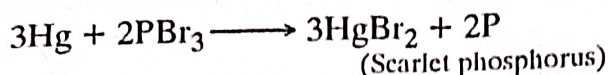


(d) **Scarlet phosphorus.** It is prepared by heating mercury with phosphorus tribromide, PBr_3 at 240°C



It is non-poisonous. It gives phosphine with alkalis.

(e) **Violet phosphorus.** It is obtained by heating red phosphorus at 530°C in a sealed tube. Its crystals have rhombohedral structure. It is bad conductor of electricity and is not oxidised by air.

2. Allotropy of arsenic. It has two allotropic forms.

(i) **Yellow arsenic.** Its molecular weight data in CS_2 solution indicates that it consists of As_4 tetrahedral units. It is an unstable plastic substance which is soft like a wax.

(ii) **Grey arsenic.** It exists in the form of **puckered sheets of atoms.** Here each atom is bonded to three neighbouring atoms. Since the sheets are held together by weak forces (than atoms within the sheets), it is soft and good conductor like graphite. It has metallic lustre and is stable form of arsenic.

3. Allotropy of antimony. It has two allotropic forms.

(i) **Yellow antimony.** It consists of Sb_4 tetrahedral units. It is unstable and has the tendency to convert into stable form.

(ii) **Silvery grey antimony.** Like grey arsenic, it exists in the form of puckered sheets of atoms. Here each atom is bonded to three neighbouring atoms. It is a stable, hard, brittle and metallic variety of antimony.

Difference between nitrogen and other group VA elements. Nitrogen differs from the rest of the elements of group VA elements in its properties. The difference is mainly due to

- (i) its small size
- (ii) its inability to increase its coordination number beyond four
- (iii) its high electronegativity and
- (iv) its more tendency to form multiple bonds with itself (catenation), carbon and oxygen.

OXYGEN FAMILY

The elements belonging to group VI A or 16 or chalcogens are given in table 3.10.

Table 3.10 Some Physical properties of group VIA elements.

Property ↓	Element Oxygen, → O	Sulphur, S	Selenium, Se	Tellurium, Te	Polonium, Po
Atomic number	8	16	34	52	84
Electronic configuration	$[\text{He}]^2 2s^2 2p^4$	$[\text{Ne}]^{10} 3s^2 3p^4$	$[\text{Ar}]^{18} 3d^{10} 4s^2 4p^4$	$[\text{Kr}]^{36} 4d^{10} 5s^2 5p^4$	$[\text{Xe}]^{54} 4f^{14} 5d^{10} 6s^2 6p^4$
Oxidation states*	-II, (-I)	-II, +IV, +VI	(-II), +II, +IV, +VI	+II, +IV, +VI	+II, (+IV)
Ionisation energies kcal/mole 1st	326	239	225	208	—
2nd	683	539	500	427	—
3rd	1097	808	786	706	—
4th	1784	1090	989	872	—
5th	2624	1670	1565	1389	—
6th	3170	2020	1878	1661	—
Total	9683	6366	5943	5263	—
Density (solid) gm/ml	1.27	2.06	4.82	6.25	9.51
Melting point ($^\circ\text{C}$)	-218.9	114.5	217.4	450	254
Boiling point ($^\circ\text{C}$)	-183	444.5	684.8	1390	962
Electronegativity (Pauling scale)	3.5	2.5	2.4	2.1	—
Atomic radii (A°)	0.74	1.04	1.17	1.37	1.64
Ionic radii M^{2-} (A°)	1.40	1.84	1.98	2.21	—
M^{2+} (A°)	—	—	—	0.89	1.02
Atomic weight	16.00	32.06	78.96	127.61	2.10
Heat of atomisation at 25°C (kcal/mole)	59.159	56.9	49.4	46.5	—

*Uncommon oxidation states are given in brackets.

Occurrence. Oxygen occurs in nature as oxygen gas. Sulphur occurs in nature as H_2S , SO_2 , sulphide ores and sulphate ores as gypsum, $MgSO_4$ and $CaSO_4$. Se, Te and Po elements have rare occurrence.

GENERAL CHARACTERISTICS

I. (a) Physical Properties. Some physical properties of group VIA elements are given in table 3.10. These properties are discussed below :

1. Electronic configuration. The electronic configuration of these elements (table 7.11) shows the presence of six electrons ($ns^2 np_x^2 np_y^1 np_z^1$) in their valence shell.

2. Oxidation states. These elements attain inert gas configuration by the following two different methods:

(a) **By transfer of electrons.** Oxygen atoms easily form doubly charged negative ions (O^{2-}) by the gain of two electrons. S, Se and Te also form a few compounds which are more than 50% ionic. The reasons are :

(i) As we move down the group, the size of element increases and attraction of nucleus for the newly added electrons decreases.

(ii) More the negative charge on the ion, more it becomes susceptible to polarisation.

(iii) A large sized anion cannot fit well in a lattice of small cations.

O^{2-} ions form stable ionic compounds with strong electropositive metals like Li, Mg and Al, e.g., Li_2O , MgO and Al_2O_3 . S^{2-} , Se^{2-} and Te^{2-} ions behave similarly but less effectively.

As we move down the group, there is gradual increase in the atomic radii and gradual decrease in electronegativity. As a result, the ability of elements to exist in +4 and +6 oxidation states decreases. Since inert pair effect increases down the group, the stability of +4 oxidation states increases and that of +6 oxidation states decreases. The oxidation states of various elements of group VI A elements are given below:

Oxidation states	0	-I	-II				
	O_2	H_2O_2	H_2O				
Oxidation States	-II	0	+II	+III	+IV	+V	+VI
	H_2S	S	$S_2O_3^{2-}$	$S_2O_4^{2-}$	H_2SO_3	$S_2O_6^{2-}$	SO_4^{2-}
	H_2Se	Se			H_2SeO_3		SeO_4^{2-}
	H_2Te	Te			$TeO_2(s)$		$H_6TeO_6(s)$

(b) **By sharing of electrons.** All these elements have two unpaired electrons in their valence shell. Thus, these elements form two covalent bonds by sharing these electrons with electrons of other atoms. For example, H_2O , H_2S etc. Compounds like CO_2 are purely covalent because of multiple bonding involved in them.

3. Metallic and non-metallic character. As we move down the group, there is a decrease in the values of electronegativity and heat of atomisation. As a result, the first four elements are non-metals. The non-metallic nature is strongest in oxygen and sulphur but weaker in selenium and tellurium. Polonium is radioactive and is markedly metallic. The above trend is indicated from the decrease in the stability of M^{2-} ions, increased tendency to form M^{2+} ions and structure of these elements.

4. Ionisation energy. As we move down the group, the screening effect of new shells becomes greater than the effective nuclear charge. As a result, the energy required to remove the valence electron becomes less and less. Thus, the ionisation energy goes on decreasing down the group. However, the first ionisation energy of VIA group elements is less (than expected than VA group elements). It is explained on the basis of increased stability of half filled p-orbitals of VA group elements. Since ionisation energy decreases down the group, the metallic character increases and ability to act as reducing agent increases.

5. Catenation. (Self-linkage). The property of catenation in group VIA elements, is only shown by sulphur.

It is observed in

(i) polysulphonic acid, $HSO_3^- S_x SO_3^- H$ ($x = 1$ to 12)

(ii) polysulphide, S_x^{2-} ($x = 6$)

(iii) Sulphanes, $H_2 S_x$ ($x = 8$)

(iv) Chlorosulphanes, $S_x Cl_2$ (x can have value equal to 100) and

(v) Polyoxides. Some examples are ; $H-O-O-H$, $H-S-S-H$, $H-S-S-S-S-H$.

6. **Elemental state.** Oxygen exists as diatomic gaseous molecule, O_2 . It is due to the ability of small sized oxygen atom to form stable $p\pi - p\pi$ multiple bond with itself. The forces holding O_2 molecules are weak van der Waal forces. Hence oxygen is a gas. Sulphur, selenium and tellurium are solids and exist as staggered S-atom rings or zig-zag chains. It is due to the inability of these large sized atoms to have $p\pi - p\pi$ overlap. The two unpaired electrons of one S-atom (say) form two covalent bonds with other S-atoms. As a result, a discrete, S_8 molecule is formed. This molecule has a puckered, saw-tooth ring structure (Fig. 3.24).

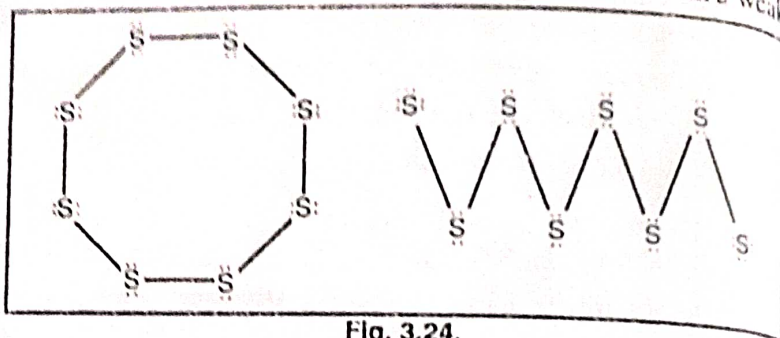


Fig. 3.24.

7. **Allotropy.** Various forms of same element having same chemical properties but different physical properties are called *allotropic forms* and the phenomenon is called **allotropy**. Oxygen sulphur, selenium and tellurium show allotropy.

(i) Oxygen exists in two allotropic forms. These are diatomic oxygen (O_2) and triatomic oxygen (O_3) i.e., ozone.

(ii) Sulphur exists in many allotropic forms. These are α (or rhombic), β (or monoclinic), γ (or plastic) and δ (or colloidal). The various allotropic forms of sulphur can be grouped into following classes.

(a) **Homocyclic species.** These contain 6 to 20 sulphur atoms. One of the examples is that of rhombic sulphur which exists as S_8 molecule.

(b) **Chain polymer species.** These contain 2 to 5 sulphur atoms and exist in liquid sulphur as unstable small molecules, S_n ($n = 2$ to 5). At temperatures of the order of 1000 K, the vapours contain S_2 molecules.

I. Allotropic forms of sulphur. (i) **Crystalline forms.** There are two crystalline forms.

(A) **Rhombic, Octahedral or α -Sulphur.** It is obtained by dissolving roll sulphur in carbon disulphide and then evaporating the solution. It is most stable form. When slowly heated to $95.5^\circ C$, it gets converted to monoclinic sulphur.

Structure. It exists as S_8 molecules. S_8 molecules are held together by weak van der Waal forces. Since these molecules are large sized and non-polar, this sulphur has low melting point ($113^\circ C$), and dissolves in non-polar solvents like CS_2 . The SSS bond angle (108°) is less than tetrahedral angle. The reduction in bond angle is caused by the repulsion of two lone pair of electrons on each atom. Its density is 2.7 gm/cc.

(B) **Monoclinic, Prismatic or β -Sulphur-Formation.** Some ordinary sulphur is melted in a china dish. On cooling, a crust is formed. A few holes are made in the crust and liquid below it is poured off. Needle shaped crystals of monoclinic sulphur are formed.

Properties. It is stable at $95.5^\circ C$. It changes to rhombic form below $95.5^\circ C$ called transition temperature. It is soluble in CS_2 but insoluble in water. Its melting point is $120^\circ C$ and density is 1.96 gm/cc.

Structure. It exists as S_8 molecules and is confirmed by X-rays.

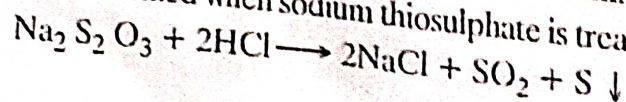
(ii) **Amorphous forms.** There are four amorphous forms.

(A) **Plastic or γ -sulphur.** It is prepared by pouring boiling ordinary roll sulphur in cold water. It is not crystalline because sudden cooling of boiling sulphur slows down the molecular motion.

Properties. It is soft and elastic. It is insoluble in CS_2 as well as H_2O . It has no sharp melting point. Its density is 1.96 gm/cc. It changes to rhombic form on standing at ordinary temperature.

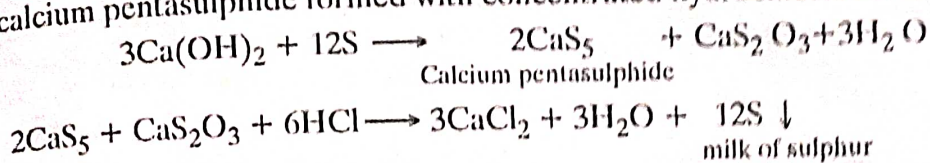
Structure. It exists in the form of helical chains of sulphur atoms. It is confirmed by X-rays.

(B) **Colloidal sulphur.** It is formed when sodium thiosulphate is treated with dilute hydrochloric acid.



Properties. It changes to ordinary form on heating on long standing. Some forms of this sulphur are soluble while others are insoluble in CS₂.

(C) **Milk of Sulphur.** It is prepared by boiling ordinary sulphur with milk of lime (calcium hydroxide) and treating the calcium pentasulphide formed with concentrated hydrochloric acid.



Properties. It is a white solid which is insoluble in H₂O as well as CS₂.

(D) **Purple sulphur vapours.** When sulphur (S₈) is heated above 250°C, the sulphur chain starts breaking. As a result, S₈ molecules dissociate into S₆, S₄ and S₂ molecules. When sulphur vapours containing S₂ species are cooled rapidly to liquid nitrogen temperature (-195°C), a purple sulphur is formed. It is paramagnetic like O₂.

2. **Allotropy of selenium.** Different allotropic forms of selenium are discussed as follows:

(i) **Grey crystalline form.** It has a metallic look and is poor conductor of electricity (conductivity = $2 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$). Its conductance increases about 1000 times when exposed to light and hence used in photoelectric cells. When light falls on grey Se, its unshared electrons get excited into slightly higher energy levels. These electrons now flow under a potential difference and its conductivity increases.

Structure. In this form, each Se-atom is covalently bonded to two other Se-atoms. The infinite chain of Se-atoms are arranged spirally around the parallel edges of the cube.

(ii) **Red amorphous form.** It is obtained in the form of Se precipitate in aqueous solution in a chemical reaction. It turns black when boiled with water. It is a meta-stable form. It is sparingly soluble in CS₂ and has density 4.26 gm/cc. It is a photoconductor.

Structure. It exists as puckered rings of Se₈ molecules (fig. 3.25).

(iii) **Yellow-vapour form.** (a) At 900°C, selenium changes to yellow vapours consisting of Se₂ molecules.

(b) At 2000°C, Se-atoms are formed.

3. **Allotropy of tellurium.** Different allotropic forms of tellurium are discussed below :

(i) **Crystalline forms.** It has metallic lustre and is good conductor of electricity. It is quite brittle and its conductivity increases to some extent when exposed to light radiations. Its density is 6.25 gm/cc.

Structure. This form consists of long zig-zag chains which are packed parallel to each other. Each Te-atom is bonded to two other Te-atoms by covalent bonds. (fig. 3.26).

(ii) **Amorphous form.** It is prepared by the reduction of tellurous acid with sulphur dioxide. Its specific gravity is 6.02

(iii) **Vapour form.** When liquid tellurium boils at 1390°C, golden yellow vapours of Te₂ molecules are formed. It represents vapour form of tellurium.

8. **Atomic radius, ionic radius (x²⁻, x²⁺ ions), atomic weight, electric conductivity, density, melting and boiling points (except Po).** These properties increase as we move down the group.

(a) As we move from oxygen to polonium, the atomic size shows a regular increase. As a result, the van der Waal forces among molecules increase regularly. Greater the van der Waal forces, greater energy is required to separate them. Hence greater will be the melting and boiling points.

(b) **Melting and boiling point of sulphur is much higher than oxygen.** It is explained in part on the basis that whereas oxygen exists as O₂ molecules, sulphur exists as S₈ molecules.

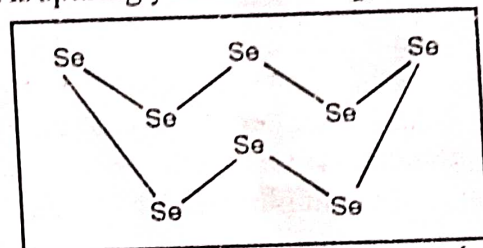


Fig. 3.25 Puckered ring structure of

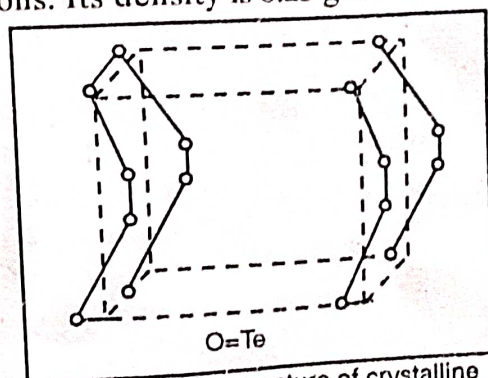


Fig. 3.26 Spiral structure of crystalline form of Te.

Melting and boiling points of polonium are less than that of tellurium. It is explained on the basis that s -electron pair in polonium is less available than tellurium due to increased inert pair effect in polonium. As a result, the van der Waal forces among Po molecules will be less than Te and hence less melting and boiling points.

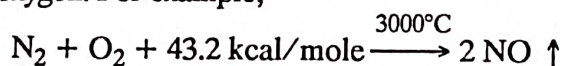
9. Oxidising property, electronegativity, heat of atomisation and oxidation potential. These properties decrease down the group. It is because as we go down the group, the screening effect of new shells becomes greater than the effective nuclear charge. The first ionisation energy decreases and hence above properties show a decreasing trend.

10. Inert nature of oxygen. ${}_8\text{O}$ atom ($1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$) shares its two unpaired electrons with unpaired electrons of another oxygen atom to form $p\pi - p\pi$ multiple bond. As a result, both O-atoms attain neon gas (stable) configuration and form $\text{O} = \text{O}$ molecule. The bond length is very short and bond dissociation energy is very high. Thus :

(i) At room temperature, strong bonding in O_2 is not disturbed by collision among O_2 molecules. Thus it is not reactive at room temperature.

(ii) At very high temperature, the O_2 molecules acquire high kinetic energy. The double bond in O_2 thus gets broken (into atoms) by the collision among molecules. The atoms so formed have high electronegativity and exhibit high chemical reactivity.

(iii) The formation of most of the oxygen compounds involve endothermic nature. It is also one of the reasons of inert nature of oxygen. For example,



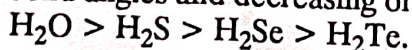
II. Chemical properties. 1. Hydrides. (i) **Covalent nature.** As we move down the group, the size of central atom in H_2O , H_2Se , H_2Te and H_2Po increases regularly. Thus $\text{H}-\text{X}$ bond length increases and electronegativity difference between H and X decreases regularly. As a result, the ionic character of $\text{H}-\text{X}$ bond decreases and *covalent bond character increases*.

The increasing trend to covalent nature of $\text{H}-\text{X}$ bond can also be explained by **Fajan's rule**. According to this rule, greater the size of negative ion, greater is the tendency to form covalent bond. Since the size of negative ion increases down the group, the covalent character of $\text{H}-\text{X}$ bond increases down the group.

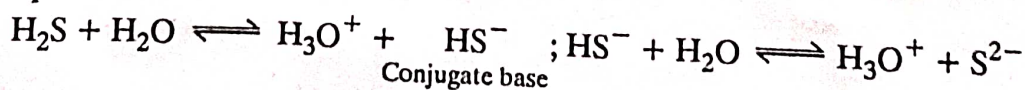
(ii) **Stability and reducing nature of hydrides.** As we go down the group, the size of negative ion increases from O^{2-} to Po^{2-} . Thus, the charge gets distributed over larger and larger volume. As a result, the stability of the hydrides goes on decreasing and reducing nature goes on increasing from H_2O to H_2Po .

(iii) **Volatile nature.** O-atom is small sized atom with high electronegativity. Thus, it forms strong intermolecular hydrogen bonding in water. Thus water is a liquid and has low volatility and high melting and boiling points. (table 3.10). As we move down the group, the size of the central atom increases while the electronegativity decreases regularly. Thus, no hydrogen bonding is possible. Thus H_2S is a gas and has high volatility. The volatile nature decreases from H_2S to H_2Se and to H_2Te . It is because of regular increase in their molecular weight and hence van der Waal forces.

(iv) **Bond angle.** As we move down the group, the electronegativity of central atom decreases. Thus the bonding electrons in $\text{M}-\text{H}$ bond of MH_2 ($\text{M} = \text{O}, \text{S}, \text{Se}, \text{Te}$) are drawn farther and farther away from M. As a result, bond pair-bond pair repulsion and lone pair-lone pair repulsion decreases regularly. This results in closing up of the bond angles and decreasing order of bond angle is



(v) **Acidity of hydrides.** Hydrides of group VIA elements behave as weak diprotic acids in aqueous solution. For example:



The acidic strength increases down the group. This behaviour can be explained on the basis of Fajan's rule. According to this rule, larger the negative ion, smaller the charge density from OH^- to HPO^- and greater is the tendency to form an ionic bond. As a result, the proton is less tightly held in higher

members and acidic character increases down the group. This effect is reflected in the dissociation constants of $\text{H}_2\text{O}(10^{-14})$, $\text{H}_2\text{S}(10^{-7})$, H_2Se , (1.7×10^{-4}) and H_2Te (2.3×10^{-3}) at 25°C .

2. Halides. Group VI A or 16 elements form following halides which are given in table 3.11.

Table 3.11 Halides of group VIA elements.

Element	Fluorides	Chlorides	Bromides	Iodides
Oxygen	OF_2 , O_2F_2	Cl_2O , ClO_2 , Cl_2O_6 , Cl_2O_7	Br_2O , BrO_2	I_2O_4 , I_4O_9 , I_2O_5
Sulphur	S_2F_2 , SF_4 , SF_6 , S_2F_{10}	S_2Cl_2 , SCl_2 , SCl_4	S_2Br_2	—
Selenium	Se_2F_2 , SeF_4 , SeF_6	Se_2Cl_2 , SeCl_4	Se_2Br_2 , SeBr_4	—
Tellurium	TeF_4 , Te_2F_{10} , TeF_6	TeCl_2 , TeCl_4	TeBr_2 , TeBr_4	TeI_4
Polonium	PoF_6	PoCl_2 , PoCl_4	PoBr_2 , PoBr_4	PoI_4

(i) **Fluorides.** Since fluorine is more electronegative than oxygen, the fluorine compounds with oxygen are called fluorides of oxygen. For example, OF_2 is called oxygen difluoride and not fluorine oxide. Since fluorine is a small sized atom, all elements except oxygen form hexafluorides, *i.e.*, SF_6 , SeF_6 , TeF_6 , PoF_6 .

(ii) **Chlorides, bromides and iodides.** Cl, Br and I are large sized atoms. The maximum coordination number of group VIA elements decreases with increase in the size of halogen atoms. Thus (a) hexachlorides are not known (b) only two tetra-iodides (TeI_4 , PoI_4) and (c) three tetrabromides (unstable) are known.

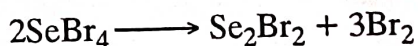
(iii) Te_2Cl_2 and Po_2Cl_2 are not known. It is because of two reasons:

(a) Te and Po atoms are large sized atoms. Thus Te-Te and Po-Po bonds are longer and hence weak.

(b) Cl-atom is more electronegative than Te or Po atoms. Thus, Cl-atom will withdraw electrons from Te-Cl and Po-Cl bonds towards itself making Te-Te and Po-Po bonds weaker.

Thermal stability. As the size of halogen atom increases, the M-X bond strength (M = S, Se, Te, Po and X = halogen) decreases. As a result, the thermal stability of these halides decreases in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$.

Stability of tetrabromides increases down the group from SeBr_4 to PoBr_4 . It is because as we move down the group, the polarity of M-Br bond (M = Se, Te, Po) increases and stability of tetrabromides increases. For example, SeBr_4 is unstable and forms Se_2Br_2 and Br_2 .



SeBr_4 also undergoes hydrolysis to form HBr and H_2SeO_3 (selenous acid).



Stability of tetra-iodides increases down the group. S and Se do not form tetra-iodides. It is because the bond between large sized I-atom and small sized S and Se atoms, is long and weak. The size of I-atoms and Te-atoms being same, TeI_4 is a stable iodide. Stability of PoI_4 can be similarly explained.

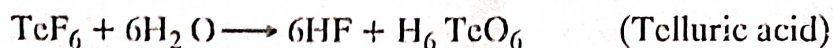
(vii) **Hexahalides.** All group VIA elements form hexafluorides of the type, MF_6 (M = S, Se, Te, Po). Oxygen does not form OF_6 because of non-availability of vacant *d*-orbitals of appropriate energy in O-atom. Some M_2F_{10} is also formed in the reaction mixture. PoF_6 is volatile.

Reactivity of hexafluorides. As we move down the group, the size of the central atom as well as length of M-F bond, (M = S, Se, Te, Po) goes on increasing. Longer the M-F bond, weaker it is. Thus the decreasing order of M-F bond strength is $\text{S} - \text{F} > \text{Se} - \text{F} > \text{Te} - \text{F} > \text{Po} - \text{F}$.

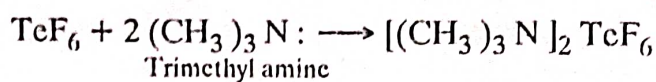
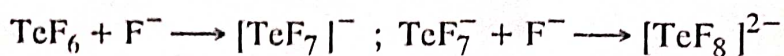
Hence the decreasing order of reactivity is $\text{PoF}_6 > \text{TeF}_6 > \text{SeF}_6 > \text{SF}_6$.

From above it is clear that SF_6 is extremely stable and inert due to high S-F bond strength, co-ordinately saturated S-atom in SF_6 and lack of polarity in SF_6 . It is used as gaseous insulator in high voltage equipment.

(a) SF_6 does not undergo hydrolysis while SeF_6 and TeF_6 react readily with water.



(b) **Lewis acid nature.** TeF_6 acts as Lewis acid because it can accept electrons from Lewis bases (like amines, F^-) in its vacant d -orbitals.



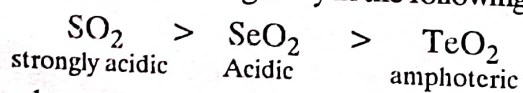
Structure. Central atom in hexafluorides is $sp^3 d^2$ hybridised. The molecules, thus, have octahedral structure.

3. Oxides. All group VIA elements form following binary oxides (table 3.12).

Table 3.12 Oxides of group VIA elements.

Element	Monoxide	Dioxide	Trioxide	Heptoxide
Sulphur	SO	SO ₂	SO ₃	S ₂ O ₇
Selenium	—	SeO ₂	SeO ₃	—
Tellurium	TeO	TeO ₂	TeO ₃	—
Polonium	PoO	PoO ₂	—	—

General trend. (i) **Acidic nature.** As we move down the group, the acidic nature of the oxides of group VIA elements (having same oxidation state) decreases regularly in the following order.



(ii) **Stability.** As we move down the group, the stability of group VIA oxides decreases. For example :

(a) SO_2 is more stable than SeO_2 . (b) SO_3 is more stable than SeO_3 (c) SO is known but SeO is not known.

(A) **Monoxides.** Except SeO, all monoxides are known.

(B) **Dioxides.** These elements burn in oxygen to form dioxides.

(a) **Solubility in water.** (i) SO_2 and SeO_2 are acidic oxides. These react with water to form H_2SO_3 (Sulphurous acid) and H_2SeO_3 (Selenous acid) respectively.

(ii) TeO_2 and PO_2 are amphoteric and are insoluble in water. These react with concentrated acids or bases to form their salts.

Nature. S-atom in SO_2 is sp^2 hybridised. SO_2 exists as monomeric covalent gaseous molecule. Se-atom is not sp^2 hybridised to form SeO_2 because of its low electronegativity and diminished ability to form multiple bonds to oxygen. Thus, it has polymeric zig-zag structure (fig. 3.27), TeO_2 and PoO_2 exist as ionic solids.

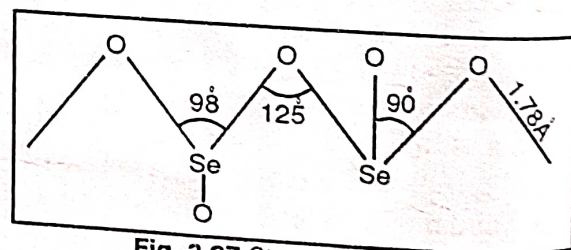
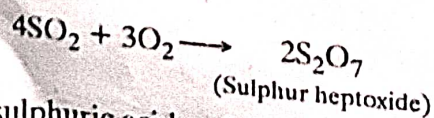


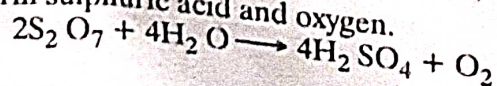
Fig. 3.27 Structure of SeO_2 .

(c) **Trioxides.** Group VIA elements form trioxides of the type MO_3 ($\text{M} = \text{S}, \text{Se}, \text{Te}$). SO_3 and SeO_3 are acidic oxides and are soluble in water. TeO_3 is insoluble in water. It is due to low electronegativity and diminished ability of large sized Te-atoms to form multiple bonds. This also explains the polymeric nature of TeO_3 .

(D) **Heptoxide.** This oxide is formed by S-atoms only. It is prepared by passing electric discharge through a mixture of SO_2 and O_2 .



It reacts with water to form sulphuric acid and oxygen.



ANOMALOUS BEHAVIOUR OF OXYGEN

Oxygen is the first member of group VIA elements. Its properties differ from rest of elements in its group due to its small size and high electronegativity. A few differences in properties are :

(i) Co-ordination of oxygen does not exceed four. Oxygen atom ($1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$) has no *d*-orbital. Thus, it cannot expand its octet to attain coordination number more than four. Other members have *d*-orbitals of low energy and can expand their octet. For example, the coordination number of S in SF_6 is six.

(ii) Nature of bonding, The electronegativity of oxygen (3.5) is highest in its group due to its small size and higher effective nuclear charge than screening effect. Thus, its compounds are more ionic as compared to other elements. Its high electronegativity is responsible for strong hydrogen bonding in its compound, water. The hydrogen bonding is not possible in large-sized S-atom. Thus H_2O is a liquid while H_2S is a gas.

(iii) Inert nature of oxygen (see page 88).

(iv) Oxygen exists as O_2 gas while other members exist as solids (see page 86).

(v) Reactivity. Weaker metals like Cu, Ag, Pb, Hg, Zn etc. occur in nature as sulphides (CuS , Ag_2S , PbS , HgS , ZnS etc.) and not oxides. The reason is that the large-sized S^{2-} ion is easily polarized by small-sized positive metal ions (Cu^{2+} , Ag^+ , Pb^{2+} , Hg^{2+} , Zn^{2+} etc.). As a result, a strong M-S bond (M = Cu, Ag etc.) is formed. On the other hand, the small-sized oxide ion O^{2-} is not easily polarised by metal ions. Thus, O^{2-} ion is called hard ion and other ions (S^{2-} , Se^{2-} etc.) of this group are called soft ions.

GENERAL CHARACTERISTICS

(a) Physical properties. Some physical properties of halogens are given in Table 3.13. These properties are discussed below.

Table 3.13 Some Physical Properties of Group 17 Elements (Halogens)

Property ↓	Fluorine (F)	Chlorine (Cl)	Bromine (Br)	Iodine (I)	Astatine (At)
Atomic number	9	17	35	53	85
Electronic configuration	$[2He] 2s^2 2p^5$	$[10Ne] 3s^2 3p^5$	$[18Ar] 3d^{10} 4s^2 4p^5$	$[36Kr] 4d^{10} 5s^2 5p^5$	$[54Xe] 4f^{14} 5d^{10} 6s^2 6p^5$
Oxidation state	-1	-1, +1, +3, +4, +5, +6, +7	-1, +1, +3, +4, +5, +6	-1, +1, +3, +7	-
Relative atomic mass	18.998	35.453	79.904	426.95	209.99
Ionisation energies ($kJ mol^{-1}$) 1st,	1680	1256	1142	1008	-
Atomic radius (pm)	72	99	114	133	-
Ionic radius X^- (pm)	133	184	196	220	-
Electronegativity	4	3.0	2.8	2.5	2.2
Electron affinity ($kcal mol^{-1}$)	333	349	325	296	-
Heat of hydration ($kJ mol^{-1}$)	515	381	347	305	-
Heat of dissociation ($kJ mol^{-1}$)	159	243	193	151	-
Melting point (K)	54	122	266	387	-
Boiling point (K)	85	239	333	458	-
Density ($g cm^{-3}$) in liquid state	1.513	1.655	3.187	3.960	-
Colour	(85 K) pale yellow	(203 K) Greenish yellow	(273 K) Reddish brown	(493 K) Violet	-
Enthalpy of vaporisation ΔH_v ($kJ mol^{-1}$)	6.54	20.41	29.56	41.95	-
Enthalpy of fusion ΔH_f ($kJ mol^{-1}$)	0.51	6.41	10.57	15.52	-
Bond enthalpy ($kJ mol^{-1}$)	158.8	242.6	192.8	151.1	-

1. Electronic configuration. The electronic configuration of these elements (Table 3.13) shows the presence of seven electrons ($ns^2 np^5$) in their valence shell. These require one electron to attain inert gas configuration. Thus, all these elements are monovalent.

2. Oxidation states. (a) **Fluorine.** It is the most electronegative element. It exists in -1 oxidation state as it needs one electron to attain stable noble gas configuration. It has no positive oxidation state because of its very high ionisation energy.

(b) **Cl₂, Br₂ and I₂.** Like fluorine, these also exist in -1 oxidation states. These also exist in positive oxidation states (see table 3.13) in oxyanions (e.g., ClO_3^- , $+5$ state of Cl) and in inter-halogen compounds (e.g., IF_7 , $+7$ state of iodine). In ICl , iodine exists as I^+ . Recently, evidence for the existence of cationic chlorine and bromine has also been reported.

3. Covalent nature of halides. As we go down the group, the size of halide ion (X^-) goes on increasing. Thus, according to Fajan's rule, the X^- ion becomes more and more polarisable. The compound, thus becomes more and more covalent. Fluorides are, however, ionic but in other halides, the ionic character decreases while covalent character increases.

4. Electron affinity. The electron affinity of elements decreases down a group due to the simultaneous increase in atomic size and nuclear charge. However, the effect of increase in size is greater than the increase in nuclear charge. As a result, the incoming electron feels less attraction by the larger atom and hence the electron affinity decreases.

Electronegativity and ionisation potential. All these elements have high electronegativity and ionisation potential. As we move down a group :

(i) The nuclear charge increases.

(ii) The electrons are added in the new shells. These new shells screen the nucleus appreciably. As a result :

The effective nuclear charge $<$ Screening effect. Thus, the force of attraction between the nucleus and the outer most electron decreases. Hence electronegativity and ionisation potential decreases regularly down the group.

Atomic and ionic radii. The atomic as well as ionic radii of these elements increase with increase in atomic number down the group. It is because of the successive addition of new orbits. Although the nuclear charge also increases down the group, yet the screening effect of the addition of new orbits is more than the effective nuclear charge. Hence size of atom and ion increases regularly down the group.

7. Diatomic nature. All the halogens exist as diatomic molecules in the form of gaseous, liquid and crystalline states. All these diatomic molecules dissociate into atoms. Except F_2 , the bond dissociation energy of halogens decreases down the group. Reasons for exceptionally low bond dissociation energy of F_2 as compared to Cl_2 are given below.

(i) Bond length in $\text{F}-\text{F}$ molecule is very small. Thus, the non-bonding electrons on both F -atoms repel each other strongly as compared to Cl_2 and other halogens in which the bond length is comparatively very large. As a result, $\text{F}-\text{F}$ bond dissociates very easily.

(ii) Except F_2 (having no d -orbital), the strength of bond in other halogens is more because of the possibility of multiple bonding involving available d -orbitals.

8. Hydrides. Halogens combine with hydrogen to form volatile halides, HX . Their tendency to react with halogens decreases down the group.

For example : (i) F_2 reacts with H_2 in the dark to form HF .

(ii) Cl_2 reacts with H_2 in presence of sun light to form HCl .

(iii) Br_2 react with H_2 above 775 K to form HBr and

(iv) I_2 reacts with H_2 only on heating in presence of platinum catalyst to form HI .

Some characteristics of these hydrides are given below.

1. Physical properties. All are colourless gases. These do not show acidic character in dry state and give sharp choking odour. *Except HF, all have low melting and boiling points.* The melting points increase with increase in atomic mass of halogen. The high boiling point of HF is due to high degree of intermolecular hydrogen bonding.

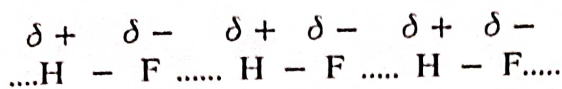
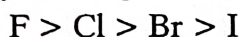


Table 3.14 Some Properties of Hydrogen Halides

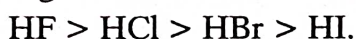
Property	HF	HCl	HBr	HI
Bond energy (kJ mol ⁻¹),	566	431	366	299
Heat of formation (ΔH_f) in kJ mol ⁻¹)	-269	-92.4	-37.2	+26.4
Ionisation constant in water	7×10^{-7}	10^7	10^9	10^{11}

2. Covalent nature. The bond between hydrogen and the halogen is covalent. It is indicated from the low melting and boiling points of these hydrides. Pure liquid hydrogen halides are poor conductor of electricity.

The order of electronegativity of halogens is :

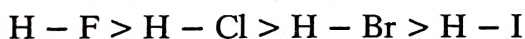


So, degree of polarity in H-halogen bond decreases in the order.



3. Heat of formation of hydrogen halides. It increases with increase in atomic mass of the halogen (table 3.14). This indicates the corresponding decrease in the quantities of energy released during the formation of hydrogen halides. Thus, the formation of hydrogen halides should become more difficult while going down the group. It is in accordance with the experimental facts.

This explains the decrease in the stability of hydrides in the following order

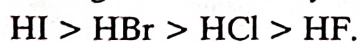


4. Reducing properties. A reducing agent is that which loses electrons easily and gets easily oxidised. Heat of formation of hydrogen halides show that their stability decreases down the group. For example.

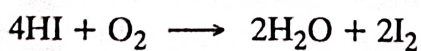
(i) HF and HCl are stable up to 1200°C.

(ii) HBr and HI dissociate to 1% and 20% respectively at 440°C.

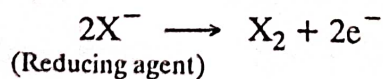
This indicates that reducing character of hydrogen halides increases down the group.



HI is such a strong reductant that it is easily oxidised by air to I₂.

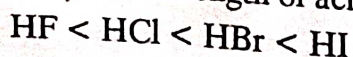


In general, the halide ion (X⁻) which is easily oxidised to X₂, is the strongest reductant.

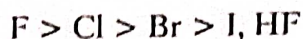


HF (i.e. F⁻) is the weakest while HI (i.e., I⁻) is the strongest reducing agent. The reason is that the electron which is to be removed during oxidation is closest to the nucleus in F⁻ and hence difficult to be removed. Thus, HF is a poor reducing agent. On the other hand, it is easy to remove an electron from large sized I⁻ and thus HI acts as a strong reducing agent.

5. Acidic strength. Hydrogen halides act as acids in their aqueous solutions. It is clear from their ionisation constant in water (table 3.13). The strength of acid increases in the order,



Although the positive charge on H-atom in HF is more than that in HCl, HBr, HI (because of decreasing order of electronegativity),



it has less tendency to lose protons to water.

It has been observed that :

“major factor contributing towards the lower acidity of HF is the high bond dissociation energy of HF”.

Group-18 (Noble Gases)

The credit of the discovery of the monoatomic gases, *helium* (${}^2\text{He}$), *neon* (${}_{10}\text{Ne}$), *argon* (${}_{18}\text{Ar}$), *krypton* (${}_{36}\text{Kr}$), *xenon* (${}_{54}\text{Xe}$) and *radon* (${}_{86}\text{Rn}$) mainly goes to Ramsay.

ELECTRONIC CONFIGURATION

Except helium which has $1s^2$ electronic configuration, all other elements of the noble gas family have $ns^2 np^6$ configuration, i.e., these have eight electrons (complete octet) in their outermost shell, (Table 3.15).

Table 3.15 Electronic Configuration of Noble Gases

Element	Atomic Number	Electronic configuration
He	2	$1s^2$
Ne	10	$1s^2 2s^2 2p^6$
Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Kr	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
Xe	54	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ $4s^2 4p^6 4d^{10} 5s^2 5p^6$
Rn	86	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ $4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

TREND IN PROPERTIES

The noble gases possess quite similar physical properties. Some important physical constants of noble gases are given in table 3.16.

Table 3.16 Some Physical Constants of Noble Gases

Property	He	Ne	Ar	Kr	Xe	Rn
Van der Waal's radius, (pm)	—	131	174	189	210	215
First Ionisation	2372	2080	1520	1351	1170	1037
Energy (kJ mol^{-1})						
ΔH_{fus} . kJ mol^{-1}	0.02	0.33	1.18	1.64	2.3	2.9
ΔH_{vap} kJ mol^{-1}	0.084	1.77	6.5	9.0	12.6	16.4

Discussion of Properties

1. Monoatomic nature. These are colourless, odourless gases and exist in the monoatomic state. These do not form diatomic molecules due to the absence of unpaired electrons in their valence shell.

2. Ionisation energy. The noble gases have high ionisation energies due to their highly stable ($ns^2 np^6$) configurations. The ionisation energies decrease down the group. Down the group, the nuclear charge goes on increasing but the electrons are added in the new shells at each successive step. These electrons screen the nucleus appreciably. The increase in screening effect being greater than the effect of the increase in nuclear charge, the force of attraction of the nucleus for the electrons goes on decreasing. As a result, the energy required to remove an electron from the valence shell goes on decreasing. Hence, the first ionisation energy of elements goes on decreasing down the group.

3. **Electron affinity.** Except helium which has the configuration ($1s^2$), all noble gases have $ns^2 np^6$ configuration, i.e., eight electrons in their outermost orbit. Thus, these elements have little tendency to accept electrons. Consequently, the electron affinity of noble gases is very small.

Compounds of helium and neon. Helium and neon do not form noble gas compounds because of the following reasons :

- (i) Both have high ionisation energies due to their small size.
- (ii) They cannot increase their covalency because of the absence of vacant d -orbitals in their valence shells.

However, xenon and krypton form compounds with oxygen, fluorine and (chlorine). It is due to the high electronegativity of fluorine (4.0), chlorine (3.0) and oxygen (3.5).

GENERAL TREND OF OXIDATION STATES AND INERT PAIR EFFECT OF P-BLOCK ELEMENTS

1. **Oxidation States.** The oxidation state of an element is the auxiliary charge which an atom has or appears to have when combined with other atoms. It can be predicted from the electronic configuration of the element. It corresponds to the number of electrons gained or lost by an element to attain a closed shell configuration of eight electrons ($ns^2 np^6$) or two electrons (ns^2).

(a) Elements of group 1, 2, 13 lose one, two and three electrons respectively and attain stable inert gas configuration. Hence these elements show +1, +2, and +3 oxidation states respectively. Thus, the oxidation state of one element in above groups is equal to the group number.

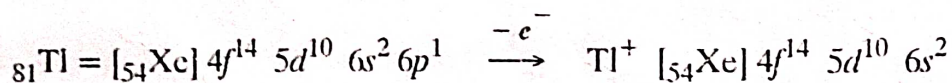
(b) Elements of group 14 are unable to lose or gain four electrons to get $ns^2 np^6$ stable configuration because of their very high ionisation energy/electron affinity. Hence these share electrons with other atoms and form covalent compounds and exhibit oxidation state equal to four.

(c) Element of group 15, 16, 17 have a tendency to gain three, two and one electron respectively to attain $ns^2 np^6$ stable configuration. Thus, the elements in these groups show -3, -2 and -1 oxidation states respectively.

(i) From above it is clear that as one moves along a period, (say third), the oxidation states increase from +1 (Na^+) to +3 (Al^{3+}) and then decreases from -3 (P^{3-}) to -1 (Cl^-). (ii) For p-block elements, the maximum oxidation state of an element in a group is equal to sum of its s and p electrons which is the same as group number.

(iii) A few p-block elements are such which in addition to usual oxidation state show an oxidation state which differ by a step of two. For example, thallium (Tl) shows +3 (Tl^{3+}) and +1 (Tl^+) oxidation states. It can be explained on the basis of inert pair effect.

2. **Inert pair effect.** p-block elements with high atomic number (usually with outer electron configuration $ns^2 np^{1-3}$) show variable valency. First of all, these elements lose outer p -subshell electrons.



This gives one value of valency. For example, ns^2 electrons which are left behind penetrate towards the nucleus to maximum extent. These are, thus, strongly attracted by the nucleus. Hence, both the ns electrons are reluctant to participate in bond formation. This pair of ns^2 electrons is called inert pair and the effect is called inert pair effect. The inert pair effect increases down the group in the periodic table. For example, the inert pair effect and stability corresponding to low valent ions and compounds of 13, 14 and 15 group elements are in the order :

Table 3.17 Oxidation States of Elements of Group

Group 13	Oxidation states	Group 14	Oxidation states
B	+3	C	+4
Al	+3	Si	+4
Ga	+3, +1	Ge	+4, +2
In	+3, +1	Sn	+4, +2
Tl	+3, +1	Pb	+4, +2

group 13 (Inert pair effect) : Tl^+ (Thallous, $Z = 81$) $>$ In^+ (Indium, $Z = 49$)

group 13 (Stability) : $TlCl > InCl$

group 14 (Inert pair effect) : Pb^{2+} (plumbous, $Z = 82$) $>$ Sn^{2+} (stannous, $Z = 50$)

group 14 (Stability) : $PbCl_2 > SnCl_2$

group 15 (Inert pair effect) : Bi^{3+} (bismuth, $Z = 83$) $>$ Sb^{3+} (antimony, $Z = 51$) $>$ As^{3+} (arsenic, $Z = 33$) $>$ P^{3+} ($Z = 15$)

The above trend is due to the decrease in the strength of the covalent bond formed by elements lying in the lower part of the group. This decrease in bond strength results from less effective overlap of electron cloud due to large distance between bonded atoms. Thus, the energy released in aqueous solution (hydration energy) due to additional bond formation is not sufficient to excite the lone pair (ns^2) of electrons. Hence, compounds showing lower valency are more stable.

Greater the inert pair effect, greater is the stability of the ion or compound and lesser is the tendency to lose electrons or get oxidised. However, ns^2 - electrons can be removed under drastic conditions to give another value of valency. The ion so formed is unstable. This will, thus, take up to two electrons from other atoms to retain its ns^2 -electrons. Hence it will behave as an oxidising agent. The oxidising character of high valent ions increase down the group. For example, gain of ns^2 electrons and oxidising nature of high valent ions or compounds of 13, 14 and 15 group elements is in the order :

group 13 (Gain of electrons) : $Tl^{3+} > In^{3+}$

group 13 (Oxidising agent) : $Tl^{3+} > In^{3+}$ or $TlCl_3 > InCl_3$

group 14 (Gain of electrons) : $Pb^{4+} > Sn^{4+}$

group 14 (Oxidising agent) : $PbCl_4 > SnCl_4$

group 15 (Gain of electrons) : $Bi^{5+} > Sb^{5+} > As^{5+} > P^{5+}$

group 15 (Oxidising agent) : $BiCl_5 > SbCl_5 > AsCl_5 > PCl_5$.

(Since inert pair effect is maximum in Bi^{3+} and least in P^{3+} , $BiCl_5$ does not exist but PCl_5 exists).

In other words, in group 13, Tl^{3+} ion will gain two electrons easily (than In^{3+} ion) to form Tl^+ ion. Thus, Tl^{3+} is better oxidising agent than In^{3+} and less stable than Tl^+ .

Similarly, we can explain that

(i) Pb^{4+} is better oxidant than Sn^{4+} and (ii) Sb^{5+} is better oxidant than As^{5+}

FIRST AND SECOND ROW ANOMALIES

It has been observed that among p -block elements, the first element in each group differs from other elements in their characteristics. It is because of its

- (i) *small size and other properties* (ionisation potential, electron affinity etc.) which depend upon size.
- (ii) *non-availability of d -orbital.*
- (iii) *tendency to form π -bond by $p\pi-p\pi$ -overlap and*
- (iv) *inability to form $p\pi-d\pi$ multiple bonding.*

Let us study the effect of above characteristics on the chemistry of first element as compared to other elements (specially second) in the same group.

(a) **Effects because of size difference.** (i) In group 14 elements, CO_2 is a gas but SiO_2 is a solid. C-atom is smaller in size as compared to silicon atom. Thus, half filled $2p$ -orbital of C-atom overlaps with half filled