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P-BLOCK ELEMENTS AND THEIR COMPOUNDS-II

SOME CHARACTERISTIC PROPERTIES OF THE ELEMENTS OF GROUP 16

- This group consists of O, S, Se, Te and Po.
- The Group 16 elements show the usual gradation from non metallic to metallic properties with increasing atomic number that occurs in any periodic group. Oxygen and sulphur are non-metals, selenium and tellurium are semiconductors and polonium is metallic.

Table 20.1: Properties of Group 16 elements

	Atomic Number.	Electronic Configuration	Atomic Radius/nm	Ionic Radius/nm	M.P. /°C	B.P. /°C
O	8	2.6 $Ls^2 2s^2 2p^4$	0·074	0.140	–218	–183
S	16	2.8.6 ....$2s^2 2p^6 3s^2 3p^4$	0.104	0.184	119*	445
Se	34	2.8.18.6 ....$3s^2 3p^6 3d^{10} 4s^2 4p^4$	0·117	0.198	217**	685
Te	52	2.8.18.18.6 ....$4s^2 4_p{}^6 4d^{10} 5s^2 5p^4$	0.137	0·221	450	990
Po	84	2.8.18.32.18.6 .... $5s^2 5p^6 5d^{10} 6s^2 6p4$	0.140		254	960

Occurrence and Abundance

- The group 16 elements of modern periodic table consist of 5 elements oxygen, sulphur, selenium, tellurium and polonium. The elements in this group are also known as the ***chalcogens*** or the ***ore-forming elements*** because many elements can be extracted from the sulphide or oxide ores. Oxygen is abundantly found on the earth.

Preparation of dioxygen

- In the laboratory, dioxygen is prepared by heating a mixture of potassium chlorate (4 parts) and manganese dioxide (1 part) in a hard glass tube to about 420 K. The manganese dioxide acts as a catalyst. The gas is collected by the downward displacement of water.

$$2KClO_3 + (MnO_2) \rightarrow 2KCl + 3O_2 + (MnO_2)$$
$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$
$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

Physical Properties

- **Oxygen** usually exists in the form of dioxygen. **Properties**: **Oxygen** is a colourless, odourless and is a highly reactive tasteless gas. Due to the presence of pπ– pπ bonding, O_2 is a discrete molecule and intermolecular forces are weak van der Waals forces, hence, O_2 is a gas.

Chemical Properties

- Phosphorus is slowly oxidised in oxygen to form its pentoxide at room temperature.

$$4P + 5O_2 \rightarrow 2P_2O_5$$

- At higher temperatures it combines with almost all the elements to form compounds with the evolution of much energy.

OXYGEN AND SULPHUR

- Oxygen and sulphur are the first two members of the 16th group of the periodic table.

Classification of Oxides

- The binary compounds of oxygen with other elements (metals or non-metals) are called oxides. Acidic oxides, Basic oxides, Amphoteric oxides and Neutral oxides.

OZONE

- Ozone or trioxygen, is an inorganic molecule with the chemical formula O. 3. It is a pale blue gas with a distinctively pungent smell. It is an allotrope of oxygen that is much less stable than the diatomic allotrope O_2, breaking down in the lower atmosphere to O.

- **Structure of Ozone:** Ozone forms a V-shaped molecule. The central O atom uses sp^2 hybrid orbitals for bonding.

- **Physical Properties of Ozone:** Ozone is a pale blue gas which turns into blue liquid at 161K. At 80K it freezes to a violet black solid. It is ten times as soluble in water as oxygen.

- **Chemical Properties of Ozone:**

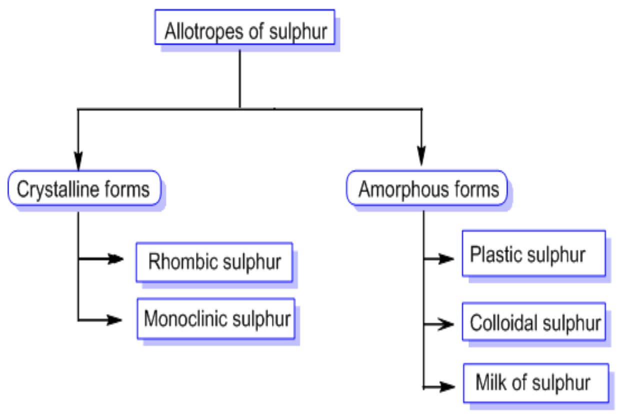
(i) **Catalytic decomposition:** Ozone in aqueous solution decomposes on standing. $2O_3 \rightarrow 3O_2$.

(ii) **Oxidizing properties:** In the presence of reducing agents ozone furnishes active atom of oxygen according to the equation.

$$O_3 \rightarrow O_2 + O$$

- Uses of Ozone: Ozone is used for water purification, air purification, refining oils, dry bleach, in industry and in the laboratory.

ALLOTROPIC FORMS OF SULPHUR



Sulphur Dioxide, SO_2

- It can be produced by the reduction of sulphuric acid.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

- **Physical properties of SO_2:** It is a colourless gas with an odour well known as that of burning sulphur. It is $2\frac{1}{4}$ times as heavy as air. It is easily liquified by compression (2.5 atm at 15°C) or by cooling in a freezing mixture.

- **Chemical properties of SO_2 :**

(i) Incombustible and non-supporter of combustion:

$$4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$$

$$2Mg + SO_2 \longrightarrow 2MgO + S$$

(ii) It is highly soluble in water forming unstable sulphurous acid.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

(iii) In presence of moisture, it acts as a fairly strong reducing agent.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

SULPHURIC ACID

- Sulfuric acid (American spelling) or sulphuric acid (Commonwealth spelling), also known as oil of vitriol, is a mineral acid composed of the elements sulfur, oxygen and hydrogen, with molecular formula H_2SO_4. It is a colorless, odorless and viscous liquid that is miscible with water.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

- **Properties of sulphuric acid:**

(i) It shows oxidizing character.

Oxidation of metals.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

$$Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + 2H_2$$

Oxidation of non-metals

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

(ii) Conc. H_2SO_4 is a strong dehydrating agent.

$$\underset{\text{blue}}{CuSO_4.5H_2O} \xrightarrow[-5H_2O]{\text{conc. } H_2SO_4} \underset{\text{white}}{CuSO_4}$$

SOME GENERAL CHARACTERISTICS PROPERTIES OF ELEMENTS OF GROUP 17

- The group 17 elements include fluorine(F), chlorine(Cl), bromine(Br), iodine(I) and astatine(At) from the top to the bottom. They are called "halogens" because they give salts when they react with metals.

Occurrence of Halogens

- Bromine compounds occur in the Dead Sea and underground brines. Iodine compounds are found in small quantities in Chile saltpeter, underground brines, and sea kelp. Iodine is essential to the function of the thyroid gland. The best sources of halogens (except iodine) are halide salts.

Table 20.2: Physical properties of Group 17 elements

	Atomic Number	Electronic Configuration	Atomic Radius/nm	Ionic Radius/nm M^{3+}	M.P. /°C	B.P. /°C
F	9	2.7 $\ldots 1s^2 2s^2 2p^5$	0.072	0.136	–220	–188
Cl	17	2.8.7 $\ldots 2s^2 2p^6 3s^2 3p^5$	0.099	0.181	–101	–34.7
Br	35	2.8.18.7 $\ldots 3s^2 3p^6 3d^{10} 4s^2 4p^5$	0.114	0.195	–7.2	58.8
I	53	2.8.18.18.7 $\ldots 4s^2 4p^6 4d^{10} 5s^2 5p^5$	0.133	0.216	114	184
At	85	2.8.18.32.18.5 $\ldots 5s^2 5p^6 5d^{10} 6s^2 6p^5$				

FLUORINE AND CHLORINE

- Fluorine and chlorine are the first two members of Group-17. Fluorine is the most electronegative element.
- **Fluorine**: The major method for preparing fluorine is electrolytic oxidation. The most common electrolysis procedure is to use a molten mixture of potassium hydrogen fluoride, KHF_2, and anhydrous hydrogen fluoride. Electrolysis causes HF to decompose, forming fluorine gas at the anode and hydrogen at the cathode.
- **Chlorine**: It is usually prepared by the oxidation of chlorides by strong oxidizing agents, such as MnO_2, $KMnO_4$.

$$MnO_2 + 2Cl^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O + Cl_2$$

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

Hydrogen Halides and Hydrohalic Acids

- Hydrohalic acids are commonly termed as Hydrogen Halides when they dissolve in water to give acids. They are diatomic organic compounds with a formula HX, X represents any of the halogens. Hydrogen chloride forms a primary component of gastric acid when present in the form of hydrochloric acid.

Preparation of Hydrogen Halides

- Industrially HF is made by heating CaF_2 with strong H_2SO_4

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

Properties of the Halogen Halides

- HF is a liquid at room temperature (b.p. 293 K), whereas HCl, HBr and HI are gases.
- The boiling point of HF is unexpectedly high as compared to HCl (189K), HBr (206K) and HI (238K). This is due to the formation of hydrogen bonds.

Oxides and Oxoacids of Halogens

- Halogens generally form four series of oxoacids namely hypohalous acids (+1 oxidation state), halous acids (+3 oxidation state), halic acids (+5 oxidation state) and perhalic acids (+7 oxidation state).
- Chlorine forms four types of oxoacids. That is HOCl (hypochlorous acid), HOClO (chlorous acid), $HOClO_2$(chloric acid) and lastly $HOClO_3$ (perchloric acid).
- Bromine forms HOBr (hypobromous acid), $HOBrO_2$(bromic acid) and $HOBrO_3$ (perbromic acid). Iodine forms HOI (hypoiodous acid), $HOIO_2$ (iodic acid) and $HOIO_3$ (periodic acid).

Chlorofluorocarbons (CFC)

- Chlorofluorocarbons (CFCs) are nontoxic, nonflammable chemicals containing atoms of carbon, chlorine, and fluorine. They are used in the manufacture of aerosol sprays, blowing agents for foams and packing materials, as solvents, and as refrigerants. Individual CFC molecules are labeled with a unique numbering system.

THE NOBLE GASES

- The gaseous elements helium, neon, argon, krypton, xenon and radon constitute the 18 group of the periodic table. Because of their low, abundance on the earth, they have been called rare gases, and due to their chemical inertness, they have been called inert or noble gases.

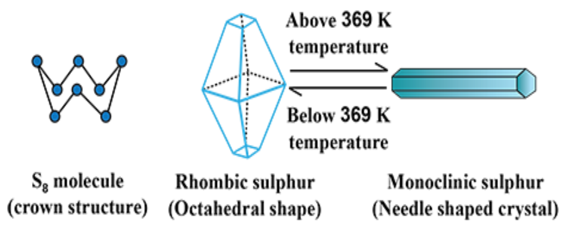
Occurrence

- All the noble gases, except radon, are present in atmosphere.

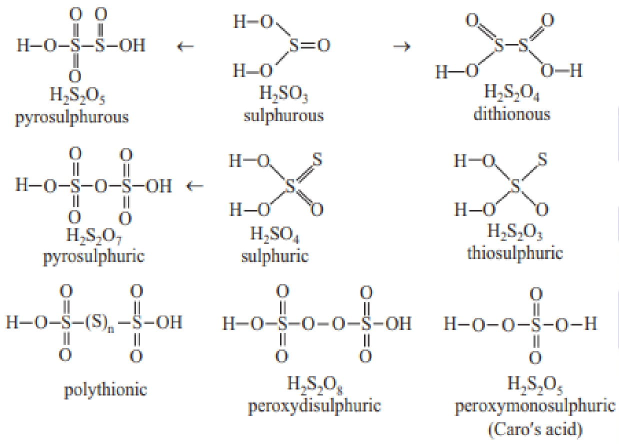
COMPOUNDS OF NOBLE GASES

- The first compound of noble gases was made by Neil Bartlett in 1962 by the reaction of xenon with PtF_6. Since then several other xenon compounds, mainly with the most electronegative elements (fluorine and oxygen), have been prepared. He, Ne and Ar do not form any compounds whereas Kr does form KrF_2. Radon is a radioactive element and all its isotopes have very short half lives.

Allotropic Forms of Sulphur:



Structures of Oxyacids of Sulphur



- The boiling point of HF is unexpectedly high as compared to HCl (189K), HBr (206K) and HI (238K). This is due to the formation of hydrogen bonds between the F atom of one molecule and the H atom of another molecule.

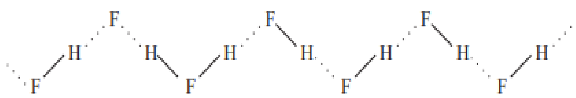


Fig. 20.2: Hydrogen bonded chain in HF

- The bond dissociation energy of the hydrogen halides follow the order **HF>HCl>HBr>HI**
- The stability of hydrogen halides to thermal decomposition therefore decreases in the order **HF > HCl > HBr > HI.**
- The acid strength of the acids increases in the order. **HF < HCl < HBr < HI.**
- Hydrogen fluoride is used to prepare certain fluorides mainly fluorocarbons or freons.

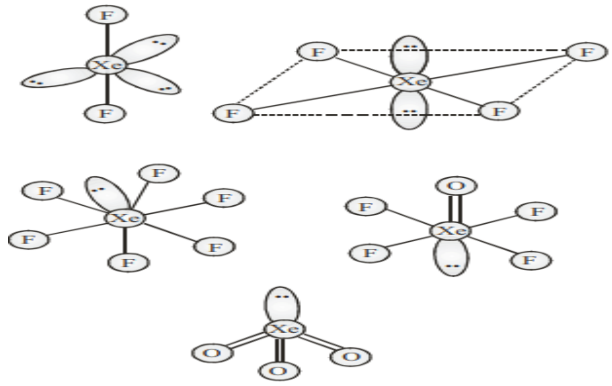


Fig. 20.3: The structures of XeF_2, XeF_4, XeF_6, XeO_3 and $XeOF_4$

Check Yourself

1. H_2S is more acidic than H_2O because

(A) Oxygen is more electronegative than sulphur.

(B) Atomic number of sulphur is higher than oxygen.

(C) H — S bond dissociation energy is less as compared to H — O bond.

(D) H — O bond dissociation energy is less also compared to H — S bond.

2. The boiling points of hydrides of group 16 are in the order

(A) $H_2O > H_2Te > H_2S > H_2Se$

(B) $H_2O > H_2S > H_2Se > H_2Te$

(C) $H_2O > H_2Te > H_2Se > H_2S$

(D) None of these

Check Yourself

3. In the manufacture of sulphuric acid by contact process Tyndall box is used to

(A) Convert SO_2 and SO_3

(B) Test the presence of dust particles

(C) Filter dust particles

(D) Remove impurities

4. Fluorine differs from rest of the halogens in some of its properties. This is due to

(A) Its smaller size and high electronegativity.

(B) Lack of d-orbitals.

(C) Low bond dissociation energy.

(D) All of these.

5. The set with correct order of acidity is

(A) $HClO < HClO_2 < HClO_3 < HClO_4$

(B) $HClO_4 < HClO_3 < HClO_2 < HClO$

(C) $HClO < HClO_4 < HClO_3 < HClO_2$

(D) $HClO_4 < HClO_2 < HClO_3 < HClO$

Stretch Yourself

1. Fluorine does not exhibit any positive oxidation state. Why?

2. Nitrogen is relatively inert as compared to phosphorus. Why?

3. Draw the structure of XeF_4 molecule.

4. Of PH_3 and H_2S which is more acidic and why?

5. Bond enthalpy of fluorine is lower than that of chlorine. Why?

Test Yourself

Question: Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Why?

Answer: Due to lack of empty d-orbitals in nitrogen, it does not form pentahalide.

Answers

Check Yourself

Answer: 1(C); 2(C); 3(C); 4(D); 5(B)

Stretch Yourself

1. This is because fluorine is the most electronegative element and is does not have d orbitals..
2. Since P-P single bond is much weaker than N≡N triple bond. Therefore phosphorus is much more reactive than nitrogen i.e. nitrogen is relatively inert as compared to phosphorus.
3. The structure of XeF_4 is shown below. The central Xe atom has 2 lone pairs and 4 bond pairs of electrons. The electron pair geometry is octahedral and molecular geometry is square planar. Xe atom undergoes sp^3d^2 hybridisation.
4. The electronegative of phosphorus is 2.2 and sulphur is 2.6. So, the electronegativity of sulphur is more than phosphorus and thus sulphur-hydrogen bond is more polar than phosphorus-hydrogen bond. So, the acidity of hydrogen sulphide is more than the acidity of phosphorus hydride.
5. Flourine is smaller as compared to Chlorine. So, there is a large electron - electron repulsion in flourine which is less in case chlorine as in chlorine the last electron enters into 3rd shell. So, Bond enthalpy of flourine is more than chlorine.