

9.4 NITROGEN

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Learning outcomes

By the end of this chapter, Students should be able to:

- Give a reason for the inertness of nitrogen and the activity of active nitrogen.
- Give chemical properties of ammonia [Action with CuSO_4 solution, water, FeCl_3 solution, Conc. HCl , Mercurous nitrate paper, O_2].
- Explain the applications of ammonia and its harmful effects.
- Write the name and formula of oxy-acids of nitrogen.
- Explain the chemical properties of nitric acid [HNO_3] as an acid and oxidising agent (action with zinc, magnesium, iron, copper, sulphur, carbon, SO_2 , and H_2S).

Nitrogen

Introduction

- Present ~ 76% by mass and ~ 78% by volume in the dry atmosphere.
- All living beings contain nitrogen in the form of proteins.
- Their abundance in natural inorganic minerals is relatively low, probably due to the inertness of N_2 .

Atomic number: 7

Atomic mass: 14 amu

E.C.: $1s^2 2s^2 2p^3$

Molecular mass: 28 Dalton

Position in the periodic table

Nitrogen is placed along with phosphorus, Arsenic, Antimony, and Bismuth in group VA (15) of the periodic table. This group is called the nitrogen family.

1. These elements have 7 electrons, so they have $ns^2 np^3$ outermost shell electronic configurations.

Nitrogen -	N (7)	$[\text{He}] 2s^2 2p^3$
Phosphorus -	P (15)	$[\text{Ne}] 3s^2 3p^3$
Arsenic-	As (33)	$[\text{Ar}] 3d^{10} 4s^2 4p^3$
Antimony-	Sb (51)	$[\text{Kr}] 4d^{10} 5s^2 5p^3$
Bismuth-	Bi (83)	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^3$

Uses of Nitrogen

- In the manufacture of Ammonia by Haber's process, which in turn is used to produce fertilisers
- to provide an inert atmosphere in metallurgy, in gas-filled electric bulbs
- Liquid nitrogen is used as a refrigerant and in cryotherapy (cryosurgery).

Reason for the inertness of nitrogen

The nitrogen molecule contains a **triple bond ($\text{N}\equiv\text{N}$)** — one sigma bond and two pi bonds — making it one of the strongest bonds in chemistry. Its key data:

The $\text{N}\equiv\text{N}$ Triple Bond

- **Bond length:** 1.09 Å (very short, indicating a very strong bond)
- **Bond dissociation energy:** 945 kJ mol^{-1} (one of the highest of any diatomic molecule)
- **Consequence:** The activation energy for most reactions of N_2 is prohibitively high at room temperature. N_2 is therefore chemically inert under ordinary conditions.

This inertness explains why nitrogen is abundant in the atmosphere but scarce in inorganic minerals — it simply refuses to react and form compounds unless forced by extreme conditions (high temperature, high pressure, or electrical discharge).

Active nitrogen

When an **electrical discharge** is passed through low-pressure N_2 gas, the molecules absorb energy and dissociate into individual nitrogen atoms. These recombine in excited electronic states, producing a characteristic **yellow-orange glow** that persists even after the gas moves away from the discharge region. This highly reactive form is called **active nitrogen**.

Active nitrogen is far more reactive than ordinary N_2 because the atoms carry excess energy. Other natural sources of active nitrogen include:

- Lightning strikes in the atmosphere
- Reaction of nitrous oxide (N_2O) with excited oxygen atoms (O^*) in the stratosphere

9.4.2 Chemical properties of Ammonia

Ammonia (NH_3) is a colourless gas with a sharp, pungent smell.

Write the Lewis structure of ammonia.

Its central nitrogen atom carries a **lone pair of electrons**, which is the key to understanding almost all of ammonia's chemistry — it makes NH_3 a **Lewis base** and gives it the ability to donate electrons, dissolve readily in water, and form complexes with metal ions.

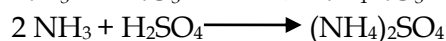
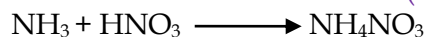
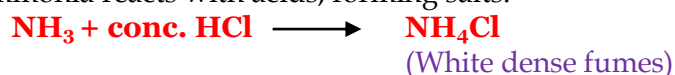
1. Basic Nature

- Ammonia dissolves in water, giving OH^- ions.



Thus, the aqueous solution of ammonia (aq. NH_3), **ammonium hydroxide**, and **ammonia solution** mean the same thing.

- Ammonia changes the colour of moist litmus blue.
- Ammonia reacts with acids, forming salts.



Think About It

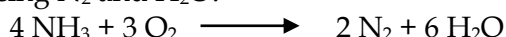
Why is ammonia so soluble in water? Two reasons: (1) NH_3 molecules form **hydrogen bonds** with water molecules; and (2) NH_3 reacts with water to form NH_4OH , which is itself highly soluble.

Why can't ammonia be dried over conc. H_2SO_4 ? Because NH_3 reacts with H_2SO_4 to form ammonium sulphate — the drying agent would consume the gas rather than simply dry it.

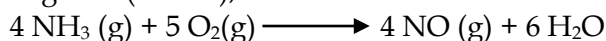
2. Oxidation reactions

Ammonia can be **oxidised** — its nitrogen is in the -3 oxidation state, which can be raised.

- a) Combustion: Ammonia burns in an atmosphere of oxygen with a greenish-yellow flame, producing N_2 and H_2O .



- b) Formation of nitric oxide: When a mixture of ammonia and oxygen gas is passed over heated platinum gauze (800°C), it is oxidised to nitric oxide.

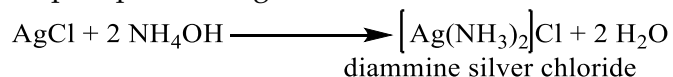


[Practice writing the ONs of all the atoms in the above equations.]

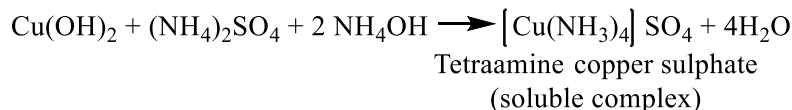
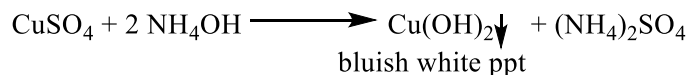
3. Complex formations

Salts of d-block elements like copper, silver, nickel, cobalt, cadmium, etc., form soluble complexes with ammonium hydroxide.

e.g., white precipitate of AgCl dissolves in ammonia solution, giving a soluble complex.

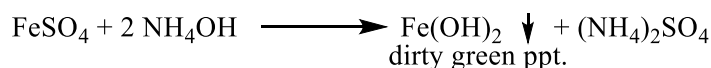
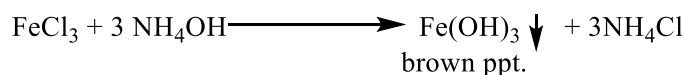


CuSO₄ solution gives a bluish-white ppt. on treatment with ammonia. On adding excess ammonia, it dissolves, giving a deep-blue solution of tetraamine copper sulphate (a complex compound).



4. Precipitation reactions

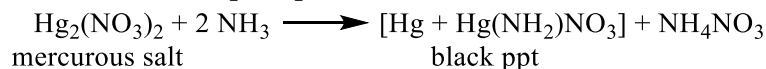
Salts of heavy metals like Iron, Chromium, Aluminium, zinc, etc., are precipitated as their hydroxides from their solutions.



These reactions serve as confirmatory tests for the presence of respective metal ions in the solution.

5. Reaction with Mercurous nitrate paper

Ammonia forms a black precipitate with mercurous salts.



This blackening test is a quick confirmatory test for ammonia gas.

9.4.3 Applications of Ammonia

Ammonia is one of the most widely produced industrial chemicals in the world. It is used:

- To produce urea, ammonium sulphate & other nitrogen fertilizers.
- To produce nitric acid, sodium carbonate, etc.
- As a laboratory reagent in the form of ammonium hydroxide.
- As a refrigerant in industrial cooling systems.

9.4.4 Harmful effects of ammonia

Despite its industrial importance, ammonia is highly toxic and must be handled with care.

Health Hazards of Ammonia

- **Respiratory system:** High concentrations cause immediate burning of the nose, throat, and airways. Severe exposure can lead to respiratory distress or failure. Even low concentrations cause persistent coughing and irritation.
- **Eyes and skin:** Brief contact with low concentrations causes stinging and irritation. Higher concentrations can cause chemical burns, permanent eye damage, or blindness.
- **Ingestion:** Swallowing ammonia solution causes severe corrosive damage to the mouth, throat, oesophagus, and stomach — potentially life-threatening.

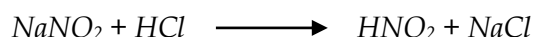
In the laboratory and industry, ammonia must always be handled in well-ventilated areas or under a fume hood. In case of exposure, flush immediately with large quantities of water and seek medical attention.

9.4.5 Oxyacids of nitrogen (Name and formula)

There are two oxyacids of nitrogen, viz. **nitrous acid** (HNO_2) and **nitric acid** (HNO_3).

The oxidation numbers of nitrogen in these two acids are +3 and +5, respectively. N_2O_3 and N_2O_5 are the anhydrides of nitrous acid and nitric acid, respectively.

Nitrous acid is relatively unstable and cannot be stored. It is prepared fresh by mixing solutions of NaNO_2 and HCl as



It easily disproportionates into HNO_3 and NO as

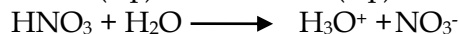


9.4.6 Chemical Properties of Nitric Acid

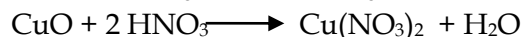
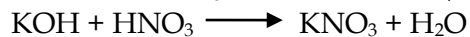
Nitric acid (HNO_3) is a colourless, fuming liquid that turns yellow on prolonged exposure to light (due to partial decomposition into NO_2). It is both a **strong acid** and a powerful **oxidising agent**.

[A] Acidic Nature

Being a very strong acid, it dissociates completely in an aqueous solution.



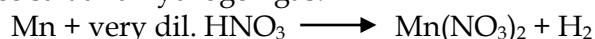
Action on bases: HNO_3 neutralises bases, forming nitrate salts.



Action with carbonates and bicarbonates: HNO_3 liberates CO_2 gas in reaction with metal carbonates and bicarbonates.



Action with highly electropositive metals: Very dilute HNO_3 reacts with **only Mg and Mn** to produce salt and hydrogen gas.



The hydrogen gas produced is not pure; it is accompanied to some extent by gaseous reduction products of acids (i.e., NO , NO_2 , etc.).

[B] Oxidising Nature

Nitric acid is a very good oxidising agent.

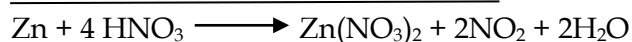
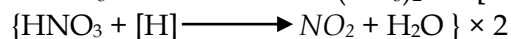
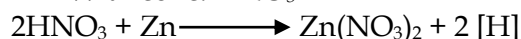
1. Action on metals:

This reacts with almost all metals, even with some that lie below hydrogen in the electrochemical series, except noble metals like Pt and Au.

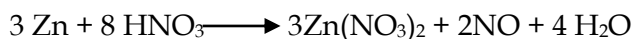
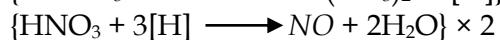
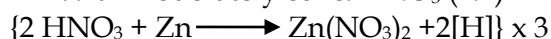
The reactions with active metals are balanced by the nascent hydrogen formation method in the partial equation method.

a. Action with Zn

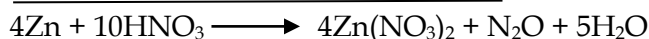
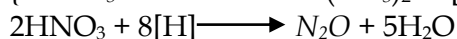
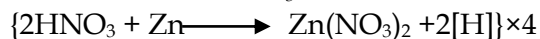
- With conc. HNO_3



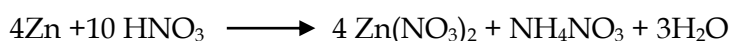
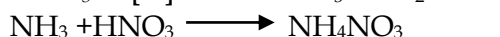
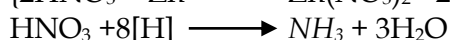
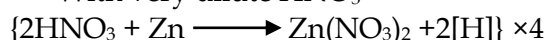
- With moderately conc. HNO_3 (1:1)



- With dilute HNO_3



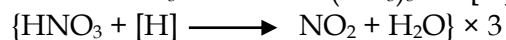
- With very dilute HNO_3



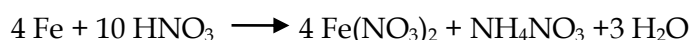
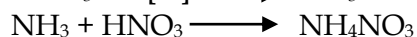
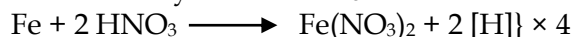
b. Action with Fe

- Highly concentrated nitric acid renders iron passive due to the formation of a layer of ferrous-ferrous oxide Fe_3O_4 . This phenomenon is used to prevent the rusting of iron.

- With moderately conc. HNO_3 (1:1)



- With very dilute HNO_3

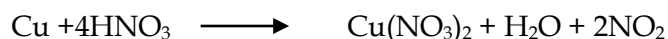
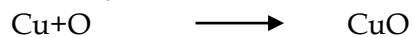


Important Note on the Partial Equation Method

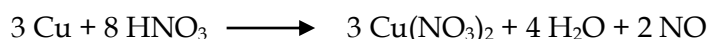
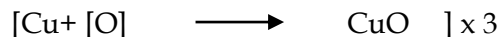
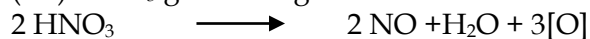
The 'nascent hydrogen' partial equation approach used above is a **balancing technique**, not a description of the actual reaction mechanism. In reality, HNO_3 acts as an oxidising agent by accepting electrons (the N^{+5} ion is reduced).

c. Action with Cu

- Conc. HNO_3 gives NO_2 gas



- (1:1) HNO_3 gives NO gas.



Summary table to remember easily:

Metal	HNO ₃ conc.	Reduction product
Zn	Conc.	NO ₂
Zn	Mod. conc.	NO
Zn	Dilute	N ₂ O
Zn	Very dilute	NH ₄ NO ₃
Cu	Conc.	NO ₂
Cu	Dilute	NO

2. Action on Non-metals

Hot and conc. Nitric acid oxidises many nonmetals, such as carbon, sulfur, phosphorus, iodine, etc., to form their oxides or oxyacids.

- a. With carbon (C is oxidised to carbonic acid)
- $$\begin{array}{l} \{ 2 \text{HNO}_3 \longrightarrow 2 \text{NO}_2 + \text{H}_2\text{O} + [\text{O}] \} \times 2 \\ \text{C} + 2 [\text{O}] \longrightarrow \text{CO}_2 \\ \text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{CO}_3 \\ \hline \text{C} + 4 \text{HNO}_3 \longrightarrow \text{H}_2\text{CO}_3 + 4 \text{NO}_2 + \text{H}_2\text{O} \end{array}$$
- b. With sulphur (S is oxidised to sulphuric acid)
- $$\begin{array}{l} 2 \text{HNO}_3 \longrightarrow 2 \text{NO}_2 + \text{H}_2\text{O} + [\text{O}] \\ \text{S} + [\text{O}] \longrightarrow \text{SO}_2 \\ \text{SO}_2 + \text{H}_2\text{O} + [\text{O}] \longrightarrow \text{H}_2\text{SO}_4 \\ \hline \text{S} + 6 \text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + 6 \text{NO}_2 + 2 \text{H}_2\text{O} \end{array}$$

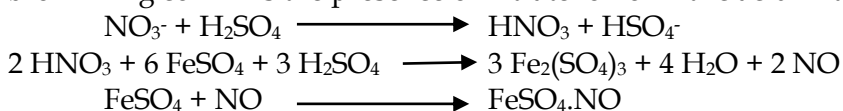
3. Action on reducing compounds

- a. It oxidises H₂S to sulphur
- $$\begin{array}{l} 2 \text{HNO}_3 \longrightarrow 2 \text{NO}_2 + \text{H}_2\text{O} + [\text{O}] \\ \text{H}_2\text{S} + \text{O} \longrightarrow \text{H}_2\text{O} + \text{S} \\ \hline 2 \text{HNO}_3 + \text{H}_2\text{S} \longrightarrow 2 \text{NO}_2 + 2 \text{H}_2\text{O} + \text{S} \end{array}$$
- b. It oxidises SO₂ to H₂SO₄
- $$\begin{array}{l} 2 \text{HNO}_3 \longrightarrow 2 \text{NO}_2 + \text{H}_2\text{O} + [\text{O}] \\ \text{SO}_2 + \text{O} \longrightarrow \text{SO}_3 \\ \text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 \\ \hline \text{SO}_2 + 2 \text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + 2 \text{NO}_2 \end{array}$$

(Practice writing all these reactions several times. These are very important)

9.4.6 Ring Test of Nitrate Ion

For the test of nitric acid or nitrate ion in a salt, the solution is first mixed with an equal volume of conc. H₂SO₄ in a test tube. The solution is cooled under tap water, and a freshly prepared FeSO₄ solution is added slowly from the wall of the test tube, tilting the test tube. The formation of a brown ring confirms the presence of nitrate ion or nitric acid in the solution.



(Nitrosyl ferrous sulphate) Brown ring

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Chapter Summary

- **$\text{N}\equiv\text{N}$ triple bond** (945 kJ mol^{-1} , length $1.09 \text{ \AA}$) makes N_2 exceptionally inert at room temperature.
- **Active nitrogen** is formed by electrical discharge through low-pressure N_2 ; it is energised and far more reactive than ordinary N_2 .
- **Ammonia is a Lewis base** due to the lone pair on N; it dissolves in water to give OH^- ions, reacts with acids to form ammonium salts, and forms deep-blue complexes with Cu^{2+} .
- **Nitrous acid (HNO_2 , O.N. of N = +3)** is unstable; nitric acid (HNO_3 , O.N. of N = +5) is stable and is both a strong acid and a strong oxidising agent.
- **Concentration controls the HNO_3 reduction product:** conc. $\rightarrow \text{NO}_2$ | mod. conc. $\rightarrow \text{NO}$ | dil. $\rightarrow \text{N}_2\text{O}$ | v. dil. $\rightarrow \text{NH}_4^+$.
- **Passivation of iron** by conc. HNO_3 forms Fe_3O_4 ; this is why iron tanks can store concentrated HNO_3 safely.
- **Ring test:** Brown ring of $[\text{FeSO}_4\cdot\text{NO}]$ confirms NO_3^- in a sample.

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