



NEET - UG

NATIONAL TESTING AGENCY

Chemistry

Volume - 4 || Part - II



NEET - UG

CHEMISTRY - CLASS - 12th

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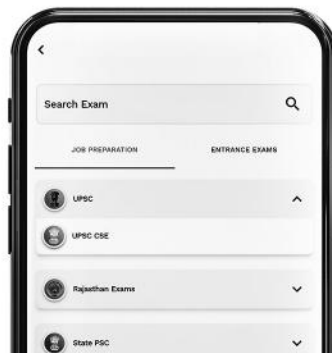
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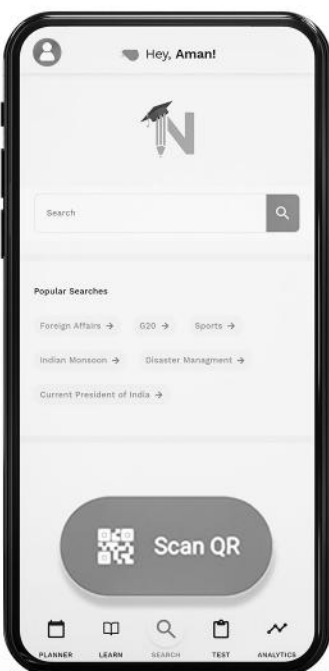
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CHAPTER 1A

The p-Block Elements (Nitrogen Family VA-Group Elements)

CHAPTER OUTLINE

- Nitrogen Family [$V(ns^2, np^3)$] - Nitrogen (N_2)
- Compounds of Nitrogen Oxides of Nitrogen
- Ammonia (NH_3) - Nitrous Acid (HNO_2) = Nitric Acid (HNO_3) - Allotropic Forms of Phosphorous Oxides of Phosphorous - Phosphorous Trioxide (P_4O_6) - Phosphorous Penta Oxide (P_4O_{10}) - Oxy Acids of Phosphorous = Hypo Phosphorous Acid (H_3PO_2)
- Phosphorous Acid (H_3PO_3) - Orthophosphoric Acid (H_3PO_4)
- Pyrophosphoric Acid ($H_4P_2O_7$) Metaphosphoric Acid (HPO_3)-Hypo phosphoric Acid ($H_4P_2O_6$) - Phosphorous Trichloride (PCl_3)
- Phosphorous Pentachloride (PCl_5)
- Phosphine (PH_3)
- Difference in ammonia and phosphine
- Fertilizer

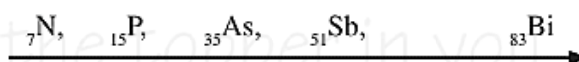
NITROGEN FAMILY [$V(ns^2, np^3)$]

- The elements which belong to this group are called **pniconides (means suffocation)**.

It includes

Nitrogen (N)	}	Non-metals
Phosphorus (P)		
Arsenic (As)	}	Metalloids
Antimony (Sb)		
Bismuth (Bi)		

- Atomic size, Metallic character, Basic nature of oxide, Acidic nature of hydride(MH_3), Reducing, poisonous nature of hydride, Gaseous nature and Rate of combustion increase.



Electronic Configuration

- The general electronic configuration of this group elements is $ns^2 np^3$.

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Nitrogen	7	[He] $2s^2 2p^3$	15	2
Phosphorus	15	[Ne] $3s^2 3p^3$	15	3
Arsenic	33	[Ar] $3d^{10} 4s^2 4p^3$	15	4
Antimony	51	[Kr] $4d^{10} 5s^2 5p^3$	15	5
Bismuth	83	[Xe] $4f^{14} 5d^{10} 6s^2 6p^3$	15	6

Physical Properties

- All elements are **polyatomic**.
- N_2 is a **gas** while other elements are **solids**.

- The metallic character increases down the group as IE decreases and atomic size increases.
- Except for nitrogen, all other elements exhibit **allotropy**.

Atomic and Chemical Properties

- **Atomic Radii:** As one moves down the group, atomic radii increase; however, from As to Bi, this increase is minimal due to the **inadequate screening effect of inner d or f orbital** electrons.

N	P	As	Sb	Bi	
70	110	120	140	150	p.m

- **Ionization Enthalpy:** Due to an increase in their atomic radii and a shielding effect, the values of ionisation enthalpy diminish as one moves down the group. As a result of their more stable half-filled electronic configuration (np^3), the ionisation energy of these elements is greater than that of the oxygen family's next-group elements.

N	P	As	Sb	Bi	
1402	1012	9477	834	703	KJ/Mole

- **Electronegativity:** They have high electronegativity values, and as atomic radii increase, electronegativity decreases and screening effect increases as follows:

N	P	As	Sb	Bi
3.0	2.1	2.0	1.9	1.9

- **Electron Affinity:** Due to their stable electronic configuration (np^3), the electron affinity of these elements is zero or extremely low; however, it increases as one goes down the group.
- **Metallic Nature:** These elements are less metallic than those of the carbon family because their nuclear charge and electronegativity values are greater. As one goes down, the metallic nature of the group increases.

N	P	As,	Sb	Bi
Non metals		Metalloid		Metal

- **Melting and Boiling Point:** As one moves down the group, the **melting and boiling points increase** from N to As due to the **increase in atomic size**, and then **decrease** from **Sb to Bi** due to their tendency to form three covalent bonds instead of five due to the inert pair effect, which reduces the force of attraction between atoms.

	N	P	As	Sb	Bi
M.P. (K)	63	317.1	1089	904	544
	N	P	As	Sb	Bi
B.P. (K)	77.2	554	888	1860	1837

- **Oxidation State:** Nitrogen exhibits oxidation states ranging from -3 to +5 because of its tiny size and high electronegativity.

-3 +5

Example – MH_3 , M_2O_5

Because of the inert pair effect, the +3 oxidation state becomes more stable as one moves down the group. As a result, in its +3 form, Bi possesses more stable compounds.

- **Catenation:** Because of its high bond energy, phosphorus has greater catenation power than nitrogen. This tendency, however, reduces as Bi moves down the group.

- **Allotropy:** All these elements except Bi show allotropy.

N: (1) α (cubic) (2) β (hexagonal)

P: (1) Red (2) White

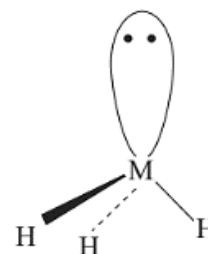
(3) Black (α, β) (4) Violet

(5) Scarlet

As: (1) Yellow (2) Grey (3) Black

Sb: (1) Yellow (2) Silver grey (3) Explosive

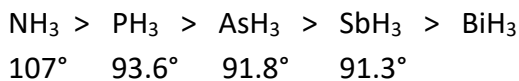
- **Reactivity Towards Hydrogen:** When these elements react with hydrogen, they produce a volatile hydride with the general formula MH_3 . M (N,P, etc.) is sp^3 hybridised with 3 bond pairs and 1 lone pair, resulting in MH_3 being pyramidal in form and of basic nature.



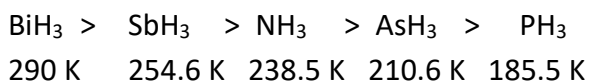
- **Properties of Hydrides**

Basic Nature: Moving from NH_3 to BiH_3 , the basic nature reduces because the increased size of the central atom implies that the lp electrons occupy a greater space, resulting in a drop in electron density on the central atom.

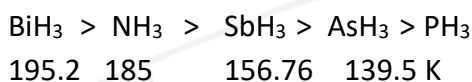
Bond Angle: Moving down the group increases the size of the central atom and lowers electronegativity, causing bp electrons to move away from it and so decreasing bond angle.



Boiling Point: As one moves along the group, the boiling point rises as the van der Waals force of attraction rises. However, because to hydrogen bonding, NH_3 has an extremely high b.p.

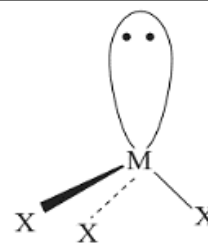


Melting Point: The melting point of the group increases as the van der Waals force of attraction increases. However, because of hydrogen bonding, NH_3 has an extremely high melting point.



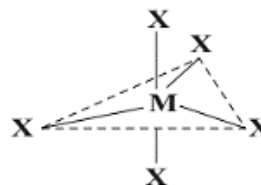
Thermal Stability and Reducing Nature: Moving from NH_3 to BiH_3 , thermal stability falls while nature rises because MH bond strength decreases as the size of the central atom increases.

- **Reactivity Towards Oxygen:** This group of elements forms two types of oxides, namely trioxides (M_2O_3) and pentoxides (M_2O_5). Nitrogen can form additional oxides due to its strong tendency to form $\pi\text{-}\pi$ multiple bonds with oxygen.
 - The acidic strength of trioxides decreases: $\text{N}_2\text{O}_3 > \text{P}_2\text{O}_3 > \text{As}_2\text{O}_3$
 - The acidic strength of pentoxides decreases: $\text{N}_2\text{O}_5 > \text{P}_2\text{O}_5 > \text{As}_2\text{O}_5 > \text{Sb}_2\text{O}_5 > \text{Bi}_2\text{O}_5$
 - The acidic strength of oxides of nitrogen increases: $\text{N}_2\text{O} < \text{NO} < \text{N}_2\text{O}_3 < \text{N}_2\text{O}_4 < \text{N}_2\text{O}_5$
- **Reactivity Towards Halogen:** The elements of this group form mainly two type of halides MX_3 and MX_5 :

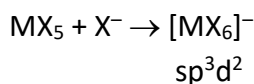


- With the exception of BiF_3 , which is ionic, MX_3 halides are pyramidal in shape with sp^3 hybridization and primarily covalent in nature.
- In the case of NX_3 , the stability of halides decreases as the magnitude of X- increases.
- NF_3 is quite stable, exothermic, and resistant to hydrolysis due to the strength of the NF bond.

MX_5



- P, As, Sb can readily form trigonal bipyramidal pentahalides (MX_5) through sp^3d hybridization.
- If X- is large, the stability is considerably reduced.
- **Nitrogen** does not form NX_5 because it **lacks d- orbitals** and therefore cannot extend its **covalency beyond four**.
- Due to their empty d-orbital, MX_5 can also act like Lewis acid.



NITROGEN (N_2)

Introduction

- Daniel Rutherford discovered it and named it foul air or mephitic air (life-killing air).
- Lavoisier determined its elemental constitution and named it azote (which means lifeless).
- The name nitrogen derives from nitre, which contains nitrogen element.
- Exists as dinitrogen, a diatomic molecule.

Occurrence

- It is found in both **free state** and **combined** state. It exists in the combined state as **Salt petre** (KNO_3) and Chile salt petre (NaNO_3).
- It comprises 70% of the volume of air. It is the fundamental constituent of all plant and animal cells.

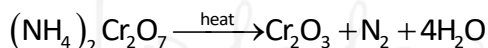
Preparation

1. By Fractional Distillation of Liquid Air

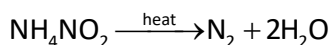
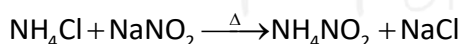
It can be produced by liquefying air containing nitrogen and oxygen, followed by fractional evaporation, as nitrogen, being more volatile than oxygen, evaporates faster than oxygen. As impurities, the nitrogen obtained from this location contains only trace amounts of oxygen and inert gases. Here, the apparatus utilised in Claude's apparatus and it is a commercial method of preparing N_2 are described.

2. From Nitrogen Containing Compounds

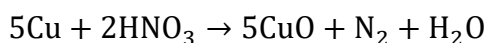
(i) From Ammonium Dichromate



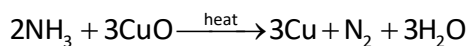
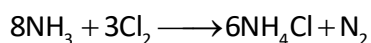
(ii) **Lab Method:** It is prepared by heating an aqueous solution of ammonium chloride and sodium nitrite.



(iii) **From Copper and Nitric Acid:** When vapours of nitric acid are passed over strongly heated copper, nitrogen is produced.

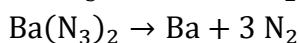
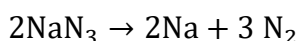


(iv) **By the Oxidation of Ammonia:** Chlorine or CuO can oxidize ammonia into nitrogen as undergoing the following reaction.



3. From Sodium or Barium Azide

On heating sodium or barium azide in vacuum, very pure form of nitrogen is obtained.



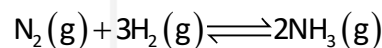
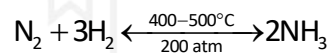
Physical Properties

- Nitrogen is a nontoxic, odourless, tasteless, and liquefiable gas that is colourless, odourless, and tasteless.
- Slightly less dense than air, its vapour density is 14.
- It is partially soluble in water and can be transformed into a colourless liquid.
- It is noncombustible and cannot sustain combustion.
- Its melting point is 63.2K, and its boiling point is 70.2K.

Chemical Properties

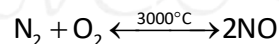
1. With Hydrogen

It reacts with hydrogen at $400 - 500^\circ\text{C}$ and 200 atmospheres of pressure in the presence of a catalyst (Fe and Mo) to produce ammonia.



2. With Oxygen

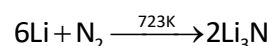
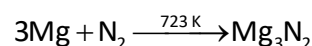
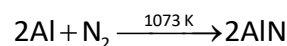
In the presence of an electric discharge, it reacts with oxygen at 3000°C to produce nitric oxide.



3. With Metals

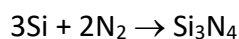
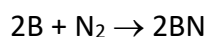
At red-hot temperature, it forms **metal nitrides**.

Example:



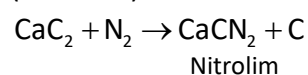
4. With Non-Metals

It reacts with boron or silicon at bright red temperatures to form boron and silicon nitrides.



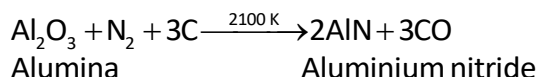
5. With Calcium Carbide

At 1273K, it forms calcium cyanamide (**Nitrolim**) with calcium carbide as follows:



6. With Al₂O₃

By heating nitrogen with alumina and carbon, aluminium nitride is produced.



Uses

- It is utilised in the production of ammonia and other chemicals, such as calcium cyanamide and nitric acid, among others.
- Liquid nitrogen is utilised as a refrigerant for the preservation of biological materials and for the freezing of food products.
- Additionally, it is used in cryosurgery.
- It is used to provide an inert atmosphere in a variety of metallurgy processes.
- It is employed as an inert diluent for reactive substances.
- It is also used to fill electric light bulbs.
 - Active Nitrogen** Nitrogen gas subjected to a low-pressure electric discharge produces active nitrogen, which is more reactive but much less stable and reverts to its normal form.

COMPOUNDS OF NITROGEN

OXIDES OF NITROGEN

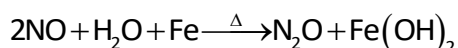
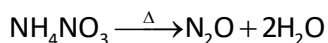
Nitrogen forms five oxides when it combines with oxygen: nitrous oxide (N₂O), nitric oxide (NO), nitrogen trioxide (N₂O₃), nitrogen dioxide (NO₂), or dinitrogen tetra oxide (N₂O₄) and dinitrogen penta oxide (N₂O₅). These are listed individually below:

N ₂ O	NO	N ₂ O ₃	NO ₂	N ₂ O ₅
Colourless Gas	Colourless gas	Bluish liquid	Brown gas	colourless solid

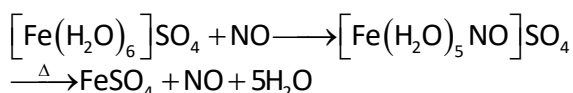
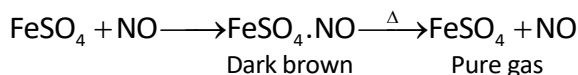
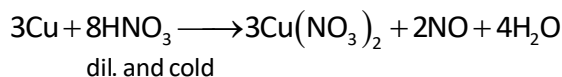
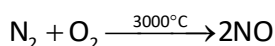
→ Acidic nature increases

Preparation

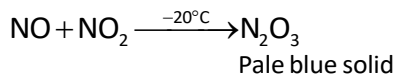
(i) Preparation of N₂O



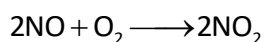
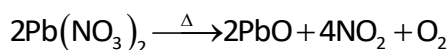
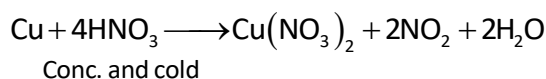
(ii) Preparation of NO



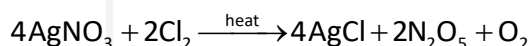
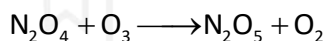
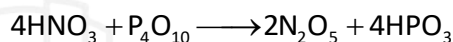
(iii) Preparation of N₂O₃



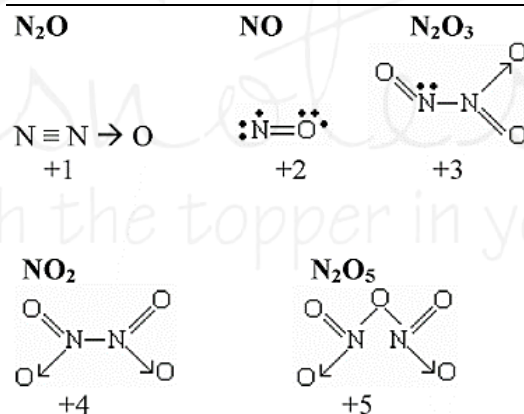
(iv) Preparation of NO₂



(v) Preparation of N₂O₅



Shapes of Nitrogen Oxides



Some Facts about Nitrogen Oxides

- N₂O is known as laughing gas and is utilised as an anaesthetic (N₂O + O₂).
- NO is a molecule with an uneven number of electrons, which makes it paramagnetic.
- NO combines with Fe (II) to produce a brown nitrosyl complex of iron(II), i.e., [Fe(H₂O)₅NO]²⁺, demonstrating the reducing nature of NO (nitrite and nitrate detection test).
- NO₂ is paramagnetic and brown, whereas N₂O₄ is diamagnetic and colourless.

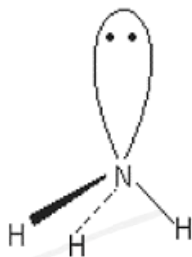
- According to X-ray diffraction, the ionic structure of N_2O_5 is $NO_2^+ + NO_3^-$; hence, it is referred to as **Nitronium nitrate**.

AMMONIA (NH_3)

Introduction

- Priestley isolated it, Berthelot proposed that it is composed of nitrogen and hydrogen, and Davy determined its molecular formula.
- It is the most important nitrogen compound and a starting material for the synthesis of several other useful compounds.

Structure



Occurrence

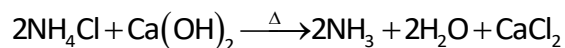
Traces of it are present in the atmosphere.

Preparation

1. From Ammonium Salts

When heated with metal oxide or hydroxide, ammonium salts produce ammonia.

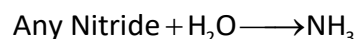
Example:



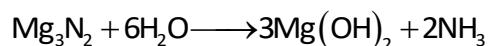
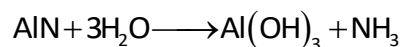
It is basically the **lab method** for the preparation of ammonia.

2. From Nitrides

Nitrides on hydrolysis forms ammonia.

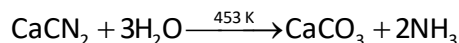
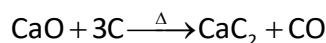
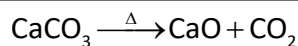


Example:



3. Cyanamide Process

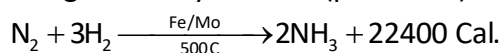
Ammonia is formed when coal and lime are heated at $1000^\circ C$ and nitrogen is passed by undergoing the following reaction.



- Here, anhydrous calcium chloride or CaF_2 is used as a catalyst.

4. Haber's Process

Ammonia is formed when nitrogen and hydrogen are heated in a 1:3 ratio at $400-500^\circ C$, 200 atmospheres of pressure, and in the presence of a catalyst (finely divided Fe filling and Molybdenum (promoter).



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

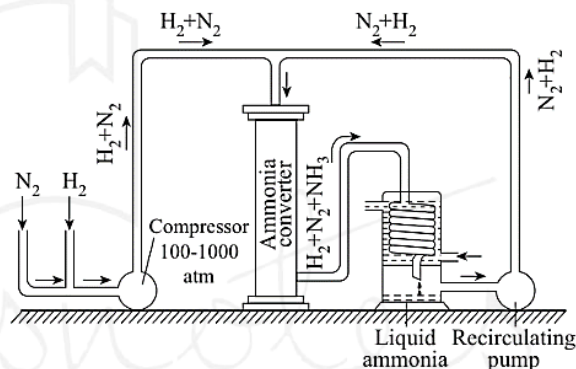


Figure: Haber's Process

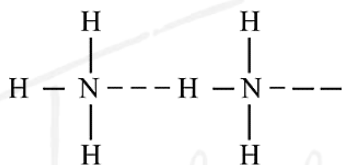
Favourable Conditions for the formation of Ammonia

Low temperature, high pressure, and a high concentration of nitrogen and hydrogen are favourable conditions for ammonia formation.

- Low temperature** is favourable for the formation of ammonia because the reaction is exothermic. It is in between $400-500^\circ C$.
- High Pressure:** Since the reaction proceeds with a decrease in volume ($\Delta n = -2$), high pressure favours the formation of additional ammonia. 200 to 900 atmosphere.
- As N_2 and H_2 are **reactants**, their **increased concentration** favours reaction in the forward direction, i.e., the formation of more ammonia.
- Continuous Ammonia Removal:** This also promotes its formation.

Physical Properties

1. It is an odourless gas with a pungent odour that induces ocular tears.
2. Because it is lighter than air, it is collected by air displacement downward.
3. Liquid NH₃ is a polar solvent.
4. Upon chilling, it readily liquefies under pressure and then solidifies into a pure white crystal.
5. As solvated electrons are formed, the reducing nature of IA metals can be increased by dissolving them in liquid NH₃.
6. Because NH₃ is highly soluble in water, it is collected over CaO or mercury. Due to hydrogen bonding, its high solubility in water is directly proportional to pressure and inversely proportional to temperature.
7. Hydrogen bonding can connect ammonia molecules to create associated molecules.

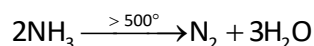
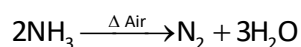


8. Because NH₃ has a high vapour density, its container is only partially filled and cooled prior to being opened to prevent any accidents.
9. Since NH₃ reacts with concentrated H₂SO₄, anhydrous CaCl₂, and P₂O₅, it cannot be dried with these substances.
10. These are used for cooling purposes.

Chemical Properties

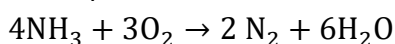
1. Decomposition

It is quite stable and can only be destroyed at extremely high temperatures or by electric charges.



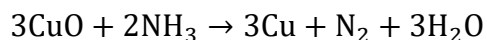
2. Combustion

It is neither combustible nor contributes to combustion, but it burns in an oxygen or air atmosphere.

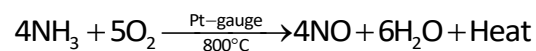


3. Oxidation

When copper oxide is exposed to heat, it is oxidised into nitrogen and water.

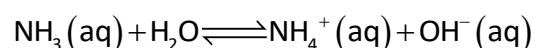


Ammonia is also oxidised by passing it with O₂ over a platinum gauge heated to 800 degrees Celsius.

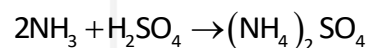
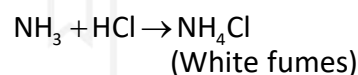


4. Basic Nature

Ammonia aqueous solution is mildly basic (Bronsted base) because the following equilibrium is reached.

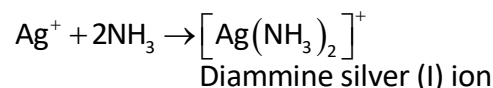
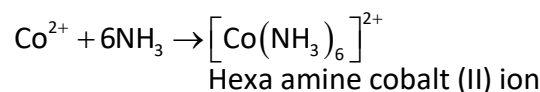
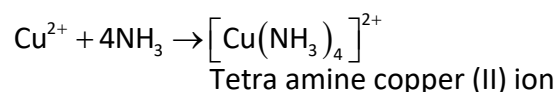


As a mild bronsted base, it can change red litmus to blue, phenolphthalein to pink, and react with acids to form the following salts:



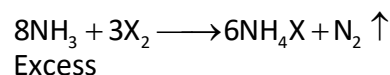
5. Formation of Complex Ions or Lewis Basic Nature

In ammonia, the nitrogen atom has one lone pair of electrons, which allows it to function as a Lewis base and form complexes by donating this lone pair to transition metal cations for the formation of coordinate bonds.

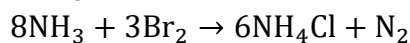
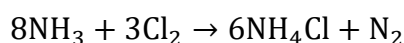


6. With Halogens

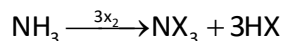
Chlorine or bromine can easily oxidized ammonia into nitrogen by undergoing the following reaction:



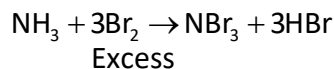
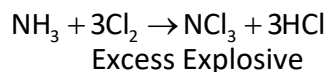
Example:



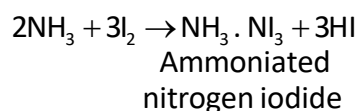
If halogen is in excess reaction is as follows:



Example:

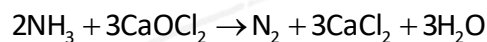
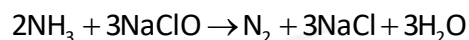


Upon rubbing iodine particles with liquor ammonia, a dark brown precipitate of ammoniated nitrogen iodide is produced.



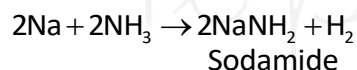
7. Reducing Nature

Ammonia can also function as a reducing agent, as it is readily oxidised by hypochlorites and bleaching powder into nitrogen, thereby reducing these substances.



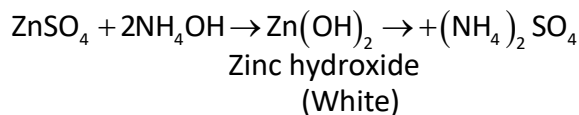
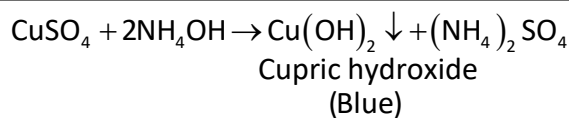
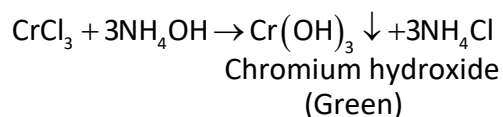
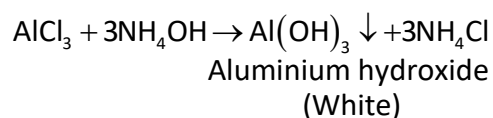
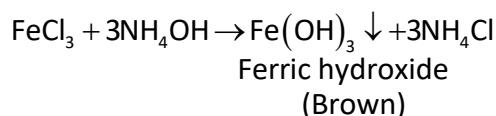
8. Formation of Amide

Amides are formed by passing dried ammonia over heated sodium or potassium.



9. Precipitation of Heavy Metal ions as Hydroxides using Aqueous Ammonia

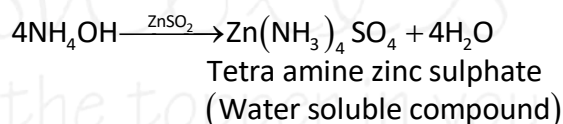
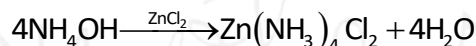
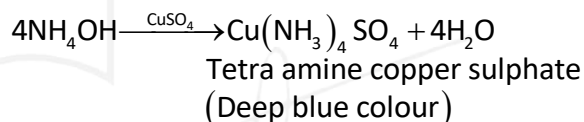
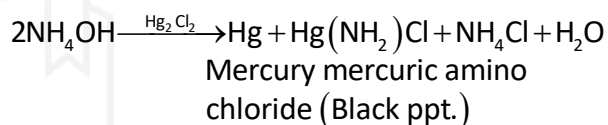
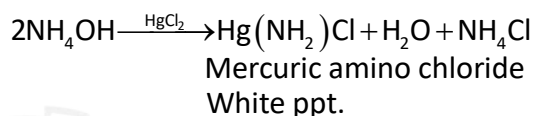
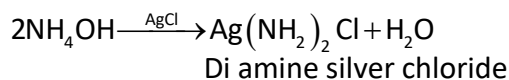
Many heavy metal ions, such as Fe^{3+} , Al^{3+} , Cr^{3+} , Cu^{2+} , Zn^{2+} etc., can be precipitated from their aqueous salt solutions using aqueous ammonia or ammonium hydroxide, as described below.



10. Formation of Complexes using Aqueous Ammonia

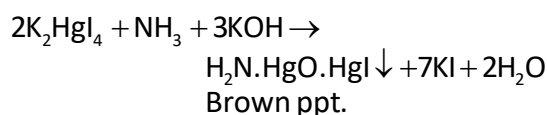
Certain compounds dissolve in excess aqueous ammonia (Bronsted base) to create soluble complexes.

Example:



11. With Nessler's Reagent

When ammonia is treated with an alkaline solution of K_2HgI_4 (Nessler's reagent), a reddish-brown precipitate of millon's base of iodide is produced.



Uses

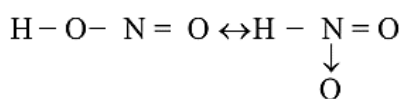
1. It's used to make nitric acid and other nitrogen compounds.
2. It is used extensively in the production of nitrogenous fertilisers, such as urea, ammonium nitrate, ammonium phosphate, and ammonium sulphate, among others.

- It is utilised in the production of synthetic silk and as a cleansing agent in dry cleaning.
- It is utilised in Solvay's production of sodium bicarbonate.
- In ice facilities, liquid ammonia is used as a refrigerant.

NITROUS ACID (HNO₂)

Structure

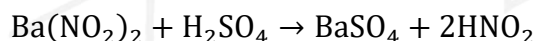
Since nitrous acid produces two series of organic derivatives, nitrites (R-ONO) and nitro compounds (R-NO₂), it is considered to be a mixture of two tautomers.



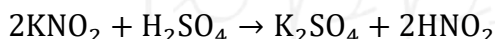
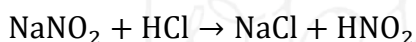
Preparation

1. From Barium Nitrate

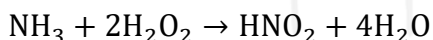
Nitrous acid is formed by adding an appropriate amount of ice and cold sulphuric acid to a well-cooled solution of barium nitrate.



2. By the action of mineral acids on nitrites

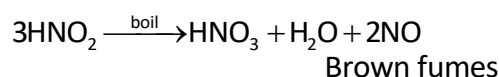


3. By the oxidation of ammonia with H₂O₂

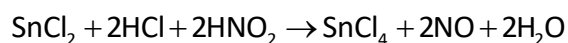
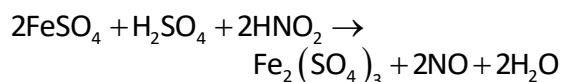
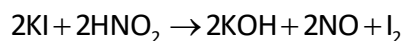
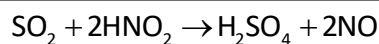
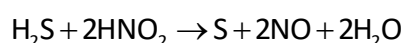


Physical-Chemical Properties

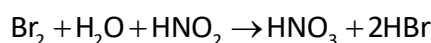
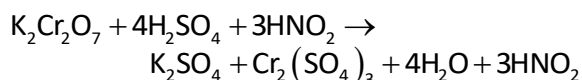
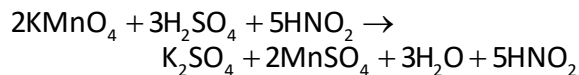
- In solution, it has a faintly bluish colour that is attributed to the anhydride N₂O₃.
- It is a weak acid (K_a = 4.5 × 10⁻⁵) that forms salts with alkalis.
- Decomposition:** Even when standing, it endures auto-oxidation due to its extreme instability. On boiling, it swiftly decomposes into acid.



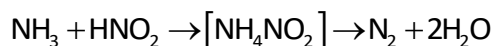
- Oxidizing Property:** It acts as an oxidizing agent.



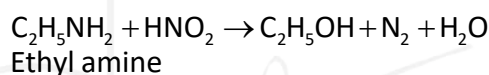
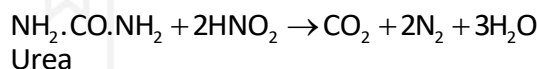
- Reducing Property:** It acts as a reducing agent towards strong oxidizing agent.



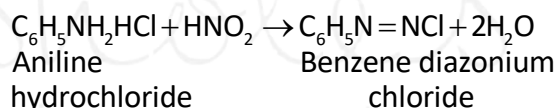
- With Ammonia:** It reacts with ammonia forms nitrogen and water.



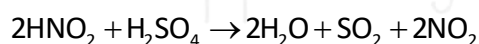
- It decomposes urea and ortho aliphatic amino compounds to give **nitrogen**.



- Diazotization:** It reacts with aromatic amines to give benzene diazonium chloride.



- With Sulphuric Acid:**



Uses

- It is used as an oxidising agent and a reducing agent.
- It is utilised in the preparation of diazo compounds, which are employed in the production of aniline dyes.
- It is used to replace the -NH₂ group in aliphatic amines with a single group.

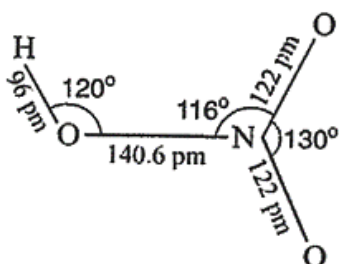
NITRIC ACID (HNO₃)

Introduction

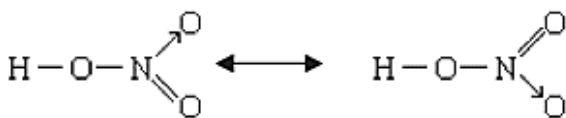
It is the most essential nitrogen oxyacids and is used for a variety of purposes in the chemical industry. Aqua Fortis is so named because it reacts with nearly all metals.

Structure

- It is a planar molecule.
- In it N – OH, N – O and O – H bond lengths are 1.41, 1.22 and 0.96 Å respectively.



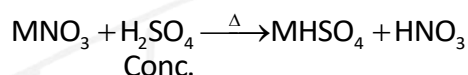
It has two resonating structures



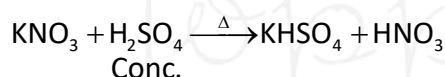
Preparation

1. Retort Method or Lab Method

In lab, it is prepared by heating a mixture of MNO_3 ($M = Na, K$) and concentrated sulphuric acid in a glass retort as follows:



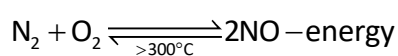
Example:



Nitric acid vapours obtained from here are condensed into liquid form in a glass receiver. It contains nitrogen oxide impurities that can be removed by further distillation or by passing CO_2 current through this acid.

2. Birkeland-Eyde Process or Arc Method

In this process, nitrogen and oxygen are initially treated at 300 degrees Celsius as follows:



According to **Le-Chatelier's principle**, this is an endothermic reaction that is favoured by high temperature. Since the volume is constant ($\Delta n_g = 0$), the pressure must be maintained at a constant level in order to increase the production of nitric oxide.

The combination of nitric oxide and oxygen yields nitrogen dioxide. Nitrogen dioxide absorbed in water produces nitric acid with a 30-40% concentration.

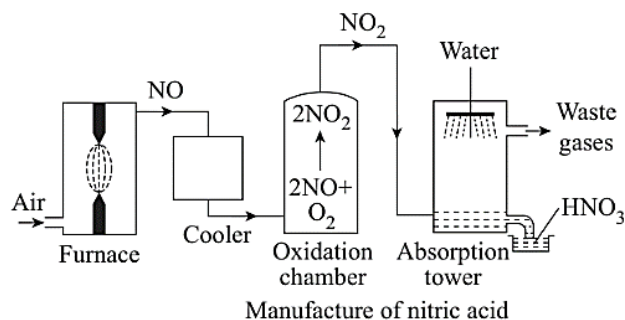
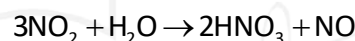
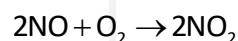
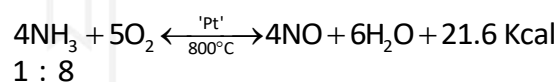


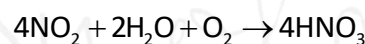
Figure: Manufacture of nitric acid

3. Ostwald Process

Here, nitric acid is produced by the oxidation of ammonia by air over platinum gauze at 1025-1175K.



or



According to Le-Chatelier's principle, formation of nitric acid is favoured by low temperature because it is exothermic and by high pressure because the volume is decreasing.

Process: The entire procedure for producing HNO_3 via this method can be described as follows:

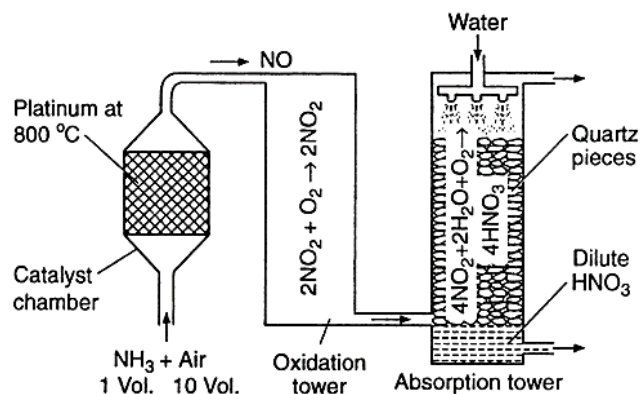
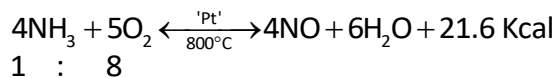


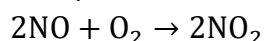
Figure: Ostwald's Process

(a) Catalyst Chamber or Converter: It possesses a platinum gauze that is initially heated to 1175.5K. When a 1: 8-10 mixture of ammonia and purified air is transmitted through it, up to 95% of the ammonia is oxidised into nitric oxide.

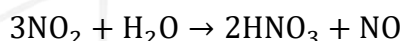


(b) Cooling Vessels: In this step, a vessel made of aluminium or chromium steel is used to chill a gaseous mixture of NO, O₂, etc., emerging from the catalyst chamber.

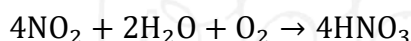
(c) Oxidizing Chamber: Here, the chilled gaseous mixture is oxidised by air, resulting in the production of NO₂.



(d) Absorption Tower: This tower is filled with quartz or acid-resistant flint, and water is distributed from the top. Here, NO₂ from the oxidising chamber is absorbed by water, resulting in the formation of diluted nitric acid.



or



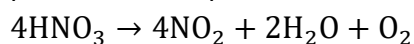
Concentration of Nitric Acid: The absorbing tower's diluted nitric acid is distilled until a constant mixture of 68% concentrated HNO₃ is produced. It becomes 98% concentrated HNO₃ (fuming nitric acid) upon further distillation with concentrated sulphuric acid. On chilling fuming nitric acid in a freeze mixture, 100% pure nitric acid crystals are produced.

Physical Properties

- In its anhydrous form, it is a colourless, pungent-smelling liquid, but in its contaminated state, it appears yellow due to its decomposition into nitrogen dioxide.
- It is miscible with water and produces a mixture with a constant boiling point (azeotropic mixture) that contains 68% HNO₃ and boils at 394K. Due to the formation of this mixture, the boiling concentration of diluted nitric acid cannot exceed 68%.

3. In its purest form, its boiling point is 355.6K, its melting point is 231.4K, and its specific gravity at 298K is 1.504.

4. Since the decomposition of fuming nitric acid (HNO₃+NO₂) into NO₂ produces brown vapours, the acid is stored in black bottles to prevent decomposition.

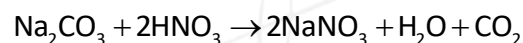
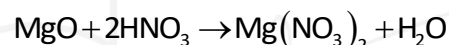
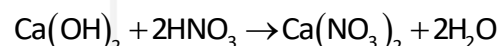
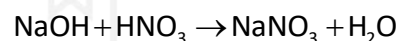
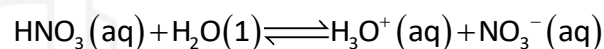


5. It has a highly corrosive effect on the outermost layer of skin, resulting in excruciating blisters or sores.

Chemical Properties

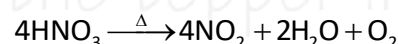
1. Acidic Nature

It is a strong monobasic acid that forms salts with basic hydroxides, oxides, and carbonates, among others.



2. Heating Effect

Due to the formation of NO₂, it decomposes slowly and turns yellow in the presence of sunlight.

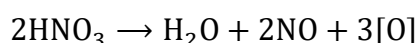


The yellow colour can be eliminated by heating the acid to 60-80 degrees Celsius and bubbling dry air through it.

3. Oxidising Nature of HNO₃

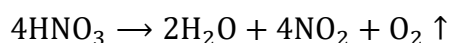
It is a powerful oxidizing agent as it easily gives nascent oxygen on decomposition under different conditions as follows:

Condition I



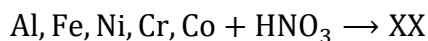
dil.

Condition II



conc.

Condition III (Oxidation of Metals)



Conc.

- **Reason:** It is due to the formation of a stable oxide layer over the metal surface (hence the storage of HNO₃ in an Al container).

(a) Oxidation of Non-Metals: It can oxidize many non metals into their oxyacids e.g.,

1. It oxidize boron into ortho boric acid.

$$B + 3HNO_3 \rightarrow H_3BO_3 + 3NO_2$$
2. It oxidize carbon into carbon dioxide.

$$C + 4HNO_3 \rightarrow CO_2 + 4NO_2 + 2H_2O$$
3. It oxidize phosphorous into ortho phosphoric acid.

$$2P + 10HNO_3 \rightarrow 2H_3PO_4 + 10NO_2 + 2H_2O$$
4. It oxidize sulphur into sulphuric acid.

$$S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$$
5. It oxidize iodine into iodic acid.

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

Iodic acid

(b) Oxidation of Metalloids: It can oxidize many metalloids into their oxyacids.

Examples:

1. It oxidize arsenic into arsenic acid.

$$2As + 10HNO_3 \rightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O$$

or

$$As + 5HNO_3 \rightarrow H_3AsO_4 + 5NO_2 + H_2O$$
2. It oxidize antimony into antimononic acid.

$$2Sb + 10HNO_3 \rightarrow 2H_3SbO_4 + 10NO_2 + 2H_2O$$

or

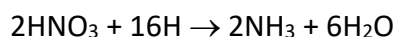
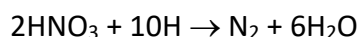
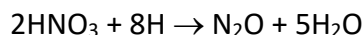
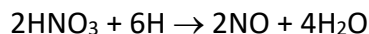
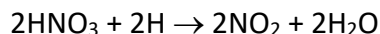
$$Sb + 5HNO_3 \rightarrow H_3SbO_4 + 5NO_2 + H_2O$$
3. It oxidize selenium into selenious acid.

$$Se + 4HNO_3 \rightarrow H_2SeO_3 + 4NO_2 + H_2O$$
4. It oxidize tin into meta stannic acid

$$Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O$$

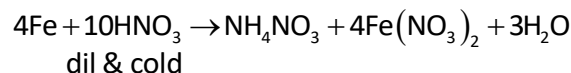
(c) Oxidation of Metals: It can react with virtually all metals besides Au and Pt to produce a variety of products. The formation of the product depends on the type of metal, the concentration of HNO₃, and the temperature.

- *Oxidation of Metals above Hydrogen in Electrochemical Series:* These metals are more electropositive than hydrogen and can therefore readily liberate hydrogen from HNO₃. This nascent hydrogen can convert nitric acid into various byproducts, including NO₂, NO, N₂O, N₂, and ammonia.

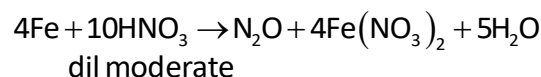


1. In Case of Iron

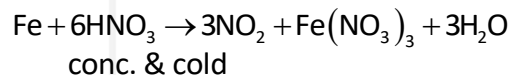
Very dilute nitric acid and iron forms ferrous nitrate and ammonium nitrate.



Dilute nitric acid and iron forms ferrous nitrate and nitrous oxide.



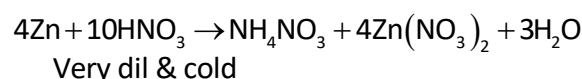
Concentrated nitric acid and iron give ferrous nitrate and nitrogen dioxide.



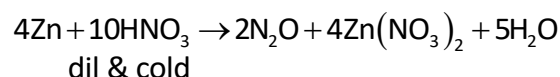
Due to the formation of a persistent oxide layer on its surface by highly concentrated HNO₃ (>80%), iron becomes passive when treated with a high concentration of the compound.

2. In Case of Zinc

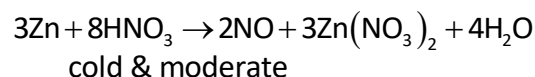
Very dilute nitric acid (6%) and zinc forms zinc nitrate and ammonium nitrate.



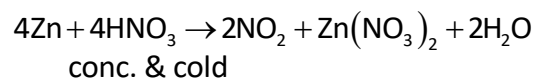
Dilute nitric acid (20%) and zinc forms zinc nitrate and nitrous oxide.



Cold and moderate nitric acid and zinc forms zinc nitrate and nitric oxide.

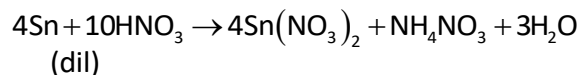


Concentrated and cold nitric acid (70%) and zinc forms zinc nitrate and nitrogen dioxide.

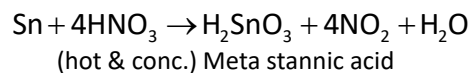


3. In Case of Tin

Dilute nitric acid and tin give tin nitrate and ammonium nitrate.

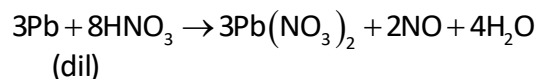


Hot and concentrated nitric acid and tin give meta stannic acid and nitrogen dioxide.

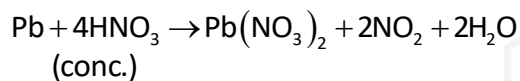


4. In Case of Lead

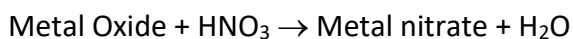
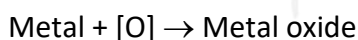
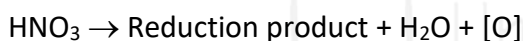
Dilute nitric acid and lead give lead nitrate and nitric oxide.



Concentrated nitric acid and lead give lead nitrate and nitrogen dioxide.

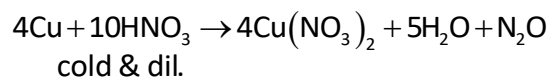


- Oxidation of Metals below Hydrogen in Electrochemical Series: As these metals are not only less electropositive than hydrogen, but also less reactive, they cannot displace the nascent hydrogen from nitric acid. Nitric acid can transform these metals into their oxides. These oxides dissolve in nitric acid to produce nitrates in the following manner:

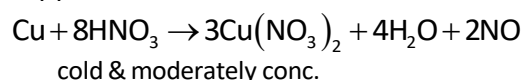


1. In Case of Copper

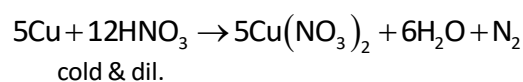
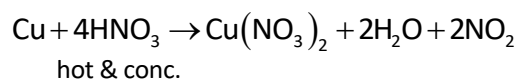
Cold and very dilute nitric acid and copper forms copper nitrate and nitrous oxide.



Cold and dilute nitric acid and copper forms copper nitrate and nitric oxide.

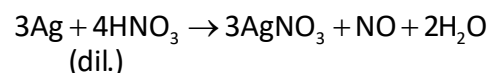


Hot and concentrated nitric acid and copper forms copper nitrate and nitrogen dioxide.

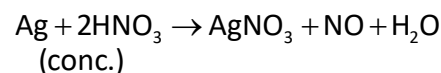


2. In Case of Silver

Dilute nitric acid and silver forms silver nitrate and nitric oxide.

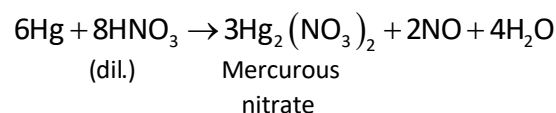


Concentrated nitric acid and silver forms silver nitrate and nitrogen dioxide.

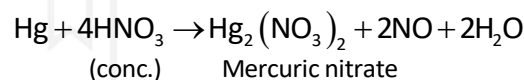


3. In case of Mercury

Dilute nitric acid and mercury forms mercurous nitrate and nitric oxide.

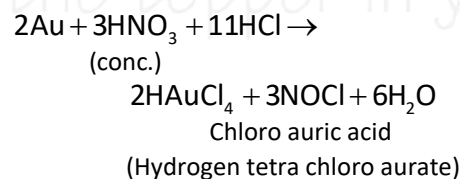


Concentrated nitric acid and mercury forms mercuric nitrate and nitrogen dioxide.

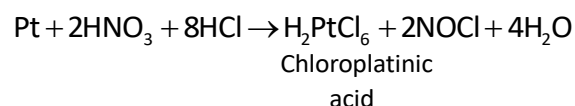


- ### 4. In case of Noble Metals:
- Noble metals such as Au, Pt, Rh, Ir, etc., are unaffected by nitric acid, but they dissolve as follows in aqua regia:

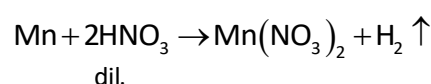
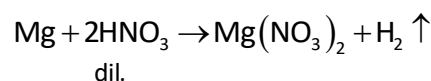
The dissolution of gold in aqua regia produces chloro auric acid and nitrosyl chloride.



Platinum dissociates in aqua regia to produce chloro platinumic acid and nitrosyl chloride.



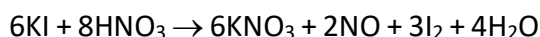
- ### 5. In Case of Mg and Mn :
- Both of these metals react with dilute nitric acid to produce nitrates and release hydrogen.



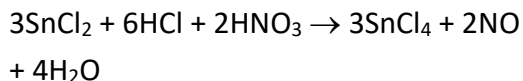
(d) Oxidation of Compounds: Nitric acid can oxidize many compounds.

Examples:

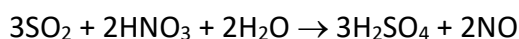
1. It oxidize KI into iodine



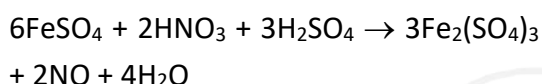
2. It oxidize stannous chloride into stannic chloride



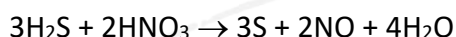
3. It oxidize sulphur dioxide into sulphuric acid



4. It oxidize ferrous sulphate into ferric sulphate

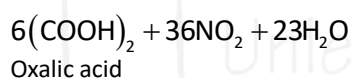
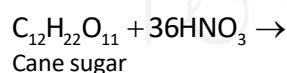


5. It can oxidize hydrogen sulphide into sulphur

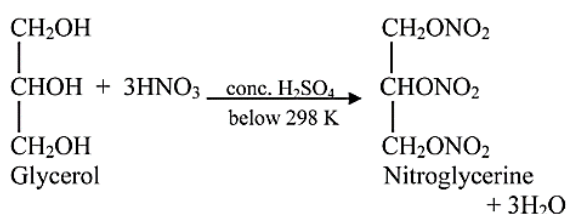
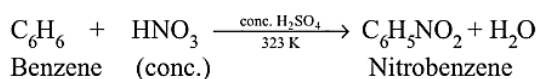


Reaction with Organic Compounds

(a) Oxidation: It can oxidize sugar into oxalic acid.



(b) Nitration: It can be used for the nitration of many organic compounds:



Facts to Remember

Finger + HNO_3 (conc.) \rightarrow Yellow (Xantho Protein)

Wood + HNO_3 \rightarrow Yellow (Nitro cellulose)

Uses

1. Not only is it used as an oxidising agent in inorganic chemistry, but also in organic chemistry.
2. Used in conjunction with concentrated H_2SO_4 as a nitrating mixture for aromatic compound nitration.
3. It is used to produce fertilisers and explosives such as TNT, nitroglycerine, rifle cotton, picric acid, etc.
4. It is utilised in the production of synthetic silk, pharmaceuticals, and pigments, etc.
5. It is utilised in stainless steel pickling and metal etching.
6. In the process of purifying silver and gold.
7. It is utilised as a rocket propellant oxidizer.

PHOSPHOROUS

Introduction

- It was discovered by Brand, isolated by Scheeley from bone ash, and verified as an element by Lavoisier.
- Because it emits light at night, it is termed phosphorous. It is toxic, but necessary for growth and survival.

Occurrence

- Phosphorous is a highly reactive element that predominately occurs in the earth's mantle as phosphate minerals.
- It is an indispensable component of both plants and vertebrates.
- It is primarily found in bones and teeth as calcium phosphate, as well as in vertebrate cells (as DNA and RNA).
- Phosphoprotein is found in brain, milk, and eggs.

Ores

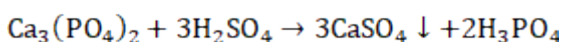
- Phosphorite or rock phosphate: $Ca_3(PO_4)_2$
- Chlorapatite: $3Ca_3(PO_4)_2 \cdot CaCl_2$
- Fluorapatite: $3Ca_3(PO_4)_2 \cdot CaF_2$
- Hydroxyapatite: $Ca_5(PO_4)_3OH$ or $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$

Extraction

It is extracted mainly from phosphorite ore by using the following methods:-

1. Old Process or Retort Process

Here, phosphorus is extracted from bone ash, which is predominantly composed of calcium phosphate. When bone ash is heated with concentrated sulphuric acid, orthophosphoric and unsolvable in calcium sulphate acids are produced.



From here, calcium sulphate is extracted by filtration, and the viscous ortho phosphoric acid is evaporated, which decomposes into meta phosphoric acid.



Now meta phosphoric acid is combined with pulverised coke and distilled in red-hot fire clay retorts to obtain phosphorous, which is vaporised and condensed under water.

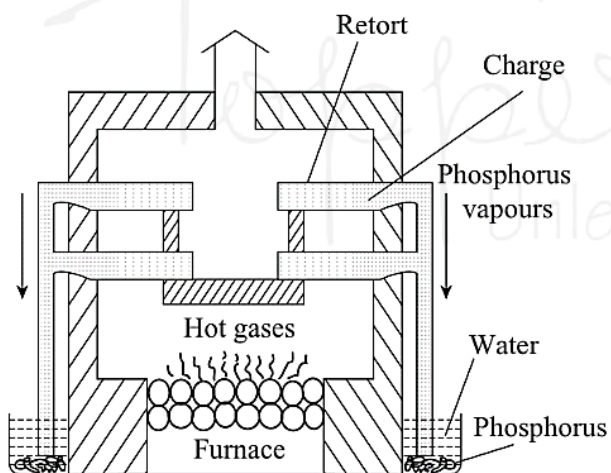
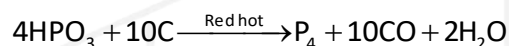
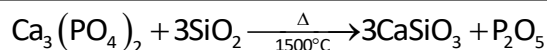


Figure: Retort Process

2. Electrothermic Process

Phosphorous is produced by heating phosphate ore, silica and charcoal in an electric furnace at 1500 degrees Celsius. This process is not electrolytic. This is accomplished by using electricity.

Intake of the solid substance into the furnace. First, the nonvolatile silica, SiO_2 , displaces the more volatile phosphorous pentoxide, P_4O_{10} , from calcium phosphate.



Which is then reduced to phosphorous by coke and carbon monoxide is formed.

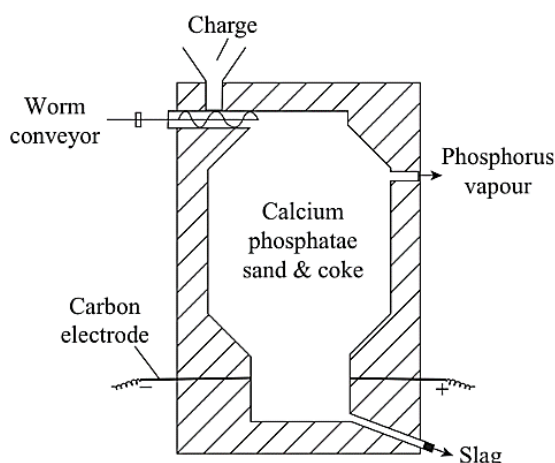
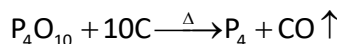


Figure: Electro Thermic Process

Purification: First, the impure phosphorous is melted in an acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$ so that the impurities can be oxidised and collected from the surface of the molten phosphorous. Now, phosphorous is redistilled in the absence of oxygen to produce pure white phosphorous vapours. Which are dissolved in water.

Allotropic Forms of Phosphorous

Types of allotropic forms:

- White (or yellow) phosphorous
- Red (or violet) phosphorous
- α -Black phosphorous
- β -Black phosphorous
- Scarlet phosphorous

Out of these allotropes **white and red forms** are of excellent phosphorous.

White Phosphorous

Structure

Given that the vapour density of white phosphorous is 62, the corresponding molecular formula is P_4 . The four phosphorous atoms in its structure occupy the vertices of a regular tetrahedron. Each phosphorous atom is covalently bonded to each of the other three atoms. The P-P bond length is 2.21 \AA , while the $\angle\text{PPP}$ bond angle is 60° . It suggests that the molecule is under stress and is therefore highly reactive.