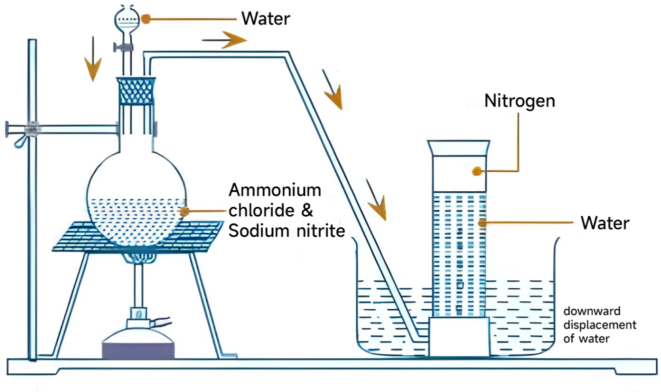
Chapter 4 - Nitrogen and Its Compounds

Nitrogen

- Nitrogen has an electronic configuration of 2.5, thus, it can
  - gain three electrons to form the **nitride ion, N^{3-}**, e.g. Mg_3N_2
  - form **covalent bonds**, e.g. N_2, NH_3
- role in lives of people
  - essential part of all living organisms, present in protein
  - essential part of many explosives

Laboratory Preparation

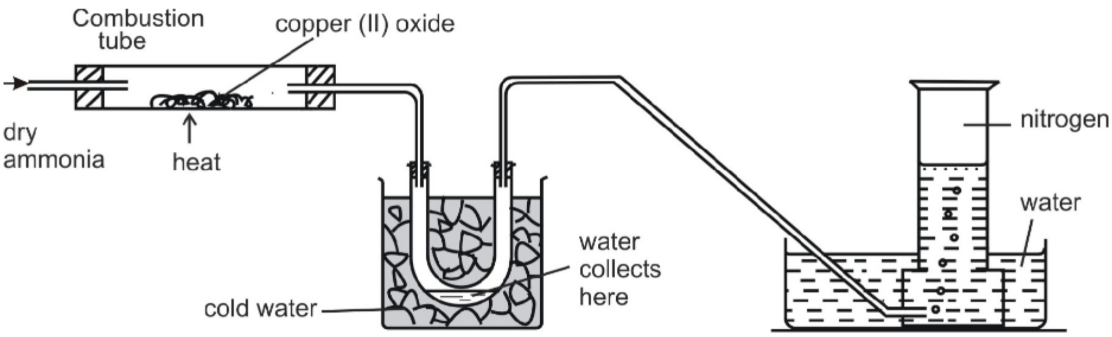
1. Preparation of nitrogen by the action of heat on ammonium chloride and sodium nitrite



$$\mathrm{NaNO_{2\,(aq)} + NH_4Cl_{(aq)} \xrightarrow{\Delta} NaCl_{(aq)} + N_{2\,(g)} + 2\,H_2O_{(l)}}$$

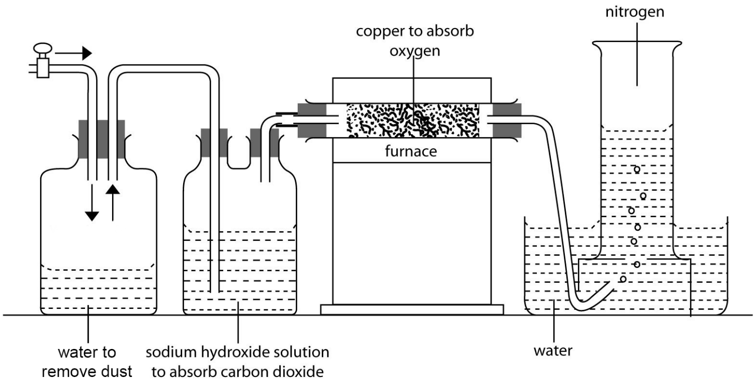
$$\mathrm{(NaNO_{2\,(aq)} + NH_4Cl_{(aq)} \xrightarrow{\Delta} NaCl_{(aq)} + NH_4NO_{2\,(aq)\,[unstable]})}$$

2. Preparation of nitrogen by action of ammonia gas on copper(II) oxide



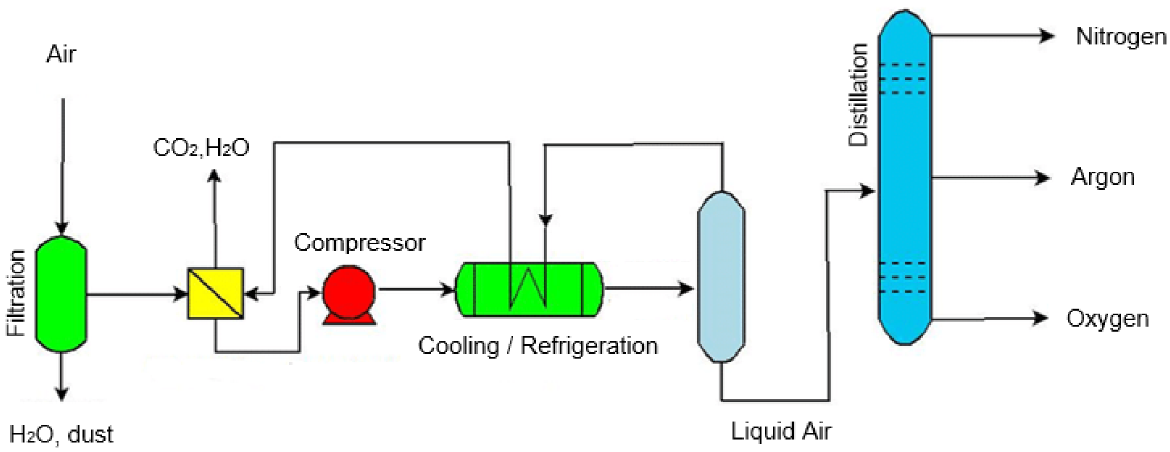
$$\mathrm{3\,CuO_{(s)} + 2\,NH_{3\,(g)} \xrightarrow{\Delta} 3\,Cu_{(s)} + N_{2\,(g)} + 3\,H_2O_{(l)}}$$

3. Preparation of nitrogen by action of air on copper (*extra one jit mentioned in class)



$$2\,NO_{(g)} + 2\,Cu_{(s)} \xrightarrow{\Delta} 2\,CuO_{(s)} + N_{2\,(g)}$$

Industrial Preparation



- **Air** is **liquefied** under pressure. When liquefied air is distilled, **liquid nitrogen boils first at -196°C** and oxygen boils off at -183°C. This process is known as **fractional distillation**.

Physical Properties

1. Colorless, odorless, tasteless. A suffocating gas, don't support life, but not poisonous.
2. Slightly lighter than air.
3. Slightly soluble in water. Two volumes of the gas dissolves in 100 volumes of water at room temperature.
4. Melts at -210°C, boils at -196°C under atmospheric pressure.

Chemical Properties

Oxidation States

NH_3	N_2	N_2O	NO	HNO_2 / N_2O_3	NO_2	NHO_3 / N_2O_5
-3	0	+1	+2	+3	+4	+5
reducing agent						oxidizing agent

- Nitrogen is chemically very inert under ordinary conditions.

- At very high temperature and pressure, nitrogen combines directly with hydrogen, oxygen and some metals to form compounds.

Reaction with metals

- Nitrogen combines directly with some metals, e.g. Ca, Mg, Al, Sr, Ba, Zn and Fe, to form **nitrides**.
- e.g. 1 Red hot magnesium combines directly with nitrogen to produce magnesium nitride. The nitride is **hydrolyzed** (water[OH^-] is added) when it is **warmed** together with a little **water**, and **ammonia gas** is produced.

$$\underset{\text{red hot}}{3\,\mathrm{Mg}_{(s)}} + \mathrm{N}_{2\,(g)} \longrightarrow \underset{\text{greenish yellow}}{\mathrm{Mg_3N}_{2\,(s)}}$$

$$\mathrm{Mg_3N}_{2\,(s)} + 6\,\mathrm{H_2O}_{(l)} \xrightarrow{\Delta} 3\,\mathrm{Mg(OH)}_{2\,(s)} + 2\,\mathrm{NH}_{3\,(g)}$$

- e.g. 2

$$2\,\mathrm{Al}_{(s)} + \mathrm{N}_{2\,(g)} \longrightarrow 2\,\mathrm{AlN}_{(s)}$$

$$\mathrm{AlN(s)} + 3\,\mathrm{H_2O}_{(l)} \xrightarrow{\Delta} \mathrm{Al(OH)}_{3\,(s)} + \mathrm{NH}_{3\,(g)}$$

Reaction with hydrogen

- Nitrogen combines reversibly with hydrogen. (**Haber Process**)

Reaction with oxygen

- Nitrogen combines with oxygen at **very high temperature** (about 2000°C) to form small amounts of nitrogen monoxide. In nature, this occurs in the atmosphere during **lightning flashes**.

$$\mathrm{N}_{2\,(g)} + \mathrm{O}_{2\,(g)} \xrightarrow{2000^\circ\mathrm{C}} 2\,\mathrm{NO}_{(g)}$$

Test for Nitrogen

- At ordinary temperatures, nitrogen is so inert that **no positive tests** can be applied. We can only show a given gas to be nitrogen by elimination of other possibilities.

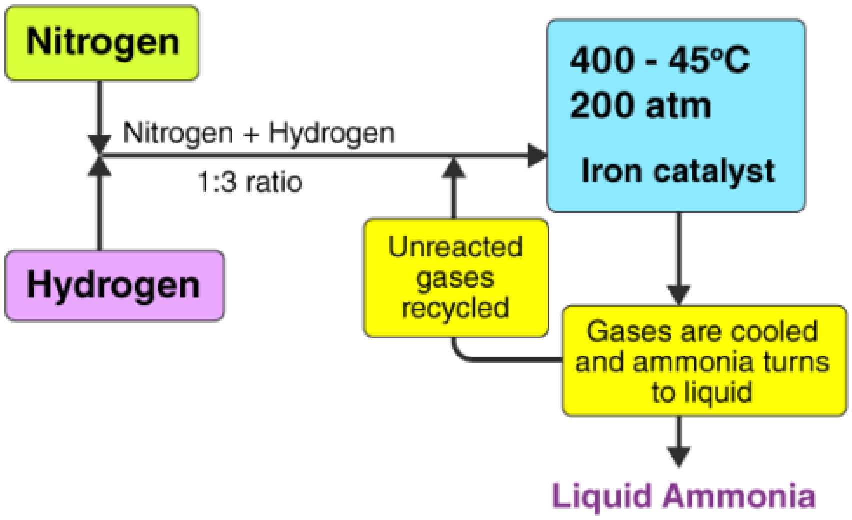
Uses

1. Manufacture of ammonia, cyanides (CN^-) and cyanamide (CNO^-, an important fertilizer)
2. Cooling agent
3. Preservative to prevent rancidity (due to the oxidation of fats) in packaged foods.
4. Carrier gas in gas chromatography

Ammonia

- hydride of nitrogen
- naturally produced when nitrogenous matter decays in the absence of air

Industrial Preparation (*Haber Process)

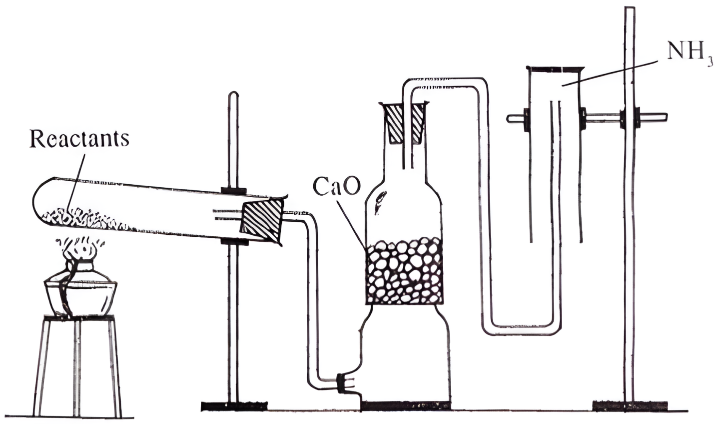


$$N_{2\,(g)} + 3\,H_{2\,(g)} \xrightleftharpoons{250-500\text{ atm},\ 500℃,\ Fe} 2\,NH_{3\,(g)}$$

- The temperature cannot be more than 550°C, this will cause the ammonia to decompose.

Laboratory Preparation

- **Heat ammonium salt with a non-volatile base**
- In the laboratory, ammonium chloride and **calcium hydroxide (slaked lime)** are used. Calcium hydroxide is chosen because it's cheap and not deliquescent like the caustic alkalis.



$$Ca(OH)_{2\,(s)} + 2\,NH_4Cl_{(s)} \xrightarrow{\text{warm}} CaCl_{2\,(s)} + 2\,H_2O_{(l)} + 2\,NH_{3\,(g)}$$

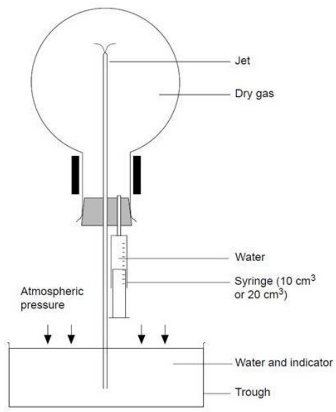
- Ammonia is collected by **downward displacement of air / upward delivery.**
- **Quicklime** (calcium oxide, **CaO**) is used as the **drying agent**.
- Concentrated sulfuric acid and calcium chloride cannot be used as the drying agents because ammonia reacts with them.

$$2\,NH_{3\,(g)} + 2\,H_2SO_{4\,(l)} \longrightarrow (NH_4)_2SO_{4\,(aq)} \text{ (acidic, absorbs the gas)}$$
$$4\,NH_{3\,(g)} + CaCl_{2\,(s)} \longrightarrow CaCl_2 \cdot 4\,NH_{3\,(g)} \text{ (forms a complex compound with ammonia)}$$

Physical Properties

- Colorless gas with characteristic choking smell
- Poisonous in large quantities, affect the respiratory muscles
- The only alkaline gas, turns red moist litmus paper blue
- 1.7 times denser than air
- Can be easily liquefied into a colorless liquid at ordinary temperatures by compression
- The most soluble gas known. (one volume of water dissolves about 700 volumes of ammonia at r.t.p.)

The Fountain Experiment



1. Half-fill the syringe with water, dry the nozzle and carefully fit it into the second hole of the two-holed stopper (see diagram).
2. Remove the plain stopper from the inverted gas-filled flask and quickly fit the stopper which holds the jet and syringe. Be careful not to prematurely inject water from the syringe.
3. Clamp (or get an assistant to hold) the flask over the trough or beaker of water so that the protruding glass tube is well below the water level. If clamping, bear in mind that the flask will be heavy when filled with water so take care that it will not overbalance.
4. Use the syringe to squirt a few cm3 of water into the flask and gently swirl to dissolve some of the ammonia gas.
5. As the gas dissolves, a partial **vacuum** forms inside the flask and the external air pressure will force water up the tube and through the jet – forming a fountain (see first diagram). The **ammonia gas dissolves** in the water emerging from the jet and the indicator changes colour.
6. The fountain continues for some minutes, depending on the size of the flask and the width of the jet. When the fountain finishes, a bubble of gas remains. This is air and its volume gives an indication of how well the flask was originally filled.

Chemical Properties

Reaction with water

- Ammonia is very soluble in water
- Ammonia molecules combine with water molecules by **hydrogen bonding** to form aqueous ammonia, $NH_3{\cdot}H_2O$, which is **slightly ionized** to produce ammonium, NH_4^+, and hydroxide, OH^-, ions.
- The **hydroxide ions** give aqueous ammonia its weakly alkaline properties.

$$\mathrm{NH_3}_{\,(\mathrm{g})} + \mathrm{H_2O}_{\,(\mathrm{l})} \rightleftharpoons \mathrm{NH_3 \cdot H_2O}_{\,(\mathrm{aq})} \rightleftharpoons \mathrm{NH_4}^{+}{}_{(\mathrm{aq})} + \mathrm{OH}^{-}{}_{(\mathrm{aq})}$$

- On **warming**, aqueous ammonia **readily decomposes** to liberate ammonia gas. We can collect jars of ammonia gas easily by warming aqueous ammonia

Reaction with oxygen

1. Ammonia **doesn't burn in air**, but it **burns readily in oxygen** with a **greenish-yellow flame** to form water vapor and nitrogen.

$$4\,\mathrm{NH_3}_{(g)} + 3\,\mathrm{O_2}_{(g)} \xrightarrow{\Delta} 6\,\mathrm{H_2O}_{(g)} + 2\,\mathrm{N_2}_{(g)}$$

2. In the presence of a **heated platinum-rhodium** or **iron(II) oxide or chromium(III) oxide as catalyst**, ammonia reacts with excess air to produce **nitrogen monoxide**. *Ostwald Process

$$4\,\mathrm{NH_3}_{(g)} + 5\,\mathrm{O_2}_{(g)} \xrightarrow{\mathrm{Pt-Rh},\,850℃} 6\,\mathrm{H_2O}_{(l)} + 4\,\mathrm{NO}_{(g)}$$

3. Ammonia is not a strong reducing agent. However, it reduced **heated copper(II) oxide** to copper while itself oxidized to water and nitrogen.

$$3\,\mathrm{CuO}_{(s)} + 2\,\mathrm{NH_3}_{(g)} \longrightarrow 3\,\mathrm{Cu}_{(s)} + 3\,\mathrm{H_2O}_{(g)} + \mathrm{N_2}_{(g)}$$

Thermal Decomposition

Ammonia is decomposed at a temperature **above 500℃**, or by prolonged **sparking**, to yield its components elements, nitrogen and hydrogen

$$2\,\mathrm{NH_3}_{(g)} \longrightarrow \mathrm{N_2}_{(g)} + 3\,\mathrm{H_2}_{(g)}$$

As a precipitating agent

Aqueous ammonia precipitates the hydroxides of most metals from solutions of their salts.

$$\mathrm{Mg^{2+}}_{(aq)} + 2\,\mathrm{NH_3\cdot H_2O}_{(aq)} \longrightarrow \underset{\text{white}}{\mathrm{Mg(OH)_2}_{(s)}} + 2\,\mathrm{NH^{4+}}_{(aq)}$$
$$\mathrm{Fe^{3+}}_{(aq)} + 3\,\mathrm{NH_3\cdot H_2O}_{(aq)} \longrightarrow \underset{\text{reddish brown}}{\mathrm{Fe(OH)_3}_{(s)}} + 3\,\mathrm{NH^{4+}}_{(aq)}$$
$$\mathrm{Zn^{2+}}_{(aq)} + 2\,\mathrm{NH_3\cdot H_2O}_{(aq)} \longrightarrow \underset{\text{white}}{\mathrm{Zn(OH)_2}_{(s)}} + 2\,\mathrm{NH^{4+}}_{(aq)}$$
$$\mathrm{Pb^{2+}}_{(aq)} + 2\,\mathrm{NH_3\cdot H_2O}_{(aq)} \longrightarrow \underset{\text{white}}{\mathrm{Pb(OH)_2}_{(s)}} + 2\,\mathrm{NH^{4+}}_{(aq)}$$
$$\mathrm{Al^{3+}}_{(aq)} + 3\,\mathrm{NH_3\cdot H_2O}_{(aq)} \longrightarrow \underset{\text{white}}{\mathrm{Al(OH)_3}_{(s)}} + 3\,\mathrm{NH^{4+}}_{(aq)}$$
$$\mathrm{Cu^{2+}}_{(aq)} + 2\,\mathrm{NH_3\cdot H_2O}_{(aq)} \longrightarrow \underset{\text{blue}}{\mathrm{Cu(OH)_2}_{(s)}} + 2\,\mathrm{NH^{4+}}_{(aq)}$$
$$\mathrm{Fe^{2+}}_{(aq)} + 2\,\mathrm{NH_3\cdot H_2O}_{(aq)} \longrightarrow \underset{\text{green}}{\mathrm{Fe(OH)_2}_{(s)}} + 2\,\mathrm{NH^{4+}}_{(aq)}$$

Two of these hydroxides dissolve in **excess ammonia** due to the formation of **water-soluble complexes**.

$$\mathrm{Cu(OH)_2}_{(s)} + 4\,\mathrm{NH_3}_{(aq)} \longrightarrow \underset{\text{deep blue}}{[\mathrm{Cu(NH_3)_4}]^{2+}}_{(aq)} + 2\,\mathrm{OH^-}_{(aq)}$$
$$\mathrm{Zn(OH)_2}_{(s)} + 4\,\mathrm{NH_3}_{(aq)} \longrightarrow \underset{\text{colorless}}{[\mathrm{Zn(NH_3)_4}]^{2+}}_{(aq)} + 2\,\mathrm{OH^-}_{(aq)}$$

Note

1. Formation of precipitate

$$\mathrm{Cu^{2+}}_{(aq)} + 2\,\mathrm{NH_3\cdot H_2O}_{(aq)} \longrightarrow \underset{\text{blue}}{\mathrm{Cu(OH)_2}_{(s)}} + 2\,\mathrm{NH^{4+}}_{(aq)}$$

2. Formation of complex ion
    - ionic equation

$$Cu(OH)_{2\,(s)} + 4\,NH_{3\,(aq)} \longrightarrow \underset{\text{deep blue}}{[Cu(NH_3)_4]^{2+}}{}_{(aq)} + 2\,OH^-{}_{(aq)}$$

    - chemical equation

$$Cu(OH)_{2\,(s)} + 4\,NH_3 \cdot H_2O_{(aq)} \longrightarrow \underset{\text{deep blue}}{[Cu(NH_3)_4](OH)_{2\,(aq)}} + 4\,H_2O_{(aq)}$$

Test for Ammonia

1. Smell: It has a characteristic choking smell that is easily recognizable. (not the best ans)
2. **Action on litmus paper**: it turns *moist/damp* red litmus paper blue.
3. **Action with concentrated hydrochloric acid**: Dip a glass rod in concentrated hydrochloric acid, and then insert it in the gas jar containing the unknown gas. *White fumes* are formed if the gas is ammonia.

$$NH_{3\,(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$$

Uses

1. Ammonia is used in laundries as a solvent for removing grease and oil stains / **cleaning agent**.
2. Liquid ammonia is used in some refrigerators as a **cooling agent**.
3. Ammonia is used in the **manufacture of nitric(V) acid** by catalytic oxidation, and washing soda, Na_2CO_3, in Solvay process.
4. The biggest use is in the **manufacture of nitrogenous fertilizers**, e.g. ammonium sulfate(IV), ammonium nitrate(V) etc.
5. One of the important uses of ammonia solution is as a **reagent to identify cations in solution**, like: Ca^{2+}. Al^{3+}, Zn^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, and Cu^{2+}. Ammonia solution reacts with these cations to give hydroxide **precipitates**. Two of these hydroxides ($Cu(OH_2)$ and $Zn(OH)_2$) dissolve in **excess ammonia** due to the formation of **water-soluble complexes**.

Ammonium Salts

Ammonia forms the **ammonium ion, NH_4^+, in solution**. Ammonium salts are prepared by **dissolving ammonia in the appropriate acid** or by **neutralizing aqueous ammonia with the appropriate acid**. The ammonium salts are then separated out of solution by **crystallization**, and not by evaporation because they're easily decomposed by dry heating.

$$\begin{aligned}&NH_{3\,(g)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}\\&NH_3 \cdot H_2O_{(aq)} + HNO_{3\,(aq)} \longrightarrow NH_4NO_{3\,(aq)} + H_2O_{(l)}\end{aligned}$$

Properties

1. All common ammonium salts are **white crystalline solids**, which readily dissolve in water.
2. All ammonium salts **decompose** to give **ammonia gas** on **heating**, except **NH_4NO_2, NH_4NO_3, $(NH_4)_2Cr_2O_7$.**

$$NH_4Cl_{(s)} \overset{\Delta}{\rightleftharpoons} NH_{3\,(g)} + HCl_{(g)}$$
$$(NH_4)_2SO_{4\,(s)} \xrightarrow{\Delta} 2\,NH_{3\,(g)} + H_2SO_{4\,(aq)}$$
$$(NH_4)_2CO_{3\,(s)} \xrightarrow{\Delta} 2\,NH_{3\,(g)} + H_2O_{(l)} + CO_{2\,(g)}$$
$$NH_4NO_{2\,(s)} \xrightarrow{\Delta} N_{2\,(g)} + 2\,H_2O_{(l)}$$
$$NH_4NO_{3\,(s)} \xrightarrow{\Delta} N_2O_{(g)} + 2\,H_2O_{(l)}$$
$$(NH_4)_2Cr_2O_{7\,(s)} \xrightarrow{\Delta} Cr_2O_{3\,(s)} + N_{2\,(g)} + 4\,H_2O_{(l)}$$

3. All ammonium salts liberate **ammonia** when **heated with bases or alkalis**.

$$NH_4Cl_{(aq)} + NaOH_{(aq)} \xrightarrow{\Delta} NaCl_{(aq)} + H_2O_{(l)} + NH_{3\,(g)}$$
$$2\,NH_4Cl_{(aq)} + Ca(OH)_{2\,(s)} \xrightarrow{\Delta} CaCl_{2\,(aq)} + 2\,H_2O_{(l)} + 2\,NH_{3\,(g)}$$

Test for ammonium salts

Ammonia gas will be evolved on heating ammonium salts with alkali. This gas can be recognized by its **'urine' smell** and its **action on moist/damp red litmus paper** which turns it blue.

$$NH_4{}^+{}_{(aq)} + OH^-{}_{(aq)} \longrightarrow H_2O_{(l)} + NH_{3\,(g)}$$

Uses

1. Many ammonium salts are used as fertilizers, e.g. ammonium sulfate(VI), ammonium phosphate(V) and ammonium nitrate(V).
2. In the concentrated form, ammonium sulfate may be used as a weed-killer.
3. Ammonium chloride is used an electrolyte in Leclanche cells.
4. Ammonium nitrate(V) is used in the manufacture of explosive.
5. Ammonium carbonate is used in smelling salts to prevent dizziness and fainting.

Oxides of nitrogen

Name of oxide	Dinitrogen monoxide	Nitrogen monoxide	Dinitrogen trioxide	Nitrogen dioxide	Dinitrogen pentoxide
Formula	N_2O	NO	N_2O_3	NO_2	N_2O_5
Oxidation stage of nitrogen	+1	+2	+3	+4	+5

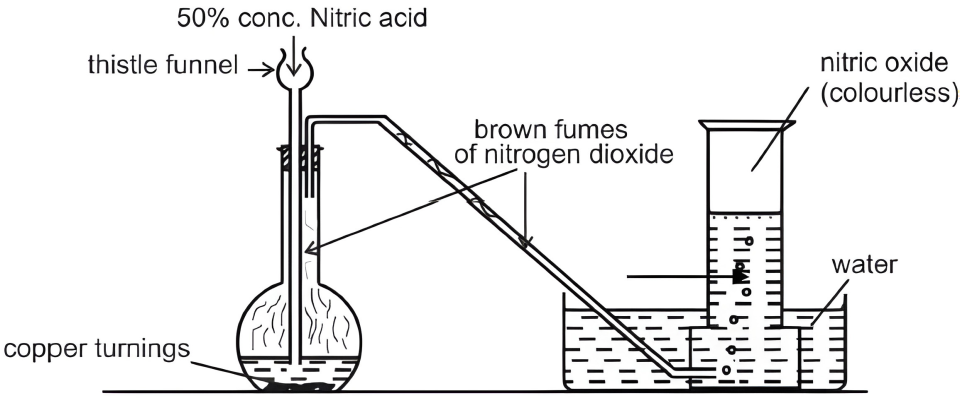
Nitrogen monoxide

It is very **difficult to obtain** the gas in its pure state because of its **great affinity for oxygen**. It reacts very readily with oxygen even at **ordinary conditions** to form nitrogen dioxide, **NO_2**.

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

Laboratory Preparation

Nitrogen monoxide can be prepared by the **action of nitric acid on most metals**. Usually, a **50% nitric(V) acid** solution and **copper turnings** are used.



Some nitrogen dioxide is produced during the process, mostly by the reaction of nitrogen monoxide formed with the oxygen in the flask. However, nitrogen dioxide is moderately soluble in water and so is removed by bubbling the gases through water.

$$3\,Cu_{(s)} + 8\underset{\text{dilute}}{HNO_{3\,(aq)}} \longrightarrow 3\,Cu(NO_3)_{2\,(aq)} + 4\,H_2O_{(l)} + 2\,NO_{(g)}$$

Physical Properties

1. colorless and poisonous gas
2. Its smell is unknown because it changes immediately to nitrogen dioxide on exposure on air.
3. It's almost insoluble in water. (5 vol of gas in 100 vol of water)
4. very slightly denser than air
5. neutral to litmus

Test

The gas turns reddish-brown on exposure to air to form nitrogen dioxide.

$$\underset{\text{colorless}}{2\,NO_{(g)}} + O_{2\,(g)} \longrightarrow \underset{\text{brown}}{2\,NO_{2\,(g)}}$$

Nitrogen dioxide

Laboratory Preparation

1. **Heating on nitrates of heavy metals**.
   - the most suitable nitrate is **lead(II) nitrate(V)** because its crystals don't contain any water of crystallization which would interfere with the preparation.

$$2\,Pb(NO_3)_{2\,(s)} \xrightarrow{\Delta} 2\,PbO_{(s)} + O_{2\,(g)} + 4\,NO_{2\,(g)}$$

2. Reaction of **copper** on **hot concentrated nitric(V) acid**.

$$Cu_{(s)} + \text{conc. } 4\,HNO_{3\,(l)} \longrightarrow Cu(NO_3)_{2\,(aq)} + 2\,NO_{2\,(g)} + 2\,H_2O_{(l)}$$

Physical Properties

1. a reddish-brown gas
2. has a pungent, irritating smell and is poisonous
3. dissolves readily in water to form an acidic solution
4. is easily liquified into a yellow liquid at 21°C
5. is much heavier than air

Chemical Properties

Action of heat

- ***Dinitrogen tetroxide*** exist as a **colorless solid** at a temperature below -11°C. When heated, the solid melts to a **pale yellow liquid** at temperature above -11°C.
- As the temperature rises, the color of the liquid deepens. The liquid boils at 21°C to produce a **reddish brown vapor**. At this state the vapor consists of about ***20% NO_2*** and 80% N_2O_4.
- As the temperature increases further, the color of the gas darkens to **brown** at about 45°C and **almost black** at 150°C. Above 150°C, the gas consists of ***entirely*** reddish brown ***NO_2*** molecules.
- With further increase in temperature, the color begins to lighten as the nitrogen dioxide molecule dissociates to the **colorless *nitrogen monoxide***. This dissociation is completed at temperatures above 600°C and the mixture is colorless.

$$\underset{\text{colorless}}{N_2O_{4\,(s)}} \xrightleftharpoons{>-11^\circ C} \underset{\text{pale yellow}}{N_2O_{4\,(l)}} \xrightleftharpoons{>21^\circ C} \underset{\text{reddish brown}}{N_2O_{4\,(g)}} \xrightleftharpoons{>150^\circ C} \underset{\text{brown}}{2\,NO_{2\,(g)}} \xrightleftharpoons{>600^\circ C} \underset{\text{colorless}}{2\,NO_{(g)}} + O_{2\,(g)}$$

Reaction with water

It disproportionates in water to form a mixture of **nitric acid** and **nitrous acid**. The gas (NO_2) is a **mixed acid anhydride**. (*disproportionation reaction)

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

Reaction with alkalis

Since the gas is a mixed acid anhydrides, it reacts with alkalis to yield a mixture of **nitrite** and **nitrate** salts. (*disproportionation reaction)

$$2\,OH^-{}_{(aq)} + 2\,NO_{2\,(g)} \longrightarrow NO_3{}^-{}_{(aq)} + NO_2{}^-{}_{(aq)} + H_2O_{(l)}$$
$$2\,NaOH_{(aq)} + 2\,NO_{2\,(g)} \longrightarrow NaNO_{3\,(aq)} + NaNO_{2\,(aq)} + H_2O_{(l)}$$

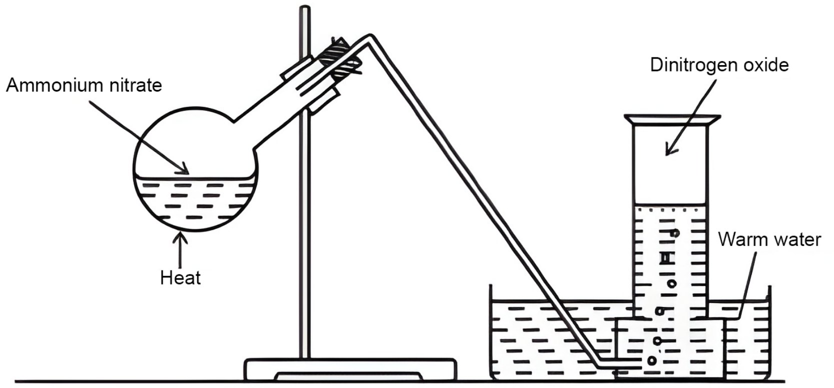
Dinitrogen monoxide

Dinitrogen monoxide, **N_2O**, known as **laughing gas**. If inhaled, produced a peculiar intoxication, which could result in uncontrollable fits of laughter.

Laboratory Preparation

Dinitrogen monoxide can be prepared by the **thermal decomposition of ammonium nitrate(V)**.

$$NH_4NO_{3\,(s)} \xrightarrow{\Delta} N_2O_{(g)} + 2\,H_2O_{(l)}$$



However, the direct heating of ammonium nitrate(V) is dangerous because the reaction may be explosive. Therefore, the gas is prepared by **heating any mixture of salts which by double decomposition will yield ammonium nitrate(V)**.

$$\mathrm{KNO_3}_{\,(s)} + \mathrm{NH_4Cl}_{(s)} \xrightarrow{\Delta} \mathrm{KCl}_{(s)} + \mathrm{N_2O}_{\,(g)} + 2\,\mathrm{H_2O}_{\,(l)}$$

Physical Properties

1. colorless gas with faint, pleasant but sickly smell, and sweetish taste
2. fairly soluble in cold water
3. 1.5 denser than air
4. neutral to moist litmus paper
5. has a boiling point of -88°C, and a melting point of -102°C

Chemical Properties

1. Action of heat
    - Dinitrogen oxide **decomposes** rapidly at about 600°C into its component elements, nitrogen and **oxygen**, the latter of which **supports combustion**.

    $$2\,\mathrm{N_2O}_{\,(g)} \xrightarrow{600^\circ\mathrm{C}} 2\,\mathrm{N_2}_{\,(g)} + \mathrm{O_2}_{\,(g)}$$

    - Thus, dinitrogen oxide **rekindles a brightly glowing splinter**, which is hot enough to decompose it to yield oxygen. However, it **extinguishes a feebly glowing one**.
    - Similarly, it **supports the combustion of any burning substance**, which is **hot enough to decompose** it to yield oxygen

    $$\mathrm{C}_{\,(s)} + 2\,\mathrm{N_2O}_{\,(g)} \xrightarrow{600^\circ\mathrm{C}} \mathrm{CO_2}_{\,(g)} + 2\,\mathrm{N_2}_{\,(g)}$$
    $$\mathrm{Mg}_{\,(s)} + \mathrm{N_2O}_{\,(g)} \xrightarrow{600^\circ\mathrm{C}} \mathrm{MgO}_{\,(s)} + \mathrm{N_2}_{\,(g)}$$

2. Reduction reaction
    - It is reduced to nitrogen when passes over heated copper or iron.

    $$\mathrm{Cu}_{\,(s)} + \mathrm{N_2O}_{\,(g)} \xrightarrow{600^\circ\mathrm{C}} \mathrm{N_2}_{\,(g)} + \mathrm{CuO}_{\,(s)}$$

Uses

1. Mild anesthetic for minor surgical operation such as dental surgery
2. Propellant in whipped cream
3. Oxidizing agent in racecars

Comparisons of the oxides of nitrogen

Comparisons of The Oxides of Nitrogen			
	Dinitrogen monoxide	**Nitrogen monoxide**	**Nitrogen dioxide**
Formula	N_2O	NO	NO_2 or N_2O_4
Physical State	gaseous	gaseous	gaseous
Colour	colorless	colorless	reddish-brown
Smell	pleasent but sickly	unknown	pungent, irritating
Solubility in Water	fairly soluble	sparingly soluble	very soluble
Density	1.5 times denser than air	very slightly denser than air	2.5 times denser than air
Effect on Damp Litmus Paper	neutral to litmus	neutral to litmus	turns blue litmus red
Effect on a Lighted Splinter	rekindles a brightly glowing splinter	extinguishes even a burning splinter	extinguishes a glowing splinter but allows a vigorously burning splinter to continue burning
As a Supporter of Combution	readily supports the combustion of burining carbon, sulfur, phosphorus, magnesium, etc.	supports the combustion of only brightly burning substances like phosphorus and magnesium	ability to support combustion is intermediate between the other two oxides
Reaction with Heated Copper	reduced to nitrogen	reduced to nitrogen	reduced to nitrogen

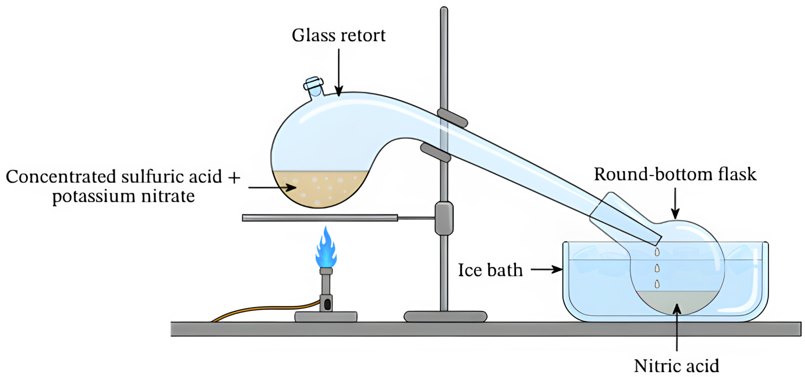
Nitric(V) Acid

Laboratory Preparation

Nitric acid can be displaced from any **nitrate(V)** by the action of **concentrated sulfuric acid**, which is a less volatile acid.

$$2\,\mathrm{NaNO_3}_{\,(aq)} + \text{conc. } \mathrm{H_2SO_4}_{\,(aq)} \xrightarrow{>200^\circ\mathrm{C}} \mathrm{Na_2SO_4}_{\,(aq)} + 2\,\mathrm{HNO_3}_{\,(l)}$$

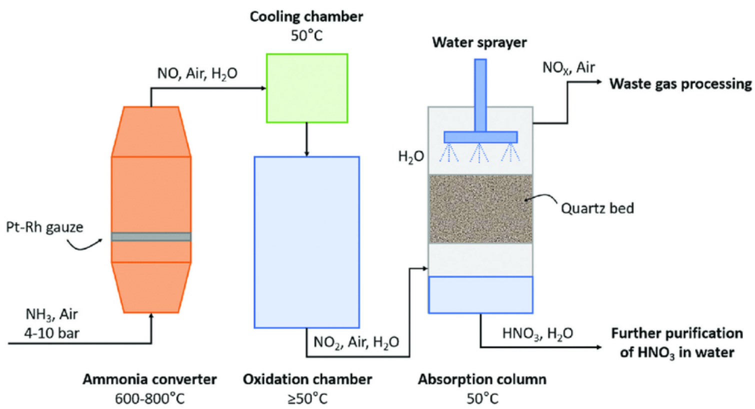
$$\mathrm{NaNO_3}_{\,(aq)} + \underset{\text{excess}}{\text{conc. } \mathrm{H_2SO_4}_{\,(aq)}} \xrightarrow{<200^\circ\mathrm{C}} \underset{\text{acid salt}}{\mathrm{NaHSO_4}_{\,(aq)}} + \mathrm{HNO_3}_{\,(l)}$$



- An all-glass apparatus must be used in this preparation because the nitric(V) acid vapor formed will rapidly attack cork or rubber.
- The yellow coloration of the acid is due to the dissolution of the nitrogen dioxide impurity in the acid. Pure acid can be obtained by bubbling air through the acid solution to remove this gas.
  - the oxygen in air oxidize nitrogen dioxide into dinitrogen pentoxide, N_2O_5, which is the anhydride of nitric acid

Industrial Preparation (*Ostwald Process)

Nitric acid is manufactured by the **catalytic oxidation of ammonia**. The process is also known as the ***Ostwald process***.



1. **Catalytic oxidation of ammonia**

$$4\,\mathrm{NH_3}_{(g)} + 5\,\mathrm{O_2}_{(g)} \xrightarrow{\text{Pt−Rh, } 850^\circ\mathrm{C}} 4\,\mathrm{NO}_{(g)} + 6\,\mathrm{H_2O}_{(g)}$$

   - The ammonia reacts with excess air, in the presence of a **platinum-rhodium catalyst at 700-900°C and 2-4 atm**, to produce nitrogen monoxide and steam.

2. **Oxidation of nitrogen monoxide**

$$2\,\mathrm{NO}_{(g)} + \mathrm{O_2}_{(g)} \xrightarrow{50^\circ\mathrm{C}} 2\,\mathrm{NO_2}_{(g)}$$

   - The nitrogen monoxide formed is cooled and mixed with **excess air** to produce nitrogen dioxide at room temperature

3. **Reaction with water to form nitric acid**

$$4\,\mathrm{NO_2}_{(g)} + 2\,\mathrm{H_2O}_{(l)} + \mathrm{O_2}_{(g)} \longrightarrow 4\,\mathrm{HNO_3}_{(g)}$$

   - In the presence of more **air**, the nitrogen dioxide is then **dissolved** in a spray of water to yield a nitric(V) acid solution up to 50% concentration. (the oxygen in air oxidize HNO_2 to HNO_3)

Physical Properties

1. Pure nitric acid is a fuming **colorless** liquid with a sharp choking smell.
2. It tends to turn **yellowish** after some time due to the **decomposition** of some of the acid to yield **nitrogen dioxide** which then dissolves in it.

$$4\,\mathrm{HNO_3}_{\,(aq)} \xrightarrow{\text{sunlight, room temp.}} 4\,\mathrm{NO_2}_{\,(g)} + \mathrm{O_2}_{\,(g)} + 2\,\mathrm{H_2O}_{\,(l)}$$

3. Boiling point = 86°C, density = 1.52gcm^{-3}.
4. The pure acid is very corrosive and rapidly destroys organic matter including our skin.
5. Dilute nitric acid turns blue litmus paper red.

Chemical Properties

In general, the chemical behavior of nitric acid depends on its **concentration**.

Dilute nitric acid	Pure / Concentrated nitric acid
almost fully ionized	poorly ionized
strongly acidic	strong oxidizing power

As an acid

1. Nitric acid **neutralizes bases and alkalis** to form **metallic nitrate(V) and water**.

$$\begin{aligned}
&\mathrm{HNO_3}_{\,(aq)} + \mathrm{NaOH}_{\,(aq)} \longrightarrow \mathrm{NaNO_3}_{\,(aq)} + \mathrm{H_2O}_{\,(l)}\\
&2\,\mathrm{HNO_3}_{\,(aq)} + \mathrm{PbO}_{\,(s)} \longrightarrow \mathrm{Pb(NO_3)_2}_{\,(aq)} + \mathrm{H_2O}_{\,(l)}\\
&2\,\mathrm{HNO_3}_{\,(aq)} + \mathrm{CuO}_{\,(s)} \longrightarrow \mathrm{Cu(NO_3)_2}_{\,(aq)} + \mathrm{H_2O}_{\,(l)}\\
&2\,\mathrm{HNO_3}_{\,(aq)} + \mathrm{CaO}_{\,(s)} \longrightarrow \mathrm{Ca(NO_3)_2}_{\,(aq)} + \mathrm{H_2O}_{\,(l)}
\end{aligned}$$

2. It reacts with **carbonates** and **hydrogencarbonates** to liberate **carbon dioxide**.

$$\begin{aligned}
&2\,\mathrm{HNO_3}_{\,(aq)} + \mathrm{Na_2CO_3}_{\,(aq)} \longrightarrow 2\,\mathrm{NaNO_3}_{\,(aq)} + \mathrm{H_2O}_{\,(l)} + \mathrm{CO_2}_{\,(g)}\\
&\mathrm{HNO_3}_{\,(aq)} + \mathrm{NaHCO_3}_{\,(aq)} \longrightarrow \mathrm{NaNO_3}_{\,(aq)} + \mathrm{H_2O}_{\,(l)} + \mathrm{CO_2}_{\,(g)}
\end{aligned}$$

3. Unlike other acids, it rarely gives **hydrogen** with metals, except in the action of **very dilute nitric acid (about 1%)** on calcium, magnesium or manganese. This is because any hydrogen that is initially formed is **immediately oxidized by more of the acid to form water**.

$$\mathrm{Mg}_{\,(s)} + \underset{\text{very dilute }(1\,\%)}{2\,\mathrm{HNO_3}_{\,(aq)}} \longrightarrow \mathrm{Mg(NO_3)_2}_{\,(aq)} + \mathrm{H_2}_{\,(g)}$$

As an oxidizing agent

Nitric acid (especially concentrated) is a **strong oxidizing agent**. A wide variety of reduction products is possible, e.g. NO_2, HNO_2, NO, N_2O, N_2, NH_2OH, N_2H_4 and NH_4^+, depending on the **acid concentration**, the **strength of the reducing agent** and the **temperature**.

1. With non-metals

Hot concentrated nitric acid oxidizes non-metals to their ***highest oxides***, which may be then **react with the water** to form the corresponding **acids**. At the same time, the acid itself is reduced to ***nitrogen dioxide***.

$$
\begin{aligned}
&C_{(s)} + 4\,HNO_{3\,(l)} \xrightarrow{\Delta} 2\,H_2O_{(l)} + CO_{2\,(g)} + 4\,NO_{2\,(g)}\\
&S_{(s)} + 6\,HNO_{3\,(l)} \xrightarrow{\Delta} H_2SO_{4\,(aq)} + 2\,H_2O_{(l)} + 6\,NO_{2\,(g)}\\
&P_{(s)} + 4\,HNO_{3\,(l)} \xrightarrow{\Delta} H_3PO_{4\,(aq)} + H_2O_{(l)} + 5\,NO_{2\,(g)}
\end{aligned}
$$

2. With metals

Generally, metals near the bottom of the electrochemical series (e.g. **lead, copper, mercury, silver**) react with nitric acid as follows.

$$
\begin{aligned}
&Cu_{(s)} + 4\,\underset{\text{conc.}}{H\overset{+5}{N}O_{3\,(l)}} \longrightarrow Cu(NO_3)_{2\,(aq)} + 2\,H_2O_{(l)} + 2\,\overset{+4}{N}O_{2\,(g)}\\
&Cu_{(s)} + 8\,\underset{\text{about }50\,\%}{H\overset{+5}{N}O_{3\,(aq)}} \longrightarrow 3\,Cu(NO_3)_{2\,(aq)} + 4\,H_2O_{(l)} + 2\,\overset{+2}{N}O_{(g)}
\end{aligned}
$$

Metals high up the electrochemical series react with nitric acid depending on the temperature and concentration of nitric acid. With **magnesium, zinc and iron**. They react with dilute nitric acid to form the respective metallic nitrates and ammonium nitrate or nitrogen monoxide.

$$
\begin{aligned}
&(4\,Zn_{(s)} + \underset{\text{very dilute }(6\,\%)}{10\,HNO_3}\ {}_{(aq)} \longrightarrow 4\,Zn(NO_3)_{2\,(aq)} + 3\,H_2O_{(l)} + \underset{\text{unstable}}{NH_4NO_{3\,(aq)}})\\
&(4\,Zn_{(s)} + \underset{\text{very dilute }(6\,\%)}{10\,H\overset{+5}{N}O_3}\ {}_{(aq)} \xrightarrow{\Delta} 4\,Zn(NO_3)_{2\,(aq)} + 5\,H_2O_{(l)} + \overset{+1}{N}{}_2O_{(g)})\\
&3\,Zn_{(s)} + 8\,\underset{\text{dilute}}{H\overset{+5}{N}O_{3\,(aq)}} \xrightarrow{\Delta} 3\,Zn(NO_3)_{2\,(aq)} + 4\,H_2O_{(l)} + 2\,\overset{+2}{N}O_{(g)}\\
&Zn_{(s)} + 4\,\underset{\text{conc.}}{H\overset{+5}{N}O_{3\,(aq)}} \xrightarrow{\Delta} Zn(NO_3)_{2\,(aq)} + 2\,H_2O_{(l)} + \overset{+4}{N}O_{2\,(g)}
\end{aligned}
$$

Some metals (e.g. **aluminum, chromium, iron**) react with concentrated nitric acid to form an oxide layer which covers the surface of the metal and protects it from further attack by he acid. Such metals are made passive by nitric acid. (**passivation**)

Certain metals such as **gold and platinum** are not affected by nitric acid. They're known as the **noble metals**.

With other reducing agents

$$
\begin{aligned}
&(3\,H_2S_{(g)} + 2\,\underset{\text{dilute}}{H\overset{+5}{N}O_{3\,(aq)}} \longrightarrow 3\,\overset{0}{S}_{(s)} + 4\,H_2O_{(l)} + 2\,\overset{+2}{N}O_{(g)})\\
&H_2S_{(g)} + \underset{\text{conc. \& cold}}{2\,H\overset{+5}{N}O_3}\ {}_{(l)} \longrightarrow \overset{0}{S}_{(s)} + 2\,H_2O_{(l)} + \overset{+4}{N}O_{2\,(g)}\\
&(H_2S_{(g)} + 2\,\underset{\text{conc. \& hot}}{H\overset{+5}{N}O_{3\,(l)}} \longrightarrow H_2\,\overset{+6}{S}\,O_{4\,(aq)} + 4\,H_2O_{(l)} + 8\,\overset{+4}{N}O_{2\,(g)})\\
&3\,Fe^{2+}{}_{(aq)} + 4\,H^+{}_{(aq)} + NO_3{}^-{}_{(aq)} \longrightarrow 3\,Fe^{3+}{}_{(aq)} + NO_{(g)} + 2\,H_2O_{(l)}
\end{aligned}
$$

Decomposition

Nitric acid decomposes slowly at room temperature (especially in the presence of sunlight), and rapidly when heated to yield nitrogen dioxide and oxygen. Nitrogen dioxide dissolve in nitric acid and causes it to become yellow.

$$
4\,HNO_{3\,(aq)} \xrightarrow{\Delta} 4\,NO_{2\,(g)} + 2\,H_2O_{(l)} + O_{2\,(g)}
$$

Uses

1. Nitric acid is used as an **acid**, an **oxidizing agent** and a **nitrating agent** in the laboratory.
2. It is used as an oxidizing agent in the production of important **polymers** like nylon and Terylene.
3. It is also used as a **rocket fuel**.
4. A mixture of three parts of hydrochloric acid and one part of nitric acid (三盐一硝), **aqua regia**, is used as a solvent for gold and platinum.
5. It is used in the making of many nitrates and organic nitro-compounds which are used as **fertilizers**, **dyes** and **explosives (e.g. TNT)**.

The nitrates

Preparation

- the neutralization of nitric acid with the appropriate alkali

$$\mathrm{HNO_3}_{\,(aq)} + \mathrm{NaOH}_{\,(aq)} \longrightarrow \mathrm{NaNO_3}_{\,(aq)} + \mathrm{H_2O}_{\,(l)}$$

- the action of nitric acid on a metal, a metallic oxide, or carbonate

$$\begin{aligned}
&2\,\mathrm{HNO_3}_{\,(aq)} + \mathrm{Na}_{\,(s)} \longrightarrow \mathrm{NaNO_3}_{\,(aq)} + \mathrm{H_2O}_{\,(l)} + \mathrm{NO_2}_{\,(g)} \\
&2\,\mathrm{HNO_3}_{\,(aq)} + \mathrm{Na_2O}_{\,(s)} \longrightarrow 2\,\mathrm{NaNO_3}_{\,(aq)} + \mathrm{H_2O}_{\,(l)} \\
&2\,\mathrm{HNO_3}_{\,(aq)} + \mathrm{Na_2CO_3}_{\,(s)} \longrightarrow 2\,\mathrm{NaNO_3}_{\,(aq)} + \mathrm{H_2O}_{\,(l)} + \mathrm{CO_2}_{\,(g)}
\end{aligned}$$

Properties

1. All nitrates are soluble in water
2. Nitrates decompose differently by heat according their thermal stability

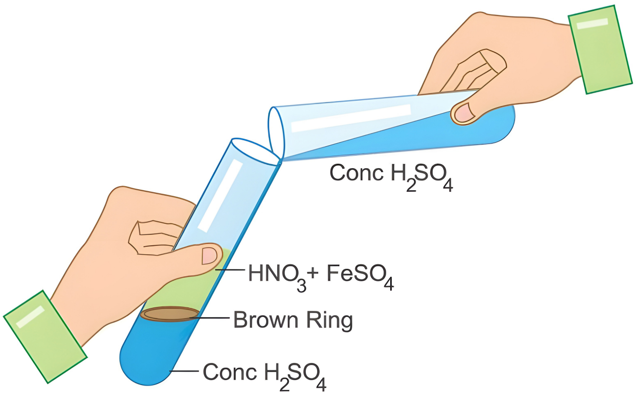
Thermal Decomposition of Metal Nitrates		
Effect of heating	**Nitrates**	**Observations**
Decompose to give oxygen and their respective metal nitrites	Potassium nitrate Sodium nitrate	$2\,KNO_{3\,(s)} \xrightarrow{\Delta} 2\,KNO_{2\,(s)} + O_{2\,(g)}$ $2\,NaNO_{3\,(s)} \xrightarrow{\Delta} 2\,NaNO_{2\,(s)} + O_{2\,(g)}$ White crystal melts to a colorless liquid, pale yellow solid left behind. Oxygen is evolved.
Decompose to give oxygen and brown fumes of nitrogen dioxide, leaving behind the respective metal oxides	Calcium nitrate	$2\,Ca(NO_3)_{2\,(s)} \xrightarrow{\Delta} 2\,CaO_{(s)} + 4\,NO_{2\,(g)} + O_{2\,(g)}$ White crystal melts, then decomposes to form a white residue. Brown fumes of nitrogen dioxide and oxygen is evolved.
	Zinc nitrate	$2\,Zn(NO_3)_{2\,(s)} \xrightarrow{\Delta} 2\,ZnO_{(s)} + 4\,NO_{2\,(g)} + O_{2\,(g)}$ White crystal melts, then decomposes to form a residue which is yellow when hot and white when cold, brown fumes of nitrogen dioxide and oxygen evolved.
	Iron(II) nitrate	$2\,Fe(NO_3)_{2\,(s)} \xrightarrow{\Delta} 2\,FeO_{(s)} + 4\,NO_{2\,(g)} + O_{2\,(g)}$ Green crystal melts, then decomposes to form a residue which is black when hot and turns reddish-brown on contact with air,
	Lead(II) nitrate	$2\,Pb(NO_3)_{2\,(s)} \xrightarrow{\Delta} 2\,PbO_{(s)} + 4\,NO_{2\,(g)} + O_{2\,(g)}$ White crystal decrepitates as it melts, then decomposes to form a residue which is orange when hot and yellow when cold. Brown fumes of nitrogen dioxide and oxygen is evolved,.
	Copper(II) nitrate	$2\,Cu(NO_3)_{2\,(s)} \xrightarrow{\Delta} 2\,CuO_{(s)} + 4\,NO_{2\,(g)} + O_{2\,(g)}$ Blue crystal melts, then decomposes to form a black residue. Brown fumes of nitrogen dioxide and oxygen evolved.
Decomposes to give oxygen and brown fumes of nitrogen dioxide, leaving behind their respective metals	Mercury(II) nitrate	$2\,HgNO_{3\,(s)} \xrightarrow{\Delta} 2\,Hg_{(l)} + 2\,NO_{2\,(g)} + O_{2\,(g)}$ White crystal melts, then decomposes to leave behind silvery mercury metal. Brown fumes of nitrogen dioxide and oxygen evolved.
	Silver nitrate	$2\,AgNO_{3\,(s)} \xrightarrow{\Delta} 2\,Ag_{(s)} + 2\,NO_{2\,(g)} + O_{2\,(g)}$ White crystal melts, then decomposes to leave behind silver metal. Brown fumes of nitrogen dioxide and oxygen evolved.

$$NH_4NO_{3\,(s)} \xrightarrow{\Delta} N_2O_{(g)} + H_2O_{(l)}$$

3. All nitrates produce nitric acid when heated with concentrated sulfuric acid.

$$NaNO_{3\,(aq)} + H_2SO_{4\,(aq)} \xrightarrow{\Delta} HNO_{3\,(aq)} + NaSO_{4\,(aq)}$$

4. Identification of NO_3^- (***Brown ring test*** for NO_3^- and HNO_3)



- When **conc. H_2SO_4** is added slowly *down the side* of a test tube containing a solution of **nitrate** and *freshly prepared* **iron(II) sulfate, $FeSO_4$**, the acid *sinks* to the bottom and two liquid layers are formed. At the junction of two layers, a **brown compound** is formed

1. The nitrate ion reacts with the concentrated sulfuric acid to yield nitric acid.

$$\mathrm{H_2SO_4}_{\,(aq)} + \mathrm{NO_3}^-{}_{(aq)} \longrightarrow \mathrm{HSO_4}^-{}_{(aq)} + \mathrm{HNO_3}_{\,(aq)}$$

2. Some of the nitric acid formed is reduced by $FeSO_4$ to yield NO.

$$2\,\mathrm{HNO_3}_{\,(aq)} + 3\,\mathrm{H_2SO_4}_{\,(aq)} + 6\,\mathrm{FeSO_4}_{\,(aq)} \longrightarrow 3\,\mathrm{Fe_2(SO_4)_3}_{\,(aq)} + 4\,\mathrm{H_2O}_{\,(l)} + 2\,\mathrm{NO}_{\,(g)}$$
$$6\,\mathrm{Fe}^{2+}{}_{(aq)} + 2\,\mathrm{NO_3}^-{}_{(aq)} + 8\,\mathrm{H}^+{}_{(aq)} \longrightarrow 6\,\mathrm{Fe}^{3+}{}_{(aq)} + 4\,\mathrm{H_2O}_{\,(l)} + 2\,\mathrm{NO}_{\,(g)}$$

3. The NO then combines with more of the $FeSO_4$ to form a brown addition compound, **$FeSO_4$·NO** which appears at the junction of two layers as a **brown ring**.

$$\mathrm{FeSO_4}_{\,(aq)} + \mathrm{NO}_{\,(g)} \longrightarrow \underbrace{\mathrm{FeSO_4 \cdot NO}_{\,(aq)}}_{\text{brown ring}} \quad {}^{*}\text{SPM}$$
$$\mathrm{FeSO_4}_{\,(aq)} + \mathrm{NO}_{\,(g)} + 5\,\mathrm{H_2O}_{\,(l)} \longrightarrow \underbrace{[\mathrm{Fe(NO)(H_2O)_5}]\mathrm{SO_4}_{\,(aq)}}_{\text{brown ring}} \quad {}^{*}\text{UEC}$$

Some Important Nitrates

- Potassium nitrate (**saltpeter**) is used in making **gun powder**.
- Sodium nitrate (**Chile saltpeter**) is poisonous, white, crystalline compound used in solid **rocket propellants**, in **matches**, in **curing meat**, and as a **fertilizer**.