Sulphur.

Electronic configuration :- $1s^2 2s^2 2p^6 3s^2 3p^4$

Group - VIA - (p-block element)

Molecular formula - S_8 (octa atomic)

Atomic no - 16

Atomic mass - 32

From ancient period it was known as brimstone (burning stone).

Occurrence.

- 0.05% in earth crust
- free as well as combine state
- Iron pyrites (FeS)
- zinc blende (ZnS)
- copper pyrites ($CuFeS_2$)
- Cinnabar (HgS).

organic compounds containing proteins like egg, hair, onion, garlic, mustard.

Allotrops of sulphur

Sulphur exist in more than one form which is physically different but chemically identical, This is called allotropy.

Sulphur exist in two allotropic form.

(I) Crystalline (II) Amorphous.

(a) crystalline

(a) Rhombic sulphur (α-sulphur)
(pale yellow colour but transpurent)
- bad conductor.
- octahedral crystal.
- insoluble in H_2O, soluble in ethere, $CHCl_3$.

(b) Monoclinic sulphur (β-sulphur)
deep-yellow crystalline but opaque
- bad conductor.

(b) Amorphous.

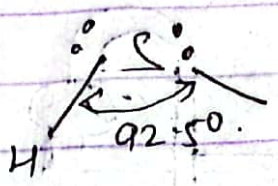
(a) plastic sulphur. (γ-sulphur)
(b) colloidal sulphur (δ-sulphur)
(c) Milk of sulphur

Uses of sulphur

(i) sulphur is used to manufacture of SO_2, H_2SO_4, (carbondisulphide) CS_2, dyes etc.
(ii) Used to manufacture of gun powder (mixture of carbon, sulphur and KNO_3)
(iii) Used to manufacture of medicine sulpha drugs and ointment for skin disease.
(iv) Used in rubber for desirable property.
(v) Used to make matchstick.
(vi) Burning sulphur is used for disinfectant room.

Hydrogen sulphide (H_2S)

- H_2S is present in volcanic gases.
- It has unpleasent smell of rotten eggs.



Laboratory preparation of H_2S by kipp's apparatus.

In laboratory, H_2S is prepared by the action of non oxidizing acid (dil H_2SO_4, or dil HCl) and Iron (II) sulphide.

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S \uparrow$$

$$FeS + 2HCl \longrightarrow FeCl_2 + H_2S \uparrow$$

It is prepared in kipps apparatus.
kipps apparatus consist of two parts.

(I) Bulb A with long stem.
(II) The base with two communicating bulb B and C.

The middle bulb B is fitted with a stop cock for for the gas. and lower bulb C has a stopper to empty apparatus.

The stem of bulb A reaches the bottom of bulb C and placed alright into

the neck of B as shown in figure.

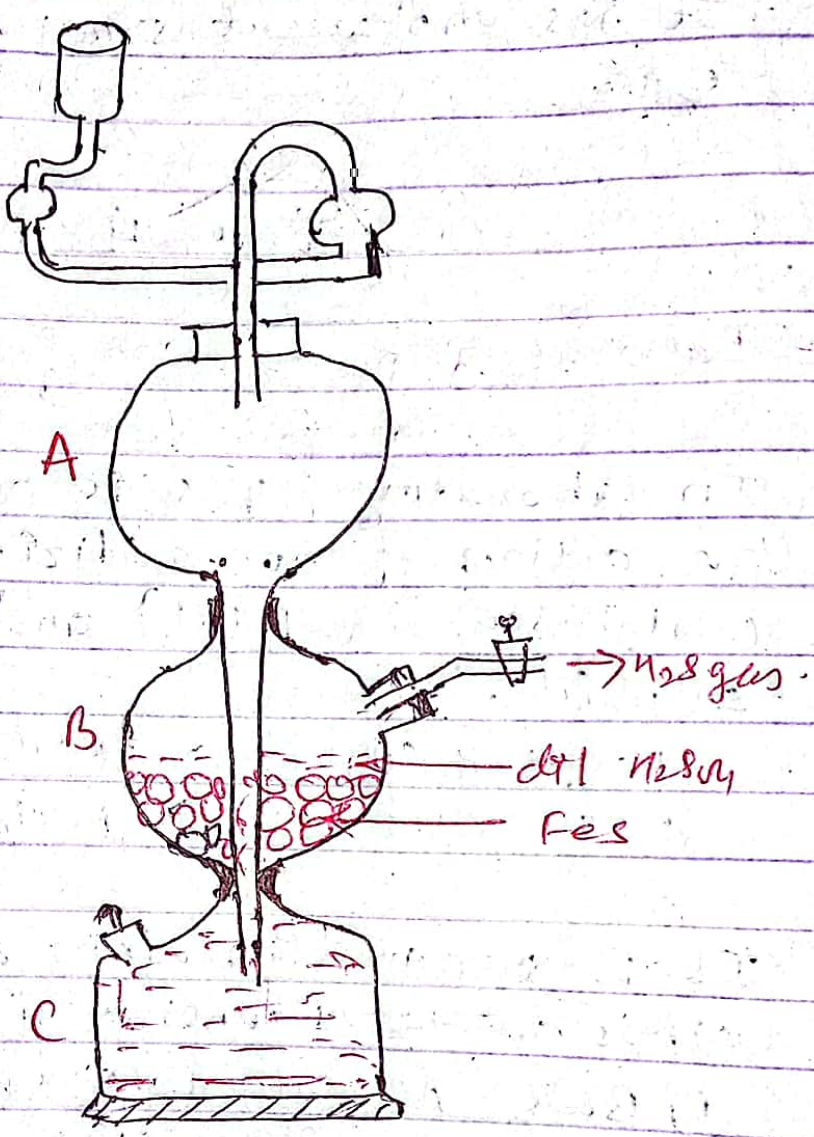


Fig: Kipp's apparatus for H_2S.

Middle bulb contains FeS (iron sulphide) and dilute H_2SO_4 poured from upper bulb 'A'.

FeS reacts with H_2SO_4 produced H_2S which

is liberated from tap when needed.

Test of H_2S.

It turns lead acetated paper into black.

$$H_2S + Pb(CH_3COO)_2 \longrightarrow PbS\downarrow + 2CH_3COOH$$

black.

(lead acetate)

Properties of hydrogen sulphide H_2S

* Colourless gas with very unpleasent smell of rotten eggs.
* It is poisonous when inhaled in excess.
* soluble in water.

1). Acidic nature:-

Aqueous H_2S is acidic. It is diprotic acid. It turns blue litmus into red.

It ionizes into two stages:

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

bisulphide ion

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

sulphide ion.

2) It H_2S react with alkali and form two series of bisulphite salt and normal salt.

aq = aqueous.

OIL RIG LEO.

$NaOH + H_2S \longrightarrow NaHS + H_2O$

Sod. bisulphide

$NaOH + H_2S \longrightarrow Na_2S + H_2O$

Sod. sulphide.

metals more reactive than hydrogen replace the hydrogen from aq. H_2S

$Zn + H_2S \longrightarrow ZnS\downarrow + H_2\uparrow$

$Pb + H_2S \longrightarrow PbS\downarrow + H_2\uparrow$.

2. Reducing properties:-

H_2S is good reducing agent due to S^{2-} ions loses two electron to another species, and itself get oxidized to sulphur.

$H_2S \rightleftharpoons 2H^+ + S^{--}$

$S^{--} \longrightarrow S + 2e^-$

(a) It reduces halogens (Cl, Br, I) to halogen acids.

$H_2S\ (aq) + X_2 \xrightarrow{H_2O} 2HX + S\downarrow$

yellow

(b) It reduces SO_2 to colloidal sulphur.

$2H_2S + SO_2 \longrightarrow 2H_2O + 3S\downarrow$.

© It reduces acidified potassium permagnet $KMnO_4$ (pink) to colourless, acidified potassium dichromate (orange colour) $K_2Cr_2O_7$ to green.

i). $KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S\downarrow$
colourless

ii). $K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + S\downarrow$
green

iii). It reduces conc. HNO_3 to NO_2.

$2HNO_3 + H_2S \longrightarrow 2NO_2 + 2H_2O + S\downarrow$.

iv). It reduces conc. H_2SO_4 to SO_2;

$H_2SO_4 + H_2S \longrightarrow SO_2 + H_2O + S\downarrow$.

3). Analytical reagent in salt Analysis.

precipitation reaction of H_2S with metal ions is highly useful to identify the basic radicals in qualitative analysis of salt.

When H_2S is passed on salt solution metal ions precipitate as coloured sulphide either in in acidic medium or in basic medium. on the basis of solubility product value.

Thus the metal ions (basic radical) classified

into two groups.

(a) Group II basic radicals.

H_2S precipitate the group (II) cations. (metal ions) in acidic medium as metal sulphide.

eg. Cu^{++}, Pb^{++}, Bi^{++}, Cd^{++}.

$$H_2S + Cu^{++} \xrightarrow[\text{or dil HCl.}]{H^+ \text{ (acidic medium)}} CuS\downarrow + 2H^+$$

black.
(metal sulphides)

$$Pb^{++} + H_2S \xrightarrow{H^+} PbS\downarrow + 2H^+$$

black

$$Cd^{++} + H_2S \xrightarrow{H^+} CdS\downarrow + 2H^+$$

yellow

The sulphide of Group II radicals have low solubility product. so addition of dil. HCl supress the ionization of weak acid (H_2S) and thus precipitates the basic radicals.

(b) Group IIIB basic radicals.

H_2S precipitates the group IIIB cations in basic medium as the metal sulphide.

eg. Zn^{++}, Ni^{++}, Co^{++} & Mn^{++} ions.

The sulphides of Group IIIB radicals have high solubility product value and are

precipitated by ~~H2S~~ passing H_2S on alkaline (basic) medium. (solution of $NH_4Cl + NH_4OH$)

$$Zn^{++} + H_2S \xrightarrow[NH_4OH]{NH_4Cl} ZnS\downarrow + 2H^+$$

White ppt.

$$Ni^{2+} + H_2S \xrightarrow[NH_4OH]{NH_4Cl} NiS\downarrow + 2H^+$$

(black)

Uses of H_2S.

i). Used in preparation of metallic sulphides used as pigments.

ii). Used as laboratory reagent in analysis of basic radicals.

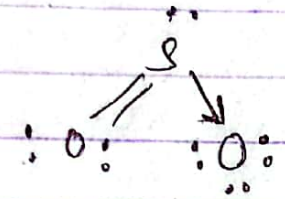
iii). Used as reducing agent.

iv) Used in preparation of hydrogen halides. like HBr & HI.

Sulphurdioxide (SO_2)

SO_2 is common oxide of sulphur.
The oxidation state of S in SO_2 is +4.

Naturally it is found in volcanic gases and also by roasting of sulphur.



properties of SO_2.

i). colourless acidic gas.
ii). It has pungent and suffocating smell of burning sulphur.
iii). Slightly soluble in water, it turns moist litmus to red.

1) Acidic nature

It dissolves in water to give sulphurous acid, and weak diprotic acid.

$$SO_2 + H_2O \longrightarrow H_2SO_3.$$

If sulphorous acid is boiled, SO_2 expelled out

$$H_2SO_3 \xrightarrow{heat} H_2O + SO_2\uparrow.$$

(a) action with NaOH.

$SO_2 + NaOH \longrightarrow NaHSO_3$ (sod. bisulphite)

$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$

$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$

excess.

(b) action with $Ca(OH)_2$.

When SO_2 is bubbled in lime water, it turns milky due to the formation of white ppt of calcium sulphite and it disappear on excess SO_2 due to formation of a colourless bisulphate solution.

$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 \downarrow + H_2O$.

white ppt.

$CaSO_3 + H_2O + SO_2 \longrightarrow Ca(HSO_3)_2$.

excess → colourless.

(c) Action with Na_2CO_3.

It gives CO_2.

$Na_2CO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3 + CO_2 \uparrow$.

27. Bleaching propert

Sulphurdioxide shows bleaching properties in presence of moisture. It changes

colouring matter into colourless product. It is used for bleaching of coloured wool, silk, sponge, flower, hair, straw. It is not permanent and colour can be restored.

It bleached by reduction.

$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$.

Vegetable colouring matter + $[H] \rightarrow$ colourless product.

3. Reducing nature.

Moist SO_2 reduces, Cl_2, Br_2, I_2, $K_2Cr_2O_7$ etc.

i) It reduces halogen to their respective halides.

$SO_2 + 2H_2O + X_2 \longrightarrow 2HX + H_2SO_4$.

(acidified)

ii) It reduces potassium permagnent to colourless.

$2KMnO_4 + H_2SO_4 + 5SO_2 \longrightarrow K_2SO_4 + \cancel{C_2(SO_4)_3} + \cancel{H_2O}$ $+2MnSO_4 + 2H_2SO_4$

pink. colourless.

iii). It reduces ferric salt to ferrous salt.

$Fe_2(SO_4)_3 + SO_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$

yellow. light green.

iv). It reduces acidified ~~$KMnO_4$~~ $K_2Cr_2O_7$ (orange) to green.

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

green

4) Oxidising property

It reduces powerful reducing agents like H_2S, Mg, Na, HI etc.

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

$Mg + SO_2 \longrightarrow 2MgO + MgS$

Uses of SO_2.

i) used for the manufacture of sulphuric acid, sulphurous acid.

ii) used for bleaching delicate articles like, silk, wool, hair etc. and in sugar industry for decolouring cane sugar solution.

iii) used as disinfectant, fungicide, and preservative.

Sulphuric acid:

(H_2SO_4)

i) It is common mineral acid.

ii) Oxidation state of sulphur in H_2SO_4 is +6

iii) It is also called king of chemical due to high consumption in world.

*. Physical properties-

i) It is colourless, hygroscopic (moisture adsorbent) liquid.

ii) Its high B.P. and viscous nature is due to intermolecular hydrogen bonding among H_2SO_4 molecules.

iii) Pure H_2SO_4 is covalent compound so bad conductor of electricity. but aqueous H_2SO_4 is conducts electricity.

iv) It is highly corrosive and produce burning sensation on skin.

Question- How concentrated H_2SO_4 is diluted?

conc. H_2SO_4 is diluted by adding acid slowly to water with constant stirring and not by adding water to acid. when water is added on acid a large amount of heat is produced which spurt the acid out of container. The produced heat evapourates the water

dibasic – two replaceable hydrogen.

and causes explosions.

$H_2SO_4 + nH_2O \longrightarrow H_2SO_4 \cdot nH_2O + \Delta$

CHEMICAL PROPERTIES OF H_2SO_4.

1) Acidic nature.

strong dibasic acid and it ionizes in two steps.

$H_2SO_4 \longrightarrow H^+ + HSO_4^-$

$HSO_4^- \rightleftharpoons H^+ + SO_4^{--}$

Being diprotic acid it gives two series of salts, like bisulphate and sulphate.

$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$

$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

It neutralises alkalis, basic oxide to form salts and water. CO_2 evolves from carbonate and bicarbonates and SO_2 gas from sulphite and bisulphites.

$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2\uparrow + H_2O$

$2NaHCO_3 + H_2HSO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O$

$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + H_2O.$

(b) It reacts with metal like Zn, Mg, Fe etc to replace hydrogen.

$Zn + dil.\ H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$.

$Mg + dil\ H_2SO_4 \longrightarrow MgSO_4 + H_2\uparrow$.

2) Oxidizing properties

Hot conc. H_2SO_4 act as an oxidising agent

$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$.

(a) This nascent oxygen oxidizes non-metals like

C to CO_2

S to SO_2

P to H_3PO_4

H_2S to S

eg: 1) carbon is oxidized to CO_2

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

2) sulphur is oxidized to sulphurdioxide

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

3) phosphorous is oxidized to phosphoric acid.

$P_4 + 10H_2SO_4 \longrightarrow 4H_3PO_4 + 10SO_2 + 4H_2O$

(b) with metal.

i) More electropositive metal like Zn, Fe, Mg, Al reduce dil H_2SO_4 to H_2 but get oxidized to metal sulphates.

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

Zn is oxidized to Zn^{++} and H^+ is reduced to H_2 gas.

ii) Hot and conc. H_2SO_4 oxidizes Zn, Cu, Ag to metal sulphates but H_2SO_4 is reduced to SO_2.

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

(3) Dehydrating properties.

H_2SO_4 is strong dehydrating agent. It has strong affinity for water, decomposes compounds like cellulose, paper, wood, sucrose by removing elements of water.

(a) Charring action.

When conc. H_2SO_4 is kept in sugar, wood, paper etc. It extracts water and causes charring.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{Conc. } H_2SO_4} 12C + 11H_2O$$

sucrose — black.

$(C_6H_{10}O_5)_n \xrightarrow{\text{conc } H_2SO_4} 6nC + H_2SO_4 \cdot 5nH_2O$.

When something is written on paper by conc. H_2SO_4 black letter will be observed.

ii) Dehydration of organic compound:-

When H_2SO_4 is dropped on oxalic acid formic acid, and ethyl alcohol, it removes elements of water from them.

$HCOOH \xrightarrow[\Delta]{\text{conc. } H_2SO_4} CO\uparrow + H_2SO_4 \cdot H_2O$

formic acid.

$C_2H_5OH \xrightarrow[\Delta\ 170^\circ C]{\text{conc. } H_2SO_4} C_2H_4 + H_2SO_4 \cdot H_2O$.

ethyl alcohol — ethylene.

$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \cdot 2H_2O \xrightarrow[\Delta]{\text{conc } H_2SO_4} CO\uparrow + CO_2\uparrow + H_2SO_4 \cdot 3H_2O$

oxalic acid

iii) It removes water of crystallization from hydrated salts. e.g.

$CuSO_4 \cdot 5H_2O \xrightarrow{\text{conc. } H_2SO_4} CuSO_4 + 5H_2O$

blue vitrol — white.

Uses of H_2SO_4.

i). Used for manufacture of dyes, drugs, explosive, fertilizer, paints, pigments etc.

ii). Used in manufacture of HCl, HNO_3, H_3PO_4 etc.

iii). Used to manufacture of nitrocellulose products like cotton, wool, rayon, rubber etc.

iv). Used as laboratory reagent

v). Used for refining petroleum.

Test of H_2SO_4

When Barium sulphate is added to H_2SO_4 solution white ppt is formed.

$$H_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2HCl$$

(White ppt)

~~Sodium~~ Sodium thiosulphate

($Na_2S_2O_3$)

It is sodium salt of thiosulphuric acid.

It is commonly called hypo.

Hydrated structure of ~~[illegible]~~ molecular formula is $Na_2S_2O_3 \cdot 5H_2O$.

→ It is used in photography.

→ Used as laboratory reagent to estimate Iodine in titration.