CHALCOGENS Section - 2

Group 16

Ionization Enthalpy

The first ionization enthalpies of the elemetnts of group 16 are unexpectedly lower than those of corresponding elements of group 15 despite their smaller atomic radii and higher nuclear charge.

Normally as the atomic radii decreases or nuclear charge increases along a period, the ionization enthalpy is expected to increase. But the ionization enthalpy of these elements is smaller than those of group 15 elements. This is due to the relatively symmetrical and stable electronic configuration of the elements of group 15 as compared to the elements of group 16 (oxygen family). e.g.

Group 15 element

$N(Z=7)\ 1s^2\ 2s^2\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$ (more symmetrical, stable)

Group 16 element

$O(Z=8)\ 1s^2\ 2s^2\ 2p_x^{\ 2}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$ (less symmetrical, less stable)

Therefore, first ionization enthalpy values of elements of oxygen family are smaller.

Metallic Character

Because of high ionization enthalpy values, the elements of group 16 are less metallic. However, as we move down the group, the ionization enthalpy decreases and hence the metallic character increases.

Electronegativity

The elements of group 16 have higher values of electronegativity than the corresponding elements of group 15. Oxygen is the second most electronegative element, the first being fluorine.

Bonding

Oxygen can form strong pπ-pπ double bonds. The double bonds formed by other elements becomes weaker as the atomic number increases. Thus CO_2 is stable, CS_2 is less stable, CSe_2 polymerises and CTe_2 is unknown.

S, Se, Te, Po can even form 4 or 6 bonds unlike oxygen due to the presence of d-orbitals. S forms strong dπ-pπ bond with O due to its small sized d-orbital which is similar to the p-orbital of O in size.

Hydrogen bonding is important for oxygen compounds.

Hydrides

$$\underbrace{H_2O}_{\text{liquid}},\quad \underbrace{H_2S,\ H_2Se,\ H_2Te,\ H_2Po}_{\text{colourless toxic gases with foul smell.}}$$

As we go down the group, Δ_fH of hydrides becomes more positive and bonding orbitals diffuse on becoming larger. This decreases stability and thus increases acidity down the group.

H_2S, H_2Se, H_2Te use almost pure p-orbitals for bonding as is indicated by their H-E-H bond angles which are close to 90°.

The boiling points usually increase as the atoms become larger and heavier but boiling point of H_2O is abnormally high due to extensive hydrogen bonding in solid and liquid state. Thus the order is :

$$H_2O >> H_2Te > H_2Se > H_2S.$$

Halides

Elements of this group form dihalides, tetrahalides and hexahalides. Among hexahalides only hexafluorides are stable.

- SF_4 is a powerful fluorinating agent.
- SCl_2 is a foul smelling red liquid. It forms poisonous 'mustard gas' which is NOT a gas but a volatile liquid.

$$\underset{\text{ethene}}{2CH_2 = CH_2} + SCl_2 \longrightarrow \underset{\substack{\text{Bis (2-Chloroethyl) sulphide} \\ \text{(Mustard gas)}}}{S(CH_2CH_2Cl)_2}$$

Oxygen and its Compounds

Preparation :

O_2 is a colourless, odourless and tasteless gas which is partially soluble in water. Liquid dioxygen is pale blue in colour and the solid is also blue. It is paramagnetic due to presence of unpaired electrons.

1. It is prepared industrially by the electrolysis of acidic or alkaline H_2O or by *Claud's Process* (fractional distillation of liquid air)

2. In laboratory it is prepared from thermal decomposition of $KClO_3$ or $Pb(NO_3)_2$.

$$2KClO_3 \xrightarrow[\text{heat}]{MnO_2} 2KCl + 3O_2 + \text{traces of } Cl_2, ClO_2$$

$$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + NO_2 + O_2$$

3. It can also be made by catalytic decomposition of hypochlorites :

$$2HOCl \xrightarrow[\text{catalyst}]{Co^{2+}} HCl + O_2 \uparrow$$

$$\underset{\text{bleaching powder}}{CaOCl_2} \xrightarrow{\Delta} CaCl_2 + O_2 \uparrow$$

Uses :

Most of the O_2 is used in the steel making industry. Some of it is used in oxy-acetylene welding and as an oxidant in rockets. It is an essential constituent of life.

[a] Oxides and their general properties

Dioxygen reacts with practically all elements to form oxides. The reactions are usually exothermic and once started often continue spontaneously.

Classification of oxides according to geometric structure :

Oxides (M_xO_y)

Normal oxides	Peroxides	Superoxides	Suboxides	Sesquioxides
They contain O(–II) and only M–O bonds are present. e.g. H_2O, MgO, Al_2O_3	They contain the peroxide ion O_2^{2-}. e.g. Na_2O_2, BaO_2 Others are covalent and contain – O – O – e.g. H_2O_2	They contain O_2^- ion. e.g. KO_2	They contain less oxygen than expected and have M–M bonds e.g. O = C = C = C = O (C_3O_2)	Any oxide containing three oxygen atom for every two atoms of another elements. e.g. B_2O_3, N_2O_3

Classification of oxides according to acid-base properties :

Oxides (M_xO_y)

Basic	Amphoteric	Acidic	Neutral
They form basic solutions in water. e.g. most metallic oxides like Na_2O, MgO	They react both with strong acids and bases. e.g. Al_2O_3, Cr_2O_3, BeO, SnO, PbO, ZnO	They are anhydrides of acids and react with only bases. e.g. most non-metallic oxides like CO_2, NO_2, SO_2, SiO_2, Cl_2O, B_2O_3	They have no acidic or basic properties. e.g. N_2O, NO, CO

- If an element exists in several oxidation states then generally lower ones are basic and higher ones are acidic

$$\underbrace{N_2O,\ NO}_{\text{neutral}},\ \underbrace{N_2O_3,\ NO_2,\ N_2O_5}_{\text{acidic}}$$

$$\underbrace{CrO}_{\text{basic}},\ \underbrace{Cr_2O_3}_{\text{amphoteric}},\ \underbrace{CrO_3}_{\text{acidic}}$$

$$\underbrace{PbO}_{\text{more basic}},\ \underbrace{PbO_2}_{\text{less basic}}$$

- The order of acidic strength of oxides can be obtained as follows :

$$K_2O,\ CaO,\ MgO,\ CuO,\ H_2O,\ SiO_2,\ CO_2,\ N_2O_5,\ SO_3$$

$$\xleftrightarrow{\hspace{6cm}}$$

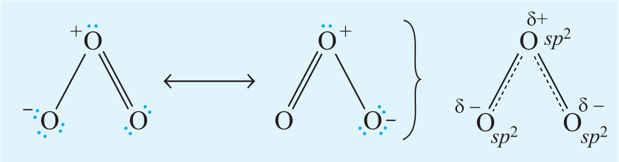
most basic most acidic

The further apart two oxides are in the series, the more stable the compound formed when they react together.

Example : $CaO + H_2O + SO_3 \longrightarrow$ more stable $CaSO_4$ ($CaO\,.\,SO_3$)

[b] Ozone O_3

O_3 is an unstable, dark blue diamagnetic toxic gas. The colour is due to intense absorption of red light. It also absorbs strongly in the UV region.



For each O atom, of the three sp^2 orbitals two are occupied by two lone pairs and one forms σ-bond. The remaining 4 electrons form π-bonds. The π system is thus a $4e^-$ 3 centre bond.

Bond order = 1.5 for O – O bonds.

Preparation :

O_3 is prepared by the action of a silent electric discharge upon dioxygen in an ozoniser.

$$3O_3 \xrightarrow[\text{discharge}]{\text{silent electric}} 2O_3\ (10\%) \xrightarrow{\text{fractional distillation}} O_3\,(\text{pure}) \qquad \Delta H > 0\ (\text{endothermic})$$

Silent electric discharge is used because sparking can generate heat and decompose O_3.

Chemical Properties :

1. O_3 turns starch iodide paper blue.
2. The amounts of O_3 in a gas mixture is determined by passing gas into KI solution buffered with a borate buffer (pH 9.2)

   Iodine liberated is titrated with sodium thiosulphate.

   $$O_3 + 2K^+ + 2I^- + H_2O \longrightarrow I_2 + KOH + O_2$$

   Alternatively, it is decomposed catalytically and the change in volume measured.

   $$\underset{\text{2 volumes}}{2O_3} \longrightarrow \underset{\text{3 volumes}}{3O_2}$$

3. Hg in the presence of ozone is oxidised to sub-oxide and starts sticking to glass and loses its meniscus. This is used as a test for ozone called 'Tailing of Mercury'
4. O_3 is an extremely powerful oxidising agent, second only to F_2.

   $$3PbS + 4O_3 \longrightarrow 3PbSO_4$$

   $$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

   $$2KOH + 5O_3 \longrightarrow \underset{\substack{\text{Potassium}\\ \text{ozonide}\\ \text{(Orange solid)}}}{2KO_3} + 5O_2 + H_2$$

5. O_3 reduces peroxides

$$O_3 + BaO_2 \longrightarrow BaO + 2O_2$$

$$O_3 + H_2O_2 \longrightarrow H_2O + 2O_2$$

Uses :

It is used as a disinfectant for water. Its advantage over chlorine is that it avoids unpleasant smell and taste of chlorine, since any excess O_3 decomposes to O_2.

[c] Hydrogen Peroxide H_2O_2 :

Pure H_2O_2 is a colourless liquid (like water), more hydrogen bonded than water (and thus has highest boiling point)

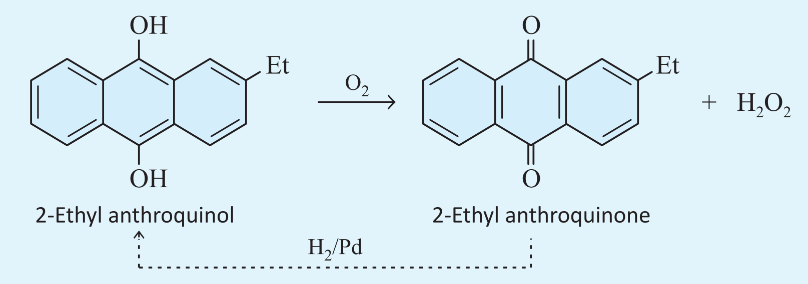
Preparation :

1. At one time H_2O_2 was obtained by electrolysis of H_2SO_4 or $(NH_4)_2SO_4$ using high current density.

$$2SO_4{}^{2-} \xrightarrow{\text{electrolysis}} S_2O_8{}^{2-} + 2e^-$$

$$\underset{\text{Peroxodisulphuric acid}}{H_2S_2O_8} + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

2. Now, it is produced industrially by a cyclic process.



H_2O_2 is extracted with water as 1% solution which is concentrated to 30% solution.

3. In laboratory :

$$Na_2O_2 + \underset{\text{(dil, cold)}}{H_2SO_4} \longrightarrow Na_2SO_4 + H_2O_2 \xrightarrow{\text{cool}} Na_2SO_4\,.10H_2O_2 \text{ crystals}$$

OR $BaO_2 + CO_2 + H_2O \longrightarrow BaCO_3\downarrow + H_2O_2$ (Merck's Process)

Chemical Properties :

1. H_2O_2 decomposes in presence of impurities like Fe^{2+}, Fe^{3+}, Ni^{2+}, Pt. to undergoes a disproportionation reaction :

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Glycerol or acetanilide is added to check its decomposition.

2. In most of its reactions H_2O_2 acts as a strong oxidising agent (slow in acidic medium while fast in alkaline).

$$H_2O_2 + 2Fe^{2+} \longrightarrow 2Fe^{3+} + 2H_2O$$

$$H_2O_2 + 2\,\underset{\text{Ferrocyanide}}{[Fe(CN)_6]^{4-}} \longrightarrow \underset{\text{Ferricyanide}}{2[Fe(CN)_6]^{3-}} + 2OH^-$$

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

$$\left[\begin{array}{l} 4\,H_2O_2 + Cr_2O_7^{2-} + 2\,H^+ \longrightarrow \underset{\substack{\text{Chromium peroxide}\\ \text{(blue)}}}{2\,CrO_5} + 5\,H_2O \\ 4\,CrO_5 + 12\,H^+ \longrightarrow 4\,Cr^{3+} + 6\,H_2O + 7\,O_2\uparrow \end{array}\right.$$

3. H_2O_2 is forced to act as a reducing agent with stronger oxidising agents and O_2 is evolved.

$$5H_2O_2 + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2\uparrow$$

$$H_2O_2 + KIO_4 \longrightarrow KIO_3 + H_2O + O_2\uparrow$$

H_2O_2 is useful to counteract chlorine :

$$H_2O_2 + Cl_2 \longrightarrow 2HCl + O_2$$

4. H_2O_2 is a mild bleaching agent for hair feathers due to the oxidation reaction :

$$H_2O_2 \longrightarrow H_2O + [O]$$

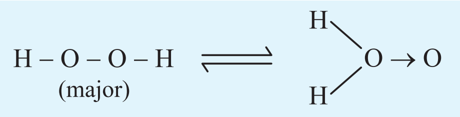
5. **Qualitative Analysis :** It is detected qualitatively by its action on KI.

$$KI \xrightarrow{H_2O_2} I_2 \xrightarrow{\text{starch}} \text{blue}$$

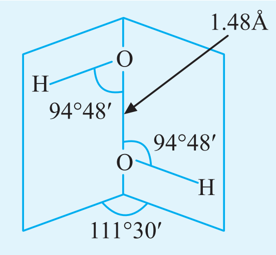
It also forms blue CrO_5 with $Cr_2O_7^{2-}/H^+$ and decolourises $KMnO_4$.

Structure :

It is proposed H_2O_2 is a tautomeric mixture of two forms :



It shows restricted rotation about O – O bond due to repulsion between two H's. The structure is same in liquid and gaseous forms but angles and bond lengths change due to hydrogen bonding.



Structure of H_2O_2 in the gas phase.

Sulphur and its Compounds

Allotropy :

Sulphur has the maximum number of allotropic structures. The two common crystalline forms are :

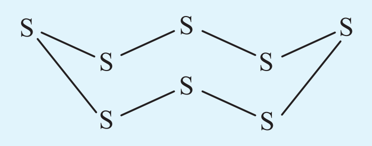
(i) α-Rhombic sulphur :

It is a yellow solid stable at room temperature, m.p. 112.8°C and specific gravity 2.06 g/cc.

(ii) β-Monoclinic sulphur :

It is a colourless solid stable above 95.5°C, mp 120°C and specific gravity 1.98 g/cc.

Note : $\alpha\text{-sulphur} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \beta\text{-sulphur}$.



At 95.5°C (transition temperature both forms are stable).

Both α and β forms contain puckered S_8 rings in crown conformation.

Other allotropic forms are :

(iii) Engels sulphur (Σ-sulphur) :

It is unstable and has S_6 rings in chair conformation.

$$Na_2S_2O_3 + \text{conc. HCl} \xrightarrow{\text{Toluene}} S$$

(iv) Plastic sulphur (χ-sulphur) :

It is elastic, dark coloured and obtained by pouring liquid sulphur into water. It can be moulded with fingers.

(v) Colloidal sulphur :

It is prepared by passing H_2S gas into an oxidising solution like HNO_3, $FeCl_3$, ...

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

Note : α, β, Σ - sulphur are soluble in CS_2 and insoluble in water while χ - sulphur is insoluble in both CS_2 and water.

Extraction :

Sulphur is obtained from natural gas plants (which contain H_2S) and from metal sulphide ores (especially iron pyrites FeS_2) which produce SO_2.

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

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

Uses :

Almost 90% of S produced is used to manufacture H_2SO_4. The rest is used in vulcanizing of rubber, making fungicides, gunpowder etc.

[a] Hydrogen sulphide H_2S (Sulphuretted Hydrogen)

It is a colourless, poisonous gas, soluble in H_2O and smells of rotten eggs.

Preparation :

It is easier to make H_2S by the action of mineral acids on metal sulphides.

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

$$Sb_2S_3 + 6HCl \longrightarrow 2SbCl_3 + \underset{\text{pure}}{3H_2S}\uparrow$$

Chemical Properties :

1. It burns with blue flame.

$$2H_2S + \underset{\text{excess}}{O_2} \longrightarrow 2H_2O + 2SO_2$$

A saturated solution of H_2S is slowly oxidised by air and sulphur is deposited.

$$2H_2S + O_2\,(\text{limited}) \longrightarrow 2H_2O + 2S$$

2. It is a very weak dibasic acid.

$$H_2S + NaOH \longrightarrow NaHS + H_2O \quad ; \quad NaHS + NaOH \longrightarrow Na_2S + H_2O$$

The two salts NaHS, Na_2S are basic and soluble in water.

3. $$H_2S + \underset{\text{dil solution}}{NH_3} \longrightarrow (NH_4)\,HS\ (\textit{not}\ (NH_4)_2S)$$

Yellow ammonium sulphide is a mixture of ammonium polysulphides and is made by dissolving sulphur in colourless $(NH_4)HS/NH_3$ solution. This solution is used to precipitate metal sulphides in qualitative analysis.

4. H_2S is a reducing agent and reduces Cl_2 to Cl^-, H_2SO_4 to SO_2, $FeCl_3$ to $FeCl_2$ and itself gets oxidised to S.

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

$$H_2S + H_2SO_4 \longrightarrow SO_2 + 2H_2O + S$$

$$H_2S + 2FeCl_3 \longrightarrow 2FeCl_2 + 2HCl + S$$

[b] Sulphur Dioxide SO_2

It is a colourless poisonous gas with a choking smell. It is highly soluble in water and almost completely present as $SO_2 . 6\,H_2O$ in water and only 1% as H_2SO_3. Liquid SO_2 has also been used as a non-aqueous solvent.

Preparation :

1. It is prepared by burning S or H_2S in air.

$$S + O_2 \longrightarrow SO_2$$

$$2H_2S + \underset{\text{excess}}{3O_2} \longrightarrow 2SO_2 + 2H_2O$$

2. It is also prepared by roasting various metal sulphides in smelters.

$$2ZnS + O_2 \longrightarrow 2ZnO + 2SO_2$$

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

Chemical Properties :

1. Most of SO_2 is oxidized to SO_3 by the contact process and used to manufacture H_2SO_4.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3 \qquad \Delta_r H^{\ominus} = -196.6 \text{ kJ/mol}$$

2. Bleaching action :

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

Bleaching by SO_2 is temporary as reduced colour is reoxidised by air to give black coloured matter.

Also, H_2SO_4 produced during bleaching may be harmful to fibres.

$$\underset{\text{coloured}}{X-OH} + SO_2 \longrightarrow \underset{\text{colourless}}{XHSO_3} \xrightarrow{HCl} XCl \xrightarrow[-HCl]{H_2O} \underset{\text{coloured}}{XOH}$$

Cl_2 although has a permanent effect as it produces [O].

3. It shows reducing properties in presence of moisture.

$$SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

$$5SO_2 + 2KIO_3 + 4H_2O \longrightarrow K_2SO_4 + 4H_2SO_4 + I_2$$

Although with stronger reducing agents it acts as an oxidising agent.

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

$$3Fe + SO_2 \longrightarrow 2FeO + FeS$$

Detection of SO_2 :

It may be detected in three ways in the laboratory :

1. By its choking smell
2. It turns filter paper moistened with $K_2Cr_2O_7/H^+$ green.

$$\underset{\text{orange}}{K_2Cr_2O_7} + 3SO_2 + H_2SO_4 \longrightarrow \underset{\text{green}}{Cr_2(SO_4)_3} + K_2SO_4 + H_2O$$

3. It turns starch iodate paper blue.

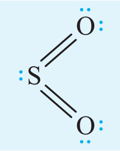
$$2KIO_3 + 5SO_2 + H_2O \longrightarrow \underset{\substack{\text{turns starch}\\\text{blue}}}{I_2} + 2KHSO_4 + 3H_2SO_4$$

Quantitative Analysis :

SO_2 is determined quantitatively by first converting to H_2SO_4 and then determining H_2SO_4 by titration or conductimetric titration.

$$SO_2 + H_2O_2 \longrightarrow H_2SO_4$$

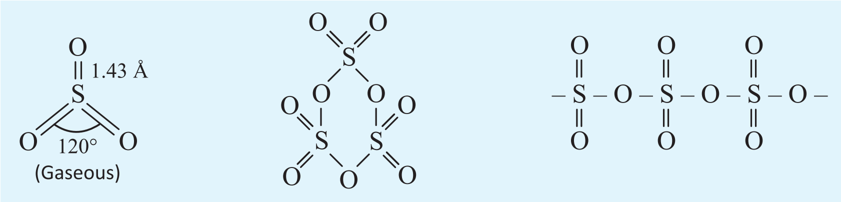
Structure :



$3d_{z^2}$ orbital of S cannot be used to form π bond as its symmetry is wrong. Instead $3d_{xz}$ orbital on S is used to make the second π bond with $2p_z$ orbital on the second O atom. Although, it is surprising that both π bonds have the same energy.

[c] Sulphur Trioxide SO_3

It is the anhydride of H_2SO_4 and is solid at room temperature. It has three forms :



In gaseous state, SO_3 has a planar triangular structure involving sp^2 hybrid sulphur atom. The lone pair of sulphur atom forms coordinate bond (σ). Therefore, bond angle is exactly 120°. Solid SO_3 possesses either cyclic trimer (α–*form*) or infinite helical chains (β - *form*).

Note : Of the three forms : α-SO_3 is most stable.

$$\alpha - SO_3 \xrightarrow{<25\,°C} \beta - SO_3 \xrightarrow{\text{dry}} \gamma - SO_3$$

Preparation :

1. It is manufactured on a huge scale by the Contact Process. Practically all of it is converted to H_2SO_4 in the same process :

$$2SO_2 + O_2 \xrightarrow{Pt\,/\,V_2O_5} 2SO_3$$

2. $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$

Chemical Properties :

1. $2SO_3 \xrightarrow{1000°C} 2SO_2 + O_2$

2. $\underset{\text{vapour}}{SO_3 + H_2O} \longrightarrow \underset{\text{dense mist}}{H_2SO_4}$

It is used to prepare oleum (mainly pyrosulphuric acid $H_2S_2O_7$)

$$SO_3(g) + \underset{98\%}{H_2SO_4} \longrightarrow \underset{\text{oleum/ fuming sulphuric acid}}{H_2S_2O_7}$$

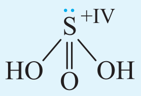
3. SO_3 is used to make sulphamic acid NH_2SO_3H (the only strong acid that can exist as a solid at room temperature).

$$\underset{\text{Urea}}{NH_2CONH_2} + SO_3 + H_2SO_4 \longrightarrow \underset{\text{Sulphamic acid}}{2\,NH_2SO_3H} + CO_2$$

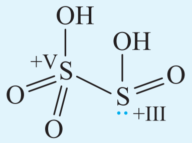
[d] Oxo Acids of Sulphur :

Oxo - acids of sulphur ending in - ous have S in the oxidation state (+IV) and form salts ending in - ite. Acid ending in –ic have S in the oxidation state (+VI) and form salts ending in -ate. Four main series exist which are :

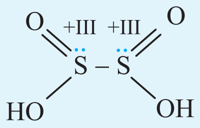
I Sulphurous Acid Series :



Sulphurous acid H_2SO_3



Disulphurous
(Pyrosulphurous) acid $H_2S_2O_5$



Dithionous acid $H_2S_2O_4$

The most important acid in this series is sulphurous acid (H_2SO_3) :

Preparation :

It is only known in solution (like carbonic acid) and as discussed SO_2 solution in water gives 1% H_2SO_3.

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

Chemical Properties of SO_3^{2-} ion :

1. H_2SO_3 being dibasic forms salt of bisulphites (HSO_3^-) and sulphites (SO_3^{2-}). HSO_3^- however undergoes internal dehydration to form $S_2O_5^{2-}$ ion.

$$2HSO_3^- \overset{\text{heat}}{\rightleftharpoons} \underset{\text{disulphite}}{S_2O_5^{2-}} + H_2O$$

2. S(+ IV) in SO_3^- and HSO_3^- is a moderately strong reducing agent and forms sulphates on oxidation.

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

$$H_2SO_3 + H_2O + 2FeCl_3 \longrightarrow H_2SO_4 + 2FeCl_2 + 2KCl$$

while with sulphur, sulphites form thiosulphates :

$$SO_3^{2-} + S \xrightarrow{OH^-} \underset{\text{thiosulphate}}{S_2O_3^{2-}}$$

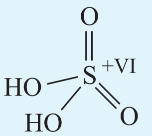
Sulphites and hydrogen sulphites liberates SO_2 on treatment with dilute acids

$$SO_3^{2-} \text{ (or } HSO_3^-) \xrightarrow{H^+ \text{(dil)}} SO_2 \uparrow$$

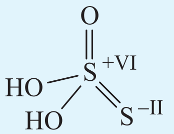
3. SO_3^{2-} acts as an oxidising agent with a strong RA like H_2S.

$$SO_3^{2-} + 2S^{2-} + 6H^+ \longrightarrow 3S\downarrow + 3H_2O$$

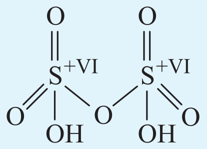
II Sulphuric Acid Series :



Sulphuric acid
H_2SO_4



Thiosulphuric acid
$H_2S_2O_3$



Pyrosulphuric acid (oleum)
$H_2S_2O_7$

(i) Sulphuric acid [oil of Vitriol] H_2SO_4 :

H_2SO_4 is the most important acid used in the chemical industry. It is a colourless syrupy liquid with boiling point 338°C and freezes into crystals at 10.5°C. It is strongly hydrogen bonded.

Preparation

1. In ancient days it was prepared from ferrous sulphate (Green vitriol) and hence called Oil of Vitriol.

$$\underset{\text{green vitriol}}{2(FeSO_4 . 7H_2O)} \xrightarrow{\text{heat}} Fe_2O_3 + SO_2 + 13H_2O + \underset{\text{(oil of vitriol)}}{H_2SO_4}$$

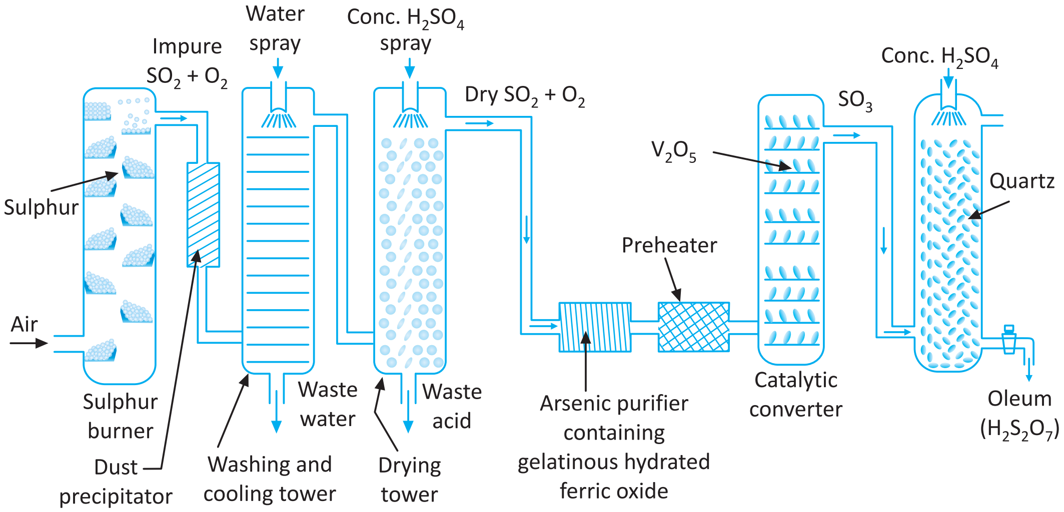
2. Lead Chamber Process

Was used to manufacture H_2SO_4 industrially but the process is now obsolete as it only produced 78% H_2SO_4. NO_2 is used as a homogeneous catalyst to oxidise SO_2 in the presence of water. NO produced combines with air to produce NO_2 which is reused. Thus, NO and NO_2 act as oxygen carriers

$$\begin{tikzcd}
NO_2 + SO_2 + H_2O \arrow[r] & H_2SO_4 + NO \arrow[d] \arrow[r] & +\frac{1}{2}O_2 \\
 & NO_2 \arrow[ul, dotted]
\end{tikzcd}$$

3. Contact Process :

It is the most important and widely used commercial process for the manufacture of H_2SO_4.



Flow diagram for the manufacture of sulphuric acid

(i) SO_2 is first collected from burning of sulphur or sulphide ores.

(ii) SO_2 is then oxidised.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The forward reaction is exothermic and is favoured by low temperature, high pressure and excess of oxygen. A catalyst (activated V_2O_5) is used to obtain a reasonable conversion. Earlier Pt gauze was used but due to high costs and its susceptibility to poisoning it has been replaced by V_2O_5.

(iii) SO_3 is then passed into 98% H_2SO_4 forming pyrosulphuric acid ($H_2S_2O_7$) called oleum. Dilution of oleum with water gives concentrated H_2SO_4 (98%).

Chemical Properties :

1. H_2SO_4 due to its low volatility is used to manufacture more volatile acids.

$$2MX + H_2SO_4 \longrightarrow 2HX + H_2SO_4$$

(M = metal ; X = F, Cl, NO_3)

2. H_2SO_4 is a powerful dehydrating agent especially for gases.

It dehydrates HNO_3 forming NO_2^+

$$2H_2SO_4 + HNO_3 \longrightarrow \underset{\text{Nitronium ion}}{NO_2^+} + H_3O^+ + 2HSO_4^-$$

It removes elements of water from organic compounds.

$$2EtOH + H_2SO_4 \longrightarrow Et-O-Et + H_2SO_4 . H_2O$$

$$(COOH)_2 + H_2SO_4 \longrightarrow CO + CO_2 + H_2SO_4 . H_2O$$

Note : H_2SO_4 mixes with water to evolve large amount of heat. If water is poured into concentrated acid, the heat evolved causes violent splashing. Thus to dilute strong acids like H_2SO_4, acid is poured into water while stirring (not water into acid).

3. H_2SO_4 is a quite strong oxidising agent.

$$\text{conc. } H_2SO_4 + Br^- \longrightarrow SO_2 + Br_2 + H_2O$$

$$2\text{conc. } H_2SO_4 + Cu \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$2\text{conc. } H_2SO_4 + C \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

4. Pure H_2SO_4 is a non-aqueous solvent and a sulphonating agent.

$$C_6H_6 + HO . SO_3H \longrightarrow \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_2OH} + H_2O$$

Uses :

1. The largest used is in making superphosphate fertilizer.

2. It is used in *Pickling* (removal of oxides from the surfaces of metals like Fe, Cu before electroplating or galvanising.

3. It is used as a dehydrating agent, oxidising agent and as strong acid.

(ii) Thiosulphuric acid $H_2S_2O_3$:

The free acid is unstable and decomposes in water into a mixture of S, H_2S, SO_2 and H_2SO_4 while the salts (thiosulphates) are stable. It forms large colourless hexagonal crystals, highly soluble in water. The most important thiosulphate is sodium thiosulphate ($Na_2S_2O_3 . 5H_2O$) also called hypo.

Preparation :

$$\underset{\text{Neutral/alkaline}}{SO_3^{2-} + S} \xrightarrow{\text{boiling}} S_2O_3^{2-}$$

Chemical Properties :

1. Hypo solutions are used for iodine titrations in volumetric analysis.

$$2\,Na_2S_2O_3 + I_2 \longrightarrow \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + 2\,NaI$$

In iodometric estimation O.A.'s like $CuSO_4$, $K_2Cr_2O_7$ are treated with KI which liberates I_2 which is determined by hypo as above.

$$2CuSO_4 + 4KI \longrightarrow 2K_2SO_4 + Cu_2I_2 + I_2$$

2. $Na_2S_2O_3$ is used to destroy excess Cl_2 on fabrics after they have been bleached and called as antichlor.

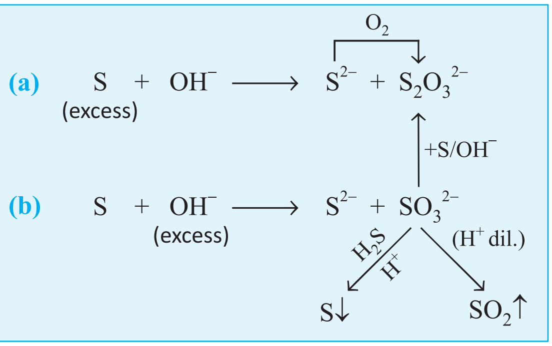
$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2\,NaHSO_4 + 8\,HCl$$

This is also used to remove the taste from heavily chlorinated drinking water.

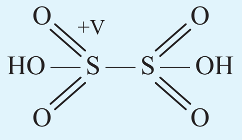
3. Hypo is used in photography for 'fixing' films and prints. It dissolves unreacted $AgNO_3$, AgBr salts.

$$Na_2S_2O_3 + AgBr \longrightarrow Ag_2S_2O_3 \downarrow \xrightarrow{+Na_2S_2O_3} \text{soluble complexes } Na_3\,[Ag\,(S_2O_3)_2]$$

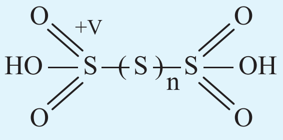
Note :



(III) Thionic Acid Series :



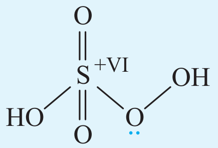
Dithionic acid
$H_2S_2O_6$



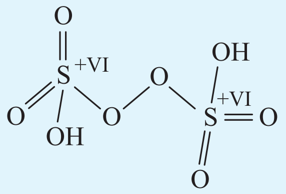
Polythionic acid
$H_2S_nO_6$

(IV) Peroxo Acid Series

They contain the peroxo linkage – O – O– .



Peroxo monosulphuric acid
(Caro's Acid) H_2SO_5



Peroxo disulphuric acid $H_2S_2O_8$
(Marshell's Acid)

IN-CHAPTER EXERCISE-B

1. *Write equations for :*

(a) *preparation of oxygen from :* (i) $KClO_3$ (ii) *Ozone* (iii) $Pb(NO_3)_2$

(b) *reaction of* H_2O_2 *with* (i) *acidified solution of* $KMnO_4$ (ii) *aqueous HI.*

2. *State reasons for the following statements*

(a) *Statues coated with white lead on long exposure to atmosphere turn black and the original colour can be restored on treatment with* H_2O_2.

(b) *Presence of water is avoided in the preparation of* H_2O_2 *from* Na_2O_2.

(c) *Hydrogen peroxide acts as an oxidizing as well as a reducing agent.*

(d) *Ozone destroys mercury meniscus.*

(e) *A white turbidity is obtained by passing* H_2S *in aqueous solution of* SO_2.

(f) *Conc.* H_2SO_4 *can't be used for drying up* H_2S *and* NH_3.

(g) *Liquid oxygen sticks to the poles of a magnet but liquid nitrogen does not.*

(h) SF_{6-} *is known but* OF_6 *is not.*

3. *Describe the differences in structure between gaseous and solid* SO_3.

4. *Which of nitric acid and sulphuric acid is the stronger Bronsted acid, i.e., which donates proton to the other ?*

5. *How are the following gases detected ?*

(a) O_2 **(b)** O_3 **(c)** H_2S **(d)** SO_2

Choose the correct alternative. Only One choice is correct.

6. *Hydrolysis of one mole of peroxodisulphuric acid produces ?*

(A) *two moles of sulphuric acid*
(B) *two moles of peroxomonosulphuric acid*
(C) *one mole of sulphuric acid and one mole of peroxomonosulphuric acid*
(D) *one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide*

7. *Which of the following will not be oxidised by* O_3 ?

(A) *KI* **(B)** $KMnO_4$ **(C)** K_2MnO_4 **(D)** $FeSO_4$

8. *Sodium thiosulphate is prepared by :*

(A) *reducing* Na_2SO_4 *solution with* H_2S
(B) *boiling* Na_2SO_3 *solution with S in alkaline medium*
(C) *neutralising* $H_2S_2O_3$ *solution with NaOH*
(D) *boiling* Na_2SO_3 *solution with S in acidic medium*

9. *Glucose on fermentation produces :*

(A) CH_3OH **(B)** CO_2 **(C)** *CO* **(D)** H_2O