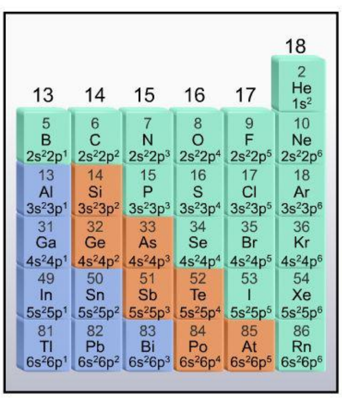
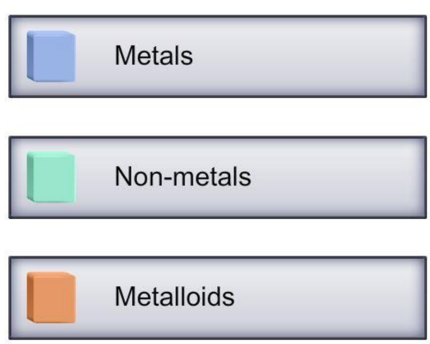
Lecture 7

Group 6A (VIA)

Oxygen Family

(Chalcogens)





- **None of the Group 6A elements behaves as a typical metal.**

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Occurrence :

- **O_2 makes up 21% of the Earth's atmosphere**
- Oxygen exists in free form as O_2 molecule in atmospheric and makes up to 21% by volume and 23% by weight of the atmosphere.
- It also occurs in combined state such as metal oxide, carbonates and bicarbonates, etc. in earths crust.
- Oxygen forms about 46.6% by mass of earth crust.
- In upper layer of atmosphere it also exists as O_3 (Ozone).

Physical properties of Oxygen

- **Oxygen gas can exists in all three physical state- solid, liquid and gases. It's is pale-blue color in liquid and solid state.**
- **Oxygen gas liquefies at 90 K and freeze at 55 K.**
- **There are three possible isotopes of oxygen; ${}_8O^{16}$, ${}_8O^{17}$, ${}_8O^{18}$.**
- **Molecular orbital theory proves that dioxygen, O_2 is paramagnetic in nature.**

- Oxygen exists as **diatomic** gaseous molecule (**O_2**).
- Oxygen undergoes Pπ - Pπ overlapping with other oxygen atoms forming double bond, O = O.
- Other elements are linked by single bonds and form **polyatomic** complex molecules

eg. Sulphur and Selenium exist as octa-atomic molecules (**S_8** and **Se_8**)

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Catenation

Catenation is the tendency of an atom to form bonds with identical atoms.

Eg. oxygen links its two atoms in **peroxides** only **$(\text{-O-O-})^{-2}$**.

- Sulphur shows greater tendency towards catenation because of stronger S-S bond than O-O bond.
- Polysulphides are existing such as H-S-S-H, H- S - S - S - S -H
- The S-S bond is very important in biological systems and occurs in several proteins and enzymes.
- Catenation tendency decreases down the group from S to Po because of decrease in element bond strength.

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Allotropy

All of 16th group elements show allotropy.

1. **Oxygen:** exists as O_2 and O_3
2. **Sulfur:** Rhombic, monoclinic
3. **Selenium:** red monoclinic, red amorphous selenium etc.
4. **Tellurium:** exists in two allotropic forms crystalline metallic and amorphous nonmetallic.
5. **Polonium:** has two forms α and ,β both metallic forms.

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Electronic Configuration

Valence electron configuration: ns^2np^4

$_{8}O$	$1s^2\underline{2s^22p^4}$	$[He]2s^22p^4$
$_{16}S$	$1s^22s^22p^6\underline{3s^23p^4}$	$[Ne]3s^22p^4$
$_{34}Se$	$1s^22s^22p^63s^23p^63d^{10}\underline{4s^24p^4}$	$[Ar]\ 4s^24p^4$
$_{52}Te$	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}\underline{5s^25p^4}$	$[Kr]\ 5s^25p^4$
$_{84}Po$	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}\underline{6s^26p^4}$	$[Xe]\ 6s^26p^4$

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Oxidation states

- Oxygen shows common oxidation state **-2**.
  - In **OF_2** oxidation state of oxygen is **+2** due to its bonding with greatest electronegative element F
  - In H_2O_2 oxidation state of oxygen is **-1**
- Tendency to show **-2** oxidation state decreases from S to Te.
- Po does not show **-2** oxidation state but can show **+2** oxidation state.

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Oxidation states

- Other elements can show **+4**, **+6** oxidation states due to their ability to promote electrons in d-subshell, which can't be done by Oxygen.
- S, Se, Te can show **+4** as well as **+6** with F.
- Stability of **+6** oxidation state decreases while stability of **+4** oxidation state increases down the group **due to inert pair effect.**

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Chemical Properties of Oxygen and its Compound

1. Combustion Reaction:

Dioxygen acts as a supporter for combustion reaction but itself not combustible.

All organic compounds like hydrocarbons burn in the presence of oxygen to give carbon dioxide gas and water vapor.

Example:

Methanol burns in air forming carbon dioxide and water:

$$2CH_3OH + 3\,O_2 \rightarrow 2CO_2 + 4H_2O$$

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Reaction with Metals

$4K + O_{2(g)} \rightarrow 2K_2O$

$2K + O_{2(g)} \rightarrow K_2O_2$

$K + O_{2(g)} \rightarrow KO_2$

With other metals, dioxygen forms metal oxides.

$2\,Zn_{(s)} + O_{2\,(g)} \rightarrow 2\,ZnO_{(s)}$

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Reaction with Non-metal

Dioxygen reacts with non-metals also like hydrogen, carbon, sulfur and phosphorus & form oxides.
Reaction occurs at high temperature or in electric discharge.

For example,

$2\ H_{2\,(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(g)}$

$C_{(s)} + O_{2\,(g)} \rightarrow CO_{(g)}$ or $CO_{2(g)}$

$P_{4(s)} + O_{2(g)} \rightarrow P_4O_{6(g)}$ or $P_4O_{10(g)}$

$S_{8(s)} + 8\ O_{2\,(g)} \rightarrow 8\ SO_{2(g)}$: $2SO_{2(g)} + O_{2(g)} \underset{V205}{\rightleftharpoons} 2SO_{3(g)}$

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With ammonia (preparation of Nitric acid)

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{Pt,\ 500\ K} 4NO_{(g)} + 6H_2O_{(g)}$$

In Decon's process,

dioxygen oxidized hydrochloric acid to form water and chlorine gas. Reaction talks place at 700 K temperature and in the presence of $CuCl_2$ catalyst.

$$4HCl_{(g)} + O_{2\,(g)} \xrightarrow{CuCl_2,\ 700\ K} 2H_2O_{(g)} + Cl_{2(g)}$$

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Respiration

It's a very important chemical property of dioxygen. It involves in respiration of all living bodies. Basically respiration is a combustion process of carbohydrates to produce carbon dioxide and water with a large amount of energy.

$$C_6H_{12}O_{6\,(aq)} + 6\ O_{2\,(g)} \rightarrow 6\ CO_{2\,(g)} + 6\ H_2O_{(l)}$$

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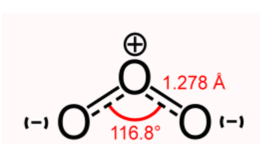
Ozone

- O_3 (ozone) exists naturally in the upper atmosphere (the stratosphere) of the Earth.
- Ozone layer absorbs UV light and acts as a screen to block most uv-radiation from reaching the Earth's surface.

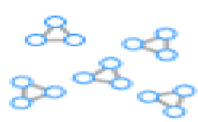


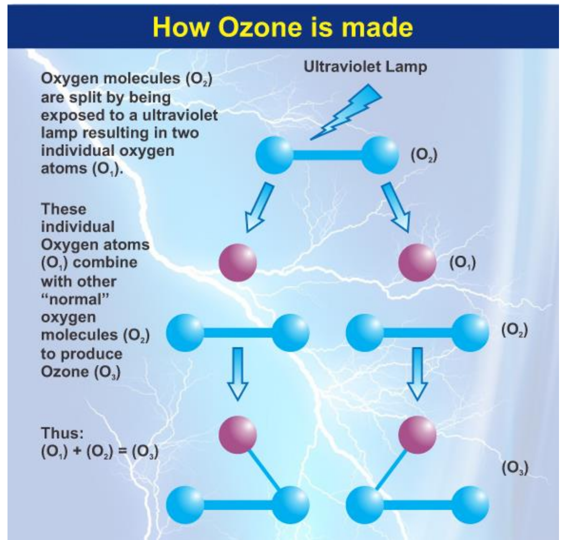
Ozone is an extremely powerful oxidizing agent.

Ozone can be used for destroying bacteria in water by oxidation.

Ozone

- ✓ allotropic form of oxygen
- ✓ important component of the atmosphere
- ✓ effect on the ozone layer
- ✓ ozone is toxic!
- ✓ used for drinking water treatment





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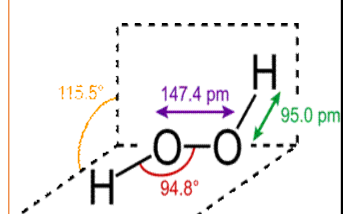
HYDROGEN PEROXIDE, PEROXIDES, AND SUPEROXIDES

- Hydrogen peroxide is a colorless, viscous liquid which boils at 150 °C.
- Like water, it is strongly associated by hydrogen bonding.
- When the pure liquid is heated, it decomposes rapidly and even explosively in a disproportionation reaction:

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g);$$

$$\Delta H° = -196 \text{ kJ}$$



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H_2O_2

Hydrogen peroxide is an important industrial chemical which has many applications; for example, it is used as:

- bleaching agent for textiles and for wood pulp and waste paper in paper making.

- Its usage for bleaching hair is well known.

- Its bleaching action is possible due to its strong oxidizing properties.

- H_2O_2 can be used as oxidizing agent and as reducing agent

Sulfur

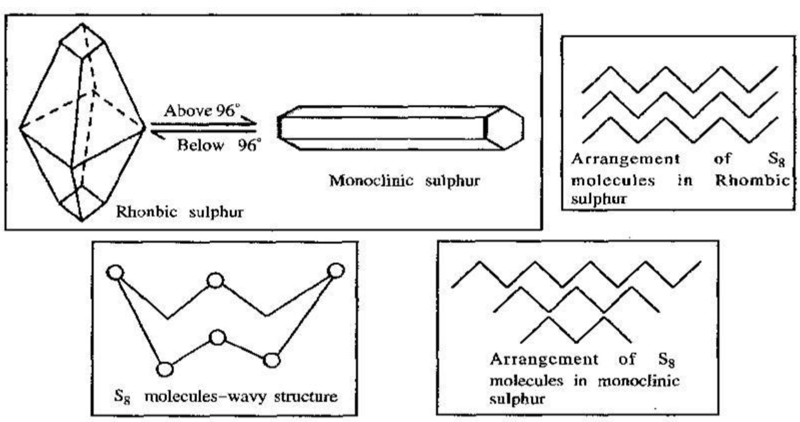
Sulfur is found in nature both in large deposits of the free element and in ores such as:

- Galena = PbS,
- Cinnabar = HgS,
- Pyrite = FeS_2,
- Gypsum = $CaSO_4 \cdot 2H_2O$),
- Epsomite = $MgSO_4.7H_2O$, and
- Glauberite = $Na_2Ca(SO_4)_2$

General properties

Allotropes:

(1) Rhombic sulphur, S_8 (room to 96^oC)
(2) Monoclinic sulphur, S_8 (stable btween. 96-119^oC)
(3) Plastic sulphur, long polymeric chains



Effect of temperature on sulphur (Figure only for information)

Plastic sulfur

- Another form of sulfur is obtained by molten sulfur quick cooling by pouring it into cold water.
- A brown rubbery material known as *plastic sulfur* is obtained.
- It is not stable and within a few hours it transformes back into crystalline orthorhombic sulfur.

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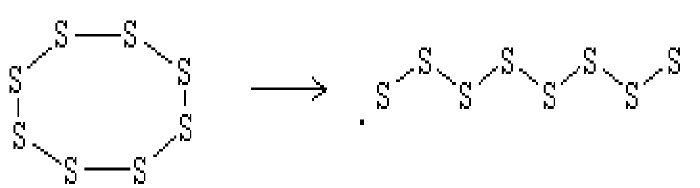
Plastic sulfur consists of very long chains of sulfur atoms rather than S_8 rings.

When liquid sulfur is heated to about 160 °C, one of the S-S bonds in some of the rings breaks, and the rings open forming chains of eight sulfur atoms.



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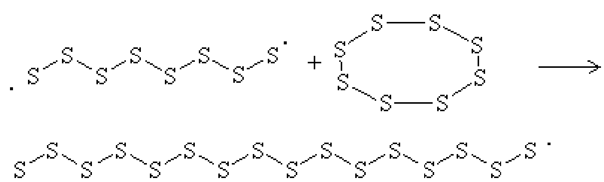
- The sulfur atoms at each end of the chain have only seven valence electrons. Therefore they have a strong tendency to attach an additional electron and are very reactive.
- An S_8 chain reacts with S_8 ring causing its opening up and thereby forming a 19-atom chain



- But the sulfur atoms at the ends of the chain have only seven electrons, so the process continues, leading to the formation of very long chains of thousands of atoms.
- When the temperature is increasing from 160 °C to 190 °C, the chains become longer and more tangle, and the liquid becomes increasingly thick and sticky, like maple syrup or molasses.
- There are still other, less important allotropes of sulfur that contain rings of six, seven, twelve, and more sulfur atoms.
-

Range of sulphur compounds

Chemical formulae	Oxidation state
S^{2-}, H_2S	-2
S_8	0
SCl_2, $S_2O_3^{2-}$	+2
SO_2, SO_3^{2-}, H_2SO_3	+4
SO_3, SO_4^{2-}, H_2SO_4	+6

Burning of sulphur

- **Sulphur burns with a dull blue flame to form sulphur dioxide**

$$S + O_2 \rightarrow SO_2$$

- **trace of misty sulphur trioxide are also formed.**

Sulphur dioxide

- A colourless gas with choking smell
- An acidic gaseous pollutant
- Readily liquefied under pressure
- Very soluble in water and reacts to form sulphuric(IV) acid
- **Can be further oxidized to SO_3, which dissolves in water to form sulphuric(VI) acid, H_2SO_4**

Oxidizing properties of SO_2

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

$2H_2S + SO_2 \rightarrow 2H_2O + 3S$

Aqueous $SO_2 \equiv SO_3^{2-}(aq)$

$2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow$
$2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \rightarrow$
$2Cr^{3+} + 3SO_4^{2-} + 4H_2O$

Sulphuric Acid

Contact Process:

$S + O_2 \rightarrow SO_2$

$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

$2SO_2 + O_2 \leftrightarrows 2SO_3$ (450°C, V_2O_5 as catalyst)

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ **(oleum)**

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

Chemical properties of H_2SO_4

Concentrated H_2SO_4

- As an oxidizing agent
  - $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$
  - $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$

As a dehydrating agent

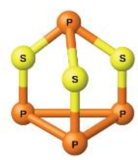
Reaction with HX

- $2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$
- $8HI + 2H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$

H_2SO_4 is used to Manufacture of detergents, dyestuffs, polymers, fibres, paints, fertilizers

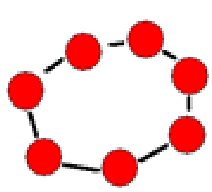
Important Compounds of Sulfur

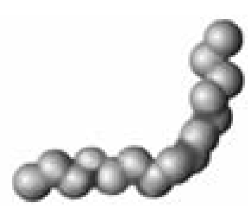
- H_2SO_4 – most important compound, for manufacture of fertilizer, soap, detergents, metal and textile processing, sugar refinery, and organic syntheses;
- SF_4 – for fluoridation
- $Na_2S_2O_3$ – as reducing agent and complexing agent for Ag^+ in photography (called "hypo");
- P_4S_3 – in "strike-anywhere" match heads



SELENIUM & TELLURIUM

- Selenium and tellurium are both large metalloids with similar properties.
- They exhibit oxidation states similar to sulfur that also range from -2 to +6.
- Their commonly found structures are different.
- Selenium is found as an 8-membered ring (like sulfur) and tellurium crystallizes in a chain-like form





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POLONIUM

- Polonium, a radioactive element, is rarely found in nature. It's made in small quantities by a nuclear reaction with bismuth.
- There are 29 known radioisotopes and more known isotopes than any other element.

$$^{209}_{83}Bi + \ ^{1}_{1}n \rightarrow \ ^{210}_{84}Po + e^{-}$$

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- Polonium crystallizes in a cubic structure.
- Due to large atomic size, Pi orbital overlap becomes difficult, therefore rarely forms double bonds.
- Following the trend, it's the least electronegative of the group, yet combines directly with most elements.

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