Chapter 19

Nitrogen and Sulphur

Student Learning Outcomes

After studying this chapter, students will be able to:

- Recognize that atmospheric oxides of nitrogen {NO and NO_2) can react with unburned hydrocarbons to form peroxyacetyl nitrate, PAN, which is a component of photochemical smog
- Describe the role of NO and NO_2 in the formation of acid rain both directly and in their catalytic role in the oxidation of atmospheric sulphur dioxide
- State the symbol equation for the production of ammonia in the Haber process, $N_{2(g)} + 3H_{2\,(g)} \longrightarrow 2NH_{3\,(g)}$
- State the sources of the hydrogen (methane) and nitrogen (air) in the Haber process
- State the typical conditions in the Haber process as 450 ° C, 20000kPa /20 atm and an iron catalyst
- State the symbol equation for the conversion of sulphur dioxide to sulphur trioxide in the Contact process, $2\,SO_{2\,(g)} + O_{2\,(g)} \longrightarrow 2\,SO_{3\,(g)}$
- State the sources of the sulphur dioxide (burning sulphur or roasting sulphide ores) and oxygen (air) in the Contact process
- State the typical conditions for the conversion of sulphur dioxide to sulphur trioxide in the Contact process as 450 °C, 200kPa /atm and a vanadium(V) oxide catalyst Oxides
- Describe amphoteric oxides as oxides that react with acids and bases to produce a salt and water
- Classify oxides as acidic, including SO_2 and CO_2, basic, including CuO and CaO, or amphoteric, limited to Al_2O_3 and ZnO, related to metallic and non-metallic character.
- properties of metal
- Identify the general chemical properties of metals, limited to their reactions with dilute acids, cold water, steam and oxygen.
- Arrange metals in order of reactivity given relevant information.

19.1 Ammonia

Ammonia gas is one of the most important chemicals produced globally for industrial use. Urea and other ammonium salts are extensively used as fertilizers. About 80% of the ammonia produced in the industries world-wide are used to produce these fertilizers. Apart from this, ammonia is also used in the production of plastics and pharmaceuticals. It is also used as a refrigerant.

Ammonia is produced industrially by Haber process discovered by a German Chemist F.J. Haber. In this process, a mixture of nitrogen and hydrogen, in the ratio of 1:3 by volume is heated at 400-500 °C under 200 atmospheric pressure and in the presence of catalyst Fe/Al_2O_3 to give ammonia.

$$N_{2\,(g)} + 3H_{2\,(g)} \underset{\text{Catalyst}}{\overset{400\text{-}500\ ^\circ c}{\rightleftharpoons}} 2NH_{3\,(g)}$$

The equilibrium mixture obtained in the above reaction contains 35% ammonia by volume. This mixture is cooled by refrigeration coils where ammonia gas changes to liquid ammonia at –33.4 °C and is removed from the mixture. The other components of the mixture, hydrogen and nitrogen gases, are then recycled back into the reaction chamber (Figure 19.1).

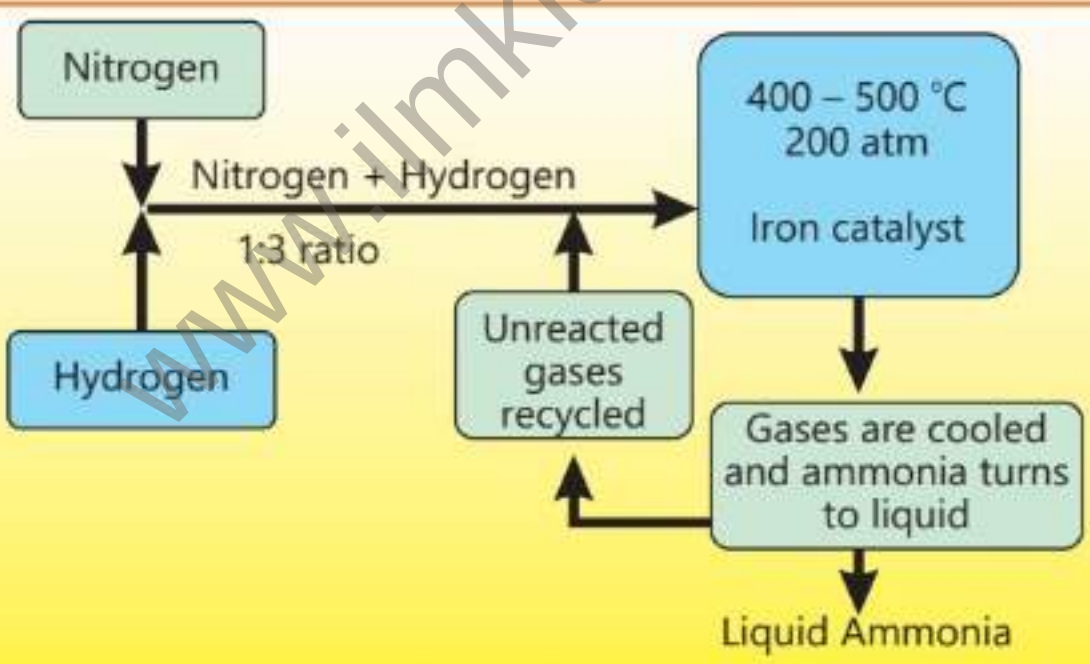

Figure 19.1: Haber process

Source of Nitrogen

One of the raw materials used for the production of ammonia is nitrogen gas and it is obtained by the fractional distillation of air. For this purpose, first of all carbon dioxide present in air is removed and the air is subjected to about 200 atmospheric pressure. This compressed air is then cooled and allowed to pass through a spiral jet. While escaping through this jet, the air suffers sudden expansion and its temperature is decreased. This process of compression and

expansion is repeated again and again till the air is liquified.

The liquid air is then fractionally distilled. Since the boiling point of nitrogen is less than oxygen, nitrogen evaporates first at -196 °C leaving behind the oxygen. The separated nitrogen is reliquified and stored in specially designed cylinders.

Source of Hydrogen

The second raw material, hydrogen, is produced by heating methane in the limited amount of oxygen that is not enough to completely oxidize methane to carbon dioxide and water. With less oxygen available, the reaction products contain primarily hydrogen and carbon monoxide and a relatively small amount of carbon dioxide. The carbon monoxide obtained is then reacted with water to form carbon dioxide and more hydrogen gas.

$$CH_{4\,(g)} + H_2O_{\,(g)} \longrightarrow CO_{(g)} + 3H_{2\,(g)}$$

$$CO_{(g)} + H_2O_{(g)} \longrightarrow CO_{2\,(g)} + H_{2\,(g)}$$

Interesting Information

13% of total Nitrogen fixation in the environment is contributed by the Haber process.

19.1 Quick Check!

1. Why is ammonia gas turned into a liquid after its production?
2. Why high pressure is maintained in the production of ammonia?

19.2 Sulphuric Acid

Sulphuric acid is one of the most important chemical compounds known. It is very commonly used in the laboratory and almost every manufacturing process makes use of this acid directly or indirectly at some stage.

Sulphuric acid is prepared industrially by the contact process. The process involves the following steps.

(1) Preparation of Sulphur dioxide gas

Sulphur dioxide gas is produced either by burning elemental sulphur in air or roasting a sulphur ore, iron pyrite, in excess of air.

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

$$4FeS_{2\,(s)} + 11O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$$

Sulphur dioxide produced above is then passed through purifying chambers and sprayed with steam. This process removes dust impurities as well as arsenic compounds present in the gas. This step is important because arsenic compounds poison the catalyst used later on. The moist gases (SO_2 and O_2) are then dried by passing through a drying tower in which concentrated sulphuric acid is being sprayed. Oxygen used in this reaction is obtained by the fractional distillation of air.

(2) Oxidation of Sulphur dioxide

The clean and dry gases (SO_2 and O_2) are then passed over vanadium (V) oxide catalyst at 450 °C and 2-3 atmospheric pressure through a contact chamber. Although the reaction is reversible yet under these conditions 98% SO_2 gas is converted to SO_3 (Figure 19.2).

$$2SO_{2\,(g)} + O_{2\,(g)} \xrightarrow[\text{2-3 atomsphere}]{\substack{V_2O_5 \\ 450\ ^\circ C}} 2SO_{3(g)}$$

Interesting Information

Sulphuric acid is called the "king of chemicals" because it is used in almost every industry.

3. Sulphur trioxide gas formed in the contact chamber is then absorbed into 98% sulphuric acid to give oleum.

$$SO_{3(g)} + H_2SO_{4(l)} \longrightarrow H_2S_2O_{7(l)}\ \text{oleum}$$

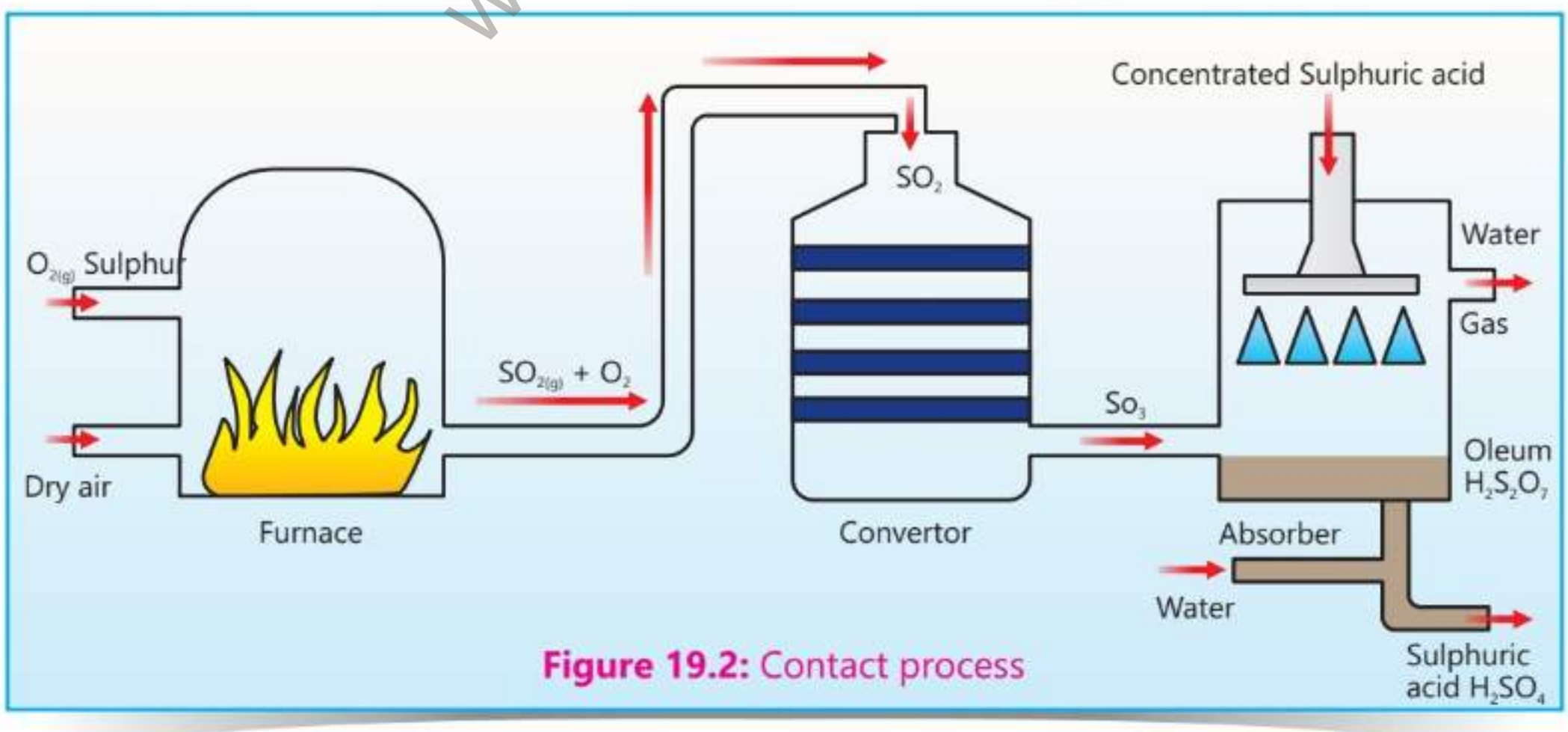

Figure 19.2: Contact process

4. The oleum is then mixed with an appropriate amount of water to produce sulphuric acid with desired concentration.

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

19.2 Quick Check!

1. How SO_2 is prepared from FeS_2?
2. Why SO_2 and oxygen are purified before they react to produce SO_3.

19.3 Oxides

Binary compounds of elements with oxygen are called oxides. Oxygen shows an oxidation state of -2 in these oxides. Metal oxides are commonly basic and amphoteric while non-metallic oxides are acidic in nature. Both basic and acidic oxides are formed when metals and non-metals are heated respectively in the presence of air or oxygen. Metal oxides are typically ionic compounds in which electrons are transferred from metals to oxygen. Non-metal oxides are covalent compounds where electrons are shared between non-metals and oxygen atom.

(i) Basic Oxides

Oxygen reacts with metals to give oxides which when dissolved in water produce hydroxides. They change red litmus blue. When treated with acids they give salts.

$$O_{2\,(g)} + 4Na_{(s)} \longrightarrow 2Na_2O_{(s)}$$

$$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$$

$$O_{2\,(g)} + 2Ca_{(s)} \longrightarrow 2CaO_{(s)}$$

$$CaO_{(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)}$$

$$O_{2\,(g)} + 2Cu_{(s)} \longrightarrow 2CuO_{(s)}$$

$$CuO_{(s)} + 2HCl_{(aq)} \longrightarrow CuCl_{2(aq)} + H_2O_{(l)}$$

(ii) Acidic Oxides

Oxygen combines with non metals (S, C, N) to give acidic oxides.

These oxides react with water to give acids which turn blue litmus red.

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

Sulphur dioxide

$$SO_{2\,(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(l)}$$

Sulphurous Acid

$$O_{2\,(g)} + C_{(s)} \longrightarrow CO_{2\,(g)}$$

$$CO_{2\,(g)} + H_2O_{(l)} \longrightarrow \underset{\text{Carbonic Acid}}{H_2CO_{3\,(aq)}}$$

Acidic oxides react with bases to give salts.

$$SO_{2\,(g)} + 2NaOH_{(aq)} \longrightarrow \underset{\text{Sodium sulphite}}{Na_2SO_3} + H_2O$$

$$CO_{2(g)} + Ca(OH)_{2\,(aq)} \longrightarrow CaCO_{3(s)} + H_2O_{(l)}$$

(iii) Neutral Oxides

Neutral oxides are those oxides which on contact with water produce neither an acid nor a base. Their aqueous solutions have no action on blue or red litmus paper. Examples are carbon monoxide (CO), nitric oxide (NO) and nitrous oxide (N_2O).

(iv) Amphoteric Oxide

Amphoteric oxides are usually formed when oxygen reacts with less electropositive metals.

$$O_{2(g)} + 2Zn_{(s)} \longrightarrow 2ZnO_{(s)}$$

$$3O_{2(g)} + 4Al_{(3)} \longrightarrow 2Al_2O_{3(s)}$$

These oxides behave both as an acid and a base. Zinc oxide and aluminium oxide behave as bases in the presence of an acid.

$$ZnO_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_2O_{(l)}$$

$$Al_2O_{3(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$$

These oxides behave as acids in the presence of an alkali.

$$ZnO_{(s)} + 2NaOH_{(aq)} + H_2O_{(l)} \longrightarrow \underset{\text{Sodium zincate}}{Na_2Zn(OH)_{4(aq)}}$$

$$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3\,H_2O_{(l)} \longrightarrow \underset{\text{Sodium aluminate}}{2NaAl(OH)_{4\,(aq)}}$$

These oxides are insoluble in water and have no action on litmus paper.

Interesting Information

Water is an amphoteric substance. It can act as both an acid and a base, depending on the other substance it reacts with.

19.3 Quick Check!

1. Why lead oxide is called an amphoteric oxide?
2. Why non-metals form covalent oxides?

19.4 Metals

Nearly three fourth elements shown in the periodic table are called metals. Metals show remarkable properties. Mostly metals occur in earth crust in the form of their oxides, hydroxides, carbonates and sulphides, etc.

Metals have a tendency to lose electrons and form cations. Usually they form ionic bonds with other elements.

Reactions of metals with cold water

Most of the elements present in the first and second group of the periodic table react vigorously with cold water producing their respective hydroxides and hydrogen gas.

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$

$$2K_{(s)} + 2H_2O_{(l)} \longrightarrow 2KOH_{(aq)} + H_{2(g)}$$

Interesting Information

If two pieces of uncoated metal touch in space, they become permanently stuck together. It does not happen on Earth because the atmosphere puts a thin layer of oxide between the surfaces which acts as a barrier preventing adhesion.

Magnesium, however, reacts with cold water slowly giving magnesium hydroxide and hydrogen gas.

$$Mg_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2\,(s)} + H_{2\,(g)}$$

Reactions of metals with steam

The more reactive the metal, the more readily it reacts with steam. Reactive metals like lithium, sodium, potassium and calcium react violently with steam and the reaction can be dangerous.

Beryllium and aluminum react with steam at high temperatures (around 700 °C) to give their respective oxides and hydrogen.

$$Be_{(s)} + H_2O_{(g)} \longrightarrow BeO_{(s)} + H_{2\,(g)}$$

Magnesium, iron and Zn have a moderate reaction with steam producing their respective oxides and hydrogen gas.

$$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$$

Reactions of metals with Oxygen

Metals react with oxygen to give metal oxides. The ease of reaction and the type of oxide which is formed, depends upon the reactivity of metals and the conditions used.

Sodium burns in air with yellow flame producing both sodium oxide and sodium per oxide.

$$4Na_{(s)} + O_{2(g)} \longrightarrow 2Na_2O_{(s)}$$

$$2Na_{(s)} + O_{2(g)} \longrightarrow Na_2O_{2(s)}$$

Magnesium, calcium, strontium and barium burn in oxygen with colour of the flame characteristic to each metal giving their respective oxides.

$$Ca_{(s)} + O_{2(g)} \longrightarrow 2CaO_{(s)}$$

Metal	Colour of flame
Mg	Intense white flame
Ca	White flame with a tinge of red
Sr	Crimson flame
Ba	A pale green flame

Figure 19.3: Strontium flame **Figure 19.4:** Barium flame

Reactions of metals with dilute acids

The more reactive the metal the more vigorous is its reaction with dilute acids. Sodium and potassium are very dangerous and react violently with dilute acids giving their respective salts and hydrogen gas.

$$2Na_{(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_{2(g)}$$

All group 2 elements react with dilute acids giving their salts, and

hydrogen gas. The reaction generally becomes more vigorous as we move down the group.

$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2\,(aq)} + H_{2(g)}$$

19.4 Quick Check!

1. Write the equation for the reaction between Ba and H_2O.
2. How do aluminum and zinc react with water.

19.5 Reactivity Series of metals

Based on their reactions with water and acids, the metals can be arranged in decreasing order of their reactivities. Such an arrangement is shown in Table 19.1 and it is called the reactivity series of metals.

Table 19.1 Reactivity Series of Metals

Most Reactive
K
Na
Li
Ba
Sr
Ca
Mg
Al
C
Mn
Zn
Fe
H
Cu
Ag
Au
Least Ractive

According to this reactivity series, calcium and metals above it react with cold water to give metal hydroxides and hydrogen gas. The metals below calcium do not react with cold water, instead they react with steam to give metal oxides and hydrogen gas.

Only metals above hydrogen will be able to liberate H_2 upon reacting with dilute acids. Unreactive metals below hydrogen do not react with dilute acids. The more reactive the metal, the more vigorous its reaction will be with dilute acids. Similarly reactive metals, like potassium and sodium, react with oxygen easily whereas the less reactive metals like silver, copper and iron react with oxygen much more slowly.

The metals at the top of the series are powerful reducing agents since they are easily oxidized. However, the reducing ability of metals decreases going down the series.

$$Zn_{(s)} + CuSO_{4\,(aq)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

19.5 Quick Check!

1. Which will react faster with HCl, Zn or Fe?
2. Name one metal which will displace Zn from its salt.

19.6 Role of oxides of nitrogen in spreading air pollution

The primary pollutants in the atmosphere include oxides of nitrogen, sulphur and carbon and various hydrocarbons etc.

These primary pollutants are then converted into secondary pollutants

through various reactions going on in the atmosphere. The main secondary pollutants are ozone, per oxyacetyl nitrate (PAN), sulphuric acid etc. All these compounds are toxic and their concentration in the atmosphere must be controlled.

Interesting Information

Air pollution is responsible for about seven to eight million deaths annually. It is a significant risk to child health.

Oxides of nitrogen which are harmful when present in the atmosphere include NO and NO_2, collectively represented by NO_x. They are generated in the atmosphere through both natural and man-made sources.

Natural sources for the production of NO_x include electrical discharges

$$N_{2(g)} + O_{2\,(g)} \xrightarrow{\text{Electric arc}} 2NO_{(g)}$$

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

during lightning which can cause atmospheric nitrogen and oxygen to react forming nitric oxide. This nitric oxide is rapidly converted into nitrogen dioxide by oxygen present in air.

Combustion of fossil fuels in vehicles, various industrial processes and electricity power plants are the main man-made sources which generate NO_x in the atmosphere. Apart from these, agricultural activities and fertilizers also contribute to NO_x emission.

Heavy traffic during morning and evening hours together with industrial processes emit a huge amount of oxides of nitrogen (NO_x) and most volatile organic compounds (VOCs) in the atmosphere.

Ultraviolet radiation present in sunlight interacts with the oxides of nitrogen and VOCs through a complex series of chemical reactions to produce secondary pollutants like ozone, aldehydes and peroxyacetyl nitrate (PAN).

Oxides of nitrogen are also responsible for the formation of another type of pollutant called acid rain. Especially NO_2 reacts with water and other chemicals presents in air, to produce vapours of nitric acid and nitrous acid.

$$2NO_{2\,(g)} + H_2O_{\,(l)} \longrightarrow HNO_{3(g)} + HNO_{2\,(g)}$$

These acidic vapours then mix with water vapours present in air and fall to earth as acid rain.

Oxides of nitrogen (NO_x) can also act as catalyst to convert, another primary pollutant, sulphur dioxide present in air, to sulphuric acid which is another major component of acid rain.

$$2SO_{2\,(g)} + O_{2\,(g)} \xrightarrow{\text{Oxides of nitrogen}} 2SO_{3(g)}$$

$$SO_{3(g)} + H_2O_{(g)} \longrightarrow H_2SO_{4\,(g)}$$

19.6 Quick Check!

1. What are the harmful effects of oxides of nitrogen on human health?
2. How do oxides of nitrogen pollute environment?

Acid rain has a pH less than 5.6. Acid rain is damaging for the ecosystem, it can corrode materials and can lead to respiratory problems.

EXERCISE

A Multiple Choice Questions

Choose and tick the correct answer from the given choices.

1. The reason for maintaining higher temperature for the production of ammonia is:
   (a) activation energy of the reaction is very high.
   (b) activation energy of the reaction is very low.
   (c) nitrogen and hydrogen are both gases.
   (d) at low temperature nitrogen and hydrogen change into liquids.
2. The contact process used for the industrial production of H_2SO_4 is sensitive to the impurities present in SO_2 and O_2 because the impurities:
   (a) affect the capability of the catalyst
   (b) affect the purity of H_2SO_4
   (c) do not let SO_2 to react with oxygen
   (d) decrease the rate of reaction appreciably
3. Which of the following oxides is neutral in character?
   (a) Al_2O_3 (b) SO_2
   (c) CO_2 (d) NO

4. Sodium is considered more reactive than magnesium because:

(a) It is more electropositive than magnesium

(b) It reacts with water slowly.

(c) It is present in second group

(d) It is the less metallic

5. Secondary pollutants present in the atmosphere are:

(a) Oxides of nitrogen (b) Oxides of Sulphur

(c) Ozone and PAN (d) Oxides of Carbon

6. SO_3 is absorbed in H_2SO_4 rather than H_2O during the production of sulphuric acid because:

(a) SO_3 does not react with H_2O

(b) reaction of SO_3 with H_2O is highly exothermic producing mist of H_2SO_4 which is difficult to condense.

(c) It gives better yield of H_2SO_4

(d) reaction of SO_3 with H_2O can cause explosion.

7. Oxides formed when oxygen reacts with metals:

(a) Acidic (b) Basic

(c) Both basic and amphoteric (d) Neutral

8. Major components of acid rain are:

(a) H_2SO_4 and HNO_3 (b) H_2SO_3 and HNO_2

(c) H_2SO_4 and HCl (d) Acetic acid and HNO_3

B Short Answer Questions

19.1 How is nitrogen obtained from air?

19.2 How is hydrogen produced from methane?

19.3 Which conditions are used to oxidize SO_2 to SO_3?

19.4 Why CO_2 is called an acidic oxide while CO is called a neutral oxide?

19.5 How do magnesium and calcium differ with each other towards their reactions with water?

19.6 How are the reactivities of metals determined?

19.7 Which secondary pollutants are produced by oxides of nitrogen?

C Constructed Response Questions

19.1 Why ammonia is regarded as an important chemical?

19.2 How SO_2 present in the atmosphere is converted to SO_3?

19.3 The burning of fossil fuels in a car engine is responsible for the production of oxides of nitrogen. Explain.

19.4 The metals present at the top of the reactivity series are regarded as more reactive than those present at the bottom. Comment on this statement.

19.5 How fossil fuels produce SO_2?

D Descriptive Questions

19.1 Explain the production of ammonia on industrial scale.

19.2 Describe the contact process for the production of sulphuric acid.

19.3 Explain the formation and properties of acidic and basic oxides.

19.4 Differentiate between first and second group metals based on their reactivities with oxygen and water.

19.5 Describe the role of oxides of nitrogen in the formation of PAN and the acid rain.