Oxygen Family / 16 A

└ chalcogen (ore forming family)

Oxide of Sulphur

$S_8 \xrightarrow[O_2]{\Delta} SO_2$

$S_8 \xrightarrow[\text{excess}]{O_2/\Delta} SO_3$

Abhishek

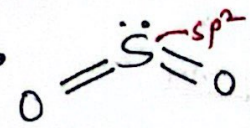
Nature :- SO_2 & SO_3 → acidic

$SO_2 \xrightarrow{H_2O} H_2SO_3$ sulphurous acid.

$SO_3 \underset{P_2O_5}{\overset{H_2O}{\rightleftharpoons}} H_2SO_4$ sulphuric acid.

(SO_3 ↓ anhydride of H_2SO_4.)

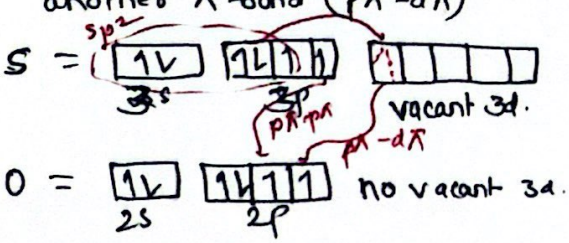
Structure :-

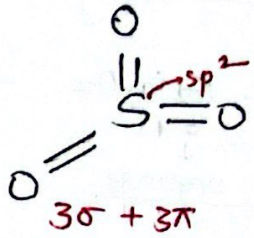
$SO_2 \rightarrow$ 

$2\sigma + 2\pi$

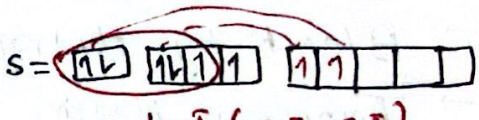
1 π-bond ($p\pi - p\pi$)

another π-bond ($p\pi - d\pi$)



$SO_3 \rightarrow$ 

$3\sigma + 3\pi$

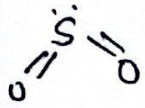


→ 1-π ($p\pi - p\pi$)

→ 2-π ($p\pi - d\pi$)

SO_2

→ sp^2

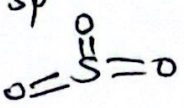
→ 

→ angular shaped or V-shaped.

($\mu \neq 0$) → polar.

SO_3

→ sp^2



→ $\mu = 0$ planar non-polar molecule

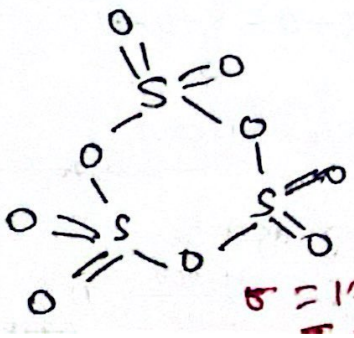
* SO_3 exist as cyclic trimer.

$SO_3 \longrightarrow S_3O_9$

SO_3 : sp^2 / monomer

S_3O_9 : sp^3 / trimer

L(S-S) → zero.



$\sigma = 12$

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SO_2 — oxidising agent, reducing agent — Both

SO_3 — oxidising state — max. O.S.

H_2S — reducing agent — min O.S.

Q. acidic $K\overset{+7}{M}nO_4$ + SO_2 → SO_3 + Mn^{+2}

($K\overset{+7}{M}nO_4$: O.A, purple)

→ $H_2\overset{-2}{S}$ + SO_2 → S.

(H_2S: R.A; SO_2: O.A)

Test of SO_2

- Turn ~~org~~ orange acidic $K_2Cr_2O_7$ to green.

acidic $K_2Cr_2O_7$ $\xrightarrow{SO_2}$ SO_3 + Cr^{+3}

($K_2Cr_2O_7$: O.A → orange; Cr^{+3}: green)

→ Bleach by Hydrogen.

→ Temporary bleach.

H_2SO_4

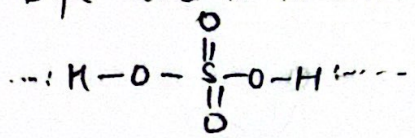
Contact process:-

→ $S + O_2 \xrightarrow{\Delta} SO_2 \xrightarrow[P_2O_5]{O_2} SO_3 \xrightarrow{H_2SO_4} H_2S_2O_7$ (oleum) $\xrightarrow{H_2O}$ $2H_2SO_4$.

(P_2O_5: catalyst)

properties

① High B.pt due to H-bond.



② Non-volatile, viscous.
↳ due to H-bond

③ Dehydrating agent

$C_{12}H_{22}O_{11}$ $\xrightarrow[-11H_2O]{H_2SO_4,\ \Delta}$ 12 C (Black). (Charring nature)

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- $HCOOH \xrightarrow[\Delta]{H_2SO_4} CO + H_2O$

- $\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{\quad} CO_2 + CO + H_2O$

④ Oxidising agent.

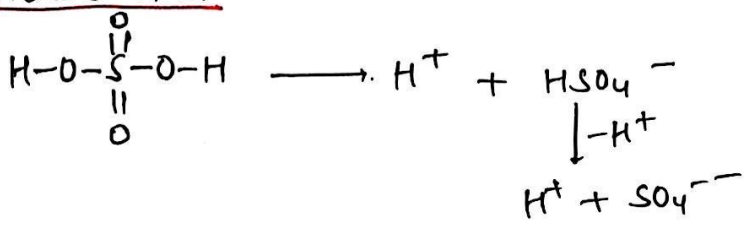
- Conc $H_2SO_4 \rightarrow$ ✓
- dil. $H_2SO_4 \rightarrow$ X.

$Zn + \text{dil. } H_2SO_4 \longrightarrow ZnSO_4 + H_2$

$Zn + \underset{\text{O.A.}}{\text{conc } H_2SO_4} \longrightarrow ZnSO_4 + H_2O + SO_2$

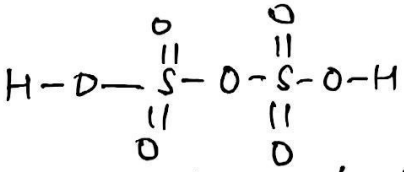
$C + \underset{\text{O.A}}{\text{conc. } H_2SO_4} \longrightarrow CO_2 + 2\,SO_2$

⑤ Dibasic acid



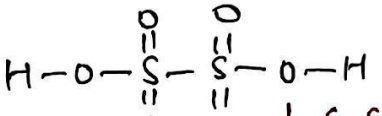
- $2H_2SO_4 \xrightarrow[-H_2O]{\Delta} H_2S_2O_7$

pyrosulphuric acid
or
oleum



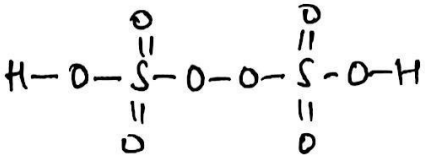
↳ no – (S-S) linkage.

but in $H_2S_2O_6$ – Dithionic acid.



↳ S-S linkage.

$H_2S_2O_8$ – Marshall acid.



↳ (peroxide linkage).
no S-S linkage.

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Q. S-S linkage absent in:-

(a) $S_2O_7^{-2}$ (b) $S_2O_6^{-2}$ (c) $S_2O_5^{-2}$ (d) $S_2O_4^{-2}$

Q. S-S linkage present in:-

(a) $H_2S_2O_7$ (b) $H_2S_2O_8$ (c) $H_2S_2O_6$ (d) S_3O_9

$H_2S_2O_8$ → peroxide linkage +ve

Introduction

O, S] - Non-metal

Se, Te] - Metalloid

Po → Metal
└ radioactive (Half life = 13 days)

O_2 → gas.

S_8 → solid.
└ crown like shape.

$\boxed{O_2}$ - - $\boxed{O_2}$ - $\boxed{O_2}$



vander waal force of attraction

→ All elements show allotropy.

① General configuration:- $ns^2\ np^4$

② O.S → $\underbrace{-2 \quad +2}_{\text{popular}}$ $\underbrace{+4 \quad +6}_{\text{most popular}}$

O → H_2O^{-2} $H_2O_2^{-1}$ OF_2^{+2} $KO_2^{-1/2}$

- SF_6 — vacant d-orbital +ve.
- OF_6 → X. due to absence of vacant d-orbital.

→ O, S, Se, Te, Po ↓ stability of +6↓es & stability of +4↑es due to inert pair effect.

Atomic Radius:-

O, S, Se, Te, Po ↓ radius ↑es, size ↑es.

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Electronegativity

O
S
Se
Te
Po

↓ E.N ↓es.

I.E

↓ I.E ↓es.

Electron affinity

O ↓least.
S.
Se
Te
Po

→ S > Se > Te > Po > O.

m.pt & B.pt

O
↓
Po

B.pt ↑es, mpt ↑es as mol. mass ↑es

Metallic character

O
↓ → ↑es.
Po

Chemical properties

① Rxn with H_2

$M + H_2 \longrightarrow H_2M$

e.g. H_2O, H_2S, H_2Se, H_2Te

H_2O: H-bond
H_2S, H_2Se, H_2Te: vander waal force

B.pt → $H_2O > H_2Te > H_2Se > H_2S$.

H_2O (solid) < H_2O (liq) — density.

→ H_2O H_2S H_2Se H_2Te

Size ↑es. B.L ↑es, Bond str. ↓es. B.D.E ↓es. acidic character ↑es, reducing power ↑es.

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② Rxn with O_2

$E + O_2 \longrightarrow EO_2 + EO_3$

e.g. SO_2 SO_3.

$(S^{+4}O_2 < S^{+6}O_3)$ — acidic

③ Rxn with Halogen

$E + X_2 \longrightarrow EX_4 + EX_6$

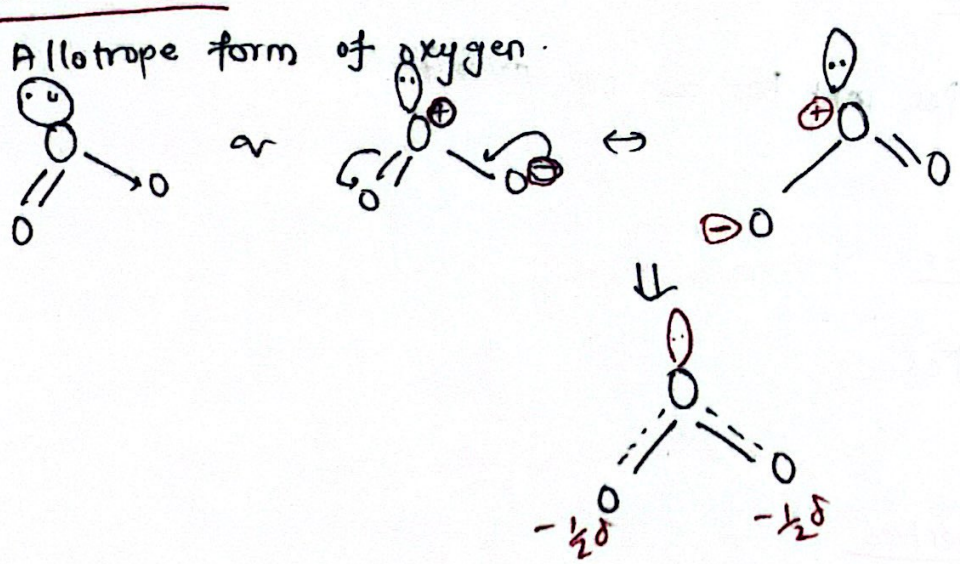
e.g. SF_4 (sp^3d) SF_6. (sp^3d^2). $(SF_4 < SF_6)$ - covale

Q. Which compound is least thermal stable?

ⓐ H_2O ⓑ H_2S ⓒ H_2Se ~~ⓓ~~ H_2Te ← weak bond easily break

Ozone (O_3)

→ Allotrope form of oxygen.



→ O-O bond length equal due to resonance.

→ Bond order → 1.5.

→ Hybridization → sp^2.

↳ bent shaped.

- polar
- $\mu \neq 0$
- Diamagnetic (but O_2 is paramag).

→ preparation of ozone is endothermic process.

→ Ozone is good oxidising agent after Fluorine.

→ Fishy smell (less conc - harmless more conc → harmful)

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→ Tailing of mercury is due to ozone.
└ Hg loses its fluidity

H_2SO_4

→ King of chemical or oil of vitriol.

→ By contact process (prepare).

→ properties

① Dibasic acid.
└→ 2 types of salt बनाउक
└ $NaHSO_4$ & Na_2SO_4.

Q. Which acid form 2 types of salt?

exist as H_2F_2 (dimer)

ⓐ HF ⓑ H_3PO_3 ⓒ H_2O_2 ⓓ H_2S ⓔ H_2SO_4 ⓕ All

KF, KHF_2 (fremith salt) — NaH_2PO_3, Na_2HPO_3 — $NaHO_2$, Na_2O_2 — NaHS, Na_2S — $NaHSO_4$, Na_2SO_4

② Dehydrating agent.

Q. When mixture of $KClO_3$, H_2SO_4 & $H_2C_2O_4$ heated, which element show maximum change in O.S?

ⓐ Cl ⓑ S ⓒ C ⓓ H ⓔ O

└ by 6

$\rightarrow 2KClO_3 \xrightarrow{\Delta} 2KCl + O_2$ (+5 → 6, −1)

$\rightarrow H_2SO_4 \xrightarrow{\Delta} SO_3 + H_2O$

$\rightarrow$ COOH, +2COOH $\xrightarrow{\Delta} CO_2 + CO + H_2O$ (+4)

③ Oxidising agent

$M + dil.H_2SO_4 \rightarrow MSO_4 + H_2\uparrow$
└ not O.A.

$M + con.H_2SO_4 \rightarrow MSO_4 + H_2O + SO_2$.
all metals except Au/pt. — O.A

ECS:
$\xrightarrow[dil.H_2SO_4]{H_2O, dil.HCl} H_2$.

— H —

$\xrightarrow[dil.HCl]{H_2O}$ No rxn.

Q. In which reaction, H_2 gas evolved:-

(a) $Cu + dil.H_2SO_4 \longrightarrow$ No rxn.

(b) $Zn + dil.\ H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$.

(c) $Zn + conc\ H_2SO_4 \longrightarrow ZnSO_4 + H_2O + SO_2$.

(d) $Cu + \underset{\text{O.A.}}{\text{con. } H_2SO_4} \longrightarrow CuSO_4 + H_2O + SO_2$.

(e) a & b both.

Q. Which reaction is possible:-

(a) $Cu + H_2O \longrightarrow X$.

(b) $Cu + dil.HCl \longrightarrow X$

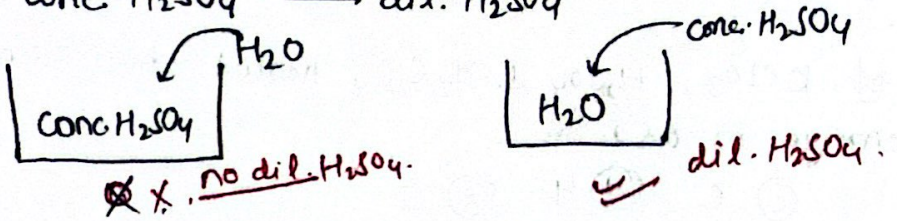
(c) $Cu + dil.\ H_2SO_4 \longrightarrow X$

(d) $Cu + \underset{\text{O.A.}}{\text{dil. } HNO_3} \longrightarrow \checkmark\ Cu(NO_3)_2 + H_2O + NO$

(e) $Cu + \underset{\text{O.A}}{\text{con. } HNO_3} \longrightarrow \checkmark\ Cu(NO_3)_2 + H_2O + NO_2$

(f) $Cu + conc\ \underset{\text{O.A.}}{H_2SO_4} \longrightarrow \checkmark\ CuSO_4 + 2H_2O + SO_2$

$\longrightarrow$ conc. $H_2SO_4 \longrightarrow$ dil. H_2SO_4



X. no dil. H_2SO_4.

Q. In which rxn, SO_2 gas evolve:-

(a) $H_2\overset{-2}{S} \xrightarrow[H_2SO_4]{\text{con.}} \overset{0}{S} + \overset{+4}{S}O_2$

(b) $C \xrightarrow{\Delta} CO_2 + SO_2$

(c) $Cu \xrightarrow{\Delta} CuSO_4 + H_2O + SO_2$

(d) $KI \xrightarrow{\Delta} HI + K_2SO_4$

(e) All

$\downarrow$ con H_2SO_4

$I_2 + SO_2$.

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Allotrope of sulphur

$\alpha\text{-}S \underset{<369K}{\overset{>369K}{\rightleftharpoons}} \beta\text{-}S$

→ At 369 K, both the form are stable. & This temperature is called transition temp^r.

* α-S (Rhombic sulphur)
  - Yellow color
  - It is insolwble in H_2O but dissolve in some extent in benzen ether & alcohol.
  - It is soluble in CS_2 (carbon disulphide)

- Monoclinic S (β-S)

S_8 – crown structure

  - → colorless
  - soluble in CS_2.

H_2S

prep – $Sb_2S_3 + HCl \longrightarrow H_2S$
- colorless
- rotten egg smell.
- moderately soluble in H_2O

→ $H_2\overset{-2}{S}$ is good reducing agent.

$$H_2\overset{-2}{S} + X_2 \longrightarrow HX + \overset{0}{S}$$

(red. agent / loss of e^-)

$$H_2S + SO_2 \longrightarrow S$$

$$H_2S + HNO_3 \longrightarrow NO_2.$$

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Sodium Thiosulphate

→ $Na_2S_2O_3 \cdot 5H_2O$ (Hypo)

prepn

- $Na_2SO_3 + S \xrightarrow{\text{boil}} Na_2S_2O_3$
- $NaOH + S \longrightarrow Na_2S_2O_3$ → colorless solid.
- $Na_2S + Na_2SO_3 + I_2 \longrightarrow NaI + Na_2S_2O_3$

→ Used as antichlor (removes chlorine).

$S_2O_3^{-2} \xrightarrow{HCl} \underset{\text{white}}{S} + SO_2\uparrow$

$SO_3^{-2} \xrightarrow{HCl}$ only SO_2

→ $Na_2S_2O_3 \cdot 5H_2O \xrightarrow{\Delta} Na_2S_2O_3 \xrightarrow{220^\circ C} Na_2SO_4 + Na_2S_5$

- $Na_2S_2O_3 + I_2 \longrightarrow NaI + Na_2S_4O_6$

  └ Sod. tetra thionate

$S_4O_6^{-2}$ └ tetrathionate ion

O_2

prepn

① By distillation of air

② By Heating oxide below Cu in E.C.S.

H
Cu
Ag_2O
Au_2O
HgO

$\Big] \xrightarrow{\Delta} M + \frac{1}{2}O_2$

Note: $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

$CuCO_3 \xrightarrow{\Delta} CuO + CO_2$

$Ag_2CO_3 \xrightarrow{\Delta} 2Ag + CO_2 + \frac{1}{2}O_2$

$AgNO_3 \xrightarrow{\Delta} Ag + NO_2 + \frac{1}{2}O_2$

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