# CHAPTER 19
# NITROGEN AND SULPHUR

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## Student Learning Outcomes

- Recognize how atmospheric oxides of nitrogen react with unburned hydrocarbons to form PAN, a component of photochemical smog.
- Describe the role of NO and $NO_2$ in acid-rain formation and their catalytic role in oxidation of atmospheric $SO_2$.
- State the Haber-process equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.
- Identify the sources of nitrogen and hydrogen used in the Haber process.
- Recall typical Haber conditions: about 450 °C, high pressure and an iron catalyst.
- State the Contact-process equation: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$.
- Identify sulphur dioxide and oxygen sources in the Contact process and its typical catalyst/conditions.
- Describe acidic, basic, neutral and amphoteric oxides with suitable examples.
- Describe general chemical reactions of metals with dilute acids, cold water, steam and oxygen.
- Arrange metals in decreasing order of reactivity and use the series to predict reactions.

## 19.1 Ammonia

- Ammonia ($NH_3$) is an important industrial chemical.
- About 80% of industrially produced ammonia is used to make fertilizers such as urea and ammonium salts.
- Ammonia is also used in plastics, pharmaceuticals and as a refrigerant.
- The industrial manufacture of ammonia is carried out by the Haber process, developed by F. J. Haber.
- Industrial feed gases are nitrogen and hydrogen in a 1:3 volume ratio.
- Typical conditions in the source are about 400–500 °C and about 200 atm, using an iron-based catalyst promoted with $Al_2O_3$.
- Reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.
- The equilibrium mixture contains about 35% ammonia by volume in the source description.
- Ammonia is cooled; at about −33.4 °C it liquefies and can be removed.
- Unreacted nitrogen and hydrogen are recycled to the reaction chamber.

### Source of Nitrogen

- Nitrogen is obtained from air by fractional distillation.
- Carbon dioxide is first removed from air.
- Air is compressed, cooled and expanded repeatedly until it becomes liquid air.
- Liquid air is fractionally distilled.
- Nitrogen has a lower boiling point than oxygen and evaporates first at about −196 °C.
- Separated nitrogen is reliquefied and stored in suitable cylinders.

### Source of Hydrogen

- Hydrogen is produced by heating methane with a limited amount of oxygen.
- The limited oxygen prevents complete oxidation of methane to carbon dioxide and water.
- The products primarily contain hydrogen and carbon monoxide, with a smaller amount of carbon dioxide.

- Carbon monoxide is reacted with water to produce more hydrogen and carbon dioxide.

**Quick Check:** Why is ammonia gas turned into a liquid after its production?

**Answer:** Cooling liquefies ammonia, allowing it to be separated and removed from the equilibrium mixture while unreacted nitrogen and hydrogen are recycled.

**Quick Check:** Why is high pressure maintained in the production of ammonia?

**Answer:** High pressure favors ammonia formation because the reaction changes 4 moles of gaseous reactants into 2 moles of gaseous product.

# 19.2 Sulphuric Acid

- Sulphuric acid ($H_2SO_4$) is one of the most important industrial chemicals.
- It is prepared industrially by the Contact process.
- Step 1: Sulphur dioxide is prepared by burning sulphur in air or roasting iron pyrite ($FeS_2$) in excess air.
- Step 2: $SO_2$ and $O_2$ are purified and dried before catalytic oxidation.
- Purification removes dust and arsenic compounds; arsenic compounds can poison the catalyst.
- The gases are dried using concentrated sulphuric acid.
- Step 3: $SO_2$ is oxidized to $SO_3$ over vanadium(V) oxide, $V_2O_5$, at about 450 °C and 2–3 atm.
- Reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$.
- About 98% conversion of $SO_2$ is stated under these conditions.
- Step 4: $SO_3$ is absorbed in 98% $H_2SO_4$ to form oleum, $H_2S_2O_7$.
- Step 5: Oleum is mixed with an appropriate amount of water to obtain sulphuric acid of the desired concentration.
- Sulphuric acid is called the 'king of chemicals' because it is used directly or indirectly in many industries.

**Quick Check:** How is $SO_2$ prepared from $FeS_2$?

**Answer:** By roasting iron pyrite in excess air: $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$.

**Quick Check:** Why are $SO_2$ and oxygen purified before they react to produce $SO_3$?

**Answer:** Impurities, especially arsenic compounds and dust, can poison the $V_2O_5$ catalyst and interfere with the catalytic conversion of $SO_2$ to $SO_3$.

# 19.3 Oxides

- Oxides are binary compounds of elements with oxygen.
- Oxygen generally has oxidation state −2 in these oxides.
- Metal oxides are commonly basic or amphoteric; non-metal oxides are commonly acidic.
- Metal oxides are generally ionic, while non-metal oxides are generally covalent.

## Basic Oxides

- Basic oxides are commonly formed when metals react with oxygen.
- Many basic oxides react with water to form hydroxides.
- Basic hydroxide solutions turn red litmus blue.
- Basic oxides react with acids to form salts and water.
- Examples include $Na_2O$, $CaO$ and $CuO$.
- $2Na + O_2 \rightarrow 2Na_2O$
- $Na_2O + H_2O \rightarrow 2NaOH$
- $CaO + 2HCl \rightarrow CaCl_2 + H_2O$

- $2Cu + O_2 \rightarrow 2CuO$
- $CuO + 2HCl \rightarrow CuCl_2 + H_2O$

### Acidic Oxides

- Acidic oxides are commonly formed when non-metals react with oxygen.
- They may react with water to form acids.
- Acidic solutions turn blue litmus red.
- Acidic oxides react with bases to form salts and water.
- Examples include $SO_2$ and $CO_2$.
- $S + O_2 \rightarrow SO_2$
- $SO_2 + H_2O \rightarrow H_2SO_3$
- $SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$
- $C + O_2 \rightarrow CO_2$
- $CO_2 + H_2O \rightarrow H_2CO_3$
- $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$

### Neutral Oxides

- Neutral oxides do not form an acid or a base on contact with water.
- Their aqueous solutions have no action on blue or red litmus paper.
- Examples given are CO, NO and $N_2O$.

### Amphoteric Oxides

- Amphoteric oxides react with both acids and bases to produce salts and water or soluble complex salts.
- They are commonly formed by less electropositive metals.
- Important examples are ZnO and $Al_2O_3$.
- They are insoluble in water and have no action on litmus paper.
- With acids, they behave as bases; with alkalis, they behave as acids.
- $ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$
- $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$
- $ZnO + 2NaOH + H_2O \rightarrow Na_2Zn(OH)_4$
- $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$

**Quick Check:** Why is lead oxide called an amphoteric oxide?

**Answer:** Because it can react with acids as a basic oxide and with strong alkalis as an acidic oxide. This dual behavior is called amphoterism.

**Quick Check:** Why do non-metals form covalent oxides?

**Answer:** Non-metals generally form compounds with oxygen by sharing electrons, producing covalent bonds; hence their oxides are commonly covalent.

## 19.4 Metals

- Metals generally have a tendency to lose electrons and form positive ions (cations).
- Metals commonly form ionic bonds with other elements.
- Most metals occur naturally in the Earth's crust as oxides, hydroxides, carbonates, sulphides and related compounds.

### Metals with Cold Water

- Many Group 1 and Group 2 metals react with cold water to form hydroxides and hydrogen.
- Potassium and sodium react very vigorously with cold water.
- Magnesium reacts slowly with cold water to form magnesium hydroxide and hydrogen.
- $2Na + 2H_2O \rightarrow 2NaOH + H_2$
- $2K + 2H_2O \rightarrow 2KOH + H_2$
- $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$

### Metals with Steam

- The more reactive a metal is, the more readily it reacts with steam.
- Some very reactive metals can react violently with steam.
- Be and Al react with steam at high temperature, around 700 °C, forming oxides and hydrogen.
- Mg, Fe and Zn react moderately with steam, forming their oxides and hydrogen.
- $Be + H_2O(g) \rightarrow BeO + H_2$
- $Mg + H_2O(g) \rightarrow MgO + H_2$

### Metals with Oxygen

- Metals react with oxygen to form metal oxides.
- The ease and type of reaction depend on metal reactivity and conditions.
- Sodium burns in air with a yellow flame and can form sodium oxide and sodium peroxide.
- Mg burns with an intense white flame; Ca gives a white flame with a tinge of red; Sr gives a crimson flame; Ba gives a pale green flame.
- $4Na + O_2 \rightarrow 2Na_2O$
- $2Na + O_2 \rightarrow Na_2O_2$
- $2Ca + O_2 \rightarrow 2CaO$

### Metals with Dilute Acids

- More reactive metals react more vigorously with dilute acids.
- Very reactive sodium and potassium react violently with dilute acids.
- Metals reacting with dilute acids generally produce a salt and hydrogen gas.
- Group 2 metals react with dilute acids; the reaction generally becomes more vigorous down the group.
- $2Na + 2HCl \rightarrow 2NaCl + H_2$
- $Mg + 2HCl \rightarrow MgCl_2 + H_2$

## 19.5 Reactivity Series of Metals

- The reactivity series arranges metals in decreasing order of reactivity.
- Source order: K > Na > Li > Ba > Sr > Ca > Mg > Al > C > Mn > Zn > Fe > H > Cu > Ag > Au.
- Calcium and metals above it react with cold water to form hydroxides and hydrogen.
- Metals below calcium generally do not react with cold water; they may react with steam to form oxides and hydrogen.
- Only metals above hydrogen liberate hydrogen gas from dilute acids.
- Metals below hydrogen generally do not react with dilute acids.
- The higher a metal is in the series, the more vigorous its reaction with dilute acids is.
- Highly reactive K and Na react readily with oxygen; less reactive Cu, Ag and Fe react more slowly.
- Metals near the top are powerful reducing agents because they are easily oxidized.
- Reducing ability decreases down the series.
- Zinc can displace copper from copper sulphate: $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$.

**Quick Check:** Write the equation for the reaction between Ba and $H_2O$.

**Answer:** $Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2$.

**Quick Check:** How do aluminium and zinc react with water?

**Answer:** Aluminium is protected by a surface oxide layer and does not readily react with cold water; zinc does not react appreciably with cold water but reacts with steam to form ZnO and $H_2$.

**Quick Check:** Which will react faster with HCl, Zn or Fe?

**Answer:** Zn, because zinc is above iron in the reactivity series and is therefore more reactive.

**Quick Check:** Name one metal which will displace Zn from its salt.

**Answer:** Any metal above Zn in the given series can displace zinc; for example, Mg.

## 19.6 Role of Oxides of Nitrogen in Spreading Air Pollution

- Primary atmospheric pollutants include oxides of nitrogen, sulphur and carbon, and various hydrocarbons.
- Primary pollutants undergo atmospheric reactions and form secondary pollutants.
- Important secondary pollutants mentioned are ozone, peroxyacetyl nitrate (PAN) and sulphuric acid.
- NO and $NO_2$ are harmful oxides of nitrogen, collectively represented as $NO_x$.
- $NO_x$ is produced naturally and by human activities.
- Lightning can produce NO when atmospheric nitrogen and oxygen react; NO is rapidly converted to $NO_2$ by oxygen.
- Major man-made sources include fossil-fuel combustion in vehicles, industrial processes and power plants.
- Agricultural activities and fertilizers also contribute to $NO_x$ emissions.
- Heavy traffic and industrial processes release $NO_x$ and volatile organic compounds (VOCs).
- Ultraviolet radiation from sunlight drives reactions involving $NO_x$ and VOCs, producing secondary pollutants such as ozone, aldehydes and PAN.
- $NO_2$ also contributes to acid rain by reacting with water and other atmospheric chemicals to form nitric acid and nitrous acid.
- These acidic vapours mix with atmospheric water and fall as acid rain.
- $NO_x$ can catalyze the conversion of $SO_2$ into $SO_3$; $SO_3$ reacts with water to form sulphuric acid.
- Acid rain has a pH below 5.6 and can damage ecosystems, corrode materials and contribute to respiratory problems.
- $N_2 + O_2 \rightarrow 2NO$
- $2NO + O_2 \rightarrow 2NO_2$
- $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$
- $2SO_2 + O_2 \rightarrow 2SO_3$
- $SO_3 + H_2O \rightarrow H_2SO_4$

**Quick Check:** What are the harmful effects of oxides of nitrogen on human health?

**Answer:** $NO_x$ contributes to harmful secondary pollutants and acid-rain chemistry; the chapter specifically notes that acid rain can contribute to respiratory problems. High atmospheric concentrations are toxic and must be controlled.

**Quick Check:** How do oxides of nitrogen pollute environment?

**Answer:** $NO_x$ contributes to photochemical smog by participating with VOCs in sunlight-driven reactions that form ozone and PAN, and it contributes to acid rain through formation of nitric/nitrous acids and catalytic oxidation of $SO_2$ to sulphuric acid.

# Chapter 19 — Rapid Revision

| Topic | Must Remember | Key Equation / Point |
|---|---|---|
| 19.1 Ammonia | Haber process; $N_2$:$H_2$ = 1:3 | $N_2 + 3H_2 \rightleftharpoons 2NH_3$ |
| 19.2 Sulphuric Acid | Contact process; $V_2O_5$ catalyst | $2SO_2 + O_2 \rightleftharpoons 2SO_3$ |
| 19.3 Oxides | Basic, acidic, neutral, amphoteric | ZnO and $Al_2O_3$ are amphoteric |
| 19.4 Metals | Water, steam, oxygen, dilute acids | More reactive → more vigorous reaction |
| 19.5 Reactivity Series | K → ... → Au | Above H metals release $H_2$ from dilute acids |
| 19.6 $NO_x$ Pollution | Smog, PAN, acid rain | $NO_x$ + VOCs + sunlight → secondary pollutants |

*Prepared as easy, exam-focused notes from the supplied Chapter 19 text.*