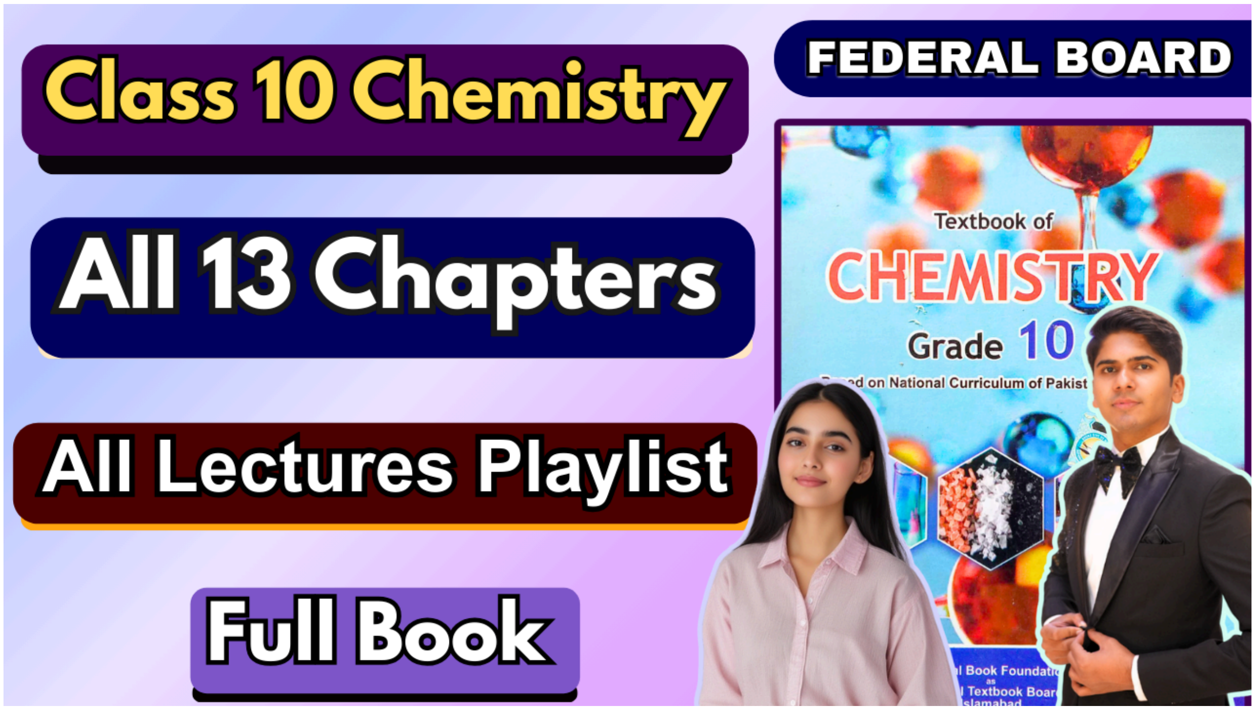
Chapter 7 - Nitrogen, Sulfur, and Metals

All Lectures Uploaded on YouTube:

https://tinyurl.com/fkm10-chemistry



Nitrogen and sulphur oxides play important roles in the environment and industrial processes. For instance, in the atmosphere, oxides such as nitric oxide (NO) and nitrogen dioxide (NOz) react with unburned hydrocarbons, resulting in the formation of peroxy acetyl nitrate, or PAN, which is a major component of photochemical smog.

7.1. Photochemical Smog

A type of air pollution formed when sunlight reacts with nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in the atmosphere.

Key Component: Peroxyacetyl Nitrate (PAN) - A major component and secondary pollutant in smog.

Formation Process (Step-by-Step):

1. **Formation of NO_2:**

   Nitric oxide (NO) from vehicles and industry reacts with oxygen. $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_2(g)$

2. **Photolysis of NO_2:**

   NO_2 absorbs UV light and breaks down, producing a highly reactive oxygen atom.

   $NO_{2\,(g)} \rightarrow NO_{\,(g)} + [O](g)$

3. **Formation of Ozone (O_3):**

   The atomic oxygen ([O]) reacts with oxygen molecules to form ozone. $O_{2(g)} + [O]_{\,(g)} \rightarrow O_3(g)$

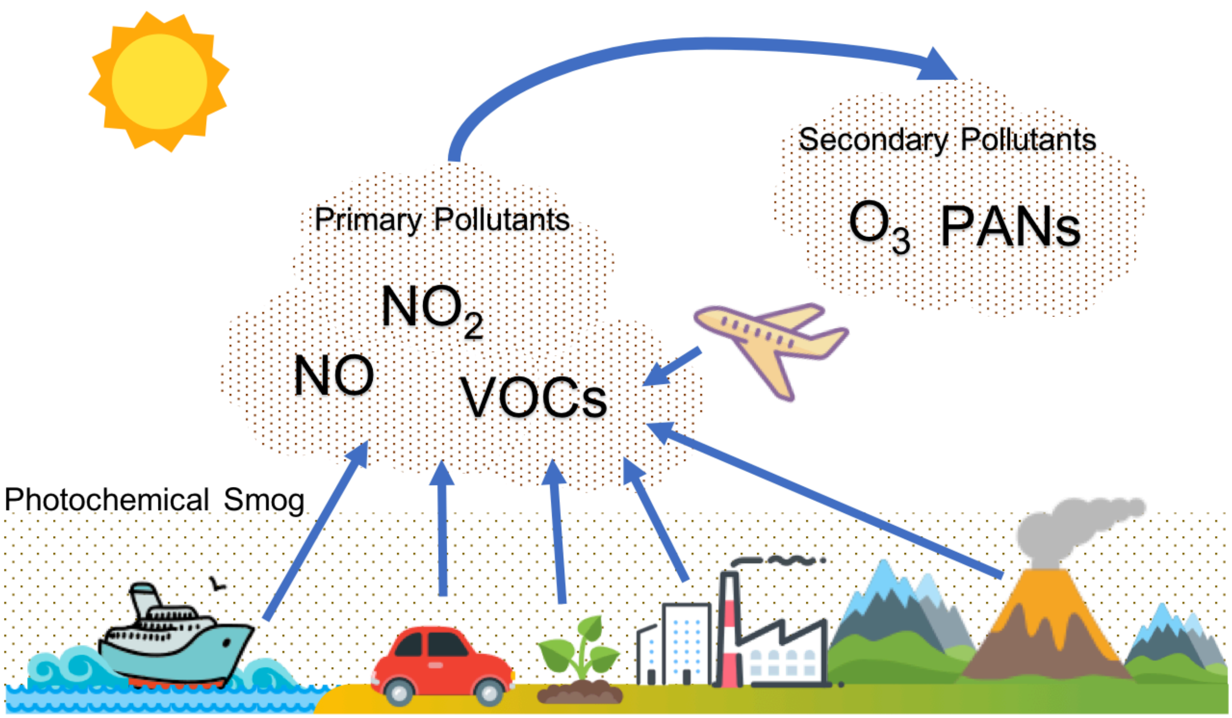
4. **Reaction with Hydrocarbons (VOCs):**

Unburned hydrocarbons react with the atomic oxygen ([O]), forming organic radicals.

$Hydrocarbon_{(g)} + [O]_{(g)} \rightarrow RCO^{\bullet}(g)$

5. **Formation of Peroxyacyl Radicals:**

The organic radicals react with oxygen to form peroxyacyl radicals.
$RCO^{\bullet}_{(g)} + O_{2\,(g)} \rightarrow RC(O)O_2^{\bullet}(g)$



6. **Formation of PAN:**

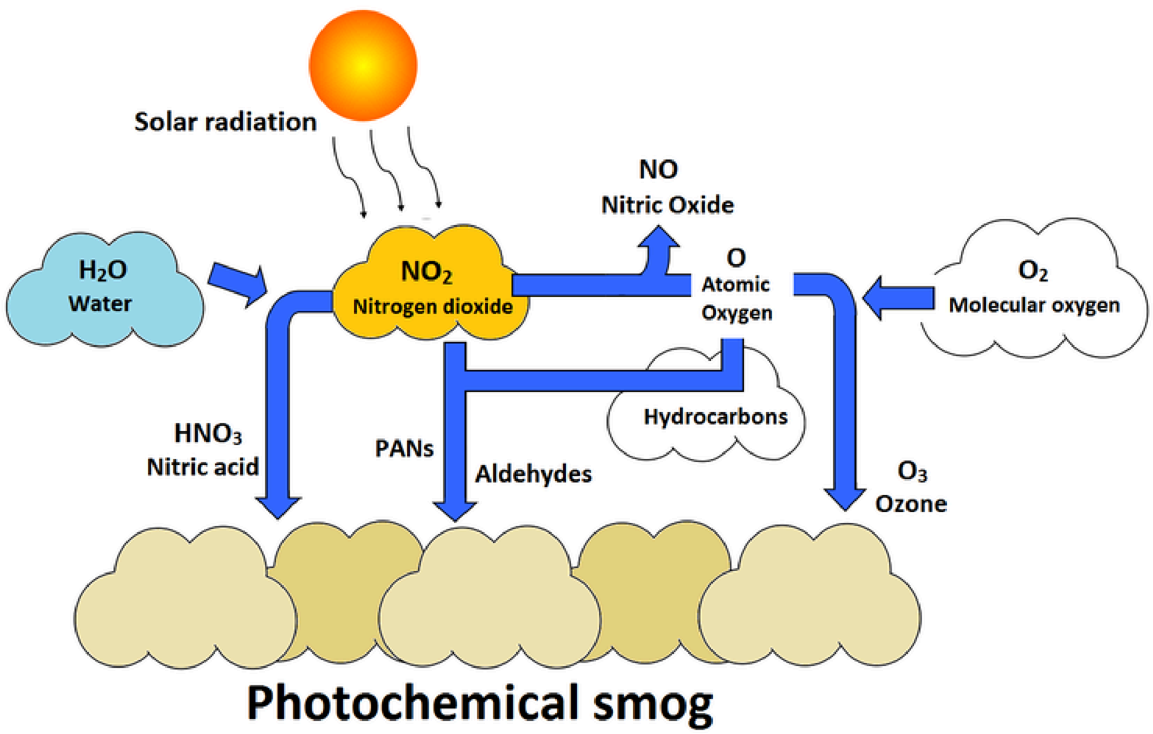
The peroxyacyl radical reacts with NO_2 to form PAN.

$RC(O)O_2^{\bullet}{}_{(g)} + NO_{2(g)} \rightarrow RC(O)O_2NO_2(g)$

Properties & Role of PAN:

· Stable at low temperatures and can travel long distances.

· Acts as a reservoir for NO_x and organic radicals, releasing them in warmer conditions, which sustains and prolongs smog formation.



7.2. Acid Rain

Rain with a pH less than 5, caused by the dissolution of acidic gases (SO_2 and NO_x) in rainwater, forming H_2SO_4 and HNO_3.

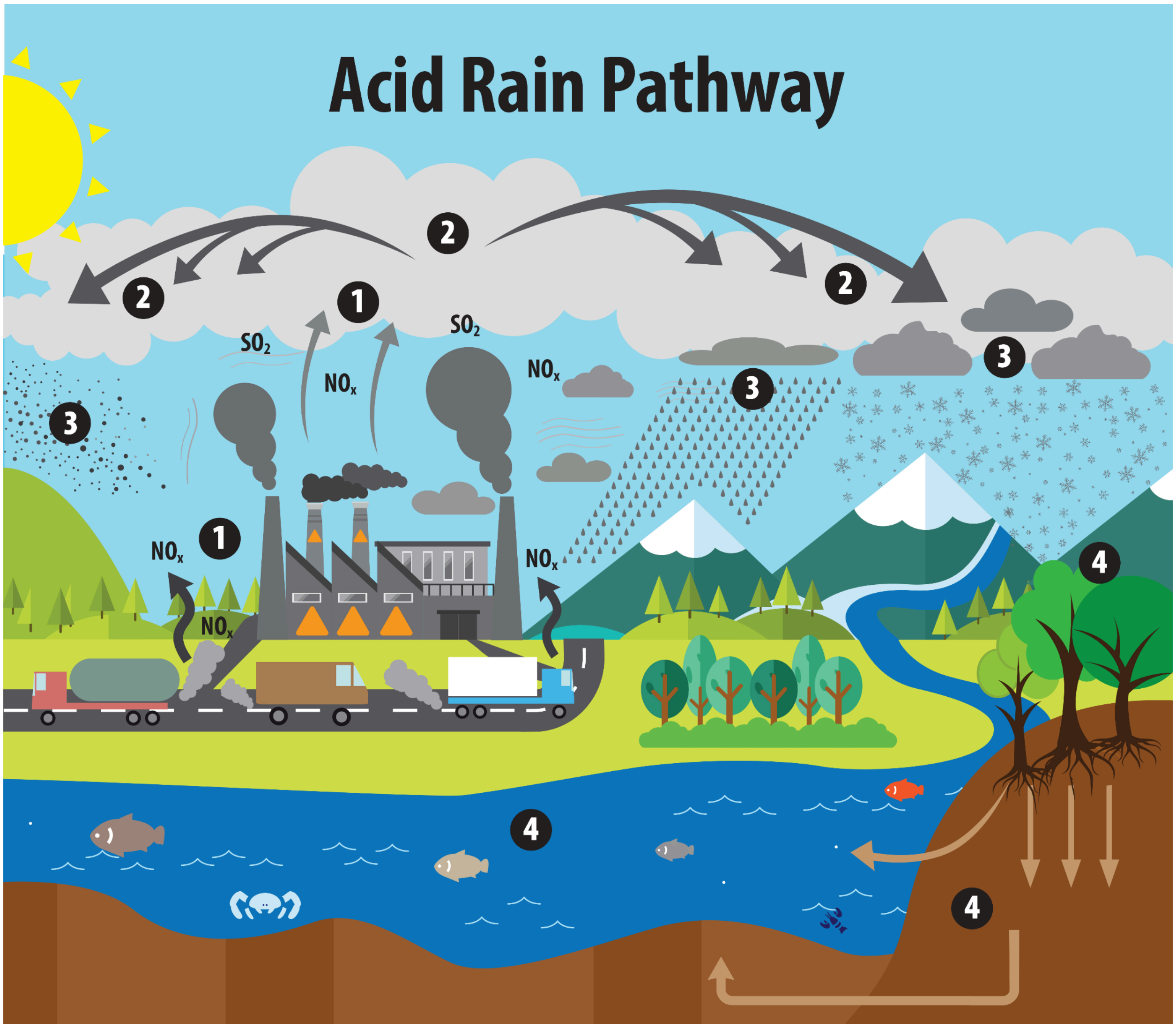
Primary Pollutants:

Sulphur Dioxide (SO_2): From burning fossil fuels.

Nitrogen Dioxide (NO_2): From automobile exhaust.

7.2.1. Role of Nitrogen Oxides (NO and NO_2) in Acid Rain

7.2.2. Direct Role in Acid Rain



A) Direct Role: Formation of Nitric Acid (HNO_3)

1. **Oxidation of NO to NO_2:**

$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_2(g)$

2. **Formation of Nitric Acid:**

NO_2 reacts with water and oxygen in the atmosphere.

$4NO_{2(g)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow 4HNO_3(aq)$

B) Catalytic Role: Oxidation of Sulphur Dioxide (SO_2)

NO_2 acts as a **catalyst** to convert SO_2 into sulphuric acid (H_2SO_4), a stronger acid. 1. **Oxidation of SO_2 to SO_3:**

NO_2 oxidizes SO_2, producing SO_3 and being reduced back to NO.

$SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$

2. **Formation of Sulphuric Acid:**

SO_3 readily dissolves in water to form H_2SO_4.

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

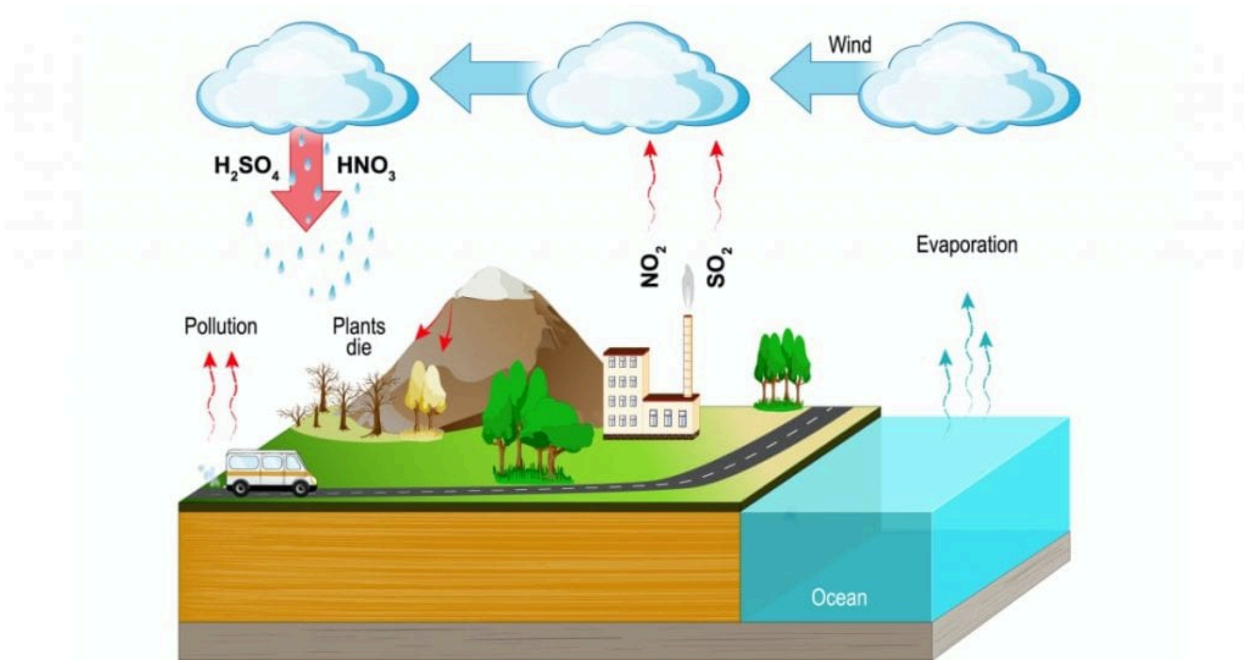
3. **Regeneration of the Catalyst (NO_2):**

The NO produced is re-oxidized by atmospheric oxygen, continuing the cycle.

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

7.3.3. Overall Impact:

A small amount of NO_2 can catalyze the conversion of a large amount of SO_2 into sulphuric acid, significantly increasing the acidity of rain.



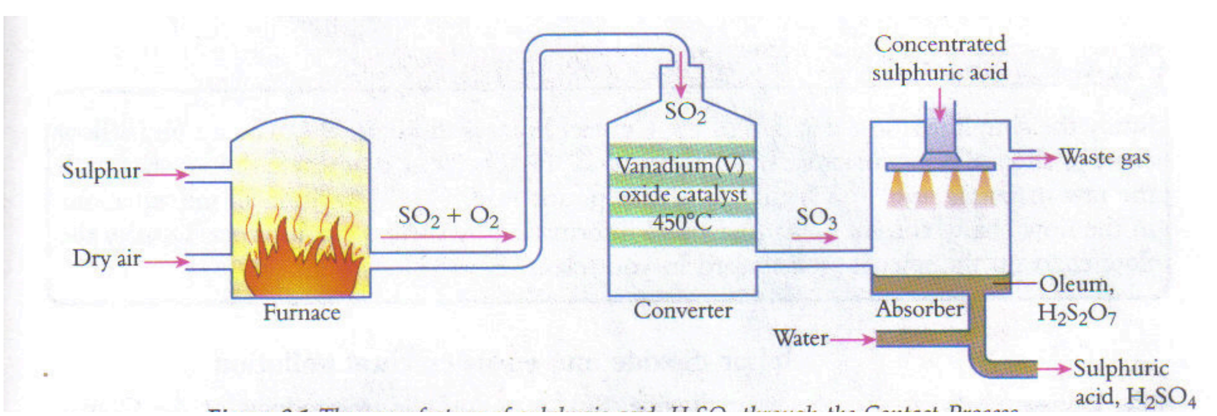
7.3. Contact Process (Manufacture of Sulphuric Acid)

Importance: Sulphuric acid (H_2SO_4) is a vital industrial chemical used in fertilizers, plastics, explosives, paints, and textiles, earning it the name "King of Chemicals."

Core Reaction: The process is based on the catalytic oxidation of Sulphur Dioxide (SO_2) to Sulphur Trioxide (SO_3).

$$2SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3\,(g)} + 45.2\ kcal$$

This reaction is **reversible** and **exothermic**.



Optimum Conditions (based on Le Chatelier's Principle):

Catalyst: Vanadium pentoxide (V_2O_5)

Temperature: ~450°C (A compromise; low temperature favors yield but high temperature is needed for a practical reaction rate).

Pressure: Around 2 atm (200 kPa). A higher pressure favors the side with fewer gas molecules, but only moderate pressure is needed for a good yield.

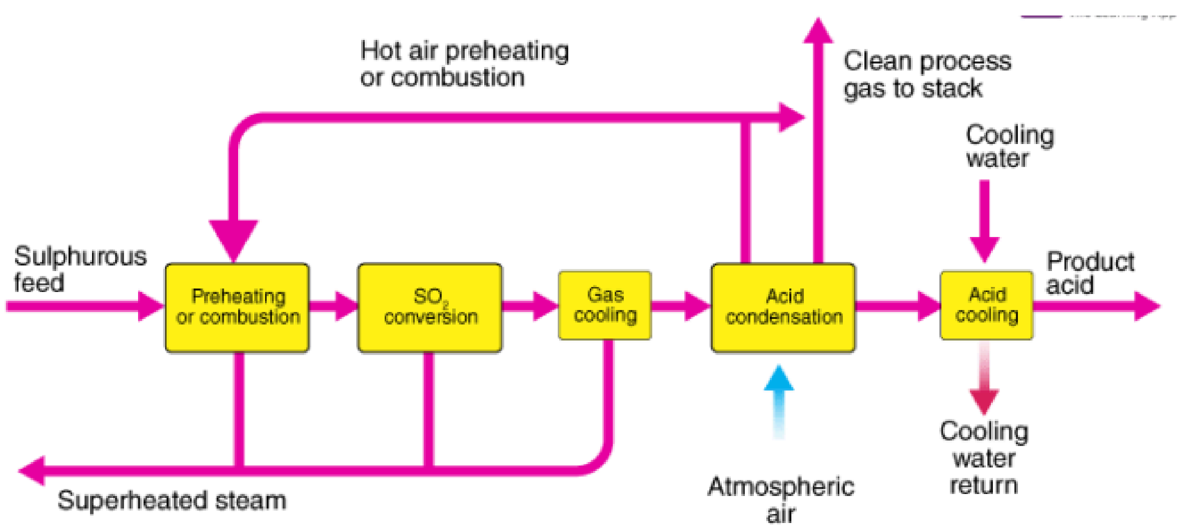
Step-by-Step Process:

1. **Production & Purification of SO_2:**

   SO_2 is produced by burning sulphur or roasting sulphide ores.

   $S(s) + O_{2\,(g)} \rightarrow SO_2\,(g)$

   The gas is cooled, filtered through coke, and dried.



2. **Conversion to SO_3:**

The purified SO_2 and air are passed over a V_2O_5 catalyst in a converter at ~450°C and 2 atm.

$2SO_{2\,(g)} + O_{2\,(g)} \rightarrow 2SO_3\,(g)$

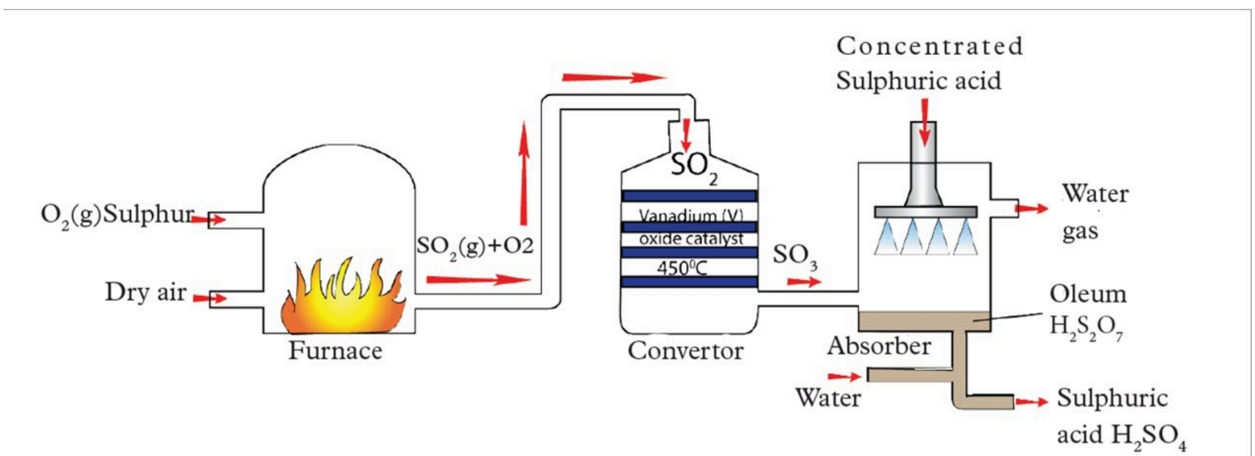
3. **Absorption & Production of H_2SO_4:**

SO_3 is **not** directly dissolved in water as it forms a corrosive mist. Instead, SO_3 is absorbed into 98% sulphuric acid to form **Oleum ($H_2S_2O_7$)**.

$H_2SO_{4\,(l)} + SO_{3\,(g)} \rightarrow H_2S_2O_7\,(l)$

Oleum is then diluted with water to produce concentrated sulphuric acid of any desired concentration.

$H_2S_2O_{7\,(l)} + H_2O_{(l)} \rightarrow 2H_2SO_4\,(l)$



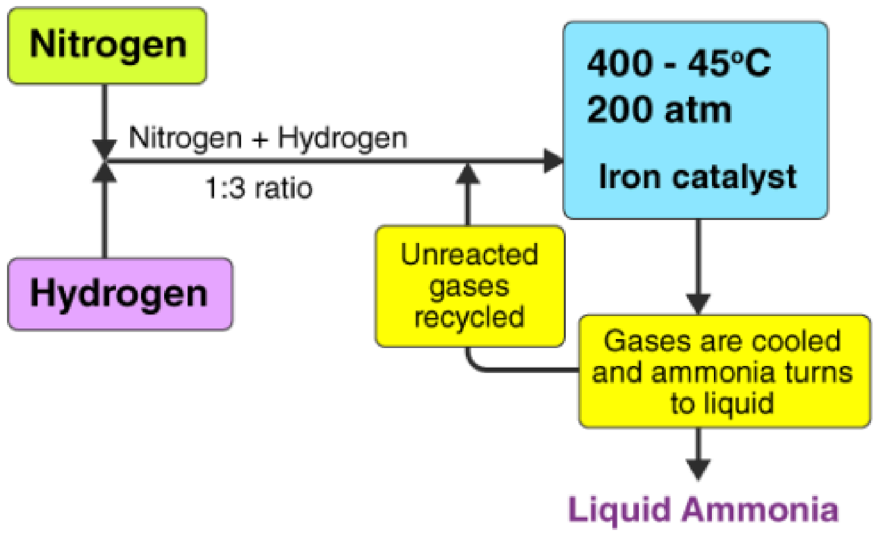
7.4. Haber Process (Manufacture of Ammonia)

Purpose: Commercial production of Ammonia (NH_3) by fixing atmospheric nitrogen.

Core Reaction:

$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$ + Heat

This reaction is **reversible**, **exothermic**, and results in a **decrease in volume**.



Sources of Reactants:

Nitrogen (N_2): Obtained from air.

Hydrogen (H_2): Obtained from the decomposition of methane (natural gas).

Optimum Conditions (based on Le Chatelier's Principle):

1. **Pressure: High pressure (200-500 atm)**. This favors the forward reaction because it decreases the total number of gas molecules.
2. **Temperature: Moderately low (450°C)**. Although low temperature favors the exothermic reaction, a higher temperature is used with a catalyst to achieve a practical reaction rate.
3. **Catalyst:** Iron promoter with Molybdenum (Fe/Mo).
4. **Reactant Ratio:** A 1:3 volume mixture of N_2 to H_2. An excess of N_2 is used to shift the equilibrium to the right.

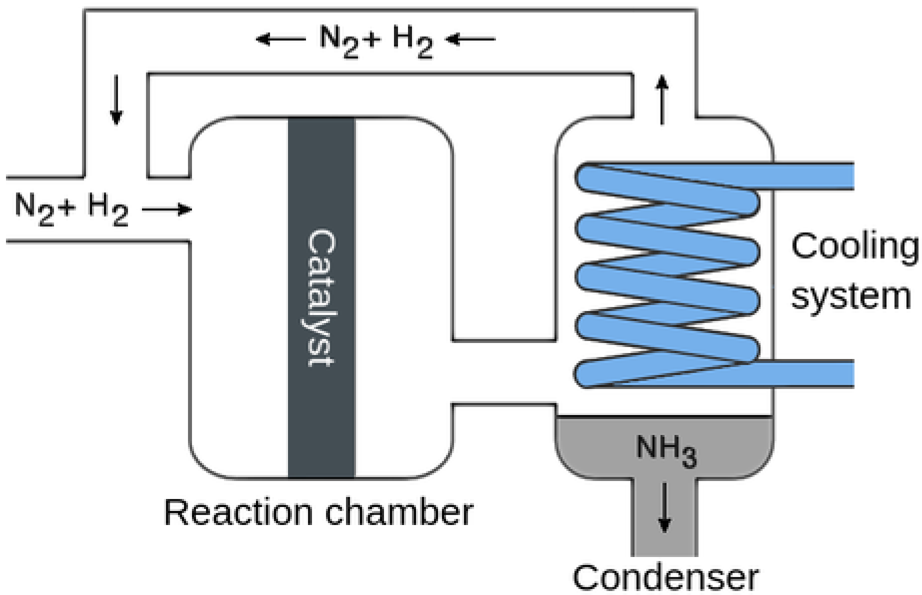
Process Flow:

1. Purified N_2 and H_2 gases are mixed, compressed, and passed over the catalyst in a heated chamber.

2. The product gas mixture (containing 10-12% ammonia) is cooled.

3. Ammonia gas is liquefied in a condenser using refrigerated brine and separated.

4. The unreacted N_2 and H_2 are **recycled** back to the reactor to improve overall yield.



7.5. Oxides

Binary compounds of an element with oxygen.

Classification:

1. Acidic Oxides

Oxides of **non-metals**.

Behavior:

React with water to form an **acid**.

React with bases to form salt and water.

Examples:

SO_2: SO_2 $_{(g)}$ + H_2O $_{(l)}$ → H_2SO_3 $_{(aq)}$ (Sulphurous acid)

CO_2: CO_2 $_{(g)}$ + H_2O $_{(l)}$ → H_2CO_3 $_{(aq)}$ (Carbonic acid)

2. Basic Oxides

Nature: Oxides of **metals**.

Behavior:

React with water to form a **base** (if soluble).

React with acids to form salt and water.

Examples:

CaO $CaO(s) + H_2O_{(l)} \rightarrow Ca(OH)_2(aq)$ (Calcium hydroxide, a base) **Na_2O & CaO with Acid:**

$Na_2O(s) + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O\ (l)$

$CaO(s) + 2HCl_{(aq)} \rightarrow CaCl_2\,_{(aq)} + H_2O\ (l)$

ACIDIC OXIDES
VERSUS
BASIC OXIDES

ACIDIC OXIDES	BASIC OXIDES
Acidic oxides are compounds that can form an acidic solution when dissolved in water	Basic oxides are compounds that can form a basic solution when dissolved in water
Formed when oxygen reacts with non-metals	Formed when oxygen reacts with metals
React with water forming acidic compounds	React with water forming basic compounds
Do not react with acids	React with acids forming a salt
React with bases forming a salt	Does not react with bases
Have covalent bonds	Have ionic bonds
pH is increased when dissolved in water	pH is decreased when dissolved in water
Also known as acid anhydrides	Also known as base anhydrides

Amphoteric Oxides & Metal Reactivity

Amphoteric Oxides

Oxides that can react with **both acids and bases**. They are typically oxides of certain metals.

Behavior: They display dual (acidic and basic) character.

Examples:

Aluminum Oxide (Al_2O_3)

With Acid: $Al_2O_3(s) + 6HCl_{(aq)} \rightarrow 2AlCl_{3\,(aq)} + 3H_2O_{(l)}$ (Behaves as a base)

With Base: $Al_2O_3(s) + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2NaAl(OH)_{4\,(aq)}$ (Sodium aluminate) (Behaves as an acid)

Zinc Oxide (ZnO)

With Acid: $ZnO(s) + 2HCl_{(aq)} \rightarrow ZnCl_{2\,(aq)} + H_2O_{(l)}$ (Behaves as a base)

With Base: $ZnO(s) + 2NaOH_{(aq)} + H_2O_{(l)} \rightarrow Na_2[Zn(OH)_4](aq)$ (Sodium zincate) (Behaves as an acid)

7.5. General Characteristics of Metals

Metals react with various substances, and their reactivity determines the products.

Reaction with Dilute Acids

Metal + Dilute Acid → Salt + Hydrogen Gas

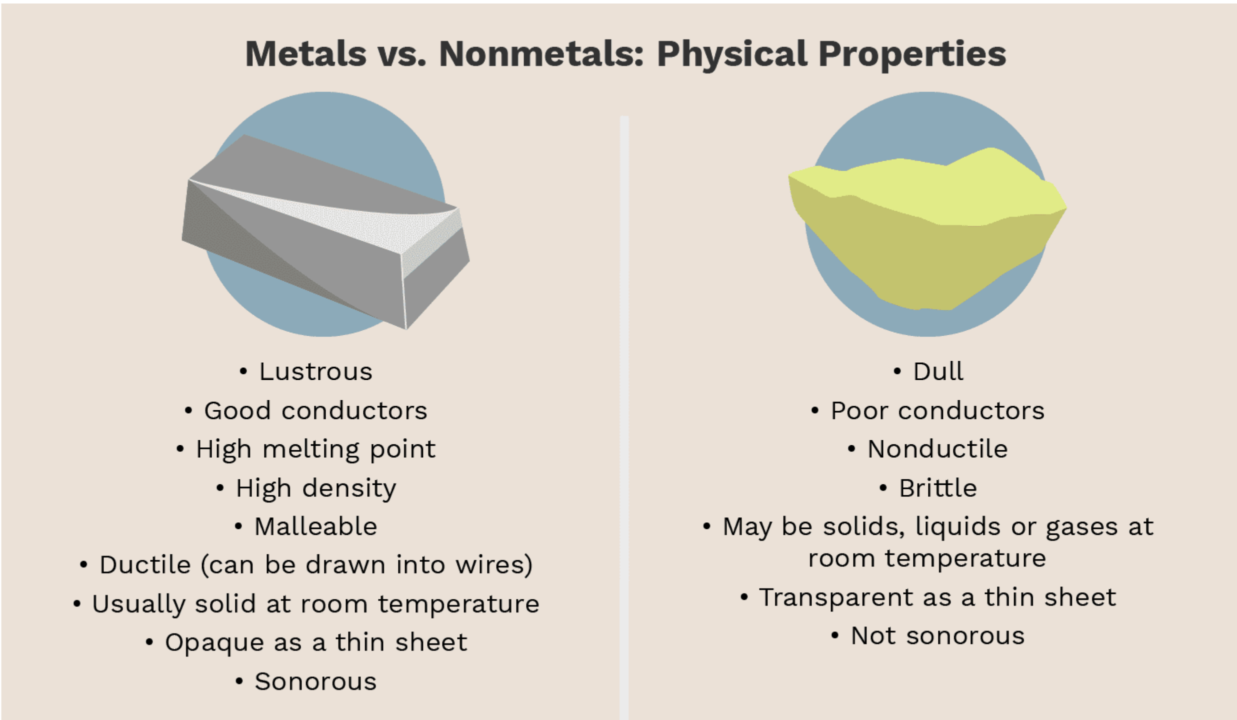
Example: $Mg(s) + 2HCl_{(aq)} \rightarrow MgCl_{2\,(aq)} + H_2(g)$

Observations:

Very Reactive (K, Na): React explosively.

Moderately Reactive (Mg, Zn, Fe): React steadily, producing bubbles of H_2.

Less/Unreactive (Cu, Ag, Au): No reaction.



2. Reaction with Cold Water

Metal + Cold Water ⟶ Metal Hydroxide + Hydrogen Gas

Example: $2Na(s) + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_2(g)$

Observations:

Very Reactive (K, Na, and Ca): React vigorously.

Moderately Reactive (Mg): Reacts slowly; faster with hot water. **Less Reactive (Zn, Fe):** Do not react significantly.

3. Reaction with Steam

Metal + Steam → Metal Oxide + Hydrogen Gas

Example: $3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4H_2(g)$

Observations:

Very Reactive (K, Na): Not tested (too violent).

Moderately Reactive (Mg, Zn, Fe): React readily.

Less Reactive (Cu): No reaction.

4. Reaction with Oxygen

Metal + Oxygen → Metal Oxide

Example: $2Mg(s) + O_{2\,(g)} \rightarrow 2MgO(s)$

Observations:

Very Reactive (K, Na): React rapidly, may form peroxides/superoxide.

Moderately Reactive (Mg, Al): Form a protective oxide layer that prevents further reaction.

Less Reactive (Cu): Oxidizes slowly, forming a patina.

Unreactive (Au, Pt): No reaction under normal conditions.

7.5.1. The Reactivity Series

Metals can be arranged in order of decreasing reactivity based on their reactions with water, steam, and acids.

Potassium > Sodium > Calcium > Magnesium > Aluminum > Zinc > Iron > Lead > Copper > Silver > Gold

Four Main Groups:

1. Highly Reactive Metals (e.g., K, Na, Ca)

Cold Water: React vigorously to form metal hydroxide and H_2 gas.
Steam & Acids: React explosively.

2. Moderately Reactive Metals (e.g., Mg, Al, Zn, Fe)

Cold Water: Slow or no reaction.

Steam: React to form metal oxide and H_2 gas. (e.g., $Mg(s) + H_2O_{(g)} \rightarrow MgO_{(s)} + H_2(g)$)

Acids: React steadily with acids to form salt and H_2 gas.

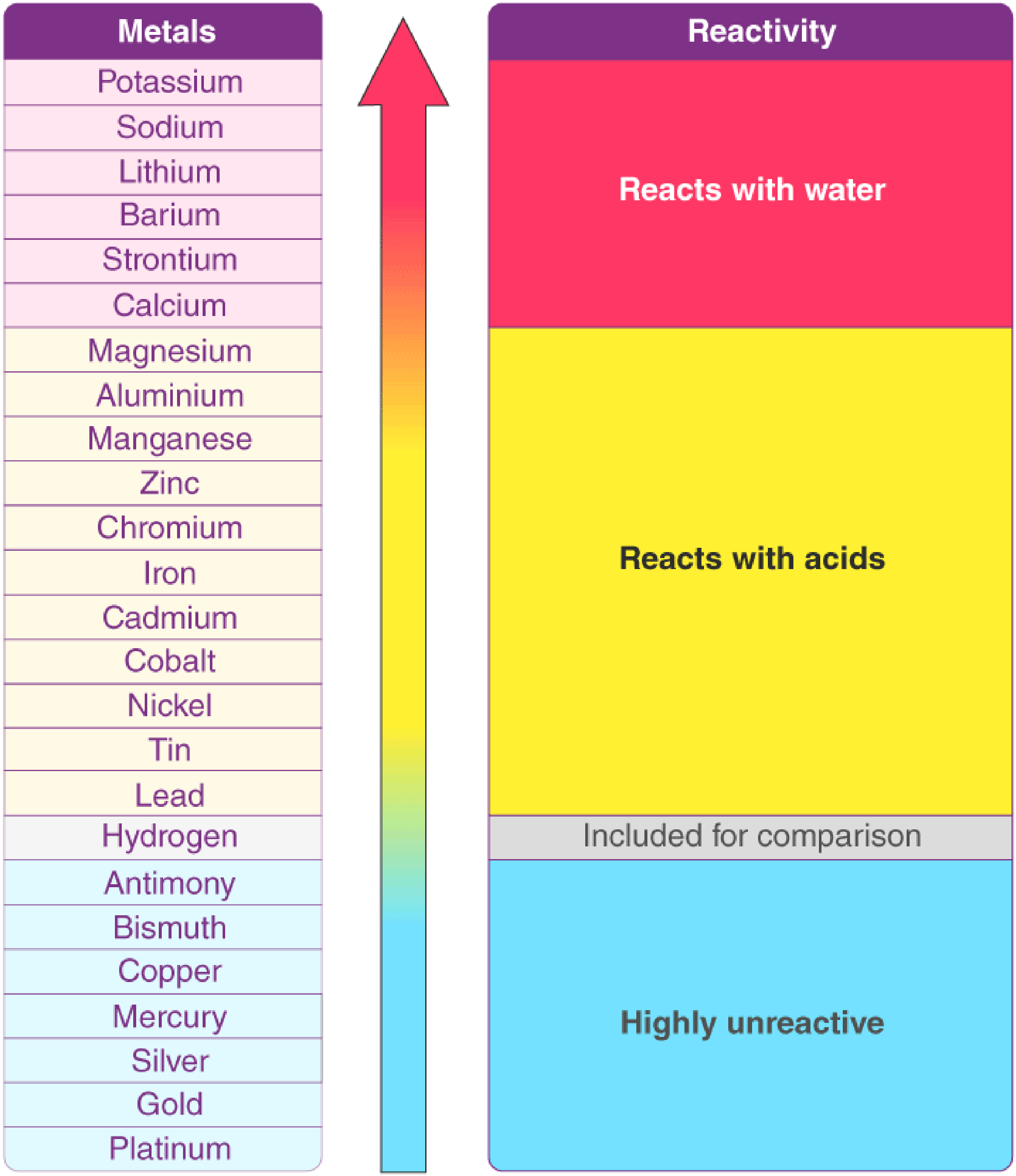
3. Less Reactive Metals (e.g., Pb, Cu, Ag)

Cold Water & Steam: No reaction.

Acids: React slowly or not at all (e.g., Cu and Ag do not react with dilute acids).

4. Unreactive Metals (e.g., Au, Pt)

Cold Water, Steam, & Acids: No reaction under normal conditions.


Metals
Potassium
Sodium
Lithium
Barium
Strontium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Iron
Cadmium
Cobalt
Nickel
Tin
Lead
Hydrogen
Antimony
Bismuth
Copper
Mercury
Silver
Gold
Platinum
Reactivity
Reacts with water
Reacts with acids
Included for comparison
Highly unreactive