TDC Part I
Paper I, Group B
Inorganic Chemistry

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TOPIC:- (Group 16) Sulphurous Acid (H_2SO_3)

Compounds of Sulphur and Nitrogen

Sulphurous Acid (H_2SO_3)

Though SO_2 is highly soluble in water, most of it is present as SO_2. H_2O (hydrate) and H_2SO_3 exists in minutes amounts. However its salts, sulphites (SO_3^{2-}) and hydrogen sulphites (HSO_3^-) are well known. Sulphurous acid possesses both oxidizing and reducing properties. It reduces iodine to HI, $KMnO_4$ to $MnSO_4$ (decolorizes $KMnO_4$) and $K_2Cr_2O_7$ to $Cr_2(SO_4)_3$ (turns $K_2Cr_2O_7$ green).

$H_2SO_3 + H_2O + I_2 \longrightarrow H_2SO_4 + 2HI$

$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

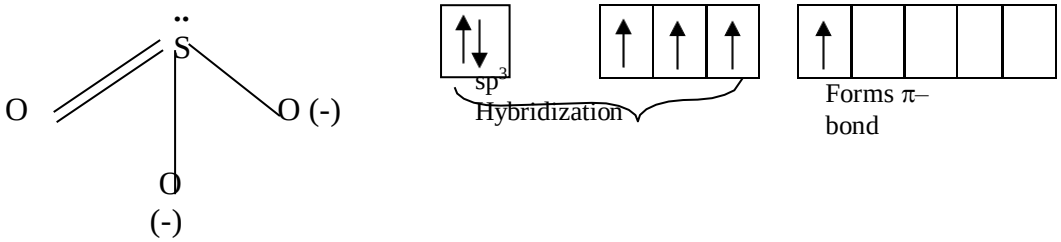
$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

In the presence of strong reducing agents it behaves as an oxidizing agent.

$2H_2S + H_2SO_3 \longrightarrow 3H_2O + 3S$

The sulphite ion has a pyramidal structure that is tetrahedral with one position occupied by a lone pair. The bond angle O-S-O is slightly distorted (106^0) due to lone pair. The bond length (151 pm) indicates double bond character.

Electronic structure of sulphur atom excited state

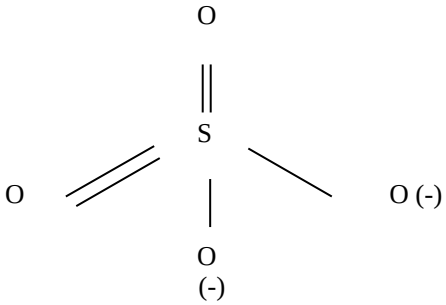


Sulphuric acid is a very important industrial chemical. It is a colourless, viscous liquid, a strong acid oxidizing agent and a powerful dehydrating agent. Some reactions of H_2SO_4 are shown in Table 22.

Table 22: Some Reactions of Sulphuric Acid

Reactant	Reaction	Remarks
Zn	$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$	Dilute Acid
Cu	$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$	Concentrated acid
C	$C + H_2SO_4 \longrightarrow CO + SO_2 + H_2O$	Conc. Acid (oxidizing agent)
NaBr	$2NaBr + 2H_2SO_4 \longrightarrow 2NaHSO_4 + Br_2$	Conc. Acid (oxidizing agent)
NaI	Similar reaction	
Sugar	$C_{12}H_{22}O_{11} \longrightarrow 12C + 11H_2O$	Conc. Acid (dehydrating agent)

H_2SO_4 is a dibasic acid forming two series of salts, hydrogen sulphate (HSO_4^-) and sulphate (SO_4^{2-}). The SO_4^{2-} ion has a tetrahedral structure



The worldwide production of sulphuric acid is ~ 180 million tons. It is used in fertilizer production, in the manufacture of chemicals, polymers, soaps and detergents, paints pigments dye intermediates and in petroleum refining.

Compounds of Sulphur and Nitrogen

Compounds containing sulphur –nitrogen rings are an area of considerable interest. N and S are diagonally related in the periodic table and have comparable charge densities and electronegativities. The compounds formed have unusual structures, which cannot be explained by the usual bonding theories. The best known is tetrasulphur tetranitride, S_4N_4 that is obtained as follows:

$$6SCl_2 + 16NH_3 \longrightarrow S_4N_4 + 2S + 14\,NH_4Cl$$

$$6S_2Cl_2 + 16\,NH_3 \xrightarrow{CCl_4} S_4N_4 + 8S + 12\,NH_4Cl$$

$$6S_2Cl_2 + 4\,NH_4Cl \longrightarrow S_4N_4 + 8S + 16\,HCl$$

S_4N_4 is a thermo chromic solid i.e. changes colour with temperature – colourless at liquid nitrogen temperature, orange at room temperature and red at 100^0C. It is stable in air, but may detonate with shock or friction, it exists as a cradle –shaped ring (Fig 27). The average S-N bond length (162 pm) indicates delocalized double bond character. The S -----S distances at top and bottom of cradle are ~ 258 pm indicating weak S-S bonding. S_4N_4 is thus a cage structure.

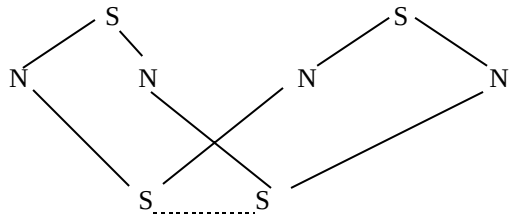


Fig. 27 : The Structure of $S_4\,N_4$

S_4N_4 is slowly hydrolyzed by water, but reacts rapidly with warm NaOH when the cage breaks.

$$S_4N_4 + 6NaOH + 3H_2O \longrightarrow Na_2S_2O_3 + 2Na_2SO_3 + 4NH_3$$