12 NITROGEN AND SULFUR

Student Learning Outcomes [C-11-B-30 to C-11-B-41]

After studying this chapter, students will be able to:

- Explain the lack of reactivity of nitrogen due to its triple bond strength and lack of polarity. **(Understanding)**
- Describe the basicity of ammonia using the Bronsted-Lowery theory. **(Understanding)**
- Identify the structure of the ammonium ion and explain how it is formed by an acid-base reaction. **(Understanding)**
- Describe how ammonia can be displaced from ammonium salts through an acid-base reaction. **(Understanding)**
- Describe natural and man-made occurrences of oxides of nitrogen and their catalytic removal from exhaust gases of internal combustion gases. **(Understanding)**
- Explain the role of NO and NO_2 in the formation of photochemical smog, specifically in the reaction with unburned hydrocarbons to form peroxyacetyl nitrate (PAN). **(Understanding)**
- Differentiate between nitrification and de-nitrification. **(Knowledge)**
- Explain the lack of reactivity of sulfur, with reference to its bonding and stability of its compounds. **(Understanding)**
- Describe the different oxidation states of sulfur and their relative stability. **(Understanding)**
- Describe the properties and uses of sulfuric acid, including its production and industrial applications. **(Understanding)**
- Describe the chemical reactions and processes involving sulfur, such as combustion and oxidation. **(Understanding)**
- Explain the uses of sulfur compounds in industry and everyday life, such as in fertilizers, gunpowder, and rubber, and in synthetic organic chemistry, including the synthesis of dyes, drugs, and fragrances. **(Understanding)**

NITROGEN

Nitrogen belongs to group 15 of the periodic table. In industrial processes, nitrogen is typically obtained by cooling air until it becomes a liquid. Liquid nitrogen is commonly used for rapid cooling purposes. In laboratory settings, nitrogen can be generated by slowly heating a solution of ammonium nitrite.

$$NH_4NO_{2(aq)} \xrightarrow{\Delta} N_{2(g)} + 2H_2O_{(\ell)}$$

Table 12.1 Physical properties of nitrogen

Atomic number	7	Ionic radius (3-)	171 pm
Relative atomic mass	14.007 u	1st Ionization energy	1402 kJ/mol
Physical appearance	Colourless Gas	Electronegativity	3.0
Electronic configuration	[He] $2s^2\ 2p^3$	Electron affinity	-7.0 kJ/mol
Melting point	-210 °C	Density	1.25 kg/m^3
Boiling point	-195.8 °C	Principal oxidation states	3+ and 5+
Covalent radius	74 pm		

12.1 REACTIVITY OF NITROGEN (N_2)

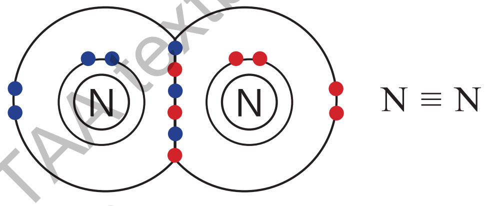


Figure 12.1 Bonding in N_2 molecule

Nitrogen is a significant component of the air, known for its low reactivity due to its small size, symmetrical electronic cloud, and nonpolar triple bond. With an electronic configuration of $1s^2\ 2s^2\ 2p^3$, nitrogen requires three electrons to complete its octet, forming a triple bond by sharing three electrons with another nitrogen atom as shown in **Figure 12.1**. This bond has a bond enthalpy of +944 $kJmol^{-1}$. High energy is required to break this bond to form new bonds, making N_2 very unreactive. The second reason for its lack of reactivity is the non-polarity of its bond. Both the atoms are the same having zero electronegativity difference. This causes equal sharing of the three bonded electrons between the two atoms making the bond nonpolar.

Interesting Information!

The high concentration of nitrogen in the air serves to dilute oxygen, preventing every spark in our atmosphere from igniting a massive fire. In the case of large shipments of hydrocarbons or edible oils, it is crucial to utilize blankets of Nitrogen or any other inert gas on ships to safeguard them from oxygen and moisture. It is also used in laboratory to carry out the reactions which require inert atmosphere.

12.2 AMMONIA (NH_3)

Ammonia (NH_3) is an important industrial compound of nitrogen, which is mainly used as a fertilizer. It is prepared industrially by Haber-Bosch process.

$$N_{2(g)} + 3H_{2(g)} \overset{\Delta}{\rightleftharpoons} 2NH_{3(g)}$$

12.2.1 Basicity of Ammonia

Ammonia behaves as a Lowry-Brønsted base by accepting a proton (H^+) from an acid to form ammonium:

$$NH_{3(aq)} + H^{1+}_{(aq)} \rightleftharpoons NH_4{}^{1+}{}_{(aq)}$$

It dissolves in water to form ammonium hydroxide (NH_4OH) and equilibrium is established between ammonia molecules and ammonium ions in the solution.

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH^{1+}_{4(aq)} + OH^{1-}_{(aq)} \qquad K_b = 1.8\times10^{-5}$$

Ammonia solution is a weak base due to the low basicity constant (K_b) and the equilibrium position being towards the far left side.

12.2.2 Structure of Ammonium (NH_4^{1+})

Ammonia molecule has pyramidal shape due to lone pair of nitrogen. But when nitrogen atom in ammonia utilizes its lone pair of electrons to form ammonium, this ion adopts a tetrahedral shape in which all the bonds are of equal length and strength, as depicted in **Figure 12.2**.

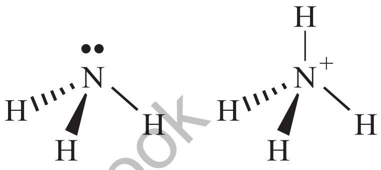


Figure 12.2 Pyramidal and tetrahedral shapes of ammonia and ammonium ion

12.2.3 Synthesis of Ammonia from Ammonium salts

In the laboratory, ammonia gas can be synthesized by heating an ammonium salt such as ammonium chloride (NH_4Cl) with a base like calcium hydroxide ($Ca(OH)_2$) as shown in **Figure 12.3.**

$$2NH_4Cl_{(s)} + Ca(OH)_{2(aq)} \longrightarrow CaCl_{2(aq)} + 2H_2O_{(\ell)} + 2NH_{3(g)}$$

In this acid-base reaction, NH_4^+ acts as an acid by donating H^+ ions, while OH^- acts as a base by accepting H^+ ions. This reaction displaces ammonia gas from the ammonium salt and produces salt and water. It is commonly used to identify ammonium in salt analysis. If a gas with a pungent smell is released and turns moistend red litmus paper blue, it indicates the presence of ammonium in the compound.

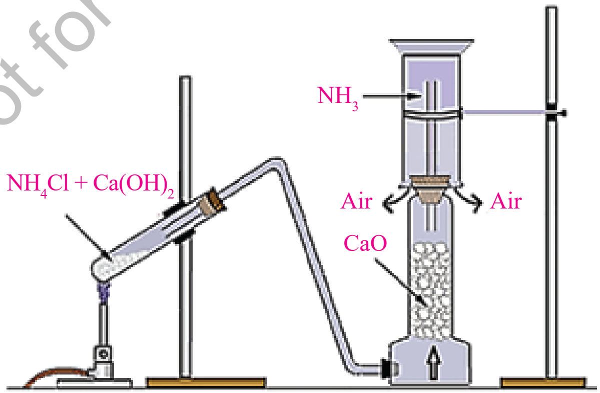


Figure 12.3 Synthesis of ammonia gas

Quick Check 12.1

a) Why N_2 gas is used in food packaging?

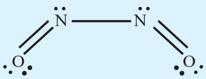
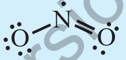
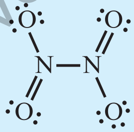
b) Both CO and N_2 have triple bonds in their molecules. Why do you think CO is more reactive than N_2?

c) Ammonium salts such as $(NH_4)_2SO_4$ or $(NH_4)_2NO_3$ are commonly used as fertilizers. Why a farmer wouldn't treat a field with an ammonium fertilizer at the same time as using lime? What would be the chemical reactions?

12.3 OXIDES OF NITROGEN

Oxides of nitrogen are NO, N_2O, NO_2, N_2O_4 and N_2O_5 in which oxidation states range from I to V. N_2O_4 and N_2O_5 decay quickly to other oxides. NO and NO_2 are collectively called as NO_x. The structures, properties and uses of these oxides are given in **Table 12.2**.

Table 12.2 Properties of some common oxides of nitrogen

Name and formula of oxide	**Structure**	Formal oxidation state	Properties	Uses
Nitrous oxide/ Nitrogen oxide (Laughing gas) N_2O	$:N\equiv N-\underset{\cdot\cdot}{\ddot{O}}:$	1+	Colourless gas, water-soluble, neutral, sweet smelling, helps in combustion	Dental anaesthetic, propellant for whipped ice cream, synthesis of NaN_3
Nitic oxide, Nitrogen dioxide NO, N_2O_2	$:N\equiv\ddot{O}$ 	2+	Colourless gas, slightly water-soluble, neutral, NO is paramagnetic while N_2O_2 is diamagnetic, oxidising as well as reducing in nature	Biochemical messenger (Lowers blood pressure and role in other body functions), synthesis of nitrosyl carbonyls
Nitrogen dioxide/Nitrogen peroxide, Nitrogen tetraoxide NO_2, N_2O_4 $\underset{Brown}{2NO_2} \underset{Heat}{\overset{Cool}{\rightleftharpoons}} \underset{Colourless}{N_2O_4}$	 	4+	NO_2 is a reddish-brown gas, paramagnetic, and reacts with water to form HNO_3 and HNO_2, N_2O_4 is colourless liquid or solid	Rocket propellant, HNO_3 formation by Ostwald process, explosives

Did you know?

The recommended name for ammonia by IUPAC is Azane and for ammonium is Azanium. These names have been derived from Azote, a Greek name for nitrogen, meaning "no life". These names are used in naming derivatives of ammonia and ammonium e.g. sodium azide (NaN_3).

12.4 SOURCES OF OXIDES OF NITROGEN

Here are the main categories of NO_x sources.

12.4.1 Natural Sources

Natural sources include lightning, volcanic eruption forest fires, and denitrifying bacteria in soil. NO is produced when N_2 and O_2 in the air react during lightning. N_2O is produced by microorganism using air N_2.

12.4.2 Anthropogenic (Man-made) Sources

The main anthropogenic sources of NO_x are the combustion of fossil fuels in vehicles and power plants. Other sources include chemical plants, biomass burning, welding, etc.

12.5 ROLE OF NO & NO_2 IN SMOG & PAN FORMATION

NO_x is responsible for numerous harmful effects on living organisms.

12.5.1 Photochemical Smog

Photochemical smog (Los Angeles smog) forms in the atmosphere from NO_x and volatile organic compounds (VOCs) in the sunlight. It is oxidising in nature. It contains photochemical oxidants, such as NO_2, ozone, and peroxyacyl nitrates (PANs). Photochemical smog is becoming more common than classical smog (London smog) due to increasing NO_x emissions. The formation of photochemical smog involves the following chemical reactions:

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$$

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

$$NO_{2(g)} \xrightarrow{h\upsilon} NO_{(g)} + O_{(g)}$$

$$O_{(g)} + O_{2(g)} \longrightarrow O_{3(g)}$$

$$RCH{=}RCH_{(g)} + O_{3(g)} \longrightarrow RCO^{\bullet}_{3(g)} + RCH^{\bullet}_{2(g)} \rightarrow\rightarrow\rightarrow RC(O)OONO_2$$

Did you know?

Lahore smog consists of volatile organic compounds (VOCs), NOx, ground level ozone (O_3), particulate matter PM2.5, CO and SO_2.

12.5.2 Formation of Peroxyacyl Nitrates (PANs)

NOx take part in a series of reactions leading to the formation of ozone (O_3), aldehydes, peroxyacyl nitrates (PANs) and peroxybenzoyl nitrate (PBN). PAN is one of the members of peroxyacyl nitrates as shown in **Figure 12.4**.

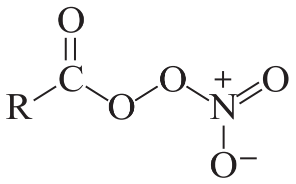


Figure 12.4 General structure of PANs

The R group in peroxyacetyl nitrate is CH_3, but other hydrocarbon chains may also be present.

The formation of PAN is illustrated in **Figure 12.5.** The main component of oxidizing smog is ozone, which oxidizes hydrocarbon to produce aldehyde. The aldehyde then reacts with hydroxyl radical to produce acyl radical. The acyl radical reacts with oxygen to produce peroxyacyl radical, which finally reacts with nitrogen peroxide to form peroxyacyl nitrate.

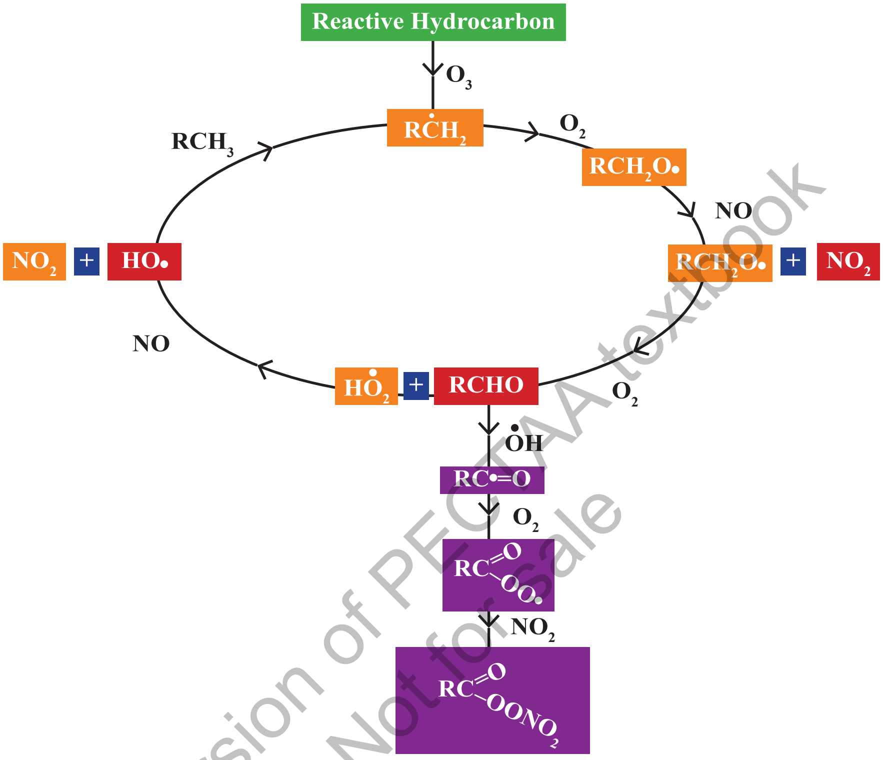


Figure 12.5 Mechanism of PAN formation

Quick Check 12.2

a) Draw the structures of the following oxides of nitrogen. Also, explain briefly their bonding.

i) N_2O ii) NO iii) NO_2

b) What does PAN stand for? Give its general formula.

c) Write down the formulas of the compounds responsible for the formation of PAN.

d) If magnesium ribbon is ignited and placed in a jar containing N_2O, it continues to burn brightly, how does the product formed in this reaction confirm the structure of N_2O?

12.6 CATALYTIC CONVERTER

A catalytic converter is a ceramic or metallic material with a honeycomb-like structure, as shown in **Figure 12.6**. Its inner channels have a layer of alumina to provide a high surface area. Noble expensive metals such as Pt (Platinum), Pd (Palladium), and Rh (Rhodium) are dispersed on the alumina.

These metals catalyze three redox reactions to remove the half harmful exhaust gases. The three-way converter converts harmful CO, NO, and hydrocarbons into CO_2, N_2, and water. These precious metals can also be recycled.

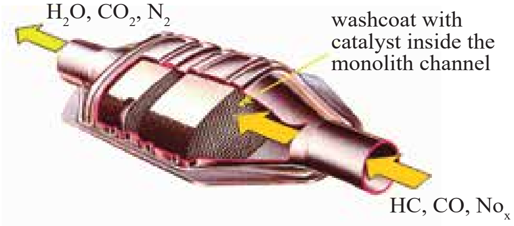


Figure 12.6 Three-way catalytic converter

Reduction

$$2NO_{(g)} + 2CO_{(g)} \xrightarrow{Pt / Rh} N_{2(g)} + 2CO_{2(g)}$$

Oxidation

$$2CO_{(g)} + O_{2(g)} \xrightarrow{Pt / Pd} 2CO_{2(g)}$$

$$2C_2H_4 + 6O_{2(g)} \xrightarrow{Pt / Pd} 4CO_{2(g)} + 4H_2O_{(g)}$$

12.7 NITRIFICATION AND DENITRIFICATION

Nitrification and denitrification are the two phases of the nitrogen cycle. Nitrification involves the conversion of ammonium (NH_4^{1+}) to nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}), while denitrification involves the conversion of nitrate (NO_3^{1-}) to Nitrogen (N_2). Some differences between nitrification and denitrification are given in **Table 12.2.**

Table 12.3 Differences between nitrification and denitrification

Nitrification	Denitrification
Ammonia NH_3/ NH_4^{1+} is converted into nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}).	Nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}) are converted back to N_2 that is released into the atmosphere.
Nitrifying bacteria, aerobic conditions, pH 6.5 – 8.0, optimum temperature 20 °C–30 °C.	Denitrifying bacteria, anaerobic conditions, pH 7.0–9.0, optimum temperature 26 °C – 38 °C.
Plants absorb these nitrites and nitrates for their nutrition as they cannot assimilate nitrogen directly from the atmosphere.	It is important in wastewater treatment and useful for aquatic life supported with Anammox that oxidizes NH_4^+ with NO_2^- to form N_2 gas.
Oxidation of nitrogen $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ $2NH^{1+}_{4(aq)} + 3O_{2(aq)} \rightarrow 2NO^{1-}_{2(aq)} + 4H^+_{(aq)} + 2H_2O_{(l)}$ $2NO^{1-}_{2(aq)} + O_{2(aq)} \rightarrow 2NO^{1-}_{3(aq)}$	**Reduction of nitrogen** $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$ $2NO^{1-}_{3(aq)} + 10e^- + 12H^+_{(aq)} \rightarrow N_{2(g)} + 6H_2O_{(l)}$

Quick Check 12.3

a) Write down the reduction and oxidation reactions that occur in the catalytic converter in the vehicle exhausts.

b) What is the basic principle of catalytic converter? Describe the role of catalyst in the catalytic converter.

c) Do hybrid and electric cars have catalytic converters? Explain why or why not.

12.8 SULFUR

Sulfur is a member of group 16 which is also called the Chalcogen family. Some physical properties of sulfur are listed in **Table 12.4.**

Table 12.4 Physical properties of Sulfur

Atomic number	16	**Ionic radius**	184 pm
Relative atomic mass	32.06 a.m.u.	**1st Ionization energy**	1000 kJ/mol
Physical appearance	Solid Yellow	**Electronegativity**	2.5
Electronic configuration	[Ne] $3s^2\ 3p^4$	**Electron affinity**	-200 kJ/mol
Melting point	113 °C (honey-yellow)	**Density**	2.07 g/cm^3
Boiling point	445 °C (dark brown)	**Common oxidation states**	+4 and +6
Covalent radius	104 pm	**Common Bonding**	Covalent bond

12.8.1 Reactivity of Sulfur

Sulfur usually forms single bonds with other sulfur atoms instead of double bonds due to poor overlapping of the orbitals. As a result, it forms larger molecules and structures through a process called catenation. S_8 is a crown-like molecule, as shown in **Figure 12.7**.

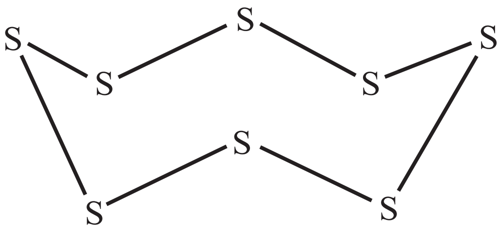


Figure 12.7 Cyclo-octasulfur, (S_8) crown molecule

12.8.2 Oxidation States of Sulfur

Sulfur exhibits oxidation states of −2, 0, +2, +4, and +6. The electronic configuration of sulfur is depicted in **Figure 12.8**, where the oxidation state is determined by the number of unpaired electrons. Under standard conditions, sulfur and oxygen react to produce sulfur dioxide (SO_2) in which sulfur has an oxidation state of +4. However, to form sulfur trioxide (SO_3) with an oxidation state of +6, high energy is required.

	2*s* / 3*s*	2*p* / 3*p*	3*d*	
a) Oxygen atom in ground state ($2s^2\,2p^4$)	↑↓	↑↓ ↑ ↑		There are no d-orbitals in 2nd shell therefore excitation is not possible.
b) Sulfur atom in ground state ($3s^2\,3p^4$)	↑↓	↑↓ ↑ ↑	□ □ □ □ □	2+ oxidation state due to two unpaired electrons
c) Sulfur atom in 1st excited state ($3s^2\,3p^3\,3d^1$)	↑↓	↑ ↑ ↑	↑ □ □ □ □	4+ oxidation state due to four unpaired electrons
d) Sulphur atom in second excited state ($3s^1\,3p^3\,3d^2$)	↑	↑ ↑ ↑	↑ ↑ □ □ □	6+ oxidation state due to six unpaired electrons

Figure 12.8 Electronic configurations of sulfur for attaining different oxidation states

12.9 STABILITY OF OXIDATION STATES OF SULFUR

Sulfur displays a range of oxidation states, principally from –2 to +6. The stability of these states is influenced by the factors like pH, temperature, nature of the compound and the chemical environment.

pH

In general, under acidic conditions, reduced forms (like H_2S, –2 oxidation state) are more stable, while under basic or neutral conditions, oxidized forms (like SO_4^{2-}, +6 oxidation state) become more stable in water.

Thermodynamics and Kinetics

Although sulfur (+6), as in SO_3, is thermodynamically the most stable, kinetic limitations can prevent it from forming readily at standard temperatures, making sulfur (+4), as in SO_2, the more frequent form.

Nature of the compound

The stability of sulfur's oxidation state can be affected by the elements it is bonded to, and the overall chemical environment. In acidic environment SO_4^{2-} is kinetically stable due to strong O-S bonds.

Catalyst

A catalyst can also enhance the rate of formation of a specific oxidation state, for example vanadium in the contact process increases the rate of formation of SO_3.

Quick Check 12.4

a) Determine the oxidation state of S in the following species:

i. SO_3 ii. H_2SO_4 iii. SO_4^{2-} iv. $S_2O_3^{2-}$

b) Which oxidation states of sulfur are the most common? Explain your answer with reason.

c) Explain the involvement of d orbital in variable oxidation states of S in its compounds.

12.10 REACTIONS OF SULFUR

Sulfur can combine with many elements to form a wide variety of inorganic and organic compounds. It is unreactive to water under normal conditions, dilute non-oxidising acids, and noble gases. Its ability to catenate allows it to form ring structures and linear chains. Here are some important reactions of sulfur:

i. Sulfur burns in the air to form SO_2 with a blue colour flame. The other main sulfur oxide is SO_3 which requires higher temperature and a catalyst for its formation.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

$$2SO_{2(g)} + O_{2(g)} \xrightarrow[Pt]{\Delta} 2SO_{3(g)}$$

Sulfur can be oxidised by nitric acid to produce NO_2 and H_2SO_4.

$$S_{(s)} + 6HNO_{3(\ell)} \longrightarrow H_2SO_{4(\ell)} + 6NO_{2(g)} + 2H_2O_{(\ell)}$$

ii. When sulfur reacts with elements that have lower electronegativity, it acts as an oxidizing agent and forms their sulfides. It tarnishes Ag, Cu, and Zn by forming a coating of metal sulfide.

$$2Ag_{(s)} + S_{(s)} \longrightarrow Ag_2S_{(s)}$$

$$Hg_{(l)} + S_{(s)} \longrightarrow HgS_{(s)}$$

$$2Cu_{(s)} + S_{(s)} \longrightarrow Cu_2S_{(s)}$$

iii. Sulfur converts cyanide into thiocyanate which is also known as pseudohalide.

$$KCN_{(s)} + S_{(\ell)} \xrightarrow{\Delta} KSCN_{(s)}$$

iv. Sulfur reacts directly with F_2 to form SF_4 and SF_6. Sulfur hexafluoride (SF_6) is a gas and is very unreactive. It is used as an insulator gas in electric devices. Sulfur readily reacts with Cl_2 to form S_2Cl_2 (yellow liquid) which further reacts with Cl_2 to form SCl_2 (red liquid).

$$S_{(\ell)} + 3F_{2(g)} \longrightarrow SF_{6(g)}$$

$$2S_{(\ell)} + Cl_{2(g)} \longrightarrow S_2Cl_{2(\ell)}$$

$$S_{(\ell)} + SCl_{2(g)} \longrightarrow SCl_{2(\ell)}$$

12.11 USES OF SULFUR AND ITS COMPOUNDS

12.11.1 Vulcanisation

Sulfur is used as a cross linker for the rubber molecular chains through di-sulfide (S–S) bridges. This is called vulcanization of rubber. It improves the strength of rubber as shown in **Figure 12.9**.

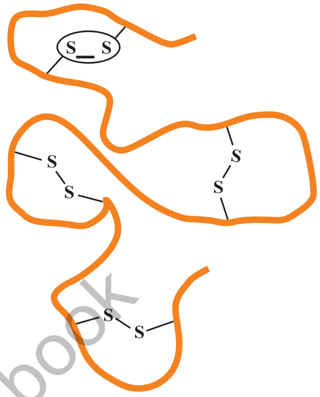


Figure 12.9 S-S cross-linkages between polymer chains

12.11.2 Fertilizer

Sulfur is an essential nutrient for plant growth. When soils become depleted in sulfate, sulfur can be restored in soil by ammonium sulfate, elemental sulfur and sulfur-coated fertilizers such as sulfur-coated urea. Soil components and microbes convert elemental sulfur into soluble forms for the use of plants. Gypsum ($CaSO_4 \cdot 5H_2O$) is also used as a fertilizer.

12.11.3 Gun powder

Gun powder is a coarse blend of 75% potassium nitrate (KNO_3), 15% wood charcoal, and 10% sulfur. Charcoal carbon is the main fuel, nitrate is the oxidiser and sulfur is the additional fuel that burns the powder faster. The following reaction in burning takes place:

$$10KNO_{3(s)} + 3S_{(s)} + 8C_{(s)} \longrightarrow 2K_2CO_{3(s)} + 3K_2SO_{4(s)} + 6CO_{2(g)} + 5N_{2(g)}$$

Quick Check 12.5

a) What is the function of SO_2 and sulfite (SO_3^{2-}) salt in preserving the food?

b) Give the reaction of S with HCl and NaOH.

12.12 ROLE OF SULFUR IN ORGANIC SYNTHESIS

Carbon-Sulfur bonds are prevalent in a wide range of compounds with biological, pharmaceutical, and material properties. These bonds form a large number of organic compounds containing a variety of functional groups such as thiols or mercaptans, thioethers, sulfoxides, sulfones, etc.

12.12.1 Drugs

Sulfa drugs are the antibacterial sulfonamides, such as penicillins and cephalosporins contain sulfur. The common drug β-lactam such as omeprazole used in GERD (Gastroesophageal reflux disease) contains sulfoxide group.

12.12.2 Dyes

Sulfur dyes are synthesized by the process of thionation or sulfurization of organic compounds that contain nitro or amino groups. These compounds contain sulfur linkages. They generally give black, brown, khaki, blue, and green colours.

Some examples are sulfur black 1, sulfur blue and sulfur brilliant green.

12.12.3 Odorants/Fragrances

Mercaptans are used to give odour to natural gas. Some thiols have pleasant odours on high dilution. For example, thioterpineol is the key ingredient in the aroma of grapefruit. cis-galbanum oxathiane is a fragrant compound. It is used in fine fragrances, soaps, shampoos and shower gels. Many naturally occurring odorants are produced synthetically and also applied as flavouring agents.

12.13 SULFURIC ACID (H_2SO_4)

The major portion of sulfur, around 85 % is used for the production of sulfuric acid (H_2SO_4). It has tetrahedral structure with two S–O and two S=O bonds as shown in **Figure 12.10**.

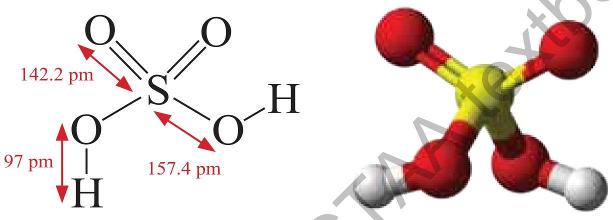


Figure 12.10 Structure of H_2SO_4

12.13.1 Contact Process

Sulfuric acid is produced by the contact process. A flow sheet diagram of the contact process is shown in **Figure 12.11.**

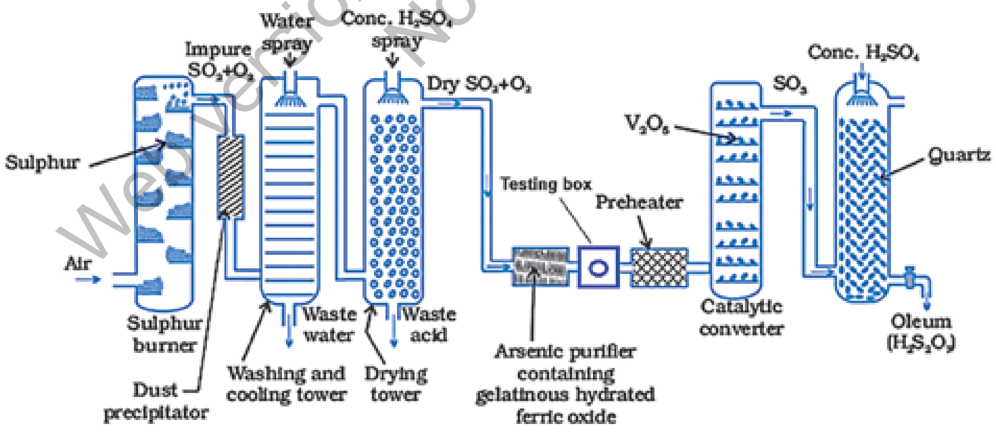


Figure 12.11 Contact process for the industrial production of sulfuric acid

Contact process can be divided into the following stages.

Sulfur / pyrite burners

The process starts with the combustion of molten sulfur or by heating pyrites such as iron pyrite (FeS) in excess of air to produce sulfur dioxide SO_2.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \qquad \Delta H = -297.03 \text{ kJ/mol}$$

$$4FeS_{(s)} + 6O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 4SO_{2(g)}$$

Purification unit

If pyrite ore is used as a sulfur source, the SO_2 gas formed may contain contaminants like dust particles, vapours, and arsenic oxide. These contaminants affect the efficiency of the catalyst. Hence, the gas needs to pass through the purification unit. In an arsenic purifier, gelatinous ferric hydroxide Fe $(OH)_3$ present in horizontal shelves, absorbs arsenic oxide As_2O_3.

$$As_2O_{3(g)} + 2Fe(OH)_{3(l)} \longrightarrow 2FeAsO_{3(l)} + 3H_2O_{(l)}$$

Contact tower and heat exchangers

Purified SO_2 and air, preheated at 420 °C– 450 °C, are fed to the first converter stage of the contact tower at 1–2 atm pressure. Here, these gases come in contact with vanadium pentoxide (V_2O_5) catalyst.

$$SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \quad \Delta H = -98.98 \text{ kJmol}^{-1}$$

V_2O_5 as catalyst works in following two steps:

Oxidation of SO_2 into SO_3 by V^{5+}:

$$SO_{2(g)} + V_2O_{5(s)} \longrightarrow SO_{3(g)} + V_2O_{4(s)}$$

Oxidation of V^{4+} back into V^{5+} by oxygen (catalyst regeneration):

$$V_2O_{4(s)} + \frac{1}{2}O_{2(g)} \longrightarrow V_2O_{5(s)}$$

Quick Check 12.6

a) Why is high temperature and catalyst needed to form SO_3?

b) Write down dehydration reactions of conc. H_2SO_4 with starch and oxalic acid.

c) How does the catalyst V_2O_5 function in the conversion of SO_2 to SO_3?

Absorption tower

Sulfur trioxide is cooled and can be converted to sulfuric acid by reacting with water.

$$H_2O_{(l)} + SO_{3(g)} \longrightarrow H_2SO_{4(l)} \qquad \Delta H = -176.6 \text{ kJ/mol}$$

Mixing SO_3 with water is not feasible because the reaction is extremely exothermic and acidic vapour or mist is produced rather than a liquid solution. Mainly, sulfur trioxide is dissolved in recirculating hot 98.5% sulfuric acid to form oleum (fuming sulfuric acid). The term fuming sulfuric acid or oleum is used for the mixture of sulfur trioxide with 100 percent sulfuric acid to form oleum.

Oleum undergoes a reaction with water to make a highly concentrated solution of H_2SO_4 whose concentration can be adjusted.

$$H_2SO_{4(\ell)} + SO_{3(g)} \longrightarrow H_2S_2O_{7(\ell)}$$

$$H_2S_2O_{7(\ell)} + H_2O_{(\ell)} \longrightarrow 2\,H_2SO_{4(\ell)}$$

12.13.2 Physical Properties

Sulfuric acid is soluble in water and hygroscopic in nature. It readily absorbs water vapour from the air. Anhydrous H_2SO_4 is a very polar liquid. It is highly corrosive to various materials. On contacting the skin, it causes chemical burns. Some physical properties of sulfuric acid are given in **Table 12.5.**

Table 12.5 Physical properties of Sulfuric acid

Molar mass	98.08 g/mol
Physical appearance	Colourless viscous liquid
Odour	Odourless
Melting point	10 °C
Boiling point	290 °C
Specific gravity (15 °C)	1.83 g/cm^3
Viscosity	25.24 centipoise
Vapour pressure (25 °C)	0.001 torr
Sulfuric acid is a highly corrosive substance. It can badly burn cloths, plastic, rubber and injured the human skin, eyes, etc,. Handle it very carefully.	

12.13.3 Chemical Properties

i. It self-ionizes or undergoes autoprotolysis as follows:

$$H_2SO_{4(\ell)} + H_2SO_{4(\ell)} \rightleftharpoons H_3SO^{1+}_{4\,(aq)} + HSO^{1-}_{4\,(aq)} \qquad K = 2.7 \times 10^{-4}$$

The equilibrium constant value is greater than that of water which makes it to be used as a non aqueous protic solvent.

Sulfuric acid is a strong acid as shown by its pK_{a1} value:

$$H_2SO_{4(aq)} \rightleftharpoons H_3O^+_{(aq)} + HSO^{1-}_{4(aq)} \quad (pK_{a1} = -2)$$

But hydrogensulfate (HSO_4^{1-}) is a far weaker acid due to a positive pK_{a2} value:

$$HSO^{1-}_{4(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + SO^{2-}_{4(aq)} \quad (pK_{a2} = 1.92)$$

ii. Concentrated sulfuric acid is a powerful dehydrating agent that removes water from many substances such as sucrose, starch, wood, and paper to produce carbon, steam, and heat.

Interesting Information!

A common laboratory demonstration is the dehydration of table sugar, where a black porous carbon mass called carbon snake protrudes out of the apparatus.

$$C_{12}H_{22}O_{11(s)} + H_2\,SO_{4(l)} \longrightarrow 12C_{(s)} + 11H_2O_{(g)} + H_2SO_{4(aq)}$$

It also dehydrates ethyl alcohol to ethene or ethoxyethane depending upon the reaction conditions.

$$C_2H_5OH_{(\ell)} + H_2SO_{4(\ell)} \longrightarrow C_2H_{4(g)} + H_2O_{(\ell)} + H_2SO_{4(aq)}$$

iii. Hydrochloric acid (HCl) gas, is formed when sulfuric acid reacts with sodium chloride.

$$NaCl_{(s)} + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(s)} + HCl_{(g)}$$

iv. Reactions of sulfuric acid with metals depend upon the metal, concentration of the acid, and temperature. Metals that are above hydrogen in electrochemical series such as Fe, Al, Zn, Mn, Ni, and Mg react directly with dilute sulfuric acid to produce hydrogen gas and metal sulfates. But with cold conc. H_2SO_4, they liberate SO_2 and metal sulfates.

$$Zn_{(s)} + \text{dil. } H_2SO_{4(aq)} \longrightarrow H_{2(g)} + Zn^{2+}_{(aq)} + SO^{2-}_{4\,(aq)}$$

$$Zn_{(s)} + H_2SO_{4(\ell)} \longrightarrow SO_{2(g)} + Zn^{2+}_{(aq)} + SO^{2-}_{4\,(aq)} + 2H_2O_{(\ell)}$$

v. Metals like Cu, Ag, and Hg react with hot conc.H_2SO_4 to form metal sulfates. Sulfuric acid is not regarded as a typical oxidising agent due to the stability of SO_4^{2-} anion. This anion is weakly oxidising. However hot concentrated sulfuric acid is a moderately strong oxidising agent due to high temperature, high concentration of protons (H^+), and formation of nascent oxygen. Hot concentrated sulfuric acid oxidises Cu, as given below:

$$Cu_{(s)} + 2H_2SO_{4(\ell)} \longrightarrow SO_{2(g)} + 2H_2O_{(\ell)} + SO^{2-}_{4(aq)} + Cu^{2+}_{(aq)}$$

Quick Check 12.7

a) Write down dehydration reactions of conc. H_2SO_4 with starch and oxalic acid.
b) How does conc. H_2SO_4 react with NaCl? What is the importance of this reaction?
c) What is the difference between the oxidizing power of cold and hot sulfuric acid?

12.13.4 Uses and Industrial Applications

Sulfuric acid is considered a king of chemicals and its consumption is an indicator of the industrial progress of a country.

1. A major portion of the acid is used in making fertilizers, normally three fourth is used to digest the phosphate rock. Sulfuric acid also reacts with ammonia to make ammonium sulfate fertilizer.
2. It is used in the extraction of metals from ores such as Cu, Ni, steel etc.
3. It is utilized as a catalyst in oil and coal refining, polymers, synthetic rubber, and plastic industries.

4. It is used in the pulp and paper industry and involved in the production of pesticides, insecticides, herbicides, varnishes, dyes, pharmaceuticals, soaps and detergents.
5. It is used for nitration in making explosives such as trinitrotoluene (TNT), nitroglycerine, picric acid, nitrocellulose, etc.
6. It is involved in the food industry for making sugar, starch, and corn syrup.
7. It is used in the paint industry for making titanium dioxide (TiO_2) pigment.
8. It is used to dry gases in industrial processes.
9. 35.67% acid is used in lead storage batteries.
10. It is used as a laboratory reagent.

Even though it is used in various industries, it is rarely contained in the final product.

Did You Know?

Calcium phosphate ($Ca_3(PO_4)_2$ and fluorapatite ($Ca_5(PO_4)_3F$) are used to make single superphosphate $Ca(H_2PO_4)_2$ and phosphoric acid (H_3PO_4). H_3PO_4 is further used to make double and triple superphosphates and ammonium phosphate.

EXERCISE

MULTIPLE CHOICE QUESTIONS

Q.1 Four choices are given for each question. Select the correct choice.

I. Despite being the most abundant gas in the Earth's atmosphere, nitrogen does not readily participate in combustion reactions because:

a) It is denser than oxygen.

b) It has a high specific heat capacity.

c) Breaking the N≡N bond requires a large amount of energy.

d) It is a noble gas.

II. A student heats a solid ammonium salt with a solution of a strong alkali. The gas produced turns damp red litmus paper blue and has a characteristic pungent smell. The gas is:

a) Hydrogen (H_2)
b) Carbon dioxide (CO_2)
c) Ammonia (NH_3)
d) Sulfur dioxide (SO_2)

III. The shape of ammonium is

a) Pyramidal
b) Triangular planar
c) Tetrahedral
d) Linear

IV. In a catalytic converter, the conversion of nitrogen oxides (NO_x) into nitrogen gas (N_2) and oxygen gas (O_2) is a process of:

a) Oxidation
b) Reduction
c) Combustion
d) Neutralization

V. PAN formation starts when______ reacts with the hydrocarbon.

a) NO
b) NO_2
c) O_3
d) $HO^\bullet$

VI. Nitrification is the process by which:

a) Atmospheric nitrogen is converted into ammonia.
b) Nitrate is converted into nitrogen gas.
c) Ammonia is converted into nitrite and then nitrate.
d) Organic nitrogen is converted into ammonia.

VII. The most stable species in an acidic environment is

a) SO_4^{2-}
b) SO_2
c) H_2S
d) S

VIII. Which gas is used in separating hard water from normal water?

a) SO_2
b) H_2S
c) NH_3
d) NO_2

IX. The oxidation state of sulfur in H_2SO_4 is

a) +1
b) +2
c) +4
d) +6

X. The drug omeprazole contains ______ group.

a) Thiol
b) Sulfoxide
c) Bisulfide
d) Sulfone

XI. Sulfur dioxide (SO_2) produced from the combustion of sulfur can be further oxidized to sulfur trioxide (SO_3) under specific conditions, such as in the presence of a:

a) Catalyst (e.g., vanadium(V) oxide) and high temperature
b) Catalyst (e.g., iron) and low temperature
c) Strong reducing agent and high pressure
d) Dilute acid and room temperature

XII. Sulfur trioxide (SO_3) is not directly dissolved in water to produce sulfuric acid in the Contact Process because this reaction is:

a) Too slow

b) Reversible and would result in a low yield

c) Highly exothermic and produces a mist of sulfuric acid

d) Requires very high pressures

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a) List two reasons for the inertness of N_2.

b) How is nitrogen isolated from air?

c) Why ammonia (NH_3) is a weak base?

d) Write down the reactions of photochemical smog formation.

e) What is the construction and function of a catalytic converter?

f) Why sulfur is quite unreactive at room temperature?

g) Which are the most stable oxidation states of sulfur in water at pH=0 and pH=14?

h) How does sulfur react with halogens?

i) Draw the structures of cyclo-octasulfur (S_8) and sulfuric acid.

j) What is the role of sulfur in the vulcanization of rubber?

k) What is the composition and the chemical reaction of gunpowder combustion?

l) What is the importance of disulfide bridges?

m) Write down self-ionization equation of sulfuric acid and its ionization in water.

n) Give two examples where sulfuric acid acts as a dehydrating agent.

o) How does V_2O_5 catalyze the formation of SO_3?

p) What is purpose of formation of oleum?

DESCRIPTIVE QUESTIONS

Q.3 Explain the preparation and basicity of ammonia.

Q.4 How oxides of nitrogen (NO_x) cause the formation of photochemical smog and PAN? Give its mechanism.

Q.5 Give flowsheet diagram and equations involved in the contact process.

Q.6 Discuss sulfuric acid as an oxidizing agent and a dehydrating agent with three reactions for each.