (pyrites, FeS_2 ; galena, PbS ; zinc blende, ZnS etc.) and metal sulphates (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; epsom salt, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; celestine, SrSO_4 etc.). Sulphur makes up ~ 0.04–0.03% of the earth's crust and oceans have a sulphur content of ~ 0.09% in the form of sulphates. Selenium occurs in trace quantities (0.00006%) and accompanies sulphide ores as metal selenides. Tellurium is even less common and occurs as minor constituents of sulphide ores. Polonium was discovered by the Curies from pitchblende in 1898. This is a decay product of radium and like radium is also an alpha emitter.

Oxygen, sulphur, selenium and tellurium are often collectively called as *chalcogens*.

20.1. COMPARATIVE STUDY OF THE GROUP VIB (GROUP 16) ELEMENTS

20.1.1. General Consideration : The outermost quantum shell of oxygen, sulphur, selenium, tellurium and polonium consists of the s^2p^4 electronic configuration. Oxygen alone does not possess any d -orbital since its $n = 2$ quantum shell cannot have any. Oxygen cannot therefore show a valence beyond 2 as it cannot expand its valence shell beyond an octet. But the other elements of the group can use their vacant d -orbitals for bonding purposes giving valences 2, 4 and 6.

The ionisation potentials (Table 20.1) are in general high but expectedly they decrease down the group. That metallic character is favoured with increasing atomic number is shown by a decrease in the resistance of the elements : sulphur is an insulator, selenium and tellurium are semiconductors and polonium a metal. Specific resistances are : $\text{S}(10^{23})$; $\text{Se}(10^{11})$; $\text{Te}(10^5)$ and ~ $\text{Po}(40)$ micro ohms cm.

* IUPAC recommendation

Selenium is not much attacked by HCl while Te dissolves to some extent in the presence of air. Polonium dissolves in HCl to give solution of polonium(II).

The elements are just two electrons short of the next noble gas configuration, which can be achieved in several ways : (a) by gaining two electrons to form dinegative ions (chalcogenides or chalconides, X^{2-}), (b) by making two single covalent bonds ($-X-$) or (c) by one double bond ($=X$). The trend in the formation of the divalent anions should be reflected in the electron affinities of the elements but these vary rather irregularly along the group. Important it is to note that although the first electron capture releases energy (conventionally taken as positive ; Chapter 4) the overall affinity ($X + 2e \rightarrow X^{2-}$) is significantly negative. The formation of X^{2-} ions is thus unfavourable. In practice, however, many ionic compounds with oxides, sulphides, etc are known, their formation being possible through favourable lattice energies (Chapter 5). Electronegativity of oxygen is only next to that of fluorine, and the values of the other chalcogens decrease down the group. Oxides of metals are therefore more ionic than the other chalcogenides of the same metal. According to the SHAB principle (Chapter 8) the large anions being the more polarisable ones will prefer to bind strongly polarisable cations. So sulphides, selenides, tellurides being soft bases combine to give stabler compounds with soft acids (class 'b' acceptors) such as Ag^+ , Cu^+ , Pd^{2+} , Pt^{2+} , Hg^{2+} etc.

Table 20.1. : Electronic Configurations and Some Properties of Group VIB (Group 16) Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential eV/atom (kJ/mole)	Electronegativity
Oxygen	8	[He] $2s^2 2p^4$	13.6, 35.11, 54.89, 77.39 113.87 (1313, 3387, 5296, 7466, 10986)	3.5
Sulphur	16	[Ne] $3s^2 3p^4$	10.36, 23.4, 35.0, 47.29, 72.5 (999, 2258, 3377, 4562, 6995)	2.5
Selenium	34	[Ar] $3d^{10} 4s^2 4p^4$	9.75, 21.5, 32.0, 42.9, 68.3 (941, 2074, 3087, 4139, 6589)	2.4
Tellurium	52	[Kr] $4d^{10} 5s^2 5p^4$	9.01, 18.6, 31, 38.60 (869, 1794, 2991, 3724)	2.1
Polonium	84	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$	8.43 (813)	2.0

In keeping with the trends in groups IVB(14) and VB(15), multiple bonds get weaker with increasing atomic number. Thus while SO_2 is multiply bonded monomer, SeO_2 is polymeric (20-XVIII) (each Se having a terminal oxygen and two bridging oxygens). TeO_2 is also polymeric (each Te being linked to four bridging oxygens in a ψ -trigonal bipyramidal geometry).

Sulphur has a prominent tendency to catenation. This is evident in its molecular forms (S_6 , S_8 and higher S_n), polysulphides (S_2^{2-} , S_3^{2-} ... S_6^{2-}) and as S_n ligands to transition metals. Tendency to catenation is less in Se although Se_8 is known.

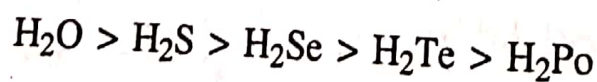
Table 20.2 records some other properties of the group VIB(16) elements. Note that with increase in atomic number the atomic radii and ionic radii also increase.

Table 20.2. : Some More Properties of Group VIB (Group 16) Elements

Element	Atomic Radius (A)(pm)	Ionic (X^{2-}) Radius (A) (pm)	M.P. ($^{\circ}\text{C}$)	B.P. ($^{\circ}\text{C}$)	Density (g/ml)
Oxygen	0.66 (66)	1.40 (140)	- 219	- 183	1.27
Sulphur	1.04 (104)	1.84 (184)	12.8* ; 119+	445	2.06
Selenium	1.17 (117)	1.98 (198)	217	685	4.80
Tellurium	1.37 (137)	2.21 (221)	450	1390	6.24
Polonium	1.64 (164)	2.30 (230)	254	962	9.51

* rhombic form ; +monoclinic form

20.1.2. Chemical Behaviour : Hydrides : All the elements form volatile covalent hydrides. Leaving aside H_2O , all the other hydrides H_2S , H_2Se , H_2Te follow the usual sequence of increasing boiling point with increasing molecular weight. H_2O is highly associated due to hydrogen bonding. The reducing properties of the hydrides increase down the group, this trend being due to their instability which again is connected with the size of the parent element. The thermal stability decreases in the order ;



The acidity of the hydrides, contrary to expectation from electronegativity, increases from H_2O to H_2Te . The factors responsible for this anomalous behaviour have been discussed in Chapter 8. As the size of the central atom increases so also the distance between hydrogen and the central atom. Release of proton (acid behaviour) is thus favoured. A summary of the general property trends of the XH_2 hydrides is given in Table 20.3.

Table 20.3. Comparative Study of Group VIB (Group 16) Hydrides

Property	H ₂ O	H ₂ S	H ₂ Se	H ₂ Te
B.P (°C)	100	- 60	- 41	- 4
K_A	1×10^{-14}	1×10^{-7}	1.7×10^{-4}	2.3×10^{-2}
$\angle \text{H}-\text{X}-\text{H}$	104°	92.2°	91°	90°
X—H. A(pm)	0.96 (96)	1.34 (134)	1.46 (146)	1.69 (169)
Association and hydrogen bonding	decreases →			
Reducing ability	increases →			
Thermal stability	decreases →			

Oxides and Oxoacids : Oxides are commonly classified from their acid-base behaviour as acidic, basic or amphoteric. Oxides of group IA/IIA (groups 1 and 2) elements are generally basic, oxides of group IV to VII (groups 14 to 17) elements are acidic, others being amphoteric. Many of the lower-valent metal oxides are ionic and form close-packed systems, the metal ions occupying the holes created by the close packing of oxide ions. As the oxidation state increases the oxides tend to be covalent (*cf* : Fajan's rules). The melting points of the oxides of group IA (group 1) and those of group IIA (group 2) metals fall down the group. This trend follows from Coulomb's law because structure type remaining the same (ionic) increasing cation-anion separation decreases the force between the ions (Chapter 5). Comparing the oxide, sulphide, selenide and telluride of the same metal ion it is observed that the heat of formation decreases from oxygen to tellurium. Small and highly charged cations (hard acids) prefer oxide ions to sulphide ions. The high oxidation states are rather easily reduced by sulphide ions.

The acidity of oxoacids of the same central element increases with increasing oxidation number (state) : $\text{H}_2\text{SO}_3 < \text{H}_2\text{SO}_4$; $\text{H}_2\text{SeO}_3 < \text{H}_2\text{SeO}_4$ etc. This is the trend expected from electronegativity. With the same oxidation number (state) acidity decreases down the series (Chapter 8 and Table 20.6).

Halides : Oxygen halides are all covalent and are restricted to a maximum of two halogens linked to one oxygen. These are of the type $\text{F}-\text{O}-\text{F}$ or $\text{Cl}-\text{O}-\text{Cl}$ or $\text{O}-\text{Cl}-\text{O}$. That one oxygen cannot bind more than two halogens must be linked with the inability of oxygen to expand its octet.

A number of hexahalides, tetrahalides and dihalides are known with S, Se and Te. In all cases combination with fluorine provides the highest halides: SF_6 , SeF_6 and TeF_6 are volatile covalent molecules of low boiling points. They have octahedral (sp^3d^2) structures. SF_6 is very stable, SeF_6 is more reactive and TeF_6 is hydrolysed by water to HF and H_6TeO_6 . Although all three S, Se and Te possess *d*-orbitals to assist nucleophilic attack by H_2O

during hydrolysis, the weakness of Te—F bonds due to decreasing non-metal character of Te is probably responsible for its easy hydrolysis. The tetrahalides often act as Lewis bases (electron donors) as in $F_4S \rightarrow BF_3$ and sometimes as Lewis acids as in $H_2[SeCl_6]$. Note that the tetrahalides possess a valence shell of $(6 + 4)$ 10 electrons. The dihalides have a valence shell of $(6 + 2)$ 8 electrons. The tetrahalides have a ψ -trigonal bipyramid (sp^3d) structure, four positions being occupied by four halogens and the fifth by a lone pair. The dihalides have tetrahedral (sp^3) array of two halogens and two lone pairs.

Donor Properties : These elements in $-X-$ or $=X$ state possess lone pairs of electrons so that they may serve as ligands. Examples are H_2O , R_2S , $(C_6H_5)_3PO$, etc. Since oxygen does not possess d -orbitals but sulphur does, oxygen donors cannot stabilise low oxidation states of metals but sulphur donors can, by virtue of their ability to receive back donated electrons from low-valent metals into their d -orbitals. With heavier elements of this group non-metal character decreases and hence donor properties fall down the group. It may be recalled that trivalent nitrogen donors (such as NH_3 , en) also cannot stabilise low oxidation states whereas trivalent P and As ligands can (Chapters 10 and 24).

20.2. STEREOCHEMICAL FEATURES OF SULPHUR

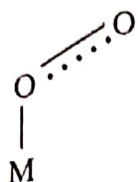
Sulphur exhibits a wide variation of stereochemical features in its compounds. The wide ranging variation is due to the many oxidation states, coordination numbers and geometries that the element can adopt. Availability of d -orbitals adds to the variety. Some of these features are given in Table 20.4.

Table 20.4. : Stereochemical Features of Sulphur

Coordination Number	Geometry	Examples	Hybridisation
1	Linear	$S = WCl_4$, $[S - C \equiv N]^-$	sp
2	Linear	$[(C_5H_5)(CO)_2 Cr \equiv S \equiv Cr (CO)_2 (C_5H_5)]$	sp
2	Bent	H_2S	sp^3
2	Triangular planar	SO_2	sp^2
3	Triangular planar	SO_3	sp^2
3	Pyramidal (ψ -tetrahedral)	SSF_2 , $OSCl_2$	sp^3
4	Tetrahedral	SO_4^{2-} , O_2SCl_2	sp^3
5	ψ -Trigonal bipyramidal	SF_4	sp^3d
5	Square pyramidal (ψ -octahedral)	SF_5^-	sp^3d^2
6	Octahedral	SF_6	sp^3d^2

20.3. MOLECULAR OXYGEN AS A LIGAND

The structure of molecular O_2 has been discussed from the view points of valence bond and molecular orbital theories in Chapter 5 and in section 20.5. Vaska in 1963 reported that $trans [IrCl(CO)(PPh_3)_2]$ reacts with dioxygen to give $[IrCl(CO)(O_2)(PPh_3)_2]$. Since then a number of dioxygen complexes have been synthesised and characterised. Dioxygen can act in a variety of ways :



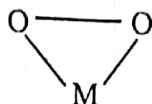
(20-I)

end-on
superoxo



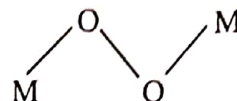
(20-II)

bridging
superoxo



(20-III)

peroxo



(20-IV)

bridging
peroxo

Of these various forms in most dioxygen complexes the O_2 molecule is linked in the peroxo form (20-III). Details appear in section 24.8.

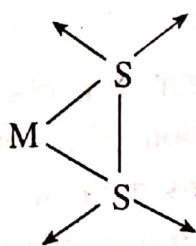
20.4. SULPHUR AS A LIGAND

Over the last twenty years or so a vast amount of coordination chemistry has accumulated where one or more sulphur atoms have participated as donor ligands. The area is too vast to be treated adequately in a text of the present size. By virtue of the larger size and easy deformability of the electron cloud sulphur is rated as a soft donor (class-b). Because of the availability of the d -orbitals the coordination number and geometries have further multiplied. It can act as a terminal and a bridging ligand. $S \equiv WCl_4$ may be taken as a simple example of sulphur acting as a terminal ligand. Its bridging behaviour is wide ranging indeed :

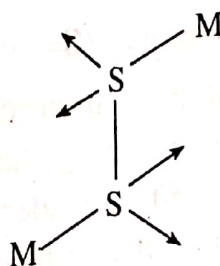
(a) bridging two atoms as in $[(Et_3P)Au-S-Au(PEt_3)]$. It acts as a two electron donor using two unpaired electrons.

(b) bridging three atoms as in $[\{(Ph_3P)Au\}_3S]$. Sulphur acts as a four electron donor using two unpaired electrons as also the lone pair.

The disulphur ligand S_2 is very versatile in its coordination mode. It can attach itself to a metal ion as a side-on S_2 (20-V) or a bridging $-S-S-$ (20-VI) with further scope of using the lone pairs for attachment :



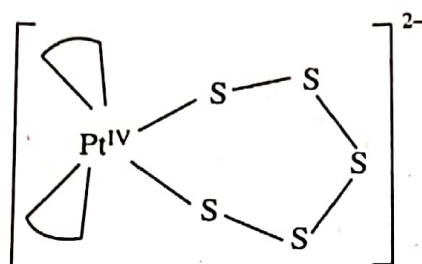
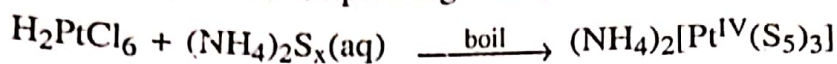
(20-V)



(20-VI)

$[\text{Mo}_2\text{O}_2\text{S}_2(\text{S}_2)_2]^{2-}$ is an example of side-on coordination while $[\text{Ru}(\text{NH}_3)_5(\text{S}_2) \text{Ru}(\text{NH}_3)_5]$ is an example of bridging -S-S-. Didentate chelation of S_2 (20-V) will be quite strained because of the three-membered ring at the metal.

Solutions of polysulphides often react with coordination complexes leading to substitution of coordinated ligands by catenated sulphur ligands (20-VII) :

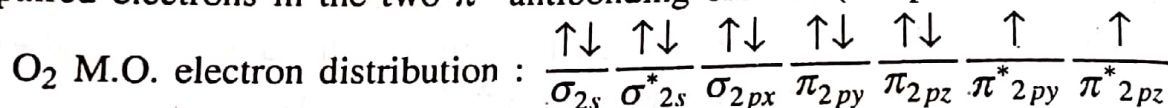


(20-VII)

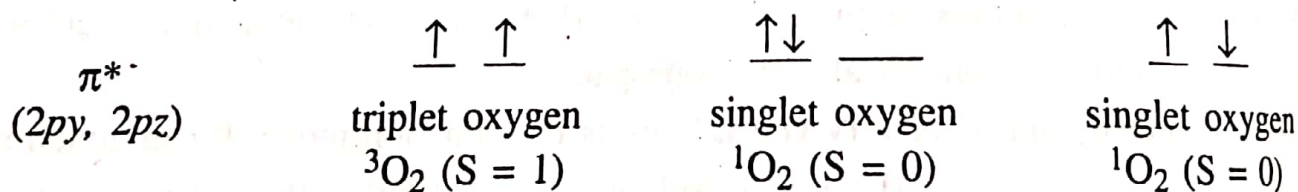
Complexes with chelating didentate $(-\text{S}_4)-$ are also known. $[\text{Mo}(=\text{S})(\text{S}_4)_2]^{2-}$ is an example.

20.5. ELEMENTARY FORMS OF THE GROUP VIB (GROUP 16) ELEMENTS

Oxygen is a diatomic molecule conventionally written with a double bond, $\text{O}=\text{O}$, having a p_x-p_x σ -bond and a p_y-p_y (or p_z-p_z) π -bond. However this valence bond picture cannot explain the paramagnetism of the O_2 molecule. Molecular orbital theory of O_2 puts two unpaired electrons in the two π^* antibonding orbitals (Chapter 5) :



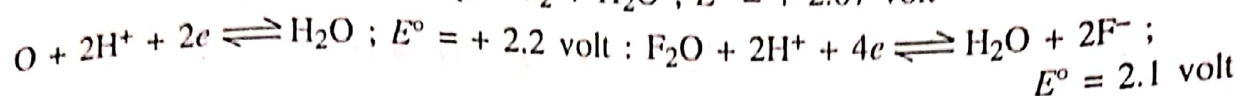
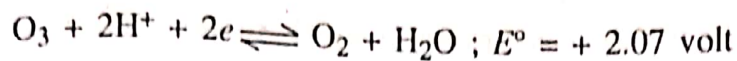
The molecular oxygen, O_2 , with two unpaired electrons in the two π^* M.O.'s is called triplet oxygen. Triplet state means it has a spin multiplicity $2S + 1 = 3$ (S being $2 \times \frac{1}{2} = 1$). Excited states of molecular oxygen are possible with the two antibonding electrons in the two π^* orbitals occupying one π^* M.O. or occupying two π^* M.O.'s with opposite spins. The singlet state ($2S + 1 = 1$; $S = 0$) with the two π^* electrons



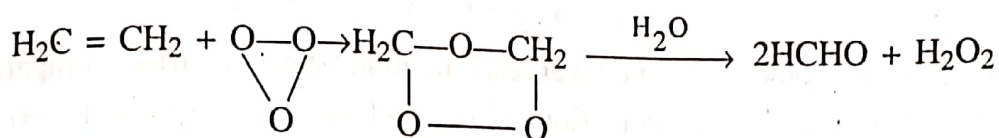
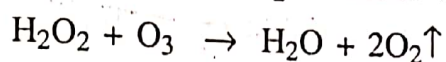
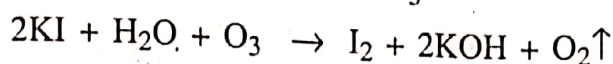
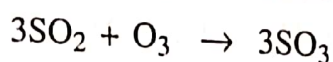
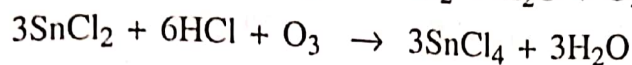
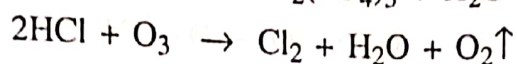
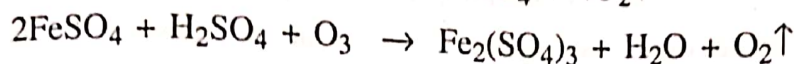
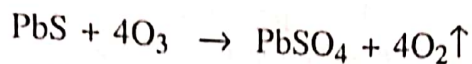
occupying the same π^* M.O. is of lower energy than the singlet state with the two π^* electrons occupying the two M.O.'s with their spins opposed. Whereas triplet oxygen is paramagnetic ($S = 1$), singlet oxygen ($S = 0$) is diamagnetic.

Ozone is an interesting molecular allotropic form of oxygen. It is obtained by passing an electric discharge through oxygen or by the anodic oxidation of a concentrated aqueous solution of perchloric acid at -50°C . Under these conditions oxidation of water occurs at the anode and ozone is liberated. It is a blue gas freezing to a purple solid at $\sim -193^\circ\text{C}$. Ozone is one of the strongest oxidants known. In acid solution the formal potential of the

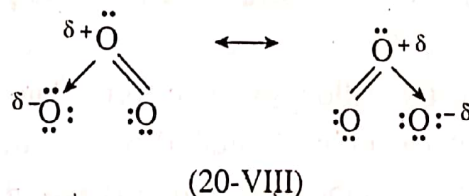
O_3/O_2 couple is 2.07 volt being lower than those of only $F_2/2F^-$, atomic oxygen/water and $F_2O/2F^-$ couples :



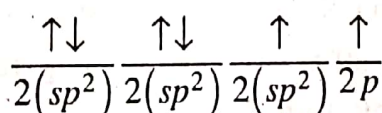
It oxidises silver(I) to silver(II) and is used in many organic oxidations. Some of the oxidising reactions of ozone are recorded below :



Ozone has a planar structure with $O-O-O$ angle $\sim 117^\circ$ and $O-O$ bond lengths intermediate between single bonds and double bonds. The oxygen-oxygen single bond and double bond lengths are 1.49A (149 pm) and 1.21A (121 pm) respectively while actual oxygen-oxygen bond length in ozone is 1.278A (127.8 pm). Following resonating structures can be written (20-VIII) :

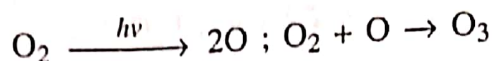


Each oxygen is sp^2 hybridised. The central oxygen has the following electron distribution in the hybridised orbitals :



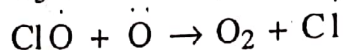
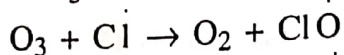
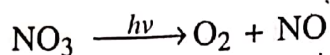
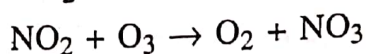
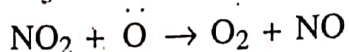
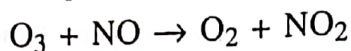
One sp^2 makes the lone pair and another the coordinate link. The third sp^2 with a proper overlap with the other oxygen orbital (with one unpaired electron) makes a sigma bond. The second electron in a $2p$ orbital then overlaps with another single electron of the other oxygen making the π -bond. The double bond is thus composed of a sigma and a pi bond.

Ozone Layer in the Stratosphere : Ozone is an important constituent of our environment. It is found mostly 15—25 km above the sea level in the stratosphere* (10—50 km). The ultraviolet radiation of the solar energy splits up O_2 to generate O_3 :



This ozone further absorbs $h\nu$ (200—350 nm) to reproduce $O + O_2$. Thus a steady state having $O_2 + O_3$ is attained. A good amount of the harmful ultraviolet radiation is held back from us.

Destruction of this ozone layer by supersonic aeroplanes discharging NO and NO_2 is undesirable. Chlorofluorocarbons ($CFCl_3$ and CF_2Cl_2) are photodecomposed to produce Cl atoms which can also catalyse decomposition of ozone to oxygen :



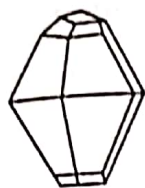
Destruction of the protective ozone layer leads to an increase of surface temperature, skin cancer etc. Unfortunately due to depletion of ozone layer, an ozone hole exists around Antarctica.

Sulphur has indeed the most varied range in its allotropic modifications. Catenation in sulphur is quite pronounced. Furthermore catenated sulphur can adopt varied arrangements within the crystal. The range of variation may be appreciated from the wide variation in S-S distance (1.8—2.6 Å ; 180-260 pm) and S-S-S angles (90° to 180°). The allotropic forms are very sensitive to variation in temperature. Many amazing varieties of sulphur units have been synthesised.

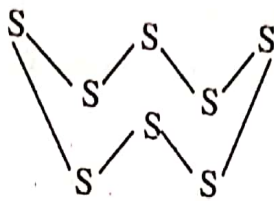
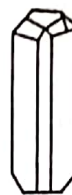
The most stable allotrope is the yellow rhombic form. The usual roll sulphur, sublimed flowers of sulphur and precipitated milk of sulphur belong to the rhombic form. It has a puckered *cyclo*- S_8 ring (Fig 20.1). As the temperature is raised to about 95°C it changes to monoclinic sulphur. The S_8 ring still persists although the packing becomes somewhat disordered. Above 119°C other structures start forming. S_8 unit is established through molecular weight determination in CS_2 and structural studies. Monoclinic S_8 is best obtained by heating ordinary sulphur to 100°C and then cooling rapidly to room temperature (to minimise formation of the rhombic form).

* (troposphere— from earth's surface upto ~ 15 km ;
stratosphere— from ~ 15 km to ~ 50 km ;
mesosphere/ionosphere— ~ 50 km to ~ 90-100 km ;
thermosphere— ~ 90 km to ~ 500 km).

Ionosphere and thermosphere contain ions such as O_2^+ , O^+ , NO^+ and also electrons.



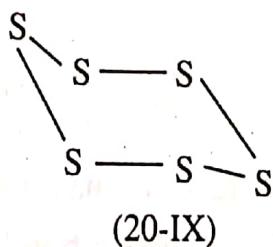
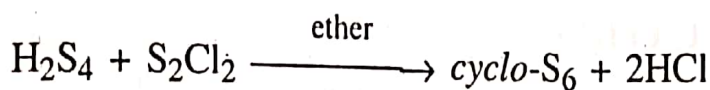
Rhombic

S₈ ring

Monoclinic

Fig. 20.1 : Crystalline forms of sulphur

Sudden cooling of the liquid sulphur from 160°C or dropping the liquid into water gives plastic sulphur. This variety of sulphur can be drawn into fibres. The fibres are made of helical chains of sulphur atoms. Plastic sulphur is insoluble in organic solvents and slowly returns to the crystalline rhombic form. Just above the boiling point sulphur still persists with the S₈ unit but further increase in temperature leads to dissociation of the S₈ units successively to S₆, S₄ and S₂. A *cyclo-S₆* form is best obtained by the reaction :



The S₆ ring has the chair conformation (20-IX). Many cyclic forms of sulphur eg. *cyclo-S₇*, *-S₁₀*, *-S₁₂*, *-S₁₈*, *-S₂₀* have been synthesised.

Note that oxygen is O₂ under all normal conditions. The difference between oxygen and sulphur supports the general rule that structures with multiple bonds are common with the first short period elements while the later period elements prefer structures with formal single bonds. Recall that nitrogen is N ≡ N whereas phosphorus and arsenic are P₄ and As₄. Also note that carbon dioxide is monomeric O = C = O whereas SiO₂ is polymeric with Si-O-Si bonds.

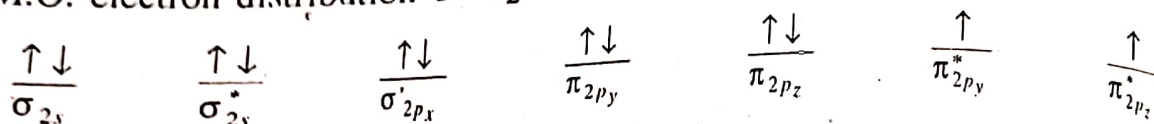
Selenium also has rhombic and monoclinic forms with Se₈ puckered rings. Both these forms are obtained on evaporation of CS₂ solution of selenium below 72°C. Both these forms are, however, unstable and slowly change to a gray, polymeric form containing infinite chains of selenium atoms spiralling around a crystal axis.

Only one form of tellurium is known, and this is isomorphous with the gray form of selenium.

Po(OH)₄ reacts with acetylacetone to form a non-electrolytic complex [Po(acac)₄].

20.7. DIOXYGENYL CATION

The M.O. electron distribution of O₂ molecule is as follows :

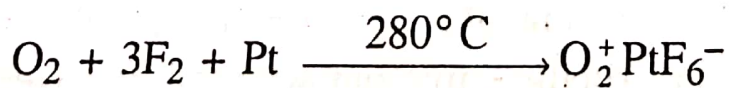
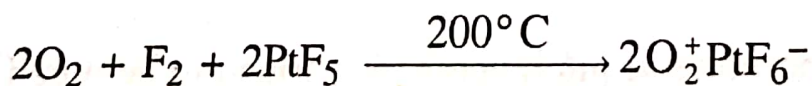
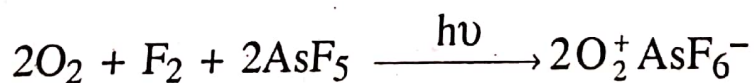
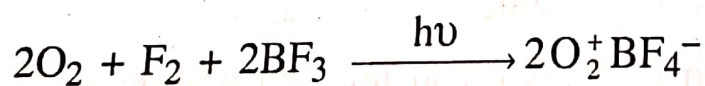


This triplet ³O₂ with two unpaired electrons has a bond order 2.0 and a bond length 1.21 Å (121 pm). The dioxygenyl cation, O₂⁺, has a bond order 2.5 and a bond length 1.12 Å (112 pm). Details of M.O. description of O₂⁺, O₂, O₂⁻ and O₂²⁻ appear in section 24.8.

Bartlett observed that oxygen reacts with PtF₆ at room-temperature to give the dioxygenyl cation compound O₂⁺ PtF₆⁻ (yellow orange). This compound is isomorphous with K⁺PtF₆⁻. Thus the oxidising agent PtF₆ was able to remove an electron from O₂ to give the cation O₂⁺. In the process PtF₆ is reduced to PtF₆⁻ (O₂ + PtF₆ → O₂⁺ PtF₆⁻).

Bartlett recognised that the ionisation potential of Xe (12.13 eV) being about the same as that of O₂ (12.12 eV), Xe could also be oxidised by PtF₆. It is now history that Bartlett succeeded (in 1962) in preparing the first ever and genuine noble gas compound XePtF₆ (section 22.3).

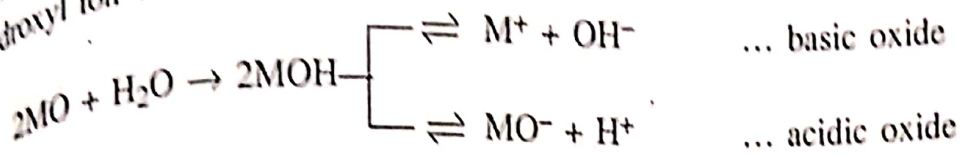
Photochemical fluorination or thermal fluorination of oxygen in the presence of Lewis acidic (i.e. electron acceptor) fluorides (eg. BF₃/AsF₅/PtF₅) also gives dioxygenyl cation.



20.8. BINARY OXIDES

Binary oxides may be classified in three different ways : (1) from their acid-base behaviour in water, (2) from structural viewpoint and (3) from the viewpoint of composition.

20.8.1. Classification of oxides based on acid base behaviour in water : When an oxide MO reacts with water to release protons we call it an acidic oxide. If it releases hydroxyl ion we term it a basic oxide :



When an oxide is capable of showing both these characteristics the oxide is termed amphoteric. Whether the intermediate MOH is acidic, basic or amphoteric will depend on which of the above equilibria becomes dominant. If the cation M^{n+} has a high polarising power (small size, large charge) it would strongly attract the oxide ion and thus will allow only the acidic dissociation (Chapter 8). Again if M^{n+} has a small polarising power the basic dissociation alone will occur. In order to have amphoteric properties the element must possess neither too much nor too low polarising power. The alkali and the alkaline earth ions are poor polarisers, and hence they form basic oxides. The group VB, VIB and VIIB (group 15, 16 and 17) elements (N, P, S, F, Cl, Br etc) can bind the oxygen via covalent bonds resulting in acidic oxides. Amphoteric behaviour of the oxides is exemplified by the oxides of Al, Be, Zn, Ga, As etc. On the basis of acid-base behaviour we have the following types :

basic oxide : Na_2O , BaO , La_2O_3 etc.

acidic oxide : CO_2 , SO_3 , N_2O_5 etc.

amphoteric oxide : BeO , Al_2O_3 , ZnO etc.

neutral oxide : these do not react with water or aqueous acids or bases : CO , NO .

Some periodic trends are now noted :

(a) In a given group basic properties increase with increasing atomic number : $BeO < MgO < CaO < SrO < BaO$.

(b) In a period the oxides gradually pass from basic through amphoteric to acidic nature :

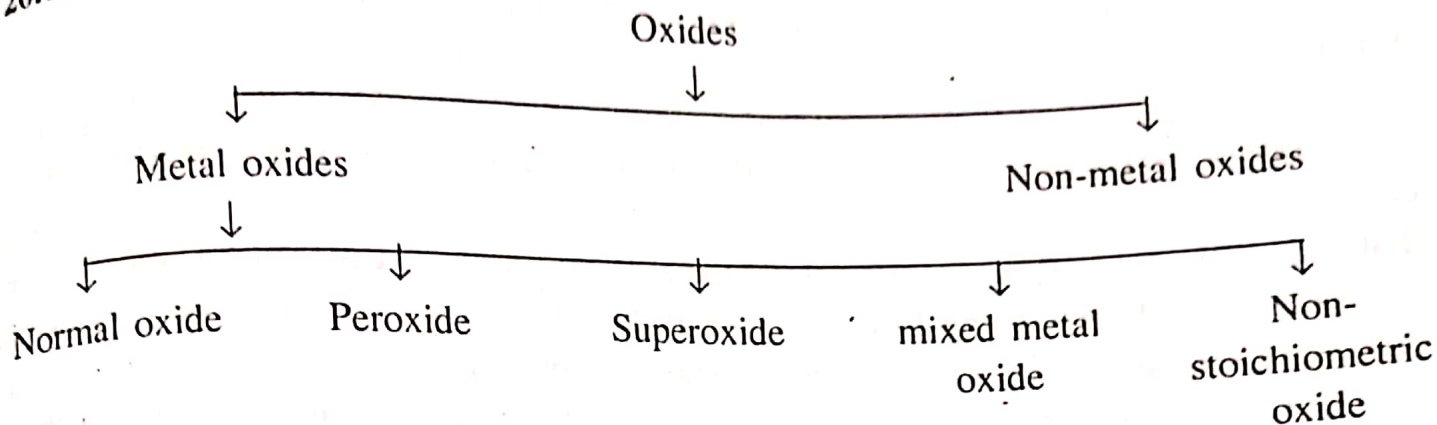
Na_2O basic	MgO basic	Al_2O_3 amphoteric	SiO_2 acidic	P_4O_{10} acidic	SO_3 acidic	ClO_2 acidic
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For a given element acidic nature increases with increasing oxidation number (state) :

oxidation number (state) of chlorine	$HClO$ + 1(I)	<	$HClO_2$ + 3(III)	<	$HClO_3$ + 5(V)	<	$HClO_4$ + 7(VII)
oxidation number (state) of manganese	MnO + 2(II)	<	MnO_2 + 4(IV)	<	Mn_2O_7 + 7(VII)		

in 10¹⁷ Fe(CO)₅, Cr(CO)₆, Co(CO)₃(NO), Fe(CO)₂(NO)₂.

20.8.3. Classification based on composition :



Normal oxides : The formulae of these oxides are decided on the basis of the oxidation number (state) ($-II$) for divalent oxygen (eg : MgO , Na_2O , etc.).

Peroxides : These are salts of hydrogen peroxide (oxidation number (state) of oxygen being $-I$) and have the peroxo links $-O-O-$. Peroxides of the alkalis and the alkaline earths and peroxosalts of S, C, P are well known.

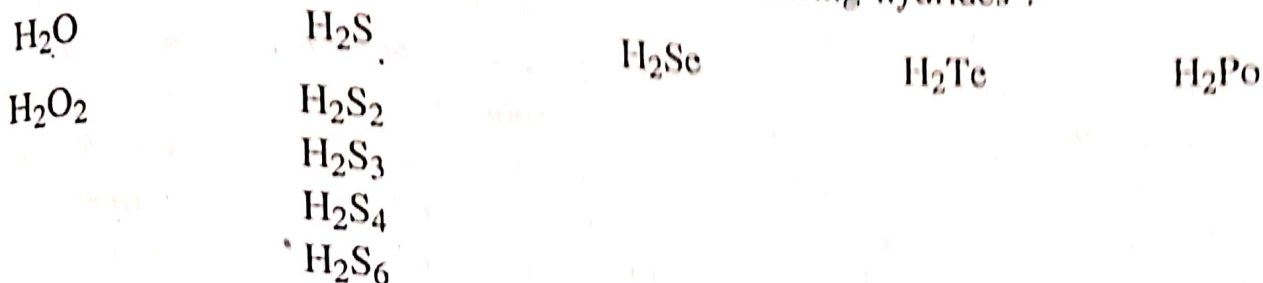
Superoxides : These are formed by the larger alkalis and the alkaline earths. They are the final products of interaction of these metals with oxygen. The superoxide ion O_2^- has a uninegative oxidation state. On changing to the heavier alkali cations the stability of the peroxide and in particular, the superoxide increases relative to the normal oxide. For larger anions we need larger cations to counteract 'rattling' in the close-packed type lattice (Chapters 6 and 15). Both peroxides and superoxides crystallise with large amounts of water due to strong hydrogen bonding. The alkali metal peroxides are among the strongest oxidants and often convert elements to their highest oxidation states.

Mixed metal oxides : On close packing of spheres (say of O^{2-} ions) two kinds of holes are created—octahedral and tetrahedral. Mixed metal oxides will arise when one metal ion occupies a particular hole and another metal ion occupies the other kind of holes. The type of holes filled depends on the size and the polarisability of the cation. *Spinel*s have the general formula AB_2O_4 (A is a divalent ion and B is a trivalent ion). In *normal spinels* divalent ions occupy the tetrahedral holes and the trivalent ions the octahedral holes. In *inverted spinels* the divalent ions occupy the octahedral holes while half of the trivalent ions

example NO_2 and N_2O_4 and Cl_2O_6 respectively.

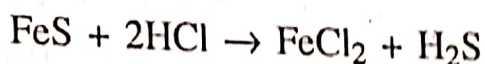
20.9. COMPOUNDS OF THE GROUP VIB (GROUP 16) ELEMENTS

20.9.1. Hydrides : The general properties and trends of the XH_2 type hydrides have already been enumerated. The elements form the following hydrides :



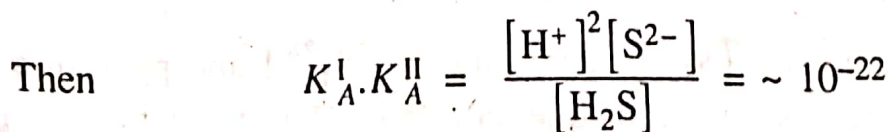
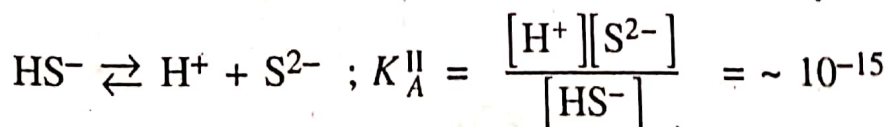
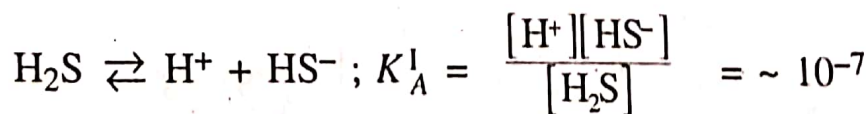
Of these hydrides H_2O alone is strongly hydrogen bonded. H_2O_2 is rather unstable, carries a peroxo $-\text{O}-\text{O}-$ linkage and behaves as a weak acid and, depending on surroundings, as an oxidant or as a reductant. Details of hydrogen peroxide and peroxo salts are given in 20.9.5.

Hydrogen sulphide : It is generally obtained in the laboratory by the action of non-oxidising acids such as HCl on iron(II) sulphide :



Direct combination of the elements at elevated temperature also provides the hydrides. By cooling the reaction mixture to $\sim -60^\circ\text{C}$ H_2S may be liquefied and then purified by distillation. A convenient laboratory method consists of heating a mixture of solid sulphur with paraffin ($\text{C}_n\text{H}_{2n+2}$, n being large). The chemistry of H_2S may be grouped under the following heads : (1) acid properties, (2) reducing properties, (3) precipitating properties (4) polysulphide forming properties.

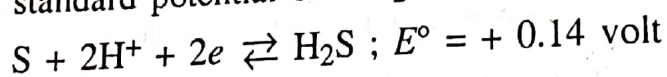
The gas is soluble in water to form $\sim 0.1M$ solution. This is a weak dibasic acid with $K_A^I \sim 10^{-7}$ and $K_A^{II} \sim 10^{-15}$:



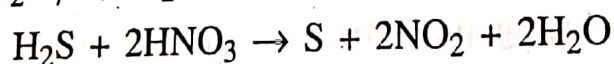
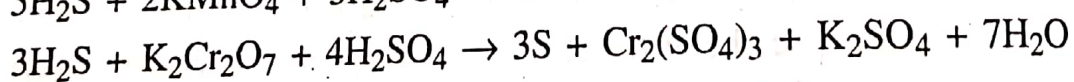
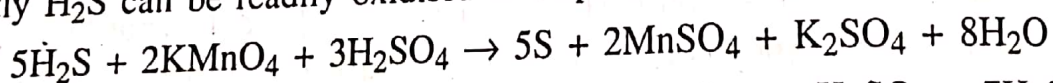
Water saturated with H_2S has $[\text{H}_2\text{S}] = 0.1 \text{ M}$. The concentration of H^+ , S^{2-} and H_2S will be regulated by the conditions prevailing in solution such that the product of K_a^1 and K_a^2 remain the same i.e. 10^{-22} . Thus addition of H^+ (acid) to a saturated solution appreciably lowers the $[\text{S}^{2-}]$ and the $[\text{HS}^-]$. Concentration of the H_2S molecules (undissociated form) is comparatively very high (0.1M) and therefore remains almost unaltered. Conversely the removal of H^+ ions (by the addition of alkali i.e. OH^- ions) appreciably increases the concentrations of both the HS^- and S^{2-} ions.

The insolubility of the metal sulphides varies to a good degree in solution. Those which form very sparingly soluble sulphides can be precipitated even in acid medium. Such ions are Cu^{2+} , Hg^{2+} , As^{3+} , Cd^{2+} etc. Metals which form more soluble sulphides need to have an alkaline medium since it is in such medium that a higher concentration of S^{2-} ions can be reached. Metal ions of this category are Zn^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} . Each sparingly soluble salt is characterised by a constant called *solubility product* (K_{sp}) which is the product of the concentrations of the two ions of the salt in a saturated solution each raised to a power equal to the coefficient of the ion. The sparingly soluble salt precipitates out of solution when the product of the concentration of the two ions in solution exceeds its K_{sp} value. A divalent metal sulphide MS will be precipitated from solution when the concentration product $([\text{M}^{2+}][\text{S}^{2-}])$ exceeds its K_{sp} . The K_{sp} value of HgS is $\sim 10^{-52}$ whereas those for MnS , NiS , ZnS are $\sim 10^{-13}$, $\sim 10^{-22}$, $\sim 10^{-23}$. A separation of metal ions becomes possible by regulating the acidity of the solution prior to introducing H_2S for precipitating the metal sulphides. Experiments show that the S^{2-} concentration in a saturated solution of H_2S in 0.3 M HCl is just high enough to precipitate insoluble sulphides like HgS ($K_{sp} \sim 10^{-52}$), CuS ($K_{sp} \sim 10^{-45}$) whereas it is too low to exceed the K_{sp} of more soluble sulphides like ZnS , NiS .

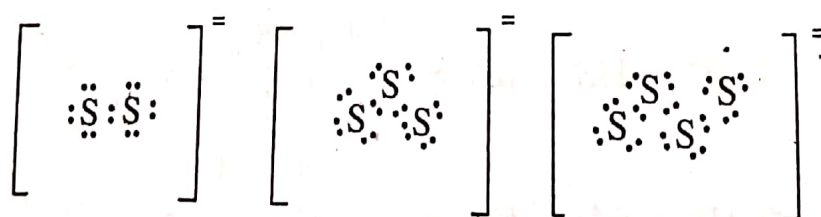
In acid solution the standard potential of $\text{S}/\text{H}_2\text{S}$ couple is + 0.14 volt.



Consequently H_2S can be readily oxidised to sulphur by a large number of oxidants :



When sulphur is boiled with solution of alkali sulphide, polysulphides are formed. The resulting solutions are yellow to dark red. Depending on the concentration of the soluble sulphide and the amount of sulphur added, the composition of the polysulphide ions varies

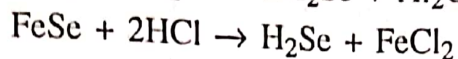
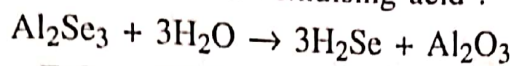


(20-X)

Disulphide (S_2^{2-}), trisulphide (S_3^{2-}), tetrakisulphide (S_4^{2-}) and pentasulphide (S_5^{2-}) are known. Some of these can be represented as in (20-X). The formation of the polysulphide

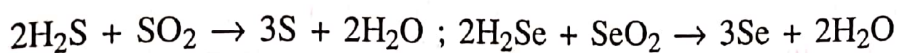
ion is an exhibition of the basic reaction (Lewis donor) of the sulphide ion. Cautious distillation of an acidified polysulphide solution provides the free hydrides H_2S_2 , H_2S_3 , H_2S_4 etc. Density, viscosity and boiling points of these hydrides increase with increasing chain length. The polysulphides on standing after acidification ultimately lead to decomposition into S^{2-} ion and S.

Hydrogen selenide : This can be obtained by the hydrolysis of a metal selenide, say aluminium selenide, in water or a dilute non-oxidising acid :



The metal selenide is obtained by the interaction of the metal and selenium at elevated temperature. The hydride can also be obtained by heating finely powdered selenium with long chain hydrocarbon at 300—400°C. Selenium is often used in synthetic organic chemistry for the dehydrogenation of hydrocarbons via H_2Se .

H_2Se is more soluble in water than H_2S . Although a weak acid it is far stronger than H_2S (K_A^1 for $\text{H}_2\text{S} \sim 10^{-7}$; K_A^1 for $\text{H}_2\text{Se} \sim 10^{-4}$). Hydrogen selenide precipitates heavy metals such as silver and lead as metal selenides from solutions of their salts. This is a reducing agent, and is oxidised to selenium by oxidants such as oxygen, nitric acid, permanganate etc. Just as H_2S does with SO_2 , H_2Se also reacts with SeO_2 to form Se :



If H_2Se is treated with sulphur a substitution occurs with the formation of H_2S and Se, the reaction being analogous to that between halogens and halogen hydrides.

Hydrogen telluride : This is formed by the hydrolysis of aluminium telluride in water or in non-oxidising acid. Aluminium telluride Al_2Te_3 can be made by heating finely divided aluminium with tellurium. H_2Te is also made by the electrolysis of 25% aqueous H_2SO_4 with Te electrodes. The gas is liberated at the cathode. It decomposes above 0°C.

20.9.2 Oxides of Group VIB (Group 16) Elements : The important and all well-established oxides of this group are included in Table 20.6.

Table 20.6. : Oxides of Group VIB (Group 16) Elements

Oxidation State	S	Se	Te	Po	
+ 1(I)	S_2O				<div style="display: flex; align-items: center;"> <div style="border-left: 1px solid black; height: 100px; margin-right: 5px;"></div> <div style="writing-mode: vertical-rl; transform: rotate(180deg);">acidity increases</div> </div>
+ 4(IV)	SO_2	SeO_2	TeO_2	PoO_2	
+ 6(VI)	SO_3	SeO_3	TeO_3		
	<div style="display: flex; align-items: center;"> <div style="border-top: 1px solid black; width: 100%;"></div> <div style="margin-left: 10px;">acidity falls</div> </div>				

The lower oxide S_2O is produced when a glow discharge is passed through SO_2 . It is very unstable decomposing to SO_2 and polymeric oxides.

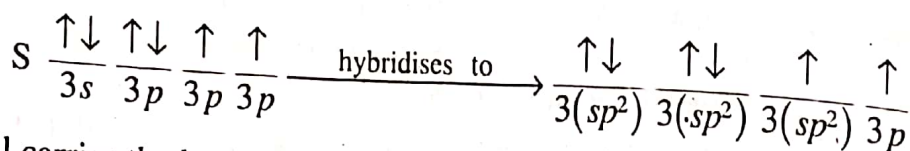
Dioxides : All the dioxides are made by burning the elements in air. Some metal sulphides, such as Cu_2S , also produce SO_2 on burning in air. On treatment with hot dilute nitric acid

selenium and tellurium produce selenic acid H_2SeO_4 and $2\text{TeO}_2 \cdot \text{HNO}_3$ respectively. When these acid solutions are heated the dioxides are obtained. The two dioxides SO_2 and SeO_2 have very different properties. Whereas SO_2 is monomeric, covalent and gaseous, SeO_2 is polymeric, covalent and comparatively high melting (sublimes, 315°C).

The structure of SO_2 can be represented by the resonating forms (20-XI). Other possible forms can also be written (Chapter 5) but these will make smaller contribution to the resonance hybrid. The bond angle $\text{O}-\text{S}-\text{O}$ is $\sim 120^\circ$ indicating sp^2 hybridisation of sulphur. The six outer orbital electrons of sulphur can be arranged in sp^2 hybridised state as :

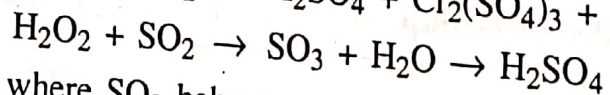
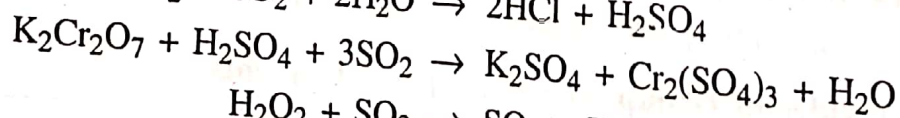
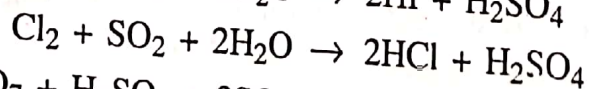
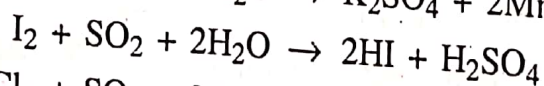
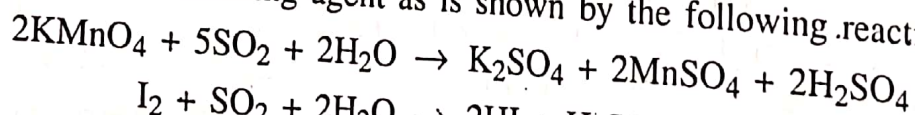


(20-XI)

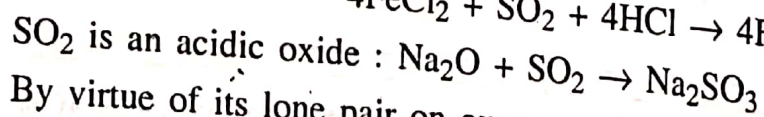
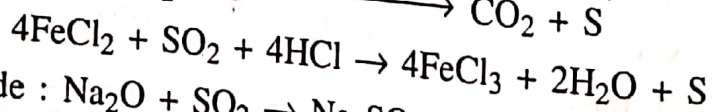
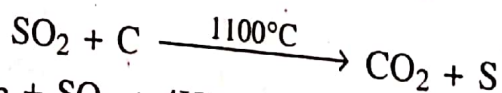
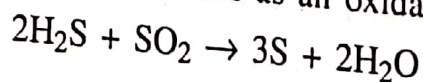


One sp^2 orbital carries the lone pair of electrons and another sp^2 orbital with paired electrons makes the coordinate bond to one oxygen. The electron in the third sp^2 orbital overlaps with unpaired electron in the second oxygen orbital. The last electron in the $3p$ orbital of sulphur then overlaps with a suitable orbital of the second oxygen (having one spin) to form the π -bond. Thus the double bond is made up. Resonance is indicated by considerable double bond character of the $\text{S}-\text{O}$ bonds.

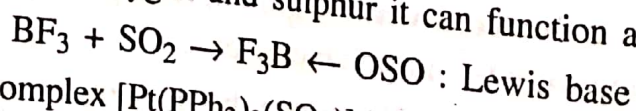
Sulphur dioxide is a reducing agent as is shown by the following reactions :



There are certain reactions where SO_2 behaves as an oxidant :

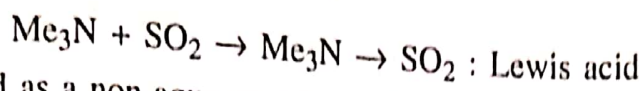


By virtue of its lone pair on oxygen and sulphur it can function as a Lewis base.



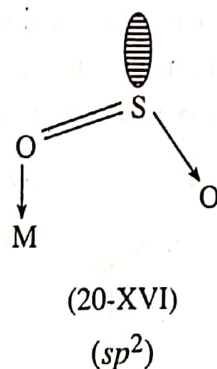
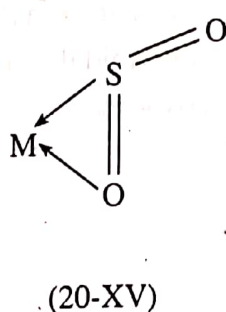
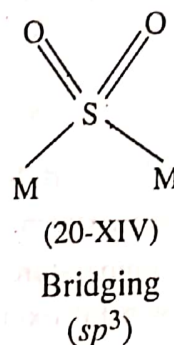
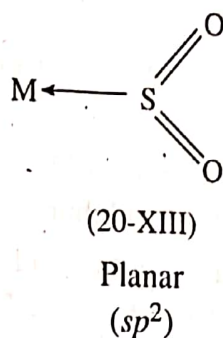
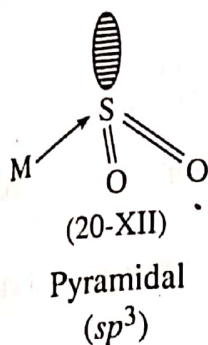
In the platinum (0) complex $[\text{Pt}(\text{PPh}_3)_3(\text{SO}_2)]$ it is also a Lewis base coordinating through sulphur.

It can also function as a Lewis acid by receiving electrons from donor molecules via expanding its valence shell :

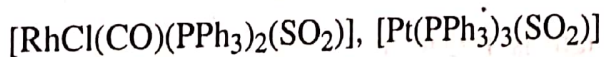


It has been studied as a non-aqueous solvent. Liquid SO_2 ionises as $2\text{SO}_2 \rightleftharpoons \text{SO}^{2+} + \text{SO}_3^{2-}$ (Chapter 9). Thionyl chloride (SOCl_2) is an acid while Cs_2SO_3 is a base in this solvent.

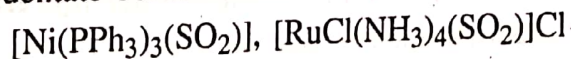
Donor behaviour of SO_2 : Several modes of coordination of SO_2 in complexes have been reported. One interesting aspect is the ability of the molecule to coordinate through sulphur or through oxygen (cf. *nitrito-N* and *nitrito-O* linkage of NO_2). The sulphur atom may offer a lone pair or receive one from a metal. It can act as a bridging ligand also. Most complexes are known to have the metal in zero or +1(I) oxidation state. Modes of coordination along with examples are given below :



Pyramidal (S-bonded) monodentate coordination :



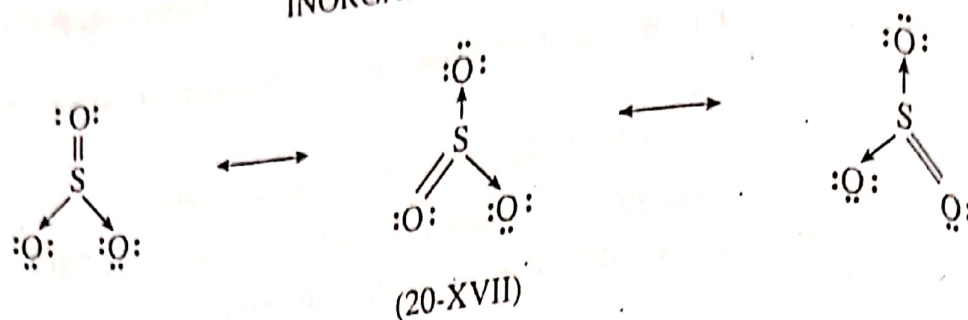
Planar (S-bonded) monodentate coordination :



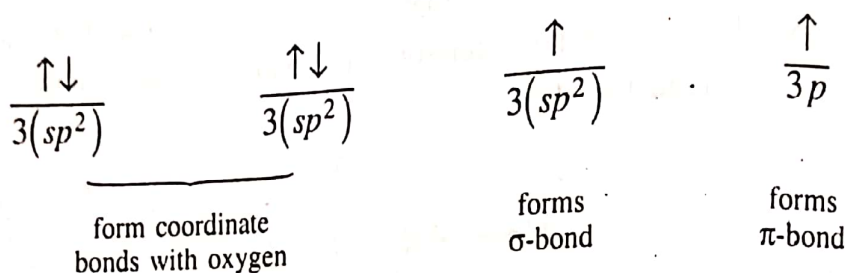
M-M bridging (S-bonded) : $[\text{Fe}_2(\text{CO})_8(\mu\text{-SO}_2)]$

(O-bonded) monodentate : $[\text{F}_5\text{Sb}(\text{OSO})]$

Sulphur trioxide, being the anhydride of sulphuric acid, is of great industrial importance. It is obtained by the oxidation of SO_2 by oxygen in the presence of a catalyst (V_2O_5 or platinum sponge). In the gas phase it may be represented as a resonance hybrid of the following planar, triangular structures (20-XVII) :



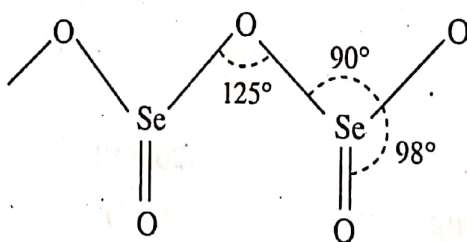
We invoke sp^2 hybridisation for sulphur : two electron pairs forming the two coordinate links ; one unpaired electron in the third sp^2 hybrid overlaps with an electron in oxygen orbital and the second electron in the remaining p -orbital of sulphur forms a π -bond with oxygen :



The extremely short S-O bond-length (1.43Å) (143 pm) points to additional π -bonding between filled oxygen p -orbitals and vacant sulphur d -orbitals.

At low temperature SO_3 stays as a polymeric solid $(SO_3)_3$ or as infinite helical chains. SO_3 is a powerful oxidant, oxidising HBr to Br_2 and P to P_4O_{10} .

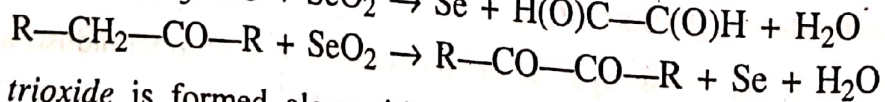
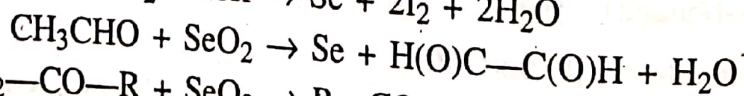
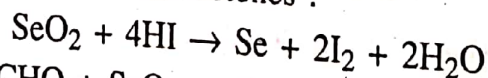
Selenium dioxide forms infinite covalently linked chain (20-XVIII). The bond angles show that the chain is non-planar. Each selenium is linked to a terminal oxygen and two bridging oxygens. The lone pair on selenium gives a flattened pyramidal shape. The polymeric structure breaks down in the gas phase to the monomeric covalent form.



(20-XVIII)

The Se = O bond-length is 1.73Å (173 pm).

Selenium dioxide behaves as an oxidant particularly towards some organic compounds. SeO_2 is used in oxidising aldehydes and ketones :



Selenium trioxide is formed alongwith much dioxide on passing electric discharge through a mixture of selenium vapour and oxygen under low pressure. It is the anhydride of H_2SeO_4 .

Tellurium dioxide is obtained by the action of oxygen on Te or by dehydrating H_2TeO_3 . It has a polymeric structure with all the oxygens shared among tellurium atoms.

Tellurium trioxide is obtained by heating H_6TeO_6 at 300°C . It is a polymeric three-dimensional structure where TeO_6 octahedra share all vertices with Te and so on.

20.9.3. Oxoacids of Sulphur : We name in Table 20.7 only the important oxoacids of sulphur. Some of the oxoacids are known only in the form of salts and the structures given in the Table are those guessed from the salts. The structures shown are but one of the several other possible resonating forms. Oxoacids with S—S links are called thioacids. There are no analogues of thioacids in tellurium and selenium.

Sulphurous Acid : This is formed when SO_2 is dissolved in water. The two acid dissociation constants of H_2SO_3 are 1.7×10^{-2} and 5.6×10^{-8} so that it is not a strong acid. It forms two series of salts, sulphites SO_3^{2-} and the hydrogensulphites HSO_3^- . *Sodium hydrogensulphite* is commercially made by passing SO_2 into a suspension of sodium carbonate or through a saturated solution of sodium sulphite :

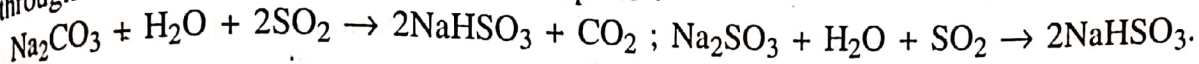


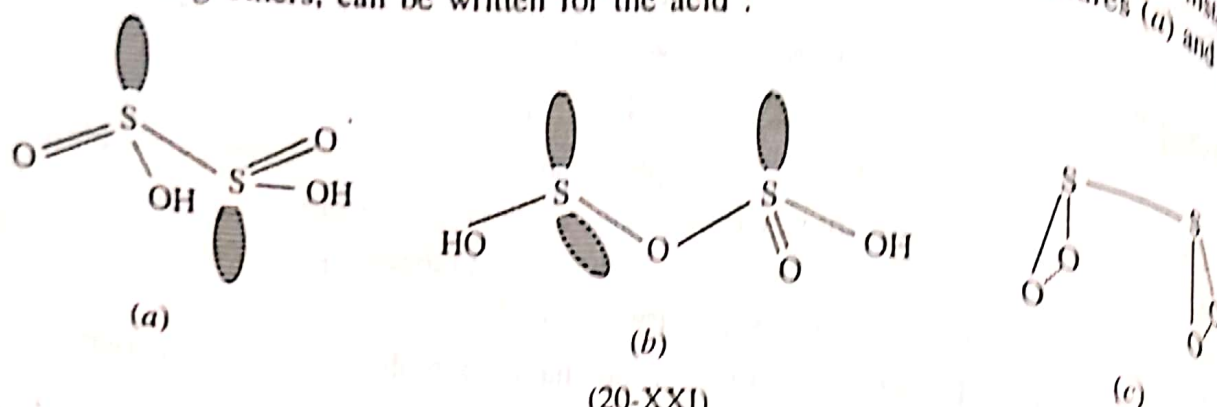
Table 20.7. : Oxoacids of Sulphur*

Formula	Structure	Name and Comments
1. Sulphurous Acid Series H_2SO_3		Sulphurous acid ; known only in solution ; salts are well known.
$\text{H}_2\text{S}_2\text{O}_4$		Dithionous (tetraoxodisulphuric) acid ; known in solution and in the form of salts ; solutions are unstable.
$\text{H}_2\text{S}_2\text{O}_5$		Pyrosulphurous acid ; known only in the form of salts.
2. Sulphuric Acid Series H_2SO_4		Sulphuric acid. Free acid and salts are well known.

* Electron counts would also be alright if the $\text{S}=\text{O}$ bonds are replaced by $\text{S} \rightarrow \text{O}$ bonds.

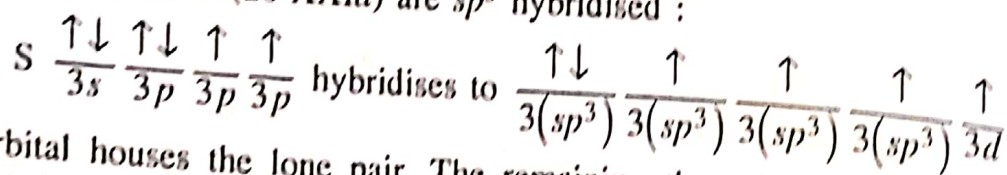
Formula	Structure	Name and Comments
$H_2S_2O_3$		Thiosulphuric acid. Free acid unstable. Salts are well known.
$H_2S_2O_7$		Pyrosulphuric acid (disulphuric acid) (μ -oxo-hexaoxodisulphuric acid)
3. Thionic Acid Series $H_2S_2O_6$		Dithionic acid (hexaoxodisulphuric acid) ; known in aqueous solution and as salts.
$H_2S_nO_6$		Polythionic acid ; known as salts. Free acids are not stable.
4. Peroxoacid Series H_2SO_5		Peroxomonosulphuric acid. IUPAC recommended name is dihydrogen trioxoperoxosulphate. Acid is well-studied. An impure potassium salt has been reported.
$H_2S_2O_8$		Peroxodisulphuric acid. IUPAC recommended name is dihydrogen μ -peroxo-hexaoxodisulphate. Acid is known. Salts are well known.

For the last mentioned reaction see Chapter 28. Among other reductions are those of chromium(VI) to chromium(III), manganese(VII) to manganese(II); iodine to iodide. **Dithionous Acid** was earlier thought to have a monomeric formula HSO_2 rather than $\text{H}_2\text{S}_2\text{O}_4$. This seemed to receive some support from the failure to obtain an acid salt, but diamagnetic behaviour of the salts ruled out the odd-electron HSO_2 formula and instead supported the dimeric even-electron $\text{H}_2\text{S}_2\text{O}_4$ formula. Two alternative structures (a) and (b) (20-XXI), among others, can be written for the acid :



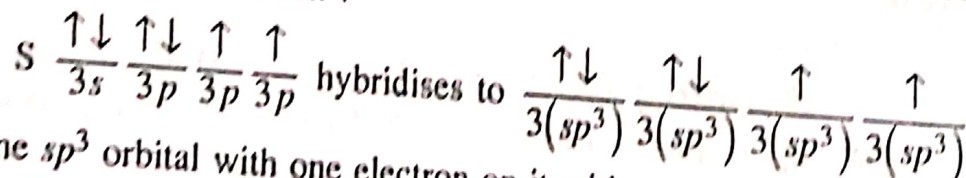
X-ray crystal structure of $\text{Na}_2\text{S}_2\text{O}_4$ supports structure (a) with very long S-S bond (2.39 Å) (239 pm) which is longer than that ($\sim 2\text{Å}$) ($\sim 200\text{ pm}$) in dithionate $-\text{O}_3\text{S}-\text{SO}_3^-$. This long bond explains the unstable character and extreme reducing ability of dithionite. Dithionite solution is used to absorb molecular oxygen.

The sulphur atoms in (20-XXIa) are sp^3 hybridised :



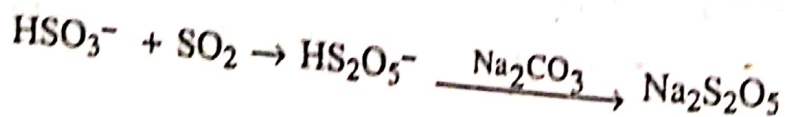
One sp^3 orbital houses the lone pair. The remaining three hybrid orbitals overlap with suitable orbitals of oxide oxygen, hydroxyl oxygen and sulphur. Finally the unpaired electron in one of the $3d$ orbitals of sulphur overlaps with a $2p$ orbital of oxygen so as to make the double bond. Strong repulsion between the lone pairs results in the long S-S bond. $\text{S}_2\text{O}_4^{2-}$ has the structure shown in (c) with the oxygen atoms in eclipsed position ($\angle \text{OSO} = 108^\circ$; $\angle \text{SSO} = 98^\circ$).

If we have assumed S \rightarrow O link instead of S=O link then the hybrid orbitals would have the following electron distribution :

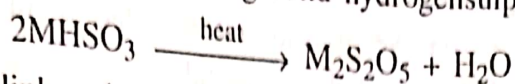


Overlap of one sp^3 orbital with one electron on it with a suitable p -orbital of oxygen gives an S-O bond. Overlap of two sp^3 orbitals of two sulphur atoms with one electron on each gives the S-S bond. One sp^3 orbital with paired spins forms the coordinate link to oxygen while the other paired spin remains as a lone pair.

Pyrosulphites (disulphites) are produced by the reaction of NaHSO_3 in solution with excess SO_2 :



Pyrosulphites are also obtained by heating solid hydrogensulphites :



Pyrosulphites have an S-S link and an unsymmetrical structure, $(\text{O}_2\text{S}-\text{SO}_3)^{2-}$.

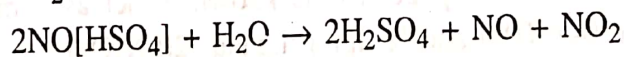
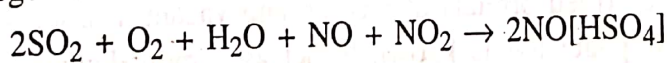
Sulphuric Acid : It is a strong dibasic acid. The first step dissociation is complete in water and the second dissociation constant is $\sim 10^{-2}$. Most metals form sulphates and acid sulphates (hydrogensulphates). The alkaline earth sulphates alone are very sparingly soluble in water.

Metal sulphates (and also tetraoxoselenates) can produce two kinds of double sulphates :

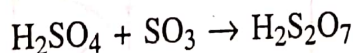
(a) between a monovalent cation and a trivalent cation, called *alums*, $\text{M}^{\text{I}}\text{M}^{\text{III}}(\text{XO}_4)_2 \cdot 12\text{H}_2\text{O}$ where $\text{M}^{\text{I}} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$; $\text{M}^{\text{III}} = \text{Al}, \text{Cr}, \text{Fe}, \text{Mn}, \text{Co}$ etc. and $\text{X} = \text{S}$ or Se ;

(b) between a monovalent cation and a divalent cation, $\text{M}_2^{\text{I}}\text{M}^{\text{II}}(\text{XO}_4)_2 \cdot 6\text{H}_2\text{O}$, called *schonites*, where $\text{M}^{\text{I}} = \text{univalent cation}$ and $\text{M}^{\text{II}} = \text{divalent cation}$. Heptahydrated dipositive metal sulphates are called *vitriols*. Common examples are $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Copper sulphate pentahydrate therefore is not a true vitriol.

Sulphuric acid is of great industrial importance. It is manufactured by two methods both involving catalytic oxidation of sulphur dioxide to sulphur trioxide. In the *contact process* a mixture of SO_2 and O_2 is passed over a catalyst (usually V_2O_5 or spongy platinum) at $450-500^\circ\text{C}$. When platinum catalyst is used the SO_2 gas must be very pure, particularly free from arsenic compounds in whose presence the platinum catalyst gets poisoned. The resulting SO_3 gas is not directly absorbed in water to produce H_2SO_4 since a fog of small droplets of H_2SO_4 is often formed. This fog dissolves in water only slowly. In practice SO_3 is absorbed into a dilute H_2SO_4 solution. The second commercial method is the *lead-chamber process* where the catalytic oxidation is carried out by nitrogen oxides in lead chambers. The oxides of nitrogen participate in the formation of some intermediate (nitrosyl sulphuric acid or nitrosyl hydrogensulphate) which on treatment with water gives sulphuric acid and regenerates the nitrogen oxides.



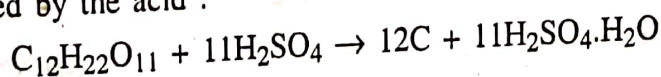
Solution of SO_3 in H_2SO_4 is called *oleum* or *fuming sulphuric acid* which contains pyrosulphuric acid (disulphuric acid) :



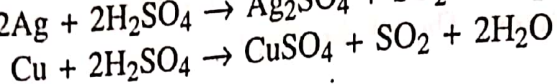
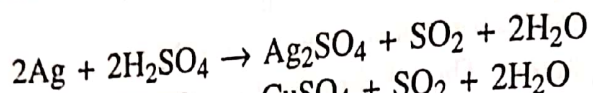
Sulphuric acid has a great affinity for water and forms several crystalline hydrates : $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (M.P. 8.5°C), $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (-39.5°C) and $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (-28°C).

On dilution with water enough heat is liberated. It is therefore the usual practice to add concentrated H_2SO_4 to water with good stirring.

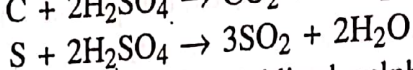
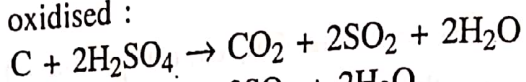
It serves as an excellent drying agent. Cellulose materials such as paper, cotton, wood, and sugar are charred by the acid :



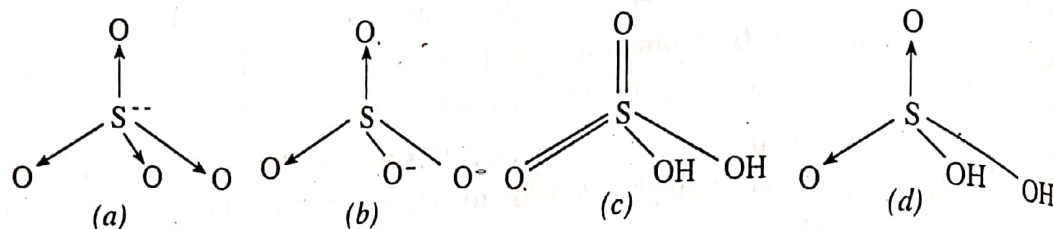
Metals above hydrogen in the electrochemical series (that is with positive standard electrode potential) do not dissolve in cold concentrated or dilute sulphuric acid, or in any other non-oxidising acid (Chapter 7). These metals, however, dissolve in hot sulphuric acid because the hot acid works as a good oxidant. Note that no hydrogen evolution occurs in these reactions :



Carbon and sulphur are also oxidised :



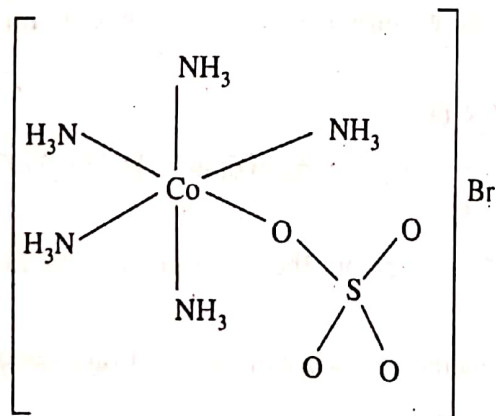
The sulphate ion is tetrahedral with sp^3 hybridised sulphur. Several structures can be written for the ion and the acid of which four are shown below (20-XXII) :



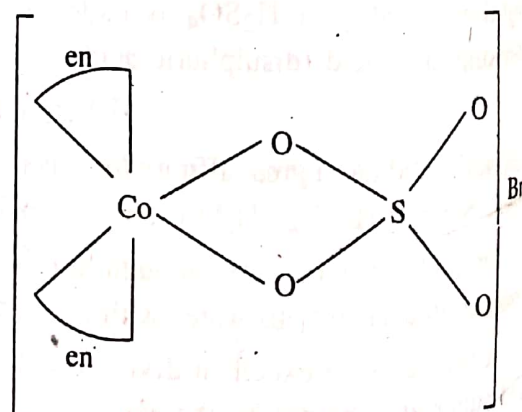
(20-XXII)

In structure (a) we assume sulphur to have a valence shell of $6 + 2 = 8$ electrons which are distributed in the four sp^3 orbitals. These orbitals make the coordinate links to the four oxygen. In structure (b) each of the two O^- ions has a valence shell of $6 + 1 = 7$ electrons. The sulphur has two pairs of electrons in the two sp^3 orbitals making the coordinate links. Two other hybrid orbitals with one electron each overlap with oxygen p -orbitals to make one sigma bond each. The two O^- ions thus take their valence shells to $6 + 1 + 1 = 8$ electrons. The other structures are left as exercises. All four S-O distances are the same (1.44Å) (144 pm) through resonance, and are considerably shorter than single bonds. Scope for double bonding via overlap of filled orbitals of oxygen and vacant d -orbitals of sulphur remains.

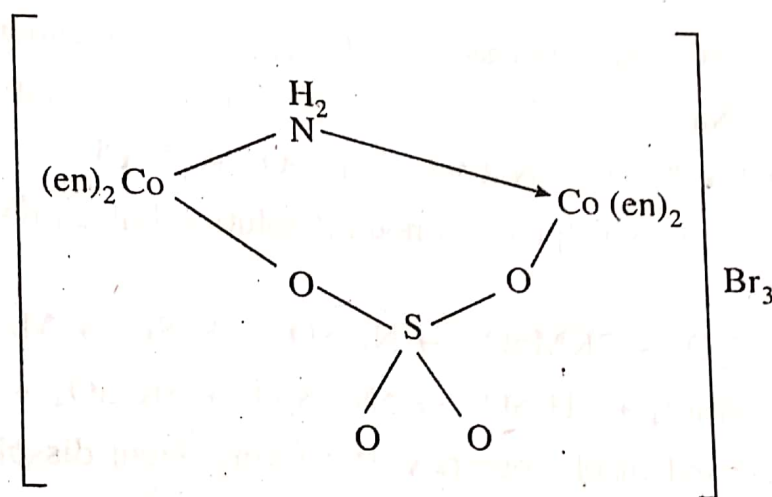
The tetrahedral sulphate ion is known to act as a monodentate (20-XXIII), chelating didentate (20-XXIV) and bridging ligand (20-XXV).



(20-XXIII)



(20-XXIV)



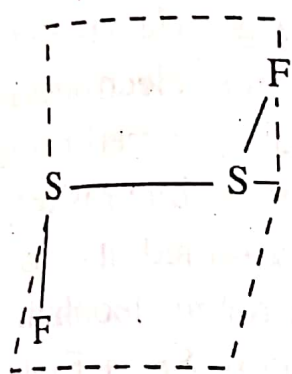
(20-XXV)

Sulphuric acid is widely used in the fertiliser industry to make ammonium sulphate and superphosphate. It is used to make esters, ethers, sulphates, other acids. Fuming sulphuric acid is used for sulphonation, that is, for introducing $-\text{SO}_3\text{H}$ group in organic compounds.

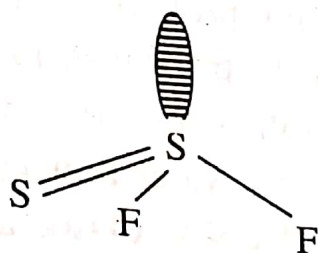
Acid Rain: It is a natural phenomenon which occurs due to the presence of sulphuric acid in the atmosphere.

of colorless compounds of the elements. For details see Chapters 25, 26 and 27.

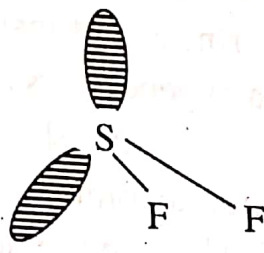
20.9.8. Halides and Oxohalides of Sulphur : Prominent sulphur fluorides are disulphur difluoride (FSSF), thiothionyl fluoride (SSF₂), sulphur difluoride (SF₂ and S₂F₄), sulphur



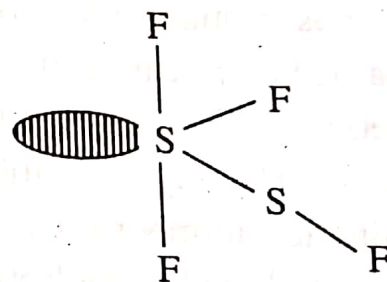
(20-XXXII)



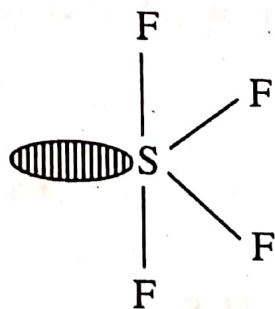
(20-XXXIII)



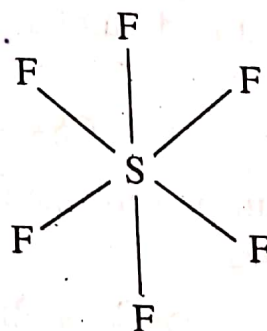
(20-XXXIV)



(20-XXXV)



(20-XXXVI)



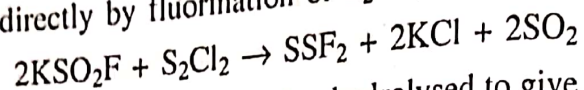
(20-XXXVII)

tetrafluoride (SF₄) and sulphur hexafluoride (SF₆). Sulphur displays a wide range of oxidation states from I (in S₂F₂) to VI (in SF₆). FSSF and SSF₂ may be regarded as linkage

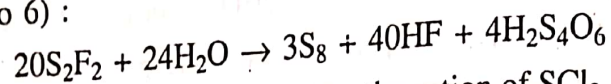
isomers while SF_2 and S_2F_4 are a monomer-dimer pair. Molecular structures of these compounds are shown in (20-XXXII) to (20-XXXVII). Structure of S_2F_2 is comparable to that of H_2O_2 .

SSF_2 has a ψ -tetrahedral structure and SF_4 a ψ -trigonal bipyramidal structure. The shapes of the molecules are those expected on VSEPR model.

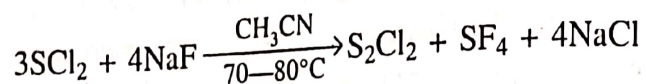
Disulphur difluoride is prepared by fluorination of sulphur with AgF in dry equipments at 125°C . It isomerises to thiothionyl fluoride, SSF_2 , in the presence of alkali metal fluorides. SSF_2 can be prepared directly by fluorination of S_2Cl_2 with KF in SO_2 :



These fluorides are very sensitive to water, being hydrolysed to give sulphur, HF and thionic acids $\text{H}_2\text{S}_n\text{O}_6$ ($n = 4$ to 6) :



Sulphur tetrafluoride, SF_4 , is best prepared by the action of SCl_2 and NaF in acetonitrile around 70 - 80°C .

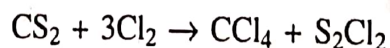


SF_4 is highly reactive and suffers nucleophilic attack by H_2O to produce SO_2 and HF :

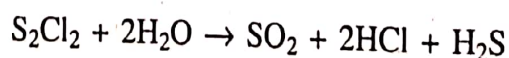
$$\text{SF}_4 + 2\text{H}_2\text{O} \rightarrow \text{SO}_2 + 4\text{HF}$$

Sulphur hexafluoride : This is made by the combination of the elements : $\text{S} + 3\text{F}_2 \rightarrow \text{SF}_6$. This is a colourless, odourless and extremely inert gas. It refuses to react with fused KOH , steam at 500°C and oxygen in an electric discharge. Hexacovalence of sulphur is brought about by fluorine which is the smallest and the most electronegative of the halogens. Because of its inertness and insulation properties the gas is sometimes used as a gaseous insulator in high voltage generators and electrical instruments. Sulphur is octahedral through sp^3d^2 hybridisation. Since in SF_6 sulphur has already attained its maximum coordination number six it cannot accommodate any water molecule for nucleophilic attack which could lead to hydrolysis. The compound suffers no dissociation to $\text{SF}_4 + \text{F}_2$ in which case the SF_4 could be hydrolysed.

Sulphur monochloride (in reality a dimer S_2Cl_2) is prepared as an orange liquid by the action of chlorine on fused sulphur. It is also formed as a by-product in the synthesis of CCl_4 from CS_2 :

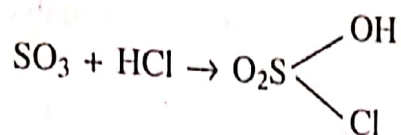


S_2Cl_2 (B.P. 138°C) can be separated from CCl_4 (B.P. 75°C) via fractional distillation. It is slowly hydrolysed by water :

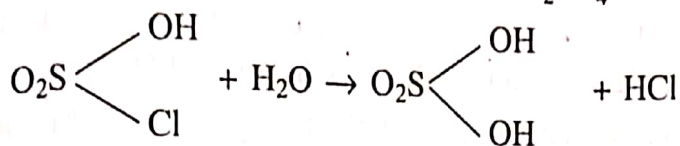


Its structure is comparable to that of H_2O_2 .

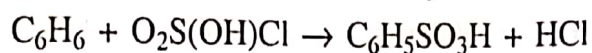
Chlorosulphonic (Chlorosulphuric) Acid (HSO_3Cl) : This may be viewed to be derived from sulphuric acid by substitution of one $-\text{OH}$ group by a chloro-group. It is prepared by passing HCl gas into fuming H_2SO_4 .



Chlorosulphuric acid (B.P. 151°C) is purified by distillation. It is violently hydrolysed by water giving HCl and H_2SO_4 :

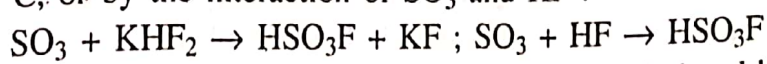


It is used as a sulphonating agent in organic chemistry :



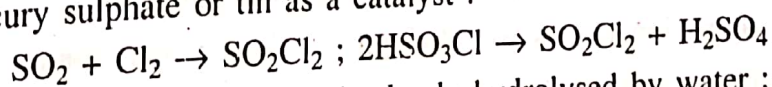
It forms no salts.

Fluorosulphuric Acid : This is made by the action of fuming sulphuric acid on KHF_2 or CaF_2 at $\sim 250^\circ\text{C}$, or by the interaction of SO_3 and HF :

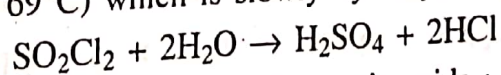


It is also a colourless liquid (B.P. 169°C) and is only slowly hydrolysed by water. Its alkali metal salts are made by the action of SO_3 on metal fluorides at $\sim 200^\circ\text{C}$. The acid is a very strong one.

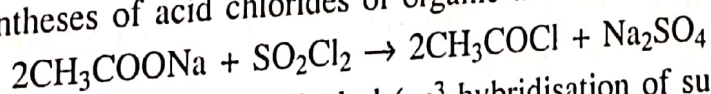
Sulphuryl (sulphonyl) Dichloride (Dichlorodioxosulphur) : SO_2Cl_2 may be considered to have been derived from H_2SO_4 by the replacement of two OH^- groups by two chloro groups. Direct interaction of SO_2 and Cl_2 in the presence of camphor, charcoal or acetic anhydride as catalysts gives SO_2Cl_2 . This is also obtained on refluxing chlorosulphonic acid with a little mercury sulphate or tin as a catalyst :



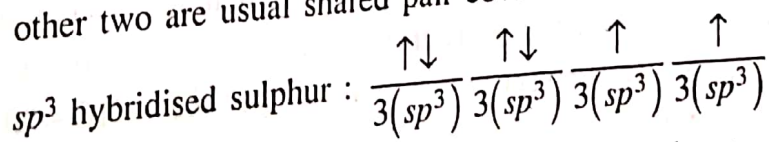
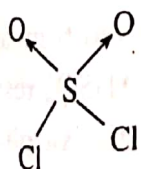
It is a fuming liquid (B.P. 69°C) which is slowly hydrolysed by water :



It is used in the syntheses of acid chlorides of organic acids :

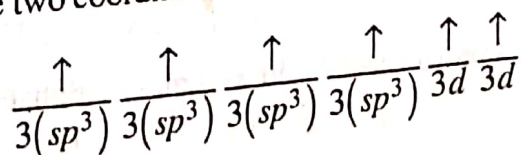


The structure of SO_2Cl_2 is roughly tetrahedral (sp^3 hybridisation of sulphur). Two sulphur lone pairs make the two coordinate links to the two oxygen. The other two are usual shared pair covalent bonds.



(20-XXXVIII)

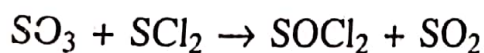
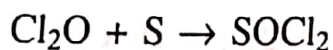
The S-O bonds have double bond character due to overlap of filled oxygen $p\pi$ orbitals with empty $d\pi$ orbitals of sulphur. An alternative structure with two double bonds in place of the two coordinate links can also be written. Then electron distribution will be :



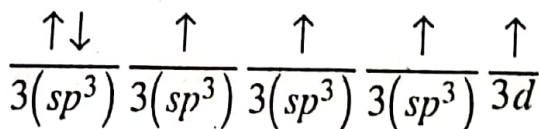
The four sp^3 orbitals will make sigma overlaps with suitable orbitals of chlorine and oxygen and the two d -orbitals will make π overlaps with oxygen forming double bonds. O-S-O angle and Cl-S-Cl angle in SO_2Cl_2 are 120° and 111° respectively. S-O bond length is 1.43A (143 pm) which is shorter than single bond (1.70A ; 170 pm).

Thionyl dichloride (Sulphinyl Chloride) (Dichlorooxosulphur) : SO_2 and PCl_5 react to give a mixture of thionyl dichloride, $SOCl_2$ (B. P. $78^\circ C$) and $POCl_3$ (B. P. $107^\circ C$). $SOCl_2$ is recovered by fractional distillation : $SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3$.

Chlorine monoxide reacts with sulphur at $-10^\circ C$ to form $SOCl_2$. An alternative method is the reaction of SCl_2 with SO_3 :

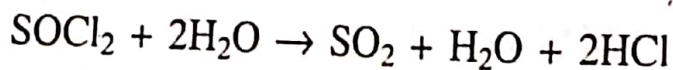


In thionyl dichloride, $SOCl_2$, roughly sp^3 hybridisation of sulphur is involved with one lone pair remaining intact on sulphur. An alternative structure with a double bond in place of the coordinate link can also be written. Then electron distribution will be :

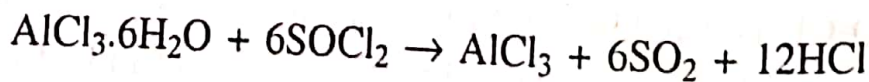


The sp^3 orbital with paired spins will be the lone pair. The other three sp^3 will overlap with suitable orbitals of chlorine and oxygen to give the three σ bonds. The $3d$ orbital will give π overlap with oxygen. O-S-Cl angle and Cl-S-Cl angle in $SOCl_2$ are 106° and 114° respectively. S-O bond-length (1.45A ; 145 pm) is shorter than single bond.

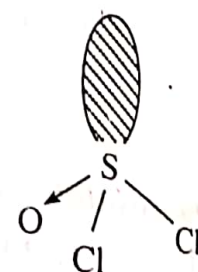
This is a colourless liquid which fumes in moist air and is hydrolysed by water :



$SOCl_2$ is used to obtain anhydrous metal halides from hydrated salts. The SO_2 and HCl formed in the reaction are removed :



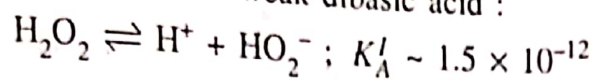
2000 Amides of Sulphuric Acid



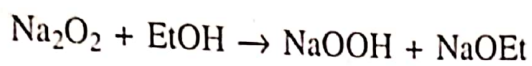
(20-XXXIX)

Reactions of Hydrogen Peroxide : In its chemical reactions H_2O_2 can function as an acid, as an oxidant and as a reductant.

1. **Acid Behaviour :** It behaves as a weak dibasic acid :

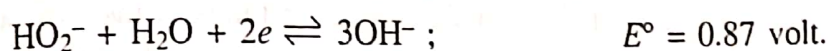
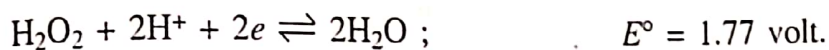


It is thus slightly more acidic than water. The second dissociation is very weak. It gives two series of salts : normal peroxides, Na_2O_2 , BaO_2 etc and the hydrogendioxide NaHO_2 . When Na_2O_2 is added to ethyl alcohol containing a little sodium ethoxide the following reaction occurs :

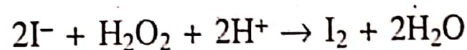
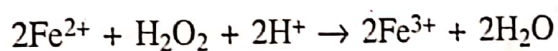


In the absence of the ethoxide, the hydrogendioxide formed reacts with ethanol to form sodium ethoxide and H_2O_2 . Alkali metal peroxides are celebrated oxidants. The hydrogendioxide is a violent oxidant unless carefully handled. It has been used to oxidise copper(II) oxide to copper(III) oxide (Cu_2O_3) in concentrated NaOH medium.

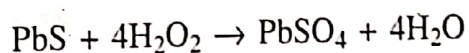
2. **Oxidising Behaviour.** This is a strong oxidant in both acid and alkaline solution. The redox potentials are :



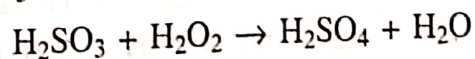
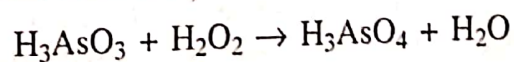
The oxygen-oxygen bond of H_2O_2 undergoes fission in presence of H^+ and electrons acquired from the reducing agents. H_2O_2 is thus converted to H_2O . The high positive potential shows that in acid solution it can easily oxidise iron(II) to iron(III) ($E^\circ = 0.77 \text{ volt}$), bromide to bromine ($E^\circ = 1.07 \text{ volt}$), iodide to iodine ($E^\circ = 0.54 \text{ volt}$) etc :



Discoloured oil-paintings in which the white lead pigment (basic lead carbonate) has been blackened due to atmospheric H_2S can be restored by scrubbing with H_2O_2 :

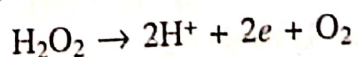


Arsenous acid and sulphurous acids are oxidised to arsenic and sulphuric acid respectively :

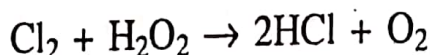
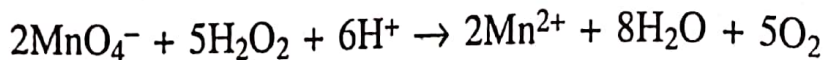


3. **Reducing Behaviour :** In presence of some very strong oxidants such as chlorine or permanganate in acid medium H_2O_2 is oxidised to oxygen. In another word H_2O_2 acts as a reducing agent. In the oxidising reactions of H_2O_2 it is reduced to H_2O while in the reducing reactions H_2O_2 is oxidised to O_2 . The hydrogen-oxygen bonds of H_2O_2 undergo fission to produce 2H^+ , $2e$ and O_2 .

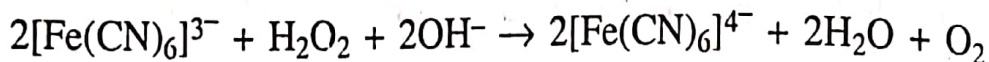
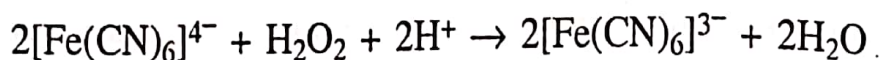
The oxidant merely removes the electrons from the hydrogen-oxygen bonds :



The released electrons bring about the reduction :

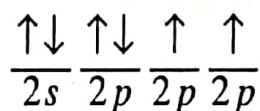


Hydrogen peroxide oxidises hexacyanoferrate(II) to hexacyanoferrate(III) in acid medium but reduces hexacyanoferrate(III) to hexacyanoferrate(II) in alkaline medium ;



Experiments with O-18 labelled H_2O_2 has shown that the oxygen that is liberated during reducing activities of H_2O_2 originates from H_2O_2 and not from the aqueous medium. This points out that the oxidants do not break the O-O link of H_2O_2 .

Hydrogen peroxide has an interesting skew structure. The two O-H planes are approximately perpendicular to each other (Fig. 20-2). Recall that oxygen has the following outer electronic configuration :



Taking the x-axis as the bond axis of O-O linkage the $2p_x$ orbitals of the two oxygen atoms overlap to give a sigma bond. Each oxygen also makes a sigma bond with a hydrogen, one oxygen using its $2p_y$ orbital and the other oxygen using its $2p_z$ orbital for the purpose. Then

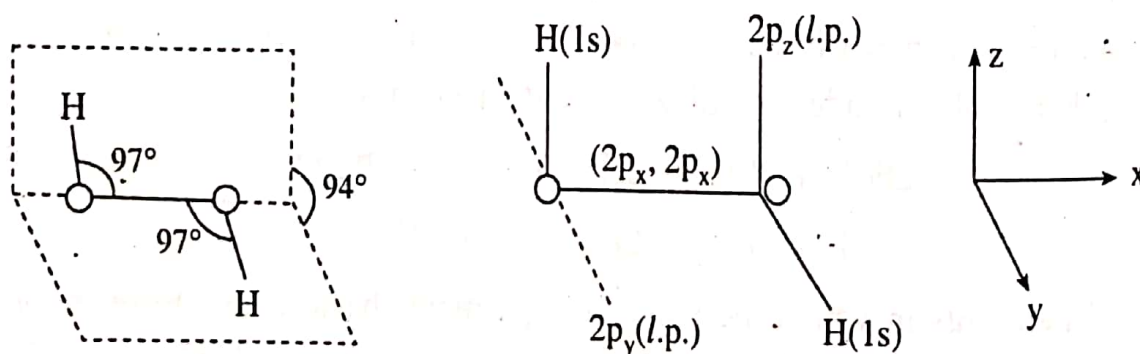


Fig. 20.2 Structure of H_2O_2 : l.p. = lone pair

the two oxygens have their third $2p$ orbital carrying the lone pairs at right angles and directed away from each other. Thus the lone pair—lone pair repulsion can be minimised.