Phosphorous Compounds

Effects of Heating

$4H_3PO_3 \xrightarrow{200^\circ C} PH_3 + 3H_3PO_4$

(compare with H_3PO_4)

+ Use of $Na_3P_3O_9$ → for softening of water

(8) Neet Test for PO_4^{-3}

$Na_2HPO_4 + 23HNO_3 + 12(NH_4)_2MoO_4$

$\longrightarrow (NH_4)_2PO_4 \cdot 12MoO_4 + 2NaNO_3 + 21NH_4NO_3 + 12H_2O$

Canary Yellow ppt. (without heating)

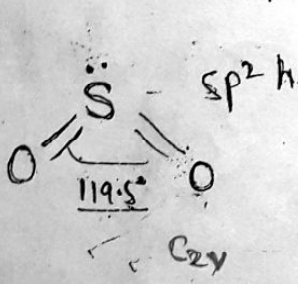
(compare with As^{+3} → It gives canary yellow ppt only on heating)

Oxides of Sulphur

(1) → SO_2 (Sulphur dioxide)

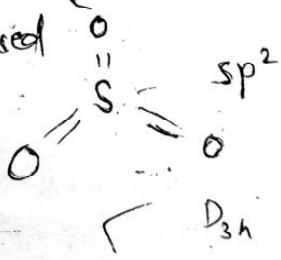
(2) → SO_3 (Sulphur trioxide)

Structures (Discrete molecules)



C_{2v}

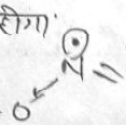
S^{+6}



D_{3h}

O=C=O
↳ l.p. absent.

* central atom पर l.p. है तो atom linear नहीं होगा।

Ex NO_2^-  paramagnetic

SO_2

Prep

(1) By burning of sulphur in air

$$S + O_2 \longrightarrow SO_2$$

(2) By burning H_2S in air

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2$$

(3) Not ✱ From Iron pyrites (by roasting)

$$4FeS_2 + 11O_2 \longrightarrow \underset{\text{हेमेटाइट}}{2Fe_2O_3} + 8SO_2$$

↳ reduction by carbon mono oxide →

It is a colorless gas with chocking smell.

It is weak reducing agent in acidic medium & strong reducing agent in basic medium e.g

$$K_2Cr_2O_7 + H_2SO_4 + SO_2 \longrightarrow Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

(+vy) (orange) (+3) (green)

Similar reaction with $KMnO_4/H^{\oplus}$

$$KIO_3 + SO_2 + H_2O \longrightarrow KHSO_4 + I_2 + H_2SO_4$$

SO_2 when dissolves in water it forms sulphurous acid

$$H_2O + SO_2 \longrightarrow H_2SO_3$$

Estimation of SO_2 (In environment) (quantitative estimation) (30) X

(1) By reaction with H_2O_2

$$H_2O_2 + SO_2 \longrightarrow H_2SO_4 \longrightarrow$$ It can be titrated with base.

(2) By burning with H_2 in flame photometer.

Spectrum of sulpher tells the quantity of sulpher in given sample.

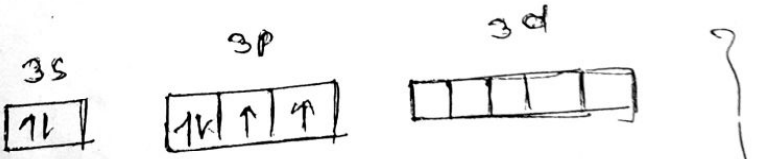
(3) By Colorimetry →

$$K_2[HgCl_4] + SO_2 + 2H_2O \longrightarrow K_2[Hg(SO_3)_2] + 4HCl$$

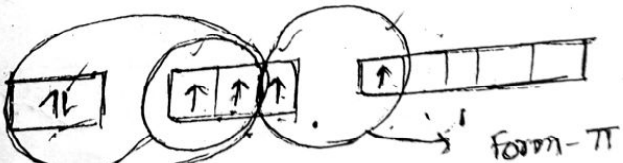
$K_2[Hg(SO_3)_2]$ + pararosaniline → Complex (dye) ← Use Colorimetry ← quantity of sulpher

Bonding

Conf. of S → (ground state)



Excited state →



Form-π bonds with O- atom

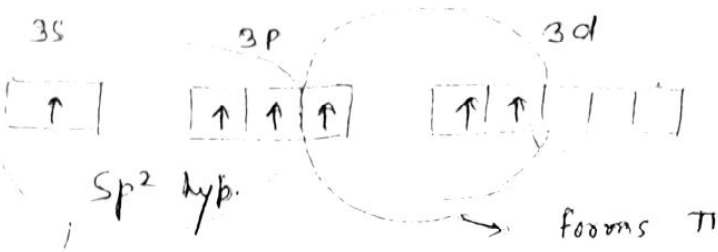
sp^2 hybridisation

Form σ Bonds with O- atom

SO_2 is mainly used in prep of SO_3 in contact process of manufacturing of H_2SO_4.

SO_3

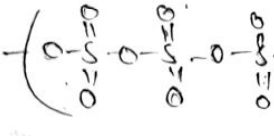
Bonding



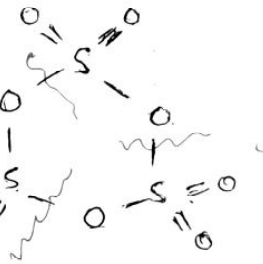
Structure in solid state

① α form ② β form ③ γ form (solid)

long chain polymer



It has helical structure in which corner are attached by -O- atoms



Cyclic Trimer of SO_3

Manufacturing of H_2SO_4

By Contact process →

① Production of SO_2

* Neb $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

It can be reduced by CO to obtain iron.

(3) Production of SO_3

$$2SO_2 + O_2 \text{ (excess)} \xrightarrow[\text{pressure, } \Delta]{V_2O_5 \text{ (catalyst)} \,/\, K_2O \text{ (promoter)},\ \text{high}} 2SO_3$$

K_2O is used as a promoter.

This reaction chamber should be dust free.

(i) Now SO_3 is treated with conc. H_2SO_4

(ii) Net

why does need to make oleum -

$$H_2SO_4 \text{ (conc.)} + SO_3 \longrightarrow H_2S_2O_7$$

Oleum (Fuming H_2SO_4)

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4 \text{ (conc.)}$$

{ here SO_3 is not mixed with H_2O because it forms (iii) Net dense fogs (fumes). }

- SO_3 can be oxidised to SO_4^{-2} ion.

Oxy acids of sulphur

Types

1. Sulphurous acid series
2. Sulphuric " "
3. Thionic " "
4. peroxo sulphuric " "

O.S. नो P.O S Pyro - 2 molequle जोड़ H_2O निकाल दे।

O.S. नो S=O (A Sulphurous acid series) (33)

Oxygen D.B.

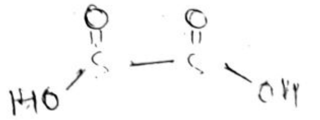
* जितने -ve charge है उतने single Bonded oxygen atom है। (Oxidation state of S)

(Sulphurous acid) +4

H_2SO_3

(di or pyro sulphurous acid) like N[...] +4

$H_2S_2O_5$ $[S_2O_5^{-2}]$

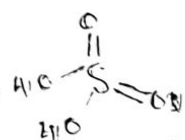


(dithionous acid) +3

$H_2S_2O_4$ $[S_2O_4^{-2}]$

- Prefix -us -ic

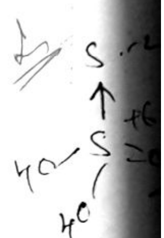
(B) Sulphuric acid series

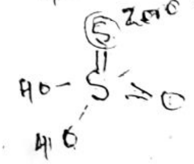


(Sulphuric acid) S (+6)

Zero O.S.

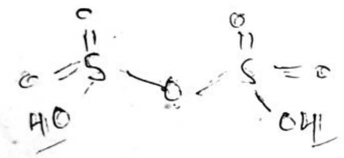
H_2SO_4. $[SO_4^{-2}]$





(Thiosulphuric acid. S (+4)

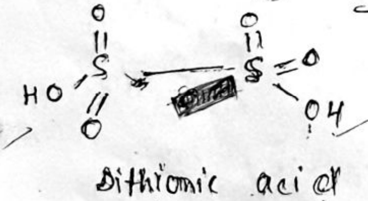
$H_2S_2O_3$ $[S_2O_3^{-2}]$



(Pyro disulphuric acid) S (+6)

$(H_2S_2O_7)$ $[S_2O_7^{-2}]$

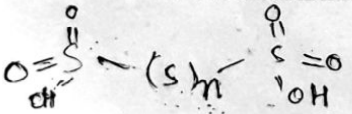
(C) Thionic acid series



$H_2S_2O_6$ S(+5)

Dithionic acid

$H_2S_{n+2}O_6$

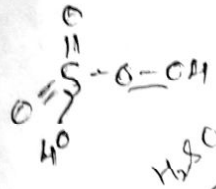


Polythionic acid

* इस सिरीज में oxygen S case - metal = bond है। $S-S$

* जितना -ve charge है उतने oxygen atom oxide $S-O^-$ form है।

(4) Peroxoacid series ⊛ Net मिलान करो



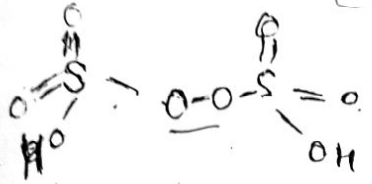
(Caro's acid, Caro's acid
peroxomonosulphuric acid)

H_2SO_5

$[SO_5^{-2}]$

$H_2SO_4 + O \rightarrow H_2SO_5$

S (+6)



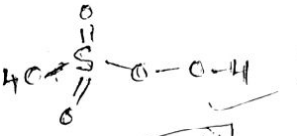
(Peroxodisulphuric acid)
(Marshall's acid)

S (+6)

6. $H_2S_2O_8$ (228) $[S_2O_8^{-2}]$

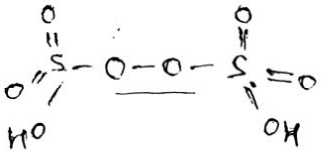
⊛ Net
Peroxo acid series

Prep → By H_2O_2 & Chlorosulphonic acid

$H_2O_2 + ClSO_3H \xrightarrow{\Delta}$  + HCl

(1 : 1)

Caro's acid — caro's acid

→ $H_2O_2 + 2\,ClSO_3H \longrightarrow$ 

(1 : 2)

+ 2HCl

(Marshalls acid) Net ⊛

H_2SO_5 is also formed as a byproduct when $H_2S_2O_8$ is formed by electrolysis of 50% H_2SO_4. Electrolysis of Net 50% H_2SO_4 (w/w) carried out at high current density & low temp on smooth Pt- electrodes.

$H_2SO_4 \rightleftharpoons H^{\oplus} + HSO_4^{\ominus}$
(50%)

$HSO_4^{\ominus}$ → on anode

$2HSO_4^{\ominus} \longrightarrow H_2S_2O_8 + 2e^{\ominus}$

$H^{\oplus}$ → On Cathode

$2H^{\oplus} + 2e \longrightarrow H_2$

Uses of salt of $H_2S_2O_8$ (Marshall's acid)

$(NH_4)_2S_2O_8$ — Ammonium persulphate
- used as an initiater in the polymerisation of vinyl acetate.

$K_2S_2O_8$ — Pot. persulphate
- used as an initiater in the polymerisation of vinyl chloride

X Sulphurous acid (H_2SO_3)

Prep → In small amount

$SO_2 + H_2O \longrightarrow H_2SO_3$

Generally it's salts are used in various reactions e.g $NaHSO_3$, Na_2SO_3

SO_2 is undergo self ionisation in non aq. media.

$2SO_2 \rightleftharpoons SO^{+2} + SO_3^{-2}$

Net

Thionyl ion Sulphite ion

Salts of H_2SO_3 are generally used in reactions

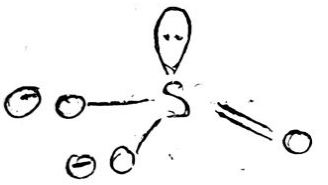
$$NaHSO_3 \underset{(aq)}{\rightleftharpoons} Na_2S_2O_5 + H_2O$$

$$NaHSO_3 \text{ or } Na_2SO_3 \xrightarrow{\text{Acid}} H_2SO_4 + SO_2$$

SO_3^{-2} is a strong reducing agent

$$H_2O_2 + SO_3^{-2} \longrightarrow H_2O + SO_4^{-2}$$

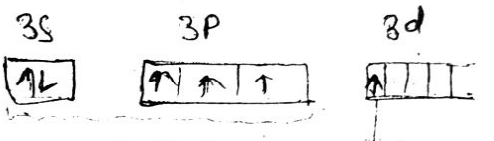
structure of SO_3^{-2}



Trigonal Pyramidal

SO_3

Excited state of S



sp^3 hyb

It forms π bond with oxygen atom ($p\pi$-$d\pi$)

× Pyro or disulphurous acid ($H_2S_2O_5$)

It is unstable but it's salts are quite stable.

$Na_2S_2O_5$

Prep.

(A) $NaHSO_3(aq) \rightleftharpoons Na_2S_2O_5 + H_2O$

(B) $RbHSO_3 \longrightarrow Rb_2S_2O_5 + H_2O$
(s)

(C) $Na_2SO_3 + SO_2 \longrightarrow Na_2S_2O_5$

sulphurous acid ($H_2S_2O_4$)

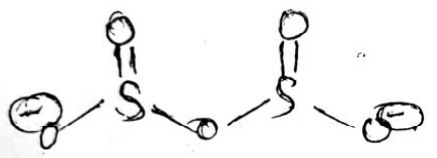
Prep.

$$2\,HSO_3^{\ominus} + SO_2 \xrightarrow{Zn} S_2O_4^{-2} + SO_3^{-2} + H_2O$$

(dithionite)

It is a strong reducing agent. It absorbs ~~oxygen~~ oxygen in alkaline media. So that it is used for estimation of oxygen.

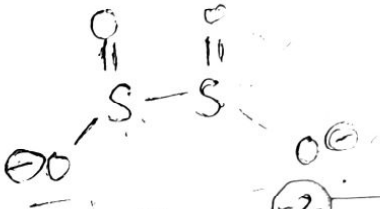
Structures of $[S_2O_5]^{-2}$ & $[S_2O_4]^{-2}$



$S_2O_5^{-2}$

disulphite ion

* Net



$[S_2O_4]$

dithionite ion

* Net

No of -ve charge is equil to No of oxygen atom in oxide

S–O and S=O

Sulphuric acid series.

(1) Sulphuric acid ⟶

Prep ⟶ (A) contact Process → Already discussed

(B) Lead Chamber Method (older method)

$$NO_2 + SO_2 + 2H_2O \longrightarrow H_2SO_4 + NO$$

NO_2: catalyst

NO: Oxygen Carrier Catalyst

$$2NO + O_2 \longrightarrow 2NO_2$$

(onc. H_2SO_4 (Anhydrous) is also used as a non aq. solvent.

Self ionisation $2H_2SO_4 \rightleftharpoons \underline{H_3SO_4^{\oplus}} + \underline{HSO_4^{\ominus}}$

× (2) Thiosulphuric acid ($H_2S_2O_3$)

Prep.

$$H_2S + SO_3 \xrightarrow{\text{ether}} H_2S_2O_3 \cdot Et_2O$$

It is unstable & decomposes to S, H_2S, SO_2, SO_3, H_2SO_4 etc,

But its salts are quite stable.

Prep. of $Na_2S_2O_3$ (sodium thiosulphate & Hypo) (STS)

(1) $Na_2SO_3 + S \xrightarrow[\text{water}]{\text{boiling}} Na_2S_2O_3$ (STS)

(2) $Na_2S_3 + O_3 \xrightarrow{\Delta} Na_2S_2O_3 + S$

(3) During the manufacturing of Na_2S in industries, Na_2SO_3, Na_2CO_3, SO_3 and present in waste liquor.

By Passing SO_2 in waste liquds, we (40
can obtain (STS)

$$2Na_2SO_3 + Na_2S + 6SO_2 \longrightarrow 4Na_2S_2O_3$$

$$Na_2CO_3 + Na_2S + SO_2 \longrightarrow Na_2S_2O_3 + CO_2$$

Reactions

(*) Net

(I) Action of heat

$$Na_2S_2O_3 \xrightarrow[>225^\circ C]{} Na_2SO_4 + Na_2S_5$$

$$Na_2S_5 \xrightarrow{\Delta\ (T^\circ)} Na_2S_4 + S$$

(B) Reaction with Cl_2 & I_2.

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

$$2Na_2S_2O_3 + Cl_2 + 2H_2O \longrightarrow 4NaHSO_4 + 4HCl$$

(C) Reaction with $AgNO_3$ → display the coloured

$$Na_2S_2O_3 + 2AgNO_3 \longrightarrow \underset{\text{White}}{Ag_2S_2O_3} + 2NaNO_3$$

$$Ag_2S_2O_3 + H_2O \longrightarrow \underset{(\text{Black})}{Ag_2S} + H_2SO_4$$

If we use excess of $Na_2S_2O_3$ then complex formation occurs

$$Na_2S_2O_3 + AgNO_3 \longrightarrow Na_5[Ag(S_2O_3)_3] + NaNO_3$$

Reaction with AgBr

$$AgBr + Na_2S_2O_3 \longrightarrow Na_5[Ag(S_2O_3)_3] + NaBr$$

Hypo is also used in titrations for estimation of I_2 conc.

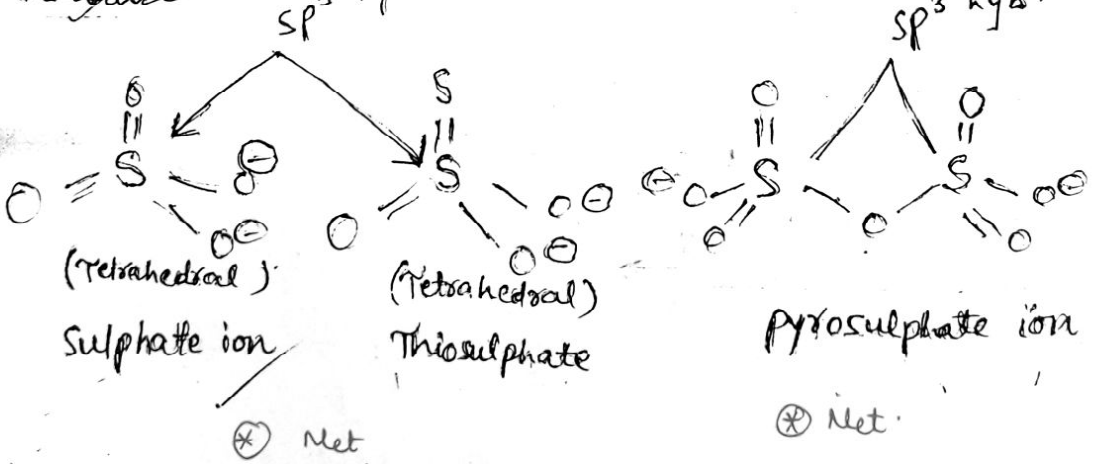
(3) Di or pyrosulphuric acid

($H_2S_2O_7$)

Prep. →

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7 \xrightarrow{H_2O} 2H_2SO_4$$

Structure



⊛ Net

⊛ Net.

Thionic acid series

(1) Dithionic acid ($H_2S_2O_6$)

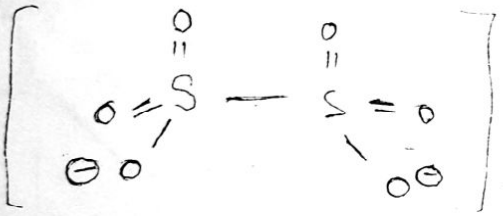
Prep →

$$MnO_2 + SO_2 \longrightarrow MnS_2O_6 + MnSO_4$$

$MnS_2O_6 \xrightarrow{H^\oplus}$ Hydrolysis → $H_2SO_4 + H_2SO_3$ and $H_2SO_4 + H_2SO_5$

$MnS_2O_6 \xrightarrow{H^\oplus} H_2S_2O_6$

Structure → $S_2O_6^{-2}$ (dithionate ion)



Polythionic acids — $H_2S_nO_6$ $\{n = 2, 3, 4 \ldots\}$

Prep. → (1)

$$SCl_2 + 2HSO_3^- \longrightarrow {}^{\ominus}O_3S - S - SO_3^{\ominus} + 2HCl$$

$$S_2Cl_2 + 2HSO_3^{\ominus} \longrightarrow {}^{\ominus}O_3S - S - S - SO_3^{\ominus} + 2HCl$$

(2) from H_2SO_3 & H_2S (Wackenroder's soln)

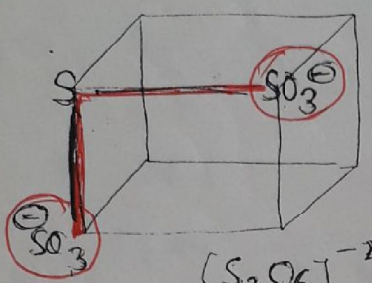
$$H_2SO_3 + H_2S \xrightarrow[\text{cold}]{\text{Ice}} H_2S_2O_3 + H_2O$$

Tetrathionic acid

$$H_2S_2O_2 + H_2SO_3 \xrightarrow{\quad} H_2S_4O_6 + H_2O$$

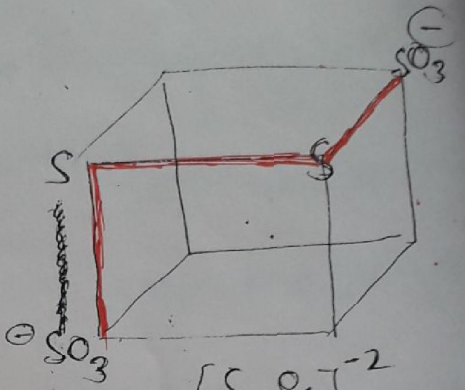
In this reaction a mixture of polythionic acids is formed which is called Wackenrodor soⁿ

structure



$[S_3O_6]^{-2}$

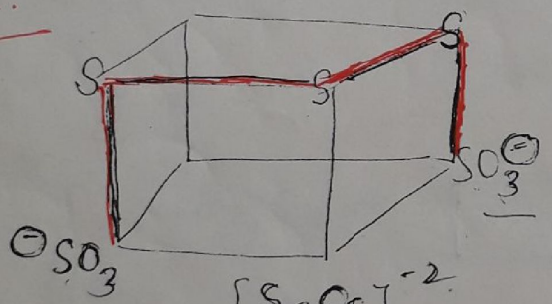
Trithionate ion



$[S_4O_6]^{-2}$

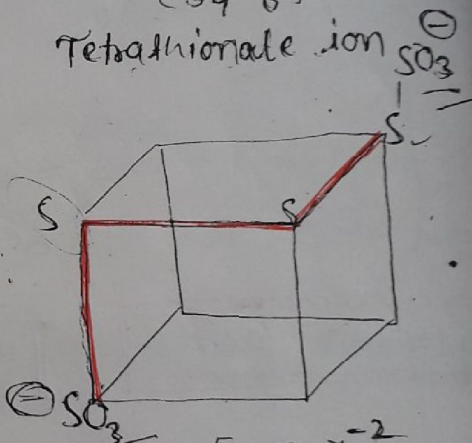
Tetrathionate ion

$S-SO_3^-$ unit



$[S_5O_6]^{-2}$

Cis-pentathionate ion



$[S_5O_6]^{-2}$

Trans-pentathionate

(*) Prefix - ate