

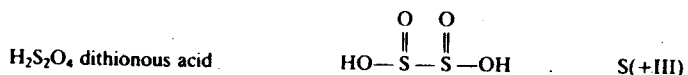
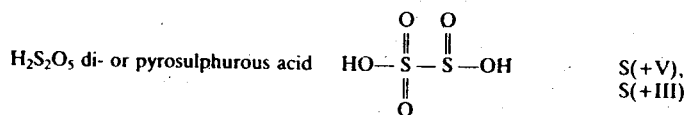
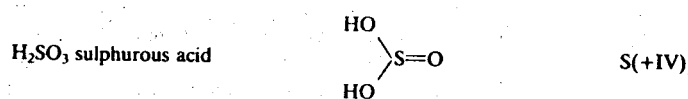
2. **Oxoacids : (a) Oxoacids of sulphur :** Sulphur forms a number of oxoacids, of which sulphuric acid is the most stable.

### Oxoacids of Sulphur

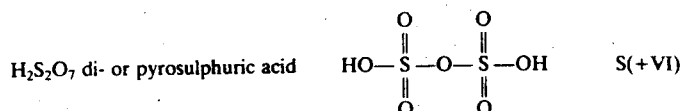
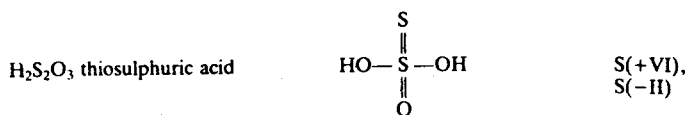
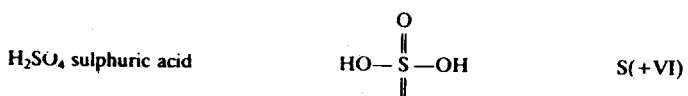
The oxoacids of sulphur are more numerous and more important than those of Se and Te. Many of the oxoacids of sulphur do not exist as free acids, but are known as anions and salts. Acids ending in-ous have S in the oxidation state (+IV), and form salts ending in-ite. Acids ending in-ic have S in the oxidation state (+VI) and form salts ending in -ate. The oxoanions have strong  $\pi$  bonds and so they have little tendency to polymerize compared with the phosphates and silicates. To emphasize structural similarities the acids are listed in four series.

1. sulphurous acid series.
2. sulphuric acid series.
3. thionic acid series.
4. peroxyacid series.

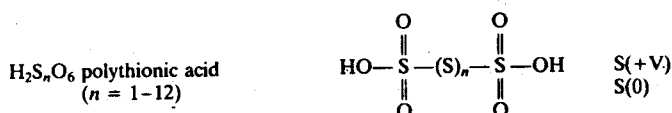
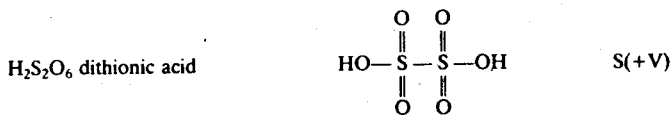
#### 1. Sulphurous acid series



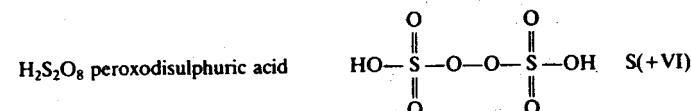
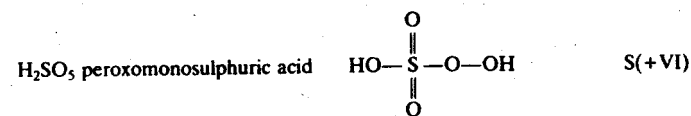
#### 2. Sulphuric acid series



#### 3. Thionic acid series



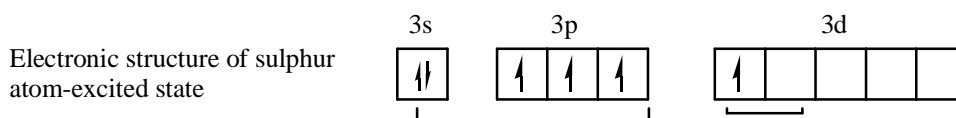
#### 4. Peroxyacid series



## 1. Sulphurous acid series

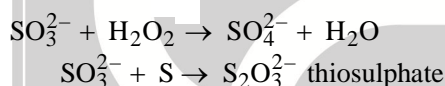
Though  $\text{SO}_2$  is very soluble in water, most is present as hydrated  $\text{SO}_2$  ( $\text{SO}_2\text{H}_2\text{O}$ ). Sulphurous acid  $\text{H}_2\text{SO}_3$  may exist in the solution in minute amounts, or not at all, though the solution is acidic. Its salts, the sulphites  $\text{SO}_3^{2-}$ , form stable crystalline solids. Many sulphites are insoluble or are sparingly soluble in water, e.g.  $\text{CaSO}_3$ ,  $\text{BaSO}_3$  or  $\text{Ag}_2\text{SO}_3$ . However, those of the Group 1 metals and ammonium are soluble in water, and in dilute solutions the hydrogen sulphite (bisulphite) ion  $\text{HSO}_3^-$  is the predominant species.

The sulphite ion exists in crystals and has a pyramidal structure that is tetrahedral with one position occupied by a lone pair. The bond angles  $\text{O—S—O}$  are slightly distorted ( $106^\circ$ ) due to the lone pair, and the bond lengths are  $1.51 \text{ \AA}$ . The  $\pi$  bond is delocalized, and hence the  $\text{S—O}$  bonds have a bond order of 1.33.

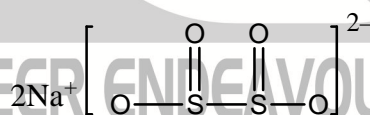
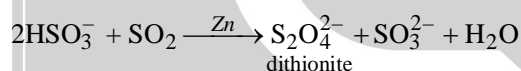


three electron form  $\sigma$ -bonds  
with three oxygen atoms  
four electron pairs,  
hence tetrahedral with one position  
occupied by a lone pair

On oxidation sulphites form sulphates and with sulphur they form thiosulphates.



Reduction of sulphite solution plus  $\text{SO}_2$  with Zn dust, or electrolytically, yields dithionites. These contain S in the oxidation state (+III).



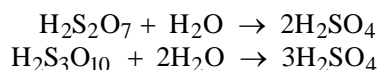
sodium dithionite

The dithionite ion has an eclipsed conformation, with a very long  $\text{S—S}$  bond ( $2.39 \text{ \AA}$ ) and  $\text{S—O}$  bond lengths of  $1.51 \text{ \AA}$ . Sodium dithionite  $\text{Na}_2\text{S}_2\text{O}_4$  crystallizes out on adding  $\text{NaCl}$  to the mixture. The parent acid does not exist.  $\text{Na}_2\text{S}_2\text{O}_4$  is a powerful reducing agent, which has a variety of industrial uses. These include bleaching paper pulp and making dyestuffs. It is used to treat water since it reduces many heavy metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Bi}^{3+}$ ) to the metal. In  $\text{NaOH}$  solution  $\text{Na}_2\text{S}_2\text{O}_4$  is used to absorb dioxygen in gas analysis. It is also used to preserve foodstuffs and fruit squashes.

## Sulphuric acid series

$\text{H}_2\text{SO}_4$  is the most important acid used in the chemical industry. By far the most important commercial process for its manufacture is the contact process, in which  $\text{SO}_2$  is oxidized by air to  $\text{SO}_3$ , using a catalytic surface. Formerly a platinum gauze or platinized asbestos was used as catalyst. This has now been replaced by vanadium pentoxide, which is slightly less efficient but is cheaper and less easily poisoned. The  $\text{SO}_3$  could be mixed with water to give  $\text{H}_2\text{SO}_4$ , but the reaction is violent and produces a dense chemical mist which is difficult to condense. Instead, the  $\text{SO}_3$  is passed into 98%  $\text{H}_2\text{SO}_4$ , forming pyrosulphuric acid  $\text{H}_2\text{S}_2\text{O}_7$ , sometimes called oleum or fuming sulphuric acid. (Some

trisulphuric acid  $\text{H}_2\text{S}_3\text{O}_{10}$  is also, formed.) This solution may be sold as oleum. or diluted with water to give concentrated sulphuric acid which is a 98% mixture with water (an 18 M solution).



Pure sulphuric acid melts at  $10.5^\circ\text{C}$ , forming a viscous liquid. It is strongly hydrogen bonded, and in the absence of water it does not react with metals to produce  $\text{H}_2$ . Many metals reduce  $\text{H}_2\text{SO}_4$  (S +VI) to  $\text{SO}_2$  (S +IV), especially if heated. If pure  $\text{H}_2\text{SO}_4$  is heated, a little  $\text{SO}_3$  is evolved, and an azeotropic mixture of 98.3%  $\text{H}_2\text{SO}_4$  and 1.7% water is produced. This boils at  $338^\circ\text{C}$ . Pure  $\text{H}_2\text{SO}_4$  is used as a non-aqueous solvent and as a sulphonating agent.

Anhydrous  $\text{H}_2\text{SO}_4$  and concentrated  $\text{H}_2\text{SO}_4$  mix with water in all proportions• and evolve a great deal of heat ( $880\text{ kJ mol}^{-1}$ ). If water is poured into concentrated acid• the heat evolved leads to boiling of the drops of water and causes violent splashing. The safe way to dilute strong acids is to carefully pour the acid into the water with stirring.

Concentrated  $\text{H}_2\text{SO}_4$  has quite strong oxidizing properties. Thus when  $\text{NaBr}$  is dissolved in concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{HBr}$  is formed but in addition some  $\text{Br}^-$  ions are oxidized to  $\text{Br}_2$ .  $\text{Cu}$  does not react with acids because it is lower than  $\text{H}$  in the electrochemical series. However, several noble metals such as  $\text{Cu}$  dissolve in concentrated  $\text{H}_2\text{SO}_4$  due to its oxidizing properties. The oxidizing properties of  $\text{SO}_4^{2-}$  convert  $\text{Cu}$  into  $\text{Cu}^{2+}$ .

Concentrated  $\text{H}_2\text{SO}_4$  absorbs water avidly. and is an effective drying agent for gases. It is sometimes used as a drying agent in desiccators. It dehydrates  $\text{HNO}_3$ , forming the nitronium ion  $\text{NO}_2^+$ , which is very important in the nitration of organic compounds.



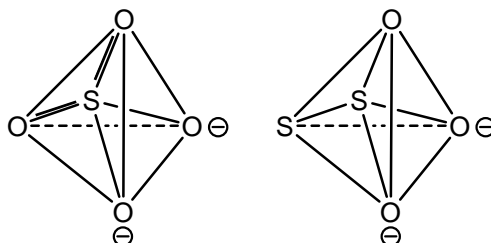
$\text{H}_2\text{SO}_4$  can also remove the elements of water, for example in the preparation of ethers.



It removes water so strongly from some organic compounds that they char, and only the carbon remains. Paper and cloth are completely destroyed.

In dilute aqueous solution  $\text{H}_2\text{SO}_4$  acts as a strong acid. The first proton dissociates very readily, and hence hydrogen sulphates  $\text{HSO}_4^-$  formed. The second proton dissociates much less readily, to form sulphates  $\text{SO}_4^{2-}$ . Because of this, solutions of hydrogen sulphates are acidic.

The thiosulphate ion is structurally similar to the sulphate ion.



**Figure:** Structure of sulphate and thiosulphate ions

Hydrated sodium thiosulphate  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  is called hypo. It forms very large colourless hexagonal crystals, m.p.  $48^\circ\text{C}$ . It is readily soluble in water and solutions are used for iodine titrations in volumetric analysis. Iodine very rapidly oxidizes thiosulphate ions  $\text{S}_2\text{O}_3^{2-}$  to tetrathionate ions  $\text{S}_4\text{O}_6^{2-}$  and the  $\text{I}_2$  is reduced to  $\text{I}^-$  ions.