Oxygen family / Chalcogen family / Group 16th / VIA family

(ore forming nature.)

Elements: O
S → Sulphur
Se → Selenium
Te → Tellurium
Po → Polonium

Properties

① General electronic configuration:

↳ [Noble gas] $ns^2 np^4$

Abundancy

O > S > Se > Te > Po

② Metal / non-metal / Metalloid

O, S } ← Non metal.

Se, Te ← Metalloid

Po ← Radioactive metal

Magnetic Nature

O ← paramagnetic

S, Se, Te, Po ← diamagnetic

catenation property:

Sulphur ⇒ Max^m

NOTE: Highest Bond strength ⇒ S-S

Oxidation state:

~~4 and 6~~

Range ⇒ −2 to +6

③ I.E. → ↓ on Group

④ Electron affinity → ↓ on.

As we know, E.A. of 3rd period > 2nd period

order: S > Se > Te > Po > O

⑤ E.N. → ↓ in ~~Group~~ group.

⑤ Allotropes:

O → O_2 and O_3

S → · α-Sulphur (Rhombic sulphur) ← octahedral ← crystalline nature
· β-Sulphur (Monoclinic ") ← prismatic
· γ = Sulphur (Plastic of sulphur)
· δ = Sulphur (Colloidal of ")
· Milk of sulphur

Se → Red form (Non-metallic) and Grey form (Metallic)

Te → α, β form

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∴ All members of group [illegible] are polymorphic in nature [illegible] phylum shows polymorphism

Hydrides

H_2O H_2S H_2Se H_2Te

∴ Boiling point : $H_2O > H_2Te > H_2Se > H_2S$

∴ Volatility :- $H_2S > H_2Se > H_2Te > H_2O$

∴ Dipole moment : $H_2O > H_2S > H_2Se > H_2Te$.

Ozone : (O_3)

Bond length = 1.278 Å

- Hybridization → sp^2, 117°
- Diamagnetic nature
- pale blue in colour.
- Fishy smell
  - poisonous.

Preparation.

↳ Siemen and Brodies Method :-

$$3O_2 \underset{\text{discharge}}{\overset{\text{silent electric}}{\rightleftharpoons}} 2O_3$$

Mechanism

$$O_2 \longrightarrow O + O$$

$$O + O_2 \longrightarrow O_3.$$

Oxygen

- Most abundant element in Earth's crust, colorless, odorless, slightly soluble in water

LAB prepn.

① $KClO_3 \xrightarrow[\Delta(240° - 250°)]{MnO_2 = \text{Pyrulocyte}} KCl + O_2$ (potassium chlorate)

② Dry metal peroxide

$$Na_2O_2 + H_2O \longrightarrow NaOH + O_2$$

↳ O_2 is paramagnetic

↳ It is 2nd most electronegative element after Fluorine.

↳ Oxygen shows +ve O.S. in F_2O.

↳ Absorbent of O_2 ⇒ • Alkaline Pyragallol Sol.
• Sodium hypo-sulphite
• Ammonical cuprous chloride

↳ Slightly heavier than air

↳ Also called fire air

↳ Non-combustible but supporter of combustion

Pure ozone can be obtained by fractional distillation.

- Depends on Boiling point
- Crystalization depends on solubility

- Ozone is a bleaching agent. (Bleaching action of ozone is ~~hydrogen~~ permanent, oxidation, Dry (@ OPD))
- Ozone acts as oxidizing agent as well as reducing agent.
- Ozone is not a dehydrating agent.

Note. Ozone act as reducing agent only with peroxide (ie H_2O_2). यहाँ पर सबसे मैं oxidizing agent.

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for properties of Ozone (O_3) → @ BF Dai Ox

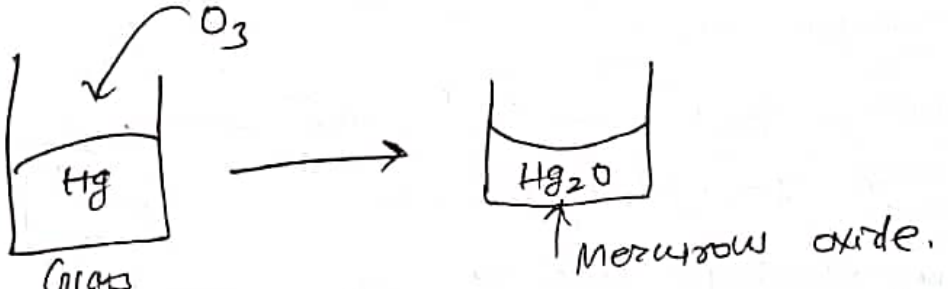
B = Blue
F = Fishy smell, fractional distillation
D = Diamagnetic
O = Oxidizing as well as reducing agent

Note:
- order of Bond length
  ↳ $H_2O_2 > O_3 > O_2$
- Bond energy / order $\propto \frac{1}{\text{Bond length}}$

- $K_4[Fe(CN)_6] + O_3 \longrightarrow K_3[Fe(CN)_6]$
  potassium ferrocyanide
- $PbS + O_3 \longrightarrow PbSO_4$

Tailing of Mercury :- When mercury is kept in glass vessel with ozone, Hg_2O (Mercurous oxide) formed due to Hg_2O formation mercury sticks to glass vessel, k/a tailing of mercury.

ie. $Hg + O_3 \longrightarrow Hg_2O + O_2$



Use of ozone
↳ Bleaching agent (Tusk of elephant)
↳ for water sterilizing ↳ Liquid ozone is used as rocket fuel.

Sulphur

→ S_2, S_6, S_8 ← crown shape.
chair form ↑ Most stable. ↑ crown shape structure.

> Allotropes of Sulphur :

(1) α-Sulphur / Rhombic Sulphur

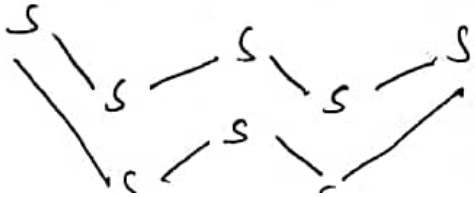
- It is most stable; pale yellow in colour, insoluble in water, Bad conductor of heat and electricity

> Preparation:

Rolled sulphur + CS_2 —evaporation→ S
↑ α-sulphur

- Crown shape structure / puckered ring structure

Structure.



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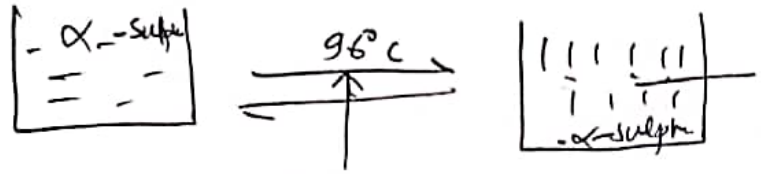
β sulphur

Note: 

This is transition tempr for α and β-sulphur.

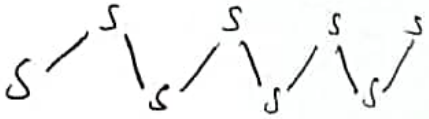
- When two allotropes at some temperature are possible, it is transition tempr.
  - Above 96°C, β sulphur is most stable whereas below 96°C, α sulphur is most stable. overall,
- β-sulphur is most unstable sulphur.

Gamma sulphur / Plastic of sulphur:-

Preparation.

Boiled sulphur + cold water ⟶ γ-sulphur.
(S at 400°C)

- It has amorphous character.
- Insoluble in water.
- P sulphur don't have fixed M.P. and B.P. due to the nature of bond.



Str. of P sulphur

- Except plastic of sulphur, all allotropes of sulphur are dissolved in CS_2
- Different str. of P sulphur is possible.

Colloidal sulphur / Delta(S) sulphur

Size: (10^{-4} cm − 10^{-7} cm)

Preparation:

- $H_2S + HNO_3$ (conc.) ⟶ S ↑ colloidal sulphur
- $Na_2S_2O_3 + HCl \longrightarrow NaCl + SO_2 + H_2O + (S)$ ↑ Colloidal sulphur

USE:

- In ointment (lotion)

Milk of Sulphur :- → obtained from ordinary sulphur by chem. process ∴ "Milk of sulphur"

- Lime mixed sulphur

CHEMICAL properties of H_2S :-

(I) Combustible but not supporter of combustion.

$H_2S + O_2$ (excess) $\longrightarrow SO_2 + H_2O$

$H_2S + O_2$ (limited) $\longrightarrow H_2O + S$

(II) H_2S is a weak diprotic / dibasic acid.

$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$

$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{--}$

↳ H_2S forms two series of salts when mixed with Base.

i.e. $H_2S + NaOH \longrightarrow NaHS$

" " $\longrightarrow Na_2S$

(III) H_2S is used as a laboratory reagent.

Test of H_2S gas

(1) Smell :- Rotten egg

(2) $(CH_3COO)_2Pb + H_2S \longrightarrow PbS + 2CH_3COOH$

Lead acetate paper — Black colour

(3) $Ag + H_2S \xrightarrow{O_2} Ag_2S + H_2O$

(Black)

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Milk of Sulphur : → obtained from ordinary sulphur by chemical process is "Milk of sulphur"

- Lime mixed sulphur
- Used as medicine.

Compounds of sulphur ↳ In EAO

H_2S (Hydrogen Sulphide)

preparation : [@ SADIS — Dilute, sulphuric acid — Iron sulphide

① Iron sulphide (FeS) + dil. H_2SO_4 ⟶ $FeSO_4 + H_2S$

- H_2S is a rotten egg smell.

Note: FeS + conc. H_2SO_4 ⟶ S

② From magnesium hydrosulphide $Mg(HS)_2 \xrightarrow{\Delta} MgS + H_2S$

③ Sb_2S_3 + conc. HCl ⟶ $SbCl_3 + H_2S$ (pure)

chemical properties:-

(I) Reducing Agent

Eg. $H_2S + FeCl_3 \longrightarrow FeCl_2 + S + HCl$

(S: −2, Fe: +3, Fe: +2, S: 0; Oxidation, Red^n)

Hint. H_2S संग reac^n गराउँदा, reactant side मा जो red^n मा बान्छ, product side मा reactant side भन्दा 1 कम oxidation state को product बन्छ।

(8.) $H_2S + \overset{0}{I_2} \longrightarrow S + \overset{(-1)}{HI}$

(9) $H_2S + \overset{(+4)}{SO_2} \longrightarrow S + H_2O$

(9) $H_2S + Cl_2 \longrightarrow S + HCl$

(9) $H_2S + \underset{+5}{HNO_3} \longrightarrow S + \underset{+4}{NO_2} + H_2O$.

(S: colloidal sulphur)

(II) H_2S is a weak dibasic acid.

(III) Used as analytical reagent

(IV) Colourless, fairy soluble in water

(V) Extremely poisonous : Antidote → Cl_2

(VI) H–S–H → Bond angle = 92.5°

(VII) H_2S is combustible but not supporter of combustion

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Oxides :

Note: Oxide हुनको लागि oxygen सँग चेडिएको atom O_2 भन्दा कम E.N. हुनु पर्छ, i.e. OF_2 is not a oxide.

(i) Normal oxides:- (जुन oxide बस्को valency 2 भएर बनिएको)

Eg- H_2O, MgO, CaO.

↳ In normal oxide, o.s. of oxygen is -2.

(ii) Polyoxides :

→ (i) peroxide (O_2^{--}) Eg- H_2O_2

↳ They give H_2O_2 with water.

→ (ii) Superoxide (O_2^-) eg. $KO_2 \rightarrow K^+ + O_2^-$

↳ They give H_2O_2 and O_2 with water.

Note: In peroxide, o.s. of Oxygen is -1 and in superoxide, o.s. of " is $-\frac{1}{2}$.

(iii) Sesquioxide :

- Oxygen no. $= 3$
- Atom attached with oxygen $= 2$ in number

Eg- N_2O_3, Al_2O_3, Fe_2O_3 etc.

(iv) Suboxide

Oxygen number < atom attached with oxygen.

- Atom should be non-metal
- E.N. of that atom should be ≥ 2.5

(Here $F = 4$, $O = 3.5$, $N = 3$, $C = 2.5$, $H = 2.1$)

Eg- N_2O, C_3O_2 (carbon suboxide)

(v) Mixed oxide :

↳ New formed oxide by mixing two normal oxides

Eg- Fe_3O_4 ($FeO + Fe_2O_3$) (ferrous oxide, ferric oxide)

(Ferrosoferic oxide)

$Pb_3O_4 = (2PbO + PbO_2)$ (plumbous oxide, plumbic oxide)

(plumbo plumbic oxide)

(Red lead, Sindur)

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(VI) Acidic oxides:

↳ All acid anhydrides are acidic oxide

Eg- CO_2, NO_2, H_2O_3, N_2O_5, SO_2, SO_3 etc.

(VII) Neutral oxide:

Eg- NO, N_2O, pure water, CO etc

(VIII) Basic oxides.

↳ Almost all metal oxide are basic oxides

Eg. → MgO

(IX) Amphoteric oxide.

Eg = BeO, Al_2O_3, ZnO, PbO, PbO_2, SnO, SnO_2, Cr_2O_3, Sb_2O_3 etc.

[@ ZAB P^2S^2C]

⊟ SO_2:

↳ Acidic in nature, colorless, poisonous, soluble in water.

↳ Acid anhydride of H_2SO_3

- Act as both oxidizing as well as reducing agent.

But SO_3 is oxidizing agent only.

Prepⁿ of SO_2.

Any metal + Hot and conc. $HNO_3 \rightarrow NO_2 + H_2O +$ metal nitrate

Cu + Hot and conc. $HNO_3 \rightarrow NO_2 + H_2O + Cu(NO_3)_2$

& ↑ Lab prepⁿ of NO_2.

- Metal + Hot and conc. $H_2SO_4 \rightarrow SO_2 + H_2O +$ Metal sulphate.

Eg

Cu + Hot and conc. $H_2SO_4 \rightarrow SO_2 + H_2O + CuSO_4$

↑ This reaⁿ is lab prepⁿ of SO_2.

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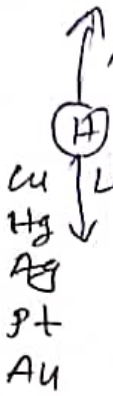
Active metal + Hot and Conc. $H_2SO_4 \rightarrow SO_2 + H_2O$ + Metal Sulphate

Note:

- Less Active metal + Hot and conc $H_2SO_4 \rightarrow SO_2 +$ H_2O + Metal Sulphate. (except platinum and Au)
- Active metal + conc. $H_2SO_4 \rightarrow SO_2 + H_2O +$ Metal sulphate.
- Active metal + dil. $H_2SO_4 \rightarrow$ Metal Sulphate + H_2
- Less active metal + dil. $H_2SO_4 \rightarrow$ No reaction.



[@ CHAPA metals are less active metal]

Bleaching Action of SO_2:

- In the presence of moisture, it shows bleaching action
  - during reduction
  - Temporary

[@ MR Temporary]

As

$$SO_2 + H_2O \xrightarrow{(air)} H_2SO_4 + [H]$$

↑ Act as reducing agent

Note: $SO_2 + H_2O \rightarrow H_2SO_3$

[H] + Colour compounds → Colour disappear → (air) → Colour regain

SO_3

- Acidic in nature
- Acid anhydride of H_2SO_4
- Oxidizing agent only.

Prep^n of SO_3:

(a) From H_2SO_4:

$$2H_2SO_4 \xrightarrow[\Delta]{P_2O_5} SO_3 + H_2O$$

(P_2O_5 acted as dehydrating agent)

Manufacture of SO_3

$$SO_2 + O_2 \xrightleftharpoons{pt} SO_3 + \text{energy}$$

- This is commercial method of prepⁿ of SO_3.

H_2SO_4

↳ King of acid (HNO_3 is the queen of acid)

→ King of Chemical

(Note: Benzene is the queen of chemical)

→ Oil of vitriol

(यदि कुनै पनि compound मा sulphate group छ भने त्यसलाई vitriol भनिन्छ).

→ The conc. H_2SO_4 is extensively used to prepare other acids as it has a high Boiling point or highly ionizing power.

Note:

- Blue vitriol → $CuSO_4 \cdot 5H_2O$
- White vitriol → $ZnSO_4 \cdot 7H_2O$
- Green vitriol → $FeSO_4 \cdot 7H_2O$

[@ Name and chemical formula को starting letters are very close)

- Epsom salt → $MgSO_4 \cdot 7H_2O$.

preparation of H_2SO_4:

(a) From HNO_3:

Non-metal + Hot and conc. HNO_3 → Acid + NO_2 + H_2O

S + " → H_2SO_4 + NO_2 + H_2O

- This is the lab method of prepⁿ of H_2SO_4.

(b) Manufacture of H_2SO_4

(i) Lead chamber process

(ii) Contact process.

(i) Lead chamber process

Used catalyst: Oxides of nitrogen (i.e. NO_2, NO)

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(ii) Contact process :

- Catalyst : → Pt
  → V_2O_5 (~~[illegible]~~ राम्रो) Best
  → Fe_2O_3

- pressure ≈ 2 atm
- Temp^r = 450°C

4 Steps involved :

(i) Formation of SO_2

$$S + O_2 \longrightarrow SO_2$$

If arsenic impurity is present, then removed by adding $Fe(OH)_3$.

(ii) Formation of SO_3

$$SO_2 + O_2 \xrightleftharpoons{Pt / V_2O_5} SO_3 + \text{energy}$$

- Most important step of contact process.

(iii) Formation of oleum

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

- (oleum)
- Pyrosulphuric acid or fuming ~~acid~~ H_2SO_4.

(iv) Dilution of oleum

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

↳ H_2SO_4 is liquid in nature due to Hydrogen Bonding

Uses of H_2SO_4

- Aq. H_2SO_4 → Good conductor of Heat & electricity
- Act as Dehydrating agent
  ie. Charring of sugar is due to dehydration
- Used in Leadstorage Battery → H_2SO_4 is consumed.

$$PbO_2 + H_2SO_4 + Pb \longrightarrow PbSO_4 + H_2O$$

- Used as Abrasive (ie Capable of polishing hard surface)
- Used in pickling agent (ie. Cleaning of metal surface by acid impurities

⑥ Dithionic acid
↳ $H_2S_2O_6$

⑦ Dithionous acid
↳ $H_2S_2O_4$

NOTE :-

- H_2SO_5 → Per monosulphuric acid
- $H_2S_2O_8$ → Per disulphuric acid

} In both of them peroxy linkage is not (i.e. O-O).

Finding the no. of S-S linkage :-

① $S_2O_2^{-2}$ $S_2O_3^{-2}$ $S_2O_4^{-2}$ $S_2O_5^{-2}$ $S_2O_7^{-2}$] ≡ $S_2O^{-2}_{(2-6)}$

⇓

1 S-S linkage.

② $S_3O_6^{-2}$ ⇒ 2 S-S linkage

③ $S_4O_6^{-2}$ ⇒ 3 S-S linkage

Finding no. of peroxy linkage (O-O linkage)

↳ Given acid में central atom में S 1 वाला नहीं है तो

- If calculated oxidation state > Maxm oxidation state then,

No. of peroxy linkage = $\frac{\text{Calculated O.S.} - \text{Maxm O.S.}}{2}$

Calculated principal :

eg- find peroxy linkage in H_2SO_5

$H_2\overset{8}{S}O_5$ ⇒ Calculated O.S. ⇒ 8

Maxm O.S. of S ⇒ 6

Now,

No. of peroxy linkage = $\frac{8-6}{2}$

= 1. //

↳ Given acid of if 2 S is present.

- If calculated O.S. > Maxm O.S.

Then,

No of peroxy linkage = Calculated O.S − Maxm. O.S

eg. $H_2S_2O_8$

↳ Calculated O.S ⇒ +7

↳ Maxm O.S. of S ⇒ +6

Now)

No of peroxy linkage = $\frac{7-6}{1}$

= 1.

↳ NOTE!- If calculated O.S < Maxm O.S. then there is no peroxy linkage

Hypo (Hypo mg.)

↳ $Na_2S_2O_3 \cdot 5H_2O$ (Sodium thiosulphate)

↳ White, crystalline

Prepn.

(1) $Na_2SO_3 + S \longrightarrow Na_2S_2O_3$

- Used in pickling agent (ie. cleaning of metal surface by acid in

(2) $Na_2S + Na_2SO_3 + I_2 \longrightarrow Na_2S_2O_3 + NaI$
(Sod. sulphide) (Sod. sulphite)

(3) $NaHSO_3 + NaHS \longrightarrow Na_2S_2O_3 + H_2O$

Chemical properties

(1) Reaxn with AgBr

$Na_2S_2O_3 + AgBr \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$
(Sod. Argentothiosulphite)

(2) Reaxn with Cl_2

$Na_2S_2O_3 + Cl_2 \xrightarrow{H_2O} Na_2SO_4 + S + HCl$

(3) Rxn with I_2

$Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + NaI$
Sod. tetrathionate

(4) Rxn with HCl

$Na_2S_2O_3 + HCl \longrightarrow NaCl + H_2O + SO_2 + S$

Imp Note:
Gun powder → S + charcoal + KNO_3.

(due e-e repulsion)

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1) Marshall acid

$2H_2SO_4$
$- H_2$ (Remove)

= Marshall acid
ie. $H_2S_2O_8$

2) Caros acid

> $H_2SO_4 + [O] \rightarrow H_2SO_5$

3) Pyrosulphuric acid

> $H_2SO_4 + H_2SO_4$

$= H_4S_2O_8$
$- H_2O$

$H_2S_2O_7$

4) Thiosulphuric acid

Thio → S (add गर्ने)
→ O (remove गर्ने)

H_2SO_4
ie. $H_2S_2O_3$.

(5) Thiosulphurous acid

H_2SO_3 → S (add गर्ने)
→ O (remove गर्ने)

ie. $H_2SO_3 \rightarrow H_2S_2O_2$.
↑ Thiosulphurous acid

Halogen family:

→ Group 17th / VII A family

F ← Gaseous
Cl ← Non-metals
Br ← Liquid
I ← solid
(At – Astatine) ← Metalloid
[It is radioactive in nature

} ← exists in diatomic form.

properties:-

(i) Atomic Radius → ↑ in group

(ii) I-E → ↓es. in group

(iii) E.A. → ↓es (Note: 3rd period > 2nd period.

ie. $Cl_2 > F_2 > Br_2 > I_2$.

(iv) E.N. → ↓e order: $F_2 > Cl_2 > Br_2 > I_2$

* Bond energy / Bond dissociation energy / Bond strength:

$Cl_2 > Br_2 > F_2 > I_2$ (@ चना बदाम Fruit आयो)

↑ due e-e repulsion)

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