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For Feedback...
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The dihalides are formed by?

16th GROUP ELEMENTS

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Special

Introduction

- Oxygen, Sulphur, Selenium, Tellurium and Polonium are the elements of VIA group or 16th vertical column of the periodic table.
- The first four elements are collectively known as **chalcogens** (ore forming elements), since many metals occur as oxides (or) sulphides in nature.
- **Polonium** is a radio active element and short lived ($t_{1/2}$ 13.8 days)
- Oxygen is the most abundant element in earth's crust.
- It constitutes 46.6 % by mass of earth's crust
- Dry air contains 20.946% of oxygen by volume
- The abundance of sulphur in earth's crust is only 0.03–0.1 %
- There are three naturally occurring isotopes of oxygen i.e.,

  $_8O^{16}$(99.762%) $_8O^{17}$(0.038%) and $_8O^{18}$(0.200%)
- Sulphur exists mainly as sulphides and sulphates. Such as gypsum $CaSO_4.2H_2O$, Epsom salt $MgSO_4.7H_2O$ baryte $BaSO_4$ and sulphides such as Zincblende ZnS, galena PbS copper pyrites $CuFeS_2$.
- Traces of sulphur is present as H_2S in eggs, garlic, onion, hair, wool, proteins
- Native sulphur is also available at volcanic areas.
- Polonium occur in nature as decay product of thorium and uranium minerals.
- Oxygen is a gas while other elements of this group are solids at room temperature.
- In oxygen molecule strong double bond is present so it exists as isolated molecules i.e as a gas.
- Atomic radius increases from O to Te.
- Ionisation energy decreases from O to Po.
- Electro negativity order is O>Se>S>Te>Po. This implies that the metallic nature increases from oxygen to Po
- Electron gain enthalpy order is S>Se>Te>Po>O
- Because of compact size of oxygen, inter electronic repulsions are high hence it has less negative electron gain enthalpy than sulphur
- Density order : $O < S_{(\alpha)} < Se_{(grey)} < Te$
- Melting point : (K) $S < Se < Po < Te$
  (monoclinic)
- Boiling point (K) $O < S < Se < Po < Te$
- The large difference between the MP and BP of oxygen and sulphur may be explained on the basis of their atomicity. oxygen exist as a diatomic molecule while sulphur exist act as poly atomic molecule (s_8).

Oxidation states and chemical reactivity

- Oxygen exists as a diatomic molecule (O_2), Sulphur, Selenium, Tellurium exist as octaatomic molecules. (S_8, Se_8, Te_8).
- Metallic character increases from O to Po.
- Oxygen, Sulphur are strongly non-metallic.
- Selenium and Tellurium are metalloids, and Polonium is a metal.
- The general outer electronic configuration of these elements is ns^2np^4
- The common oxidation state of these elements is -2, because they have s^2p^4 configuration in their outer most orbit.
- The stability of -2 oxidation state decreases down the group. Polonium hardly shows -2 oxidation state
- Oxygen shows positive oxidation states in fluorides. Oxidation state of oxygen in O_2F_2 is +1 and in OF_2 is +2.
- The Oxidation state of oxygen in a peroxide is -1 (H_2O_2) and in a super oxide is $-\frac{1}{2}(KO_2)$
- Oxygen cannot exhibit oxidation number beyond +2, due to absence of vacant d-orbitals.
- The other elements exhibit +2, +4, +6 oxidation states due to availability of vacant d orbitals in its valency shell. but +4 and +6 are most common
- S, Se and Te show +4 in oxides and +6 in fluorides. stability of +6 oxidation state decreases down the group and stability of +4 oxidation state increases (Inert pair effect)
- Bonding in +4 and +6 oxidation states is covalent
- The anamolous behaviour of oxygen is due to its small size and high electronegativity
- The absence of d-orbitals in oxygen limits its covalency to four and in practice rarely exceeds two, while in other elements covalence exceeds four.

Reactivity with Hydrogen

- VIA group elements can form the hydrides of the formula H_2M (M=VIA group element).
- All these hydrides are covalent compounds.

H_2O	-	hydrogen oxide (water)
H_2S	-	hydrogen sulphide
H_2Se	-	hydrogen selenide
H_2Te	-	hydrogen telluride
H_2Po	-	hydrogen polonide

- The ease of formation and thermal stability decrease from H_2O to H_2Po (as M-H bond energy decreases)

The thermal stability Order

$H_2O > H_2S > H_2Se > H_2Te$

Water dissociates at about 2273K, H_2S at 673-873 K, H_2Se at 433K and H_2Te at ordinary room temperatures. H_2Po is unstable at room temperature.

- At room temperature, water is a liquid and the other hydrides are colourless, foul smelling, toxic gases.
- M-H bond length in the hydrides increases from H_2O to H_2Po.
- The reducing property increases from H_2O to H_2Po.
- The aqueous solutions of these hydrides behave as weak acids. The acidic strength increases from H_2O to H_2Te.

Order: $H_2O < H_2S < H_2Se < H_2Te$

- K_a (dissociation constant) of aqueous solutions of these hydrides increases from H_2O to H_2Te.

Ka	H_2O	H_2S	H_2Se	H_2Te
at 25°C	1.0×10^{-14}	1.0×10^{-7}	1.7×10^{-4}	2.3×10^{-3}

- In the formation of H_2O, Oxygen atom is sp^3 hybridised.
- In H_2S and other hydrides pure p-orbitals are involved in bonding.
- The molecules have bent structures (VSEPR theory).
- The bond angle decreases from H_2O to H_2Po.

  $(H_2O - 104^0 28'; H_2S - 92^0 30';$
  $H_2Se - 91^0; H_2Te - 90^0; H_2Po - 90^0)$
- When compared to other hydrides, water has abnormal high boiling point. This is due to intermolecular hydrogen bonding in water.
- Boiling point order: $H_2S < H_2Se < H_2Te < H_2O$
- Order of volatile nature is $H_2S > H_2Se > H_2Te > H_2O$

Reactivity with oxygen

- VIA group elements can form two types of oxides.
  (a) Dioxides eg: SO_2, SeO_2, TeO_2
  (b) Trioxides eg: SO_3, SeO_3, TeO_3
- O_3 may be treated as oxygen dioxide (OO_2)
- SO_2 is a gas, SeO_2 is a volatile solid and TeO_2 is a white non-volatile solid
- TeO_2 and PoO_2 are crystalline ionic solids.
- Order of acidic strength: $SO_2 > SeO_2 > TeO_2$ and $SO_3 > SeO_3 > TeO_3$.
- Trioxides are more acidic than dioxides. PoO_2 is basic.
- Reducing property of dioxides decreases from SO_2 to TeO_2
- SO_2 is reducing while TeO_2 is an oxidising agent

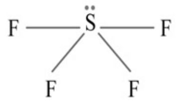
Reactivity towards Halogen

- VIA group elements can form mono halides of the type M_2X_2; dihalides (MX_2); tetrahalides (MX_4) and hexa halides (MX_6).
- Since the electronegativity of fluorine is greater than oxygen, the compounds of fluorine and oxygen are called fluorides of oxygen.
- The stability of the halides decreases in the order $F^- > Cl^- > Br^- > I^-$
- Amongst hexahalides, hexafluorides are the only stable halides
- All the hexa fluorides are gaseous in nature
- SF_6 is exceptionally stable for steric reasons
- Among tetrafluorides SF_4 is a gas, SeF_4 a liquid and TeF_4 is solid
- Sulphur reacts with fluorine (diluted with nitrogen) to form SF_4 and SF_6.
  $S + F_2(\text{dilute with } N_2) \rightarrow SF_4$ & SF_6
- SF_4 is also prepared by reaction between Cobalt trifluoride with Sulphur.
  $S + 4CoF_3 \rightarrow SF_{4(g)} + 4CoF_2$
- SF_4 is thermally more stable than lower fluorides.
- SF_4 is highly reactive gas and a good fluorinating agent.
- Tetra halides undergo hydrolysis to give the corresponding 'ous' acids.(except SF_4)

  Eg : $SCl_4 + 4H_2O \rightarrow S(OH)_4 + 4HCl$

  $$S(OH)_4 \downarrow \; H_2SO_3 + H_2O$$
- SF_4 and SCl_4 are Lewis acids since they can accept lone pairs of electrons readily to form hexahalides using halide ions.
- SF_4 and SCl_4 can act as Lewis bases by donating lone pairs of electrons.
- In SF_4 and SCl_4, sulphur atom undergoes sp^3d hybridisation ,
- Tetra halide(SF_4, SCl_4) molecules have trigonal bipyramidal structure with one corner of equatorial position occupied by a lone pair of electrons(see-saw structure) SP^3d hybridisation

Structure of SF_4



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- All elements except selenium form dichloride and dibromides
- The dihalides are formed by SP^3 hybridisation and thus have tetra hedral geometry
- In SCl_2 the sulphur atom is in sp^3 hybridisation, with two positions occupied by lone pairs.
- In SCl_2, the lone pairs distort the tetrahedral angle from $109^0 28^1$ to 103^0
- SCl_2 molecule has angular shape.
- Sulphur can form monohalides, S_2F_2 and S_2Cl_2. (dimers)
- The best known dihalide is SCl_2. It is a foul smelling red liquid.
- Sulphur on heating with chlorine gives S_2Cl_2. This on saturation with chlorine gives SCl_2.
  $2S + Cl_2 \rightarrow S_2Cl_2$
  $S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$
- Sulphur monochloride reacts with ethylene to form di (2-chloro ethyl) sulphide, commonly known as mustard gas.

  $S_2Cl_2 + 2CH_2{=}CH_2 \rightarrow (ClCH_2\text{-}CH_2)_2S + S$
  musturd gas
- The few monohalides are dimeric in nature.
  Examples are $S_2F_2, S_2Cl_2, Se_2Cl_2, Se_2Br_2$
- These dimeric monohalides undergo disproportionation as $2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$
- The structure of S_2Cl_2 is similar to H_2O_2 with the bond angle 104^0. Hybridization of S is Sp^3 in S_2Cl_2 & dihedral bond angle is $108^0 18^!$.

Oxygen preparation

Laboratory preparations

- By heating oxygen containing salts such as chlorates, nitrates & permanganates

  $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$
  $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$
  $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$
- Thermal decomposition of oxides of metals which are in lower part of electrochemical series

  $2Ag_2O_{(s)} \rightarrow 4Ag_{(s)} + O_{2(g)}$

  $2HgO(S) \rightarrow 2Hg(l) + O_2(g)$
  $2Pb_3O_4(S) \rightarrow 6PbO(S) + O_2(g)$
  $2PbO_2(S) \rightarrow 2PbO(S) + O_2(g)$
- By decomposition by H_2O_2 in presence of catalyst like metals and metal oxides like MnO_2

  $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
- On large scale it can be prepared from water or air. electrolysis of water leads to the release of oxygen at anode.