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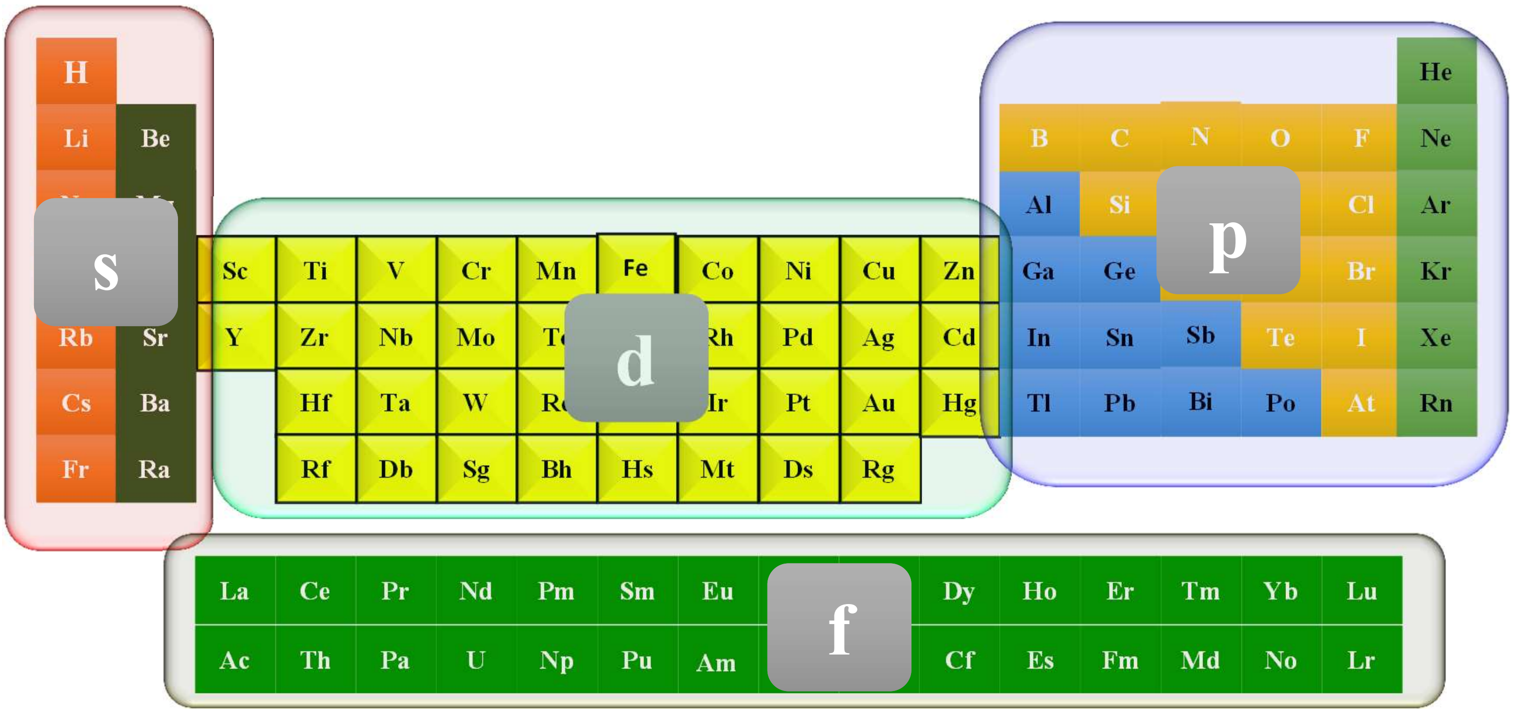
An Initiative by अमरउजाला

# 15$^{TH}$ GROUP ELEMENTS

# INTRODUCTION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Tm
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Th
Pa
U
Np
Pu
Am
Cf
Es
Fm
Md
No
Lr

| Group 15 | | Atomic number |
| --- | --- | --- |
| N | Nitrogen | 7 |
| P | Phosphorus | 15 |
| As | Arsenic | 33 |
| Sb | Antimony | 51 |
| Bi | Bismuth | 83 |

Nitrogen family members are also called Pnicogens

Because compounds of these elements are poisonous in nature or form suffocating compounds

# Occurrence

| | |
|---|---|
| **Elements** | **NITROGEN** |
| **Occurrence** | **Atmosphere (78%)(free state ), Nitrates (combined) Example – Chile salt petre ($NaNO_3$) Indian salt petre ($KNO_3$)** |

## Occurance

| | |
|---|---|
| **Elements** | **PHOSPHOROUS** occurs in apatite family |
| **Occurence** | $Ca_9\ [PO_4]_6.CaX_2$ $(3Ca_3(PO_4)_2\ .CaX_2\ )$ (X = F, Cl, OR, OH) $3Ca_3\ (PO_4)_2.CaF_2$ (FLUORAPATITE)Present in bones as well as living cells. |

# Occurrence

| | |
|---|---|
| **Elements** | **BISMUTH, ARSENIC, ANTIMONY** |
| **Occurrence** | **Oxide–BISMUTHITE ($Bi_2O_3$) sulphide-BISMUTHGLANCE($Bi_2S_3$)** |

MCQs

**1. The element belonging to group 15 is ...**

a) H

b) O

c) P

d) Mg

**2. The atomic number of Bismuth is ...**

**a) 7**

**b) 33**

**c) 51**

**d) 83**

**3. Indian salt petre is …**

**a) $KNO_3$**

**b) $NaNO_3$**

**c) $Mg(NO_3)_2$**

**d) None of these**

4. Phosphorous occurs in _______family.

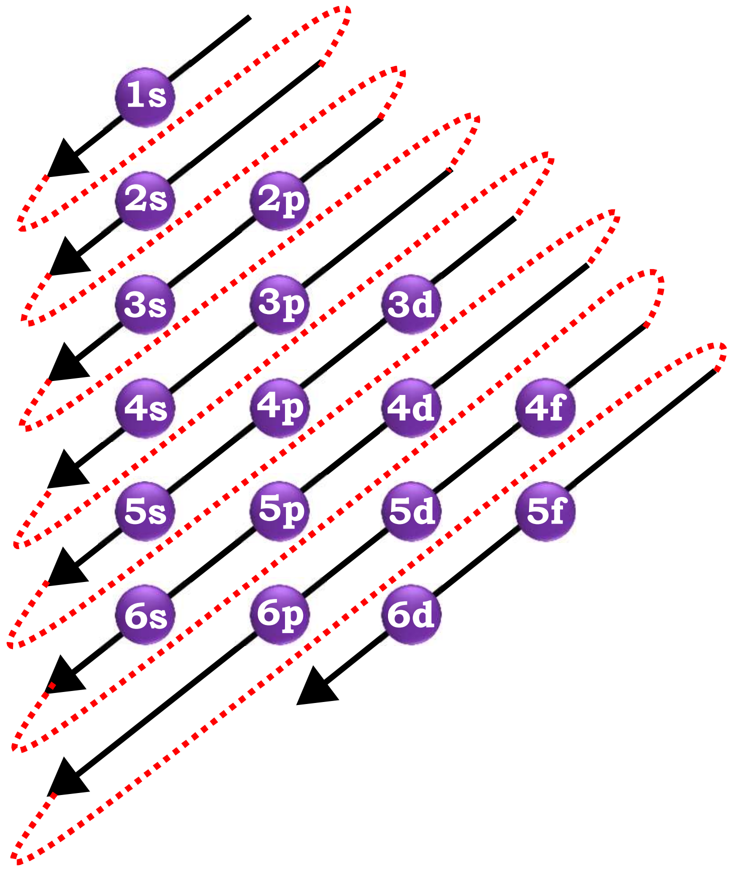
a) Nitrate

b) Apatite

c) Oxide

d) None of these

# ELECTRONIC CONFIGURATION PHYSICAL PROPERTIES OF 15$^{TH}$ GROUP ELEMENTS

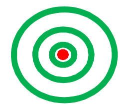
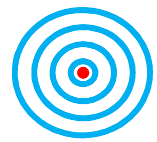
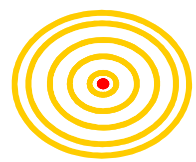
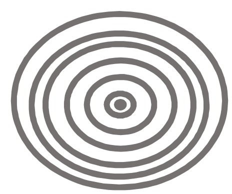


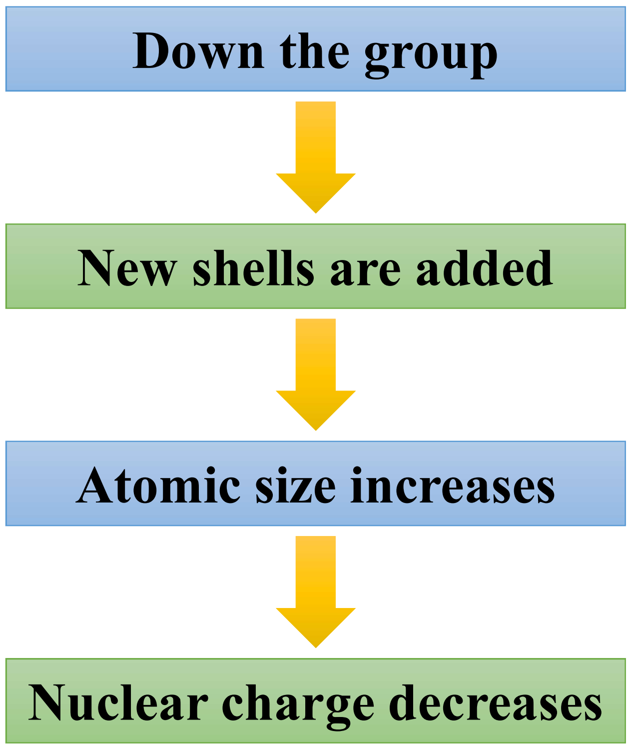

According to Aufbau Principle an atom is "built up" by progressively adding electrons

| Elements | Symbol & Atomic Number | | Electronic Configuration | Brief rep of electronic configuration |
|---|---|---|---|---|
| Nitrogen | N | 7 | $1s^2$ $2s^2$ $2p^3$ | [He] $2s^2$ $2p^3$ |
| Phosphorous | P | 15 | $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^3$ | [Ne] $3s^2$ $3p^3$ |
| Arsenic | As | 33 | $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^3$ | [Ar] $3d^{10}$ $4s^2$ $4p^3$ |
| Antimony | Sb | 51 | $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $5s^2$ $5p^3$ | [Kr]$4d^{10}$ $5s^2$ $5p^3$ |
| Bismuth | Bi | 83 | $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ $5s^2$ $5p^6$ $5d^{10}$ $6s^2$ $6p^3$ | [Xe]$4f^{14}$ $5d^{10}$ $6s^2$ $6p^3$ |

**$\therefore$ GEC $\rightarrow$ $ns^2\ np^3$**

## Atomic size

| Elements | Elec. Config. | Diagram |
| --- | --- | --- |
| N | [He] $2s^2\ 2p^3$ |  2-Energy levels |
| P | [Ne] $3s^2\ 3p^3$ |  3-Energy levels |
| As | [Ar] $3d^{10}\ 4s^2\ 4p^3$ |  4-Energy levels |
| Sb | [Kr] $4d^{10}\ 5s^2\ 5p^3$ |  5-Energy levels |
| Bi | [Xe] $4f^{14}5d^{10}\ 6s^2\ 6p^3$ |  6-Energy levels |


Down the group
New shells are added
Atomic size increases
Nuclear charge decreases

## Ionization Energy

It is the minimum amount of energy required to remove the most loosely bound $e^-$ from the outer most shell of an isolated atom in the gaseous state

What is Ionization energy ?

Ionization energy decreases down the group from Nitrogen to Bismuth due to the increase in atomic size.

# METALLIC CHARACTER

| ELEMENT | METALLIC CHARACTER |
|---|---|
| N | Non-metal |
| P | Non-metal |
| As | Metalloid |
| Sb | Metalloid |
| Bi | Metal |

# MCQs

**1. Down the group, atomic size …**

- a) Increases
- b) Decreases
- c) No change
- d) Can’t say

2. The ionization enthalpies of removal of 1st , 2nd, & 3rd electrons i.e. $\Delta H_1$, $\Delta H_2$ , $\Delta H_3$ are in the order …

a) $\Delta H_1 > \Delta H_2 > \Delta H_3$

b) $\Delta H_1 > \Delta H_2 < \Delta H_3$

c) $\Delta H_1 < \Delta H_2 < \Delta H_3$

d) $\Delta H_1 < \Delta H_2 > \Delta H_3$

3. In group 15, __________ is the most electro negative element

a) P

b) As

c) Sb

d) N

**4. Antimony is a…**

a) Metal

b) Non metal

c) Metalloid

d) None of these

# OXIDATION STATE

## OXIDATION STATES

| Compound | NAME | Oxidation State of N |
|---|---|---|
| $NH_3$ | AMMONIA | $-3$ |
| $N_2H_4$ | HYDRAZINE | $-2$ |
| $NH_2OH$ | HYDROXYL AMINE | $-1$ |
| $N_3H$ | HYDRAZOIC ACID | $-\frac{1}{3}$ |
| $N_2$ | DINITROGEN | $0$ |
| $N_2O$ | DINITROGEN MONOXIDE (LAUGHING GAS) | $+1$ |

# OXIDATION STATES

| Compound | NAME | Oxidation State of N |
|---|---|---|
| NO | Nitrogen monoxide | + 2 |
| $HNO_2$ or $N_2O_3$ | nitrous acid or dinitrogen trioxide | + 3 |
| $NO_2$ or $N_2O_4$ | nitrogen dioxide or Dinitrogen tetroxide | + 4 |
| $HNO_3$ or $N_2O_5$ | nitric acid or dinitrogen pentoxide | + 5 |

# OXIDATION STATES

**Characteristic electronic configuration : $ns^2\ np^3$**

**This suggests common oxidation states :- +3, +5, and –3**

N

P

As

Sb

Bi

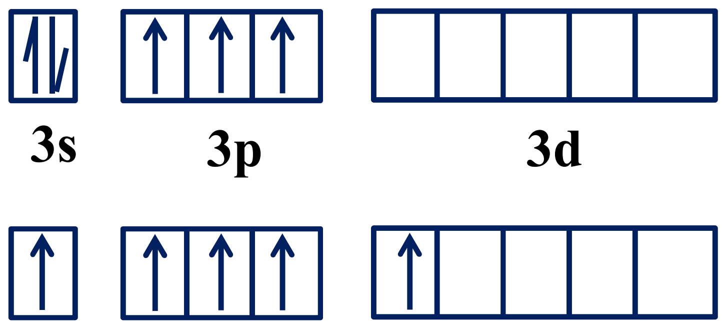
**Stability of + 3 oxidation state increases and that of + 5 oxidation state decreases**

**Reason : - Inert Pair effect**

**N cannot form compounds like $NF_5$ or $NCl_5$ while P can form compounds like $PCl_5$**

**Explain : P $_{\text{(Ground state)}}$**

**P $_{\text{(Excited state)}}$**




**This cannot happen in Nitrogen due to lack of d orbitals**

# MCQs

**1. Stability of + 5 state decreases down the group due to … effect.**

a) Inert pair

b) Reactive pair

c) Joule - Thomson

d) None of these

2. The characteristic oxidation states of group 15 elements are…

a) +3, -3, +5

b) -5, +3, -3

c) -5, -3, +2

d) -2, +5, +3

3. **Stability of +3 oxidation state, down a group …**

**a) Decreases**

**b) Increases**

**c) Does not change**

**d) Can not predict**

**4. The electronic configuration of As (33) is…**

a) [Kr] $4d^{10}$, $5s^2$, $5p^3$

b) [Ne] $3s^2$, $3p^3$

c) [Ar] $3d^{10}$, $4s^2$, $4p^3$

d) [He] $2s^2$,$2p^3$

# CHEMICAL PROPERTIES OF $15^{TH}$ GROUP ELEMENTS

## Reactivity Towards Hydrogen

**Type of hydride formed – $MH_3$ ($NH_3$ , $PH_3$ , $AsH_3$ , $SbH_3$ , $BiH_3$)**

**Stability of hydride.**

**Down the group** ↓ **Decreases**

**Due to the decrease in dissociation enthalpy.**

## Reactivity Towards Hydrogen

**Type of hydride formed – $MH_3$ ($NH_3$ , $PH_3$ , $AsH_3$ , $SbH_3$ , $BiH_3$)**
**(M= N, P, As, Sb, and Bi**

**All the hydrides of the type $MH_3$ are prepared by the action of water are dilute acids on their metal compounds.**

**Ex :** $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$

**Order of Reducing character of hydrides**

$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

**Order of Basic nature of hydrides**

$NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$

## Chemical properties

### Reactivity towards Oxygen:

- These elements react with Oxygen to form two types of oxides

- Trioxides - $M_2O_3$
- Pentoxides - $M_2O_5$

- The Oxides in the higher oxidation state of the element is more acidic than that of lower oxidation state.

- Acidic character decreases down the group

- The trioxides of Nitrogen and Phosphorus are purely acidic, that of Arsenic and Antimony are amphoteric and that of Bismuth is predominantly basic .

- All Pentoxides are acidic.

- Except Bi other elements form pentoxides represented by $M_4O_{10}$.

- Tri-oxides dissolve in water giving – Ous acids

- Pentoxides dissolve in water giving – ic acids

## Reactivity towards metals :

**These elements react with metals to form binary compounds in which VA group element exhibits – 3 oxidization state.**

**Example:**

$$6Mg + N_2 \longrightarrow 2Mg_3N_2$$

**Magnesium nitride**

$$6Ca + P_4 \longrightarrow 2Ca_3P_2$$

**Calcium phosphide**

## Reactivity towards halogens:

- These elements form two types of halides
- Trihalides - $MX_3$
- Pentahalides - $MX_5$
- Nitrogen does not form petahalides due to non availability of the d-orbitals in it's valence shell.
- Pentahalides are more covalent than trihalides because the elements in the higher oxidation state exert more polarizing power
- All trihalides of these elements except nitrogen are stable.
- In case of nitrogen halides only $NF_3$ is stable
- Trihalides except $BiF_3$ are predominantly covalent in nature

MCQs

1. $N_2$ reacts with metals to give…

a) Nitrites

b) Nitrates

c) Nitrides

d) Nitriles

2. **The most basic group 15  hydride is….**

**a) $NH_3$**

**b) $BiH_3$**

**c) $SbH_3$**

**d) $AsH_3$**

3. $P_4 + NaOH + H_2O \longrightarrow$

a) $PH_3$

b) $H_3PO_4$

c) $P_2O_5$

d) All of these

4. $N_2 + O_2 \xrightarrow[\text{arc}]{\text{electric}}$

a) $NO_2$

b) $NO$

c) $N_2O$

d) $N_2O_5$

# DINITROGEN

# ($N_2$)

# PREPARATION:-

## 1. Laboratory method:

- **In the laboratory Dinitrogen prepared by treating an aqueous solution of Ammonium chloride with Sodium nitrite**

$$NH_4Cl + NaNO_2 \xrightarrow{\Delta} N_2 + 2H_2O + NaCl$$

| ammonium chloride | Sodium nitrite | Dinitrogen |
|---|---|---|

**Make a note**

**Small amounts of NO and $HNO_3$ formed, removed by passing the gas through aq. $H_2SO_4 + K_2Cr_2O_7$.**

## 2. Commercial method :

$$\text{Air} \xrightarrow{\text{Liquification}} \text{Liquid Air} \xrightarrow{\text{Fractional distillation}} \text{Dinitrogen}$$

## 3. By thermal decomposition of ammonium dichromate :

- $N_2$ can also be obtained by the thermal decomposition of ammonium dichoromate.

$$\underset{\text{Ammonium dichromate}}{(NH_4)_2Cr_2O_7} \xrightarrow{(\Delta)} \underset{\text{Dinitrogen}}{N_2} + Cr_2O_3 + 4H_2O$$

## 4. From suspension of bleaching powder and ammonia

$$3CaOCl_2 + 2\,NH_3 \longrightarrow N_2 + 3CaCl_2 + 3H_2O$$

**Calcium oxychloride**    **Ammonia**    **Dinitrogen**

## 5. Thermal decomposition of metal azides :

- Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide

$$2NaN_3 \xrightarrow{(\Delta)} 2Na + 3N_2$$

Sodium azide — Dinitrogen

$$Ba(N_3)_2 \xrightarrow{(\Delta)} Ba + 3N_2$$

Barium azide — Dinitrogen

**Highly pure** form of dinitrogen is obtained by this method.

**Note :**

$$\overset{\ominus}{:\ddot{N}} - \overset{\oplus}{N} \equiv \ddot{N}$$

(or)

$$N_3^{\ominus}$$

Azide ion

## PROPERTIES OF DINITROGEN ($N_2$) : -

1. **Di nitrogen is a colourless, odorless, tasteless and non ionic gas.**
2. **It has two stable isotopes $^{11}N$ and $^{15}N$**
3. **It has a very low solubility in water (23.2 cm per litre of water at 273k and 1 bar pressure). And low freezing and boiling points.**
4. **Di nitrogen is inert at room temperature because of the high bond enthalpy of N≡N bond. And reactivity increases rapidly with rise in temperature**

## MCQs

1. Commercial method of preparation of $N_2$ involves…

a) Sublimation

b) Fractional distillation of liquid air

c) Freezing

d) Evaporation

**2. An azide ion is…**

**a) $NO_3^-$**

**b) $N_2$**

**c) $N_3^-$**

**d) Any of these**

**3. In the lab method , $NH_4Cl$ is reacted with ______ to produce $N_2$ gas**

a) $NaNO_3$

b) $NaNO_2$

c) $HNO_3$

d) $HNO_2$

**4. $N_2$ can be produced by thermal decomposition of metal . . .**

**a) Sulphates**

**b) Nitrates**

**c) Sulphides**

**d) Azides**

# CHEMICAL PROPERTIES OF NITROGEN

# Chemical reactions

**1. Action on metals :** At high temperature $N_2$ directly combines with Li and Mg metals to form nitrides

$$6Li + N_2 \xrightarrow{\text{(heat)}} 2Li_3N \quad \text{Lithium nitride}$$

$$3Mg + N_2 \xrightarrow{\text{(heat)}} Mg_3N_2 \quad \text{Magnesium nitride}$$

$$2Al + N_2 \xrightarrow{\text{(heat)}} 2AlN \quad \text{Aluminium nitride}$$

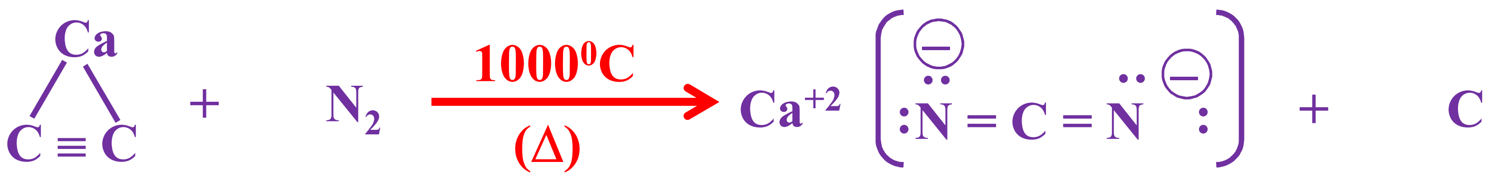
**2. Action of dioxygen :**

$$N_2 + O_2 \underset{\text{2000 K}}{\overset{(\Delta \text{ or heat})}{\rightleftharpoons}} 2NO$$

Nitric oxide

# Chemical reactions

**3. Action of calcium carbide :**




or $CaC_2$ Calcium carbide

Dinitrogen

or $CaCN_2$ Calcium cyanamide

Carbon(graphite)

## Chemical reactions

**4. Action of dihydrogen:**

$$N_{2\,(g)} + 3H_{2\,(g)} \xrightleftharpoons{773\ K} 2NH_{3(g)}$$

ammonia

**Uses :**

- Di nitrogen is mainly used in the manufacture of Ammonia and other industrial chemical containing nitrogen (Eg ; $CaCN_2$)
- It is used to maintain the inert atmosphere (Eg: In iron and steel industry)
- Liquid dinitrogen is used as a refrigerant to pressure biological materially food items and in cryo surgery

# MCQs

1. $CaC_2 + N_2 \xrightarrow{1000^oC}$ ______ + C

a) $CaCO_3$

b) $CaCN_2$

c) CaNC

d) $Ca(CN)_2$

2. $N_2$ + metal $\longrightarrow$ metal ______

a) Nitride

b) Nitrate

c) Nitrite

d) None of these

3. **Dinitrogen and Dihydrogen** $\xrightarrow{\Delta}$

**a) Amine**

**b) Amide**

**c) Ammonia**

**d) None of these**

4. $N_2 + O_2 \xrightarrow{\Delta 2000K}$ ------------------

a) $NO_2$

b) $N_2O$

c) $NO$

d) $N_2O_3$

# ANOMALOUS PROPERTIES OF NITROGEN

## Anomalous properties of nitrogen

**Nitrogen differs from the rest of the members of this group due to its small size, high electronegativity, high ionisation enthalpy and non-availability of d orbitals.**

**Nitrogen has unique ability to form pπ - pπ multiple bonds with itself and with other elements having small size and high electronegativity (Eg: C, O). Heavier elements of this group do not form pπ - pπ bonds as their atomic orbitals are so large and diffuse that they can not have effective overlapping.**

**thus, nitrogen exists as a diatomic molecule with a triple bond between the two atoms. Consequently, its bond enthalpy is very high. On the contrary, phosphorous, arsenic and antimony form single bonds as P-P, As – As and Sb – Sb.**
**While Bismuth forms metallic bonds in elemental state however the single N-N bond is weaker than the single P-P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length .**

**As a result, the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four, nitrogen can not form $d\pi$ - $p\pi$ bond e.g., $R_3P{=}O$.**

**Or $R_3P = CH_2$ (R= Alkyl group), phosphorous and arsenic can form dπ - dπ bond also with transition metals.**

**Examples: $P(C_2H_5)_3$ , $As(C_6H_5)_3$**

# PREPARATION OF AMMONIA

## Preparation of Ammonia

### 1. Laboratory method :

$$2NH_4Cl + Ca(OH)_2 \xrightarrow{(\Delta)} 2NH_3 + CaCl_2 + 2H_2O$$

Ammonium chloride | Calcium hydroxide | Ammonia

## Preparation of Ammonia

### 2. Commercial method (Haber's process):

$$N_{2\,(g)} + 3H_{2\,(g)} \underset{773K,\ 200atm}{\overset{\text{Fe-catalyst, Mo-Promoter}}{\rightleftharpoons}} 2NH_{3(g)} \quad (\Delta H = -92.4\ kJ \cdot mol^{-1})$$

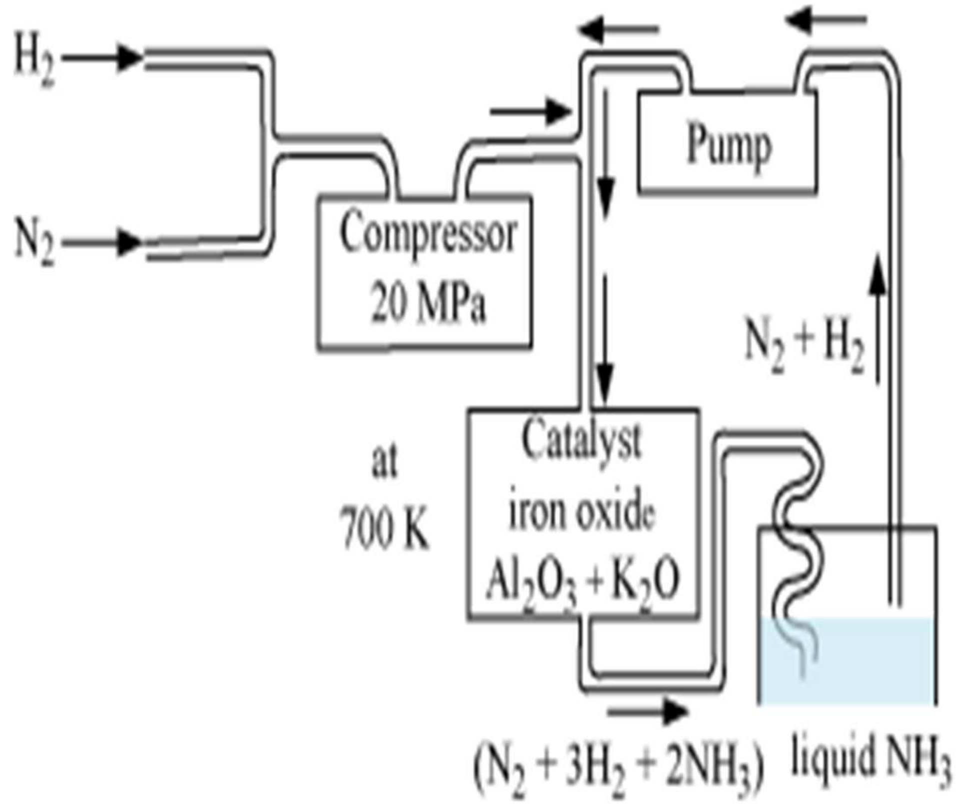
Dinitrogen   Dihydrogen   Ammonia

## Preparation of Ammonia

## 2. Commercial method (Haber's process):

**Optimum conditions :**

| | | |
|---|---|---|
| **Pressure** | = | **200 atm** |
| **Temperature** | = | **about 700 K** |
| **Catalyst** | = | **porous and finely divided IRON oxide** |
| **Promoters** | = | **Molybdenum or ($K_2O$ and $Al_2O_3$)** |



H2
N2
Compressor
20 MPa
Pump
N2 + H2
at
700 K
Catalyst
iron oxide
Al2O3 + K2O
(N2 + 3H2 + 2NH3)
liquid NH3

**Note :** Dehydrating agents cannot be used

$H_2SO_4$
Acidic
$\therefore$ reacts with $NH_3$

$P_2O_5$
Acidic
$\therefore$ reacts with $NH_3$

anhy. $CaCl_2$
Forms a complex
$CaCl_2 . 8NH_3$

Therefore, moist $NH_3$ is dried over quicklime i.e., CaO

# Preparation of Ammonia

## 3. Action of calcium carbide (Cynamide process):

(I)

$$CaC_2 + N_2 \xrightarrow[(\Delta)]{1000^0C} \underbrace{CaCN_2 + C}_{\text{NITROLIM}}$$

Calcium carbide + Dinitrogen → Calcium cyanamide + Carbon(graphite)

(II)

$$CaCN_2 + 3H_2O \longrightarrow NH_3 + CaCO_3$$

Calcium Cyanamide + Super heated Steam → Ammonia + Calcium carbonate

MCQs

**1. Ammonia is commercially prepared by ______ process.**

a) Haber's

b) Vulcanization

c) Contact

d) Any of these

2. In the laboratory method of preparation of $NH_3$, _____ and $Ca(OH)_2$ are used.

a) $NH_4NO_3$

b) $(NH_4)_2\ CO_3$

c) $NH_4Cl$

d) None of these

3. In Haber’s process, the catalyst used is...

a) Iron oxide

b) Copper oxide

c) Carbon monoxide

d) All of the above

4. Low temperatures are used in Haber's process, as the forward reaction is...

a) Endothermic

b) Exothermic

c) Either a & b

d) None of these

# CHEMICAL PROPERTIES OF AMMONIA

## Action of halogens :

**1. Chlorine :**

$$\underset{\text{(excess)}}{8\,NH_3} + 3Cl_2 \longrightarrow \underset{\text{Ammonium chloride}}{6NH_4Cl} + N_2$$

$$NH_3 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow \underset{\text{Nitrogen trichloride}}{NCl_3} + 3HCl$$

## Action of halogens :

**2. Bromine :**

$$8\,NH_3 + 3Br_2 \longrightarrow 6\,NH_4Br + N_2$$

Ammonium bromide

**3. Iodine :**

$$2NH_3 + 3I_2 \longrightarrow NH_3NI_3 + 3HI$$

Nitrogen triodide ammonia

$$8NH_3NI_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$$

Ammonium iodide

- Ammonia precipitates the hydroxides of many metals from their salt solutions

$$ZnSO_{4(aq)} + 2NH_4OH_{(aq)} \longrightarrow Zn(OH)_2(S) + (NH_4)_2\ SO_4(aq)$$

(White ppt)

$$FeCl_3\ (aq) + NH_4OH(aq) \longrightarrow Fe_2O_3\ .\ xH_2O(S) + NH_4Cl(aq)$$

(brown ppt)

- **Due to the presence of lone pair in ammonia, ammonia is used in detection of metal ions such as $Cu^{+2}$, Ag+**

**Examples**

$AgCl_{(s)} + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]\,Cl_{(aq)}$ **Colourless**

**White ppt**

$Cu^{+2}{}_{(aq)} + 4\,NH_{3(aq)} \longrightarrow \left[Cu(NH_3)_4\right]^{2+}$ **Deep Blue Colour**

**Reaction of ammonia with Nessler's reagent:**

$HgI_{2(aq)} + 2KI_{(aq)} \longrightarrow K_2HgI_{4(aq)}$ **(formation of Nessler's reagent)**

$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow H_2N - Hg - O - Hg - I + 7KI + H_2O$

**(Nessler's reagent)** **(Iodide of Millon's base)**

- **Due to the presence of lone pair of electrons in the nitrogen atom of the Ammonia $NH_3$ behaves as a Lewis base.**
- **Hence it donates the electron pair and forms bond with metal ions.**
- **So $NH_3$ is used in the detection of metal ions such as $Cu^{+2}$ or $Ag^{+}$.**

**Question**

**Why does $NH_3$ act as a Lewis base?**

**Answer:**

**Nitrogen atom in $NH_3$ has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base .**

**Question**

**How does ammonia (aqueous solution is ammonium hydroxide) react with a solution of $Cu^{2+}$, a deep blue solution is obtained due to the formation of tertraamine copper(II) ion.?**

**Answer:**

$$Cu^{2+}_{(aq)} + 4NH_4OH_{(aq)} \longrightarrow [Cu(NH_3)_4]^{2+} + 4\,H_2O$$

**Tetraamine copper (II)ion(deep blue solution**

*MCQs*

**1. ______ is the Nessler's reagent.**

a) $K_3HgI_2$

b) $K_2HgI_4$

c) $K_2Hg_2I_3$

d) All of these

**2.** $NH_3 + Cl_2$ (excess) $\longrightarrow$

a) $NH_4Cl$

b) $NCl_5$

c) $NCl_3$

d) All of these

3. The brown colour obtained in Nessler's reagent test is due to iodide of ______ base.

a) Millon's

b) Billion's

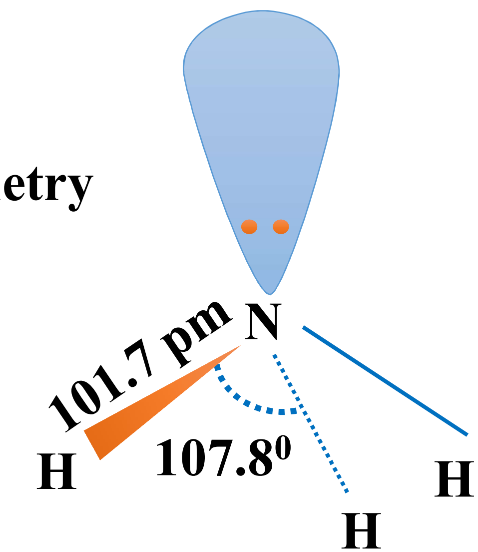
c) Trillion's

d) None of these

# STRUCTURE
# &
# USES OF AMMONIA

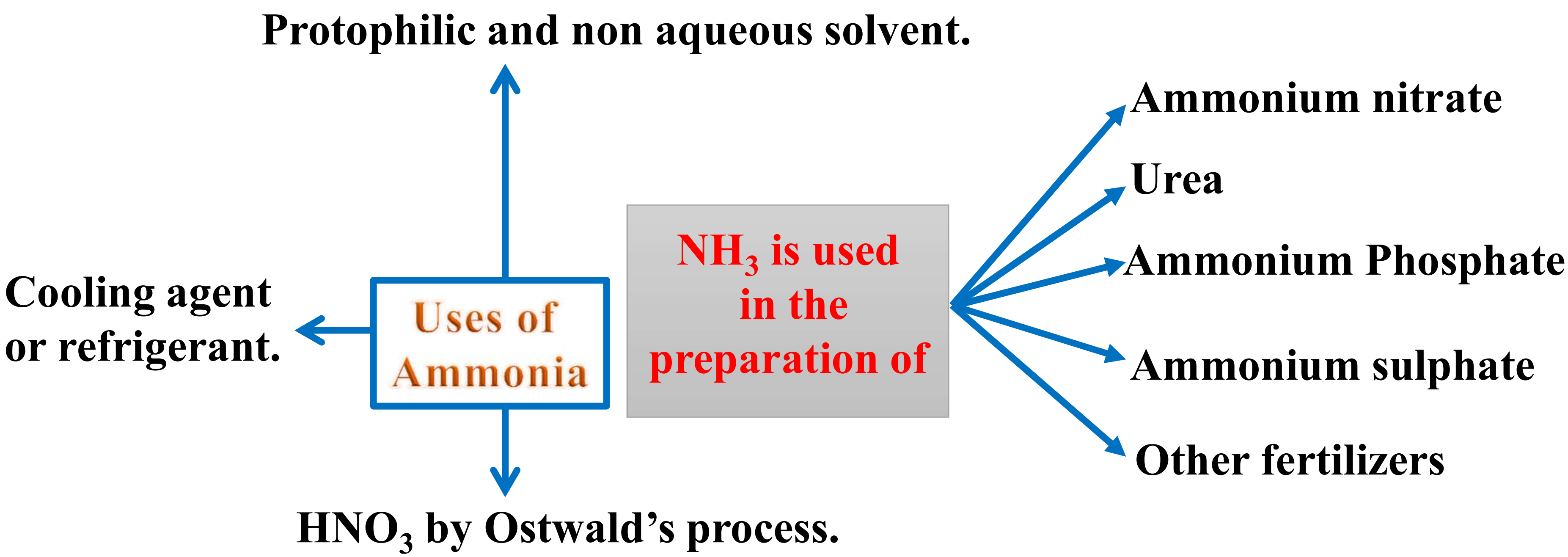
## Structure of Ammonia

- ➢ **Ammonia is expected to have a tetrahedral geometry**
- ➢ **The central nitrogen atom invloves $sp^3$ hybridisation.**
- ➢ **one position is occupied by a lone pair.**
- ➢ **Three bond pairs and one lone pair of electrons as shown in the structure.**



## Structure of Ammonia

- lone pair distorts its geometry and the molecule has pyramidal geometry with nitrogen atom at the apex.
- N–H bond length is 101.7 pm.
- HNH bond angle is $107.8^0$


Protophilic and non aqueous solvent.
Cooling agent or refrigerant.
Uses of Ammonia
HNO3 by Ostwald's process.
NH3 is used in the preparation of
Ammonium nitrate
Urea
Ammonium Phosphate
Ammonium sulphate
Other fertilizers

# MCQs

**1. In $NH_3$, the central nitrogen atom is _____ hybridized**

**a) $sp^2$**

**b) sp**

**c) $sp^3$**

**d) $dsp^2$**

**2. Ammonia has ______ geometry.**

**a) Tetrahedral**

**b) Pyramidal**

**c) Square planar**

**d) Linear**

3. The HNH bond angle is ...

a) $109^0\ 28''$

b) $120^0$

c) $90^0$

d) $107.\ 8^0$

**4. Ammonia is ________ solvent.**

**a) Protogenic**

**b) Protophilic**

**c) Aprotic**

**d) Both a & b**

# OXIDES OF NITROGEN

## Oxides of Nitrogen

| Name | Formula | Oxidation state of nitrogen | Common methods of preparation | Physical appearance and chemical nature |
|---|---|---|---|---|
| Dinitrogen Monoxide or nitrous oxide (Nitrogen (I) oxide) (laughing gas) | $N_2O$ | + 1 | $NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$ | Colourless gas, neutral |
| Nitrogen monoxide or Nitric oxide (Nitrogen (II) oxide) | NO | + 2 | $2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$ | Colourless gas, neutral |
| Dinitrogen trioxide (Nitrogen (III) oxide) | $N_2O_3$ | + 3 | $2NO + N_2O_4 \xrightarrow{250\ K} 2N_2O_3$<br>$NO + NO_2 \rightarrow N_2O_3$ | Blue solid , acidic |

# Oxides of Nitrogen

| Name | Formula | Oxidation state of nitrogen | Common methods of preparation | Physical appearance and chemical nature |
|---|---|---|---|---|
| Nitrogen dioxide (Nitrogen (IV) oxide) | $NO_2$ | + 4 | $2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 2PbO + O_2$ | Brown gas, acidic |
| Dinitrogen tetroxide (Nitrogen (IV) oxide) | $N_2O_4$ | + 4 | $2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$ | Colourless solid/ liquid, acidic |
| Dinitrogen pentoxide (Nitrogen (V) oxide) | $N_2O_5$ | + 5 | $4\ HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$ | Colourless solid ,acidic |

MCQs

**1. ______ is also called as laughing gas.**

**a) $NO_2$**

**b) NO**

**c) $N_2O_5$**

**d) $N_2O$**

2. ______ is called as Nitrogen (III) oxide

a) $NO_2$

b) $N_2O_5$

c) $N_2O_3$

d) $NO$

**3. The oxidation state of Nitrogen in $NO_2$ and $N_2O_4$ is ______ and ______.**

a) +4, +4

b) +4, +2

c) +2, +4

d) +1, +4

4. $N_2O_3$ is prepared from ______ and ______

a) $NO$, $NO_2$

b) $N_2O_5$, $NO$

c) $NO_2$, $N_2$

d) $NO$, $N_2O_4$

# NITRIC ACID

# Nitric Acid

## Preparation of Nitric acid

**Laboratory method to prepare nitric acid.**

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

**Sodium nitrate** **Nitric acid**

**Preparation of nitric acid on a large scale by Ostwald's process.**

Step 1 $4NH_{3(g)} + 5O_2 \xrightarrow[\text{500 K 9 bar}]{\text{Pt/ Rh gauze catalyst}} 4NO_{(g)} + 6H_2O_{(g)}$

Nitric oxide

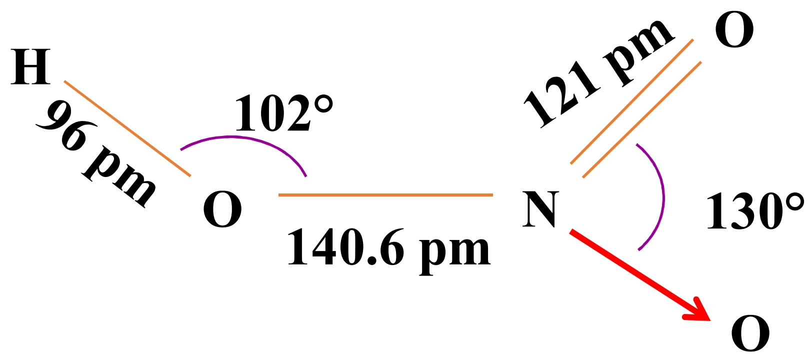
Step 2 $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$

Nitrogen Dioxide

Step 3 $NO_2 + H_2O_{(l)} \longrightarrow 2HNO_{3(l)} + NO_{(g)}$

Nitric acid

## Structure of Nitric Acid




- $HNO_3$ is a planar molecule.
- Bond length between H–O is 96 pm
- O–N is 140.6 pm
- Bond angle between H–O–N is $102^0$
- Bond angle between O–N–O is $130^0$.

MCQs

**1. Nitric acid is commercially prepared by ______ process.**

**a) Haber's**

**b) Contact**

**c) Ostwald's**

**d) All of the above**

2. The catalyst used in commercial preparation of nitric acid is …

a) FeO

b) Pt/ Rh

c) Pd/Rh

d) PtO

**3. In the structure of $HNO_3$, the O – N – O bond angle is ______**

a) $109^0$

b) $180^0$

c) $120^0$

d) $130^0$

4. ______ + $H_2SO_4$ $\longrightarrow$ ______ + $HNO_3$

a) $NaNO_2$, $NaHSO_4$

b) $NaHSO_4$, $NaNO_2$

c) $NaNO_3$, $NaHSO_4$

d) $NaHSO_4$, $NaNO_3$

# REACTIONS OF NITRIC ACID

## Reactions of NITRIC ACID

### With copper

Metal + acid $\longrightarrow$ Metal salt

$3Cu + 8HNO_{3(dil)} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

Copper nitrate  Nitric oxide

$Cu + 4HNO_{3(conc.)} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Copper nitrate  Nitrogen dioxide

## Reactions of NITRIC ACID

### With Zinc

Metal + acid $\longrightarrow$ Metal salt

$4Zn + 10HNO_{3(dil)} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

Zinc nitrate    nitrous oxide

$Zn + 4HNO_{3(conc.)} \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$

Zinc nitrate    Nitrogen dioxide

## Reactions of NITRIC ACID

### With Phosphorous

Non metal + acid $\rightarrow$ Acid

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Phosphoric acid

### With Iodine

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

Iodic acid.

# Reactions of NITRIC ACID

## With Sulphur

$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

Sulphuric acid

## With Carbon

$$C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2$$

(hot, conc.)

Carbon dioxide

**The brown ring test.**

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$$

**(Brown ring)**

## Action of $HNO_3$ on Gold and Platinum

$$HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2[Cl]$$

Nitrosyl chloride

$$Au + 3[Cl] + 3HCl \longrightarrow 4AuCl_4$$

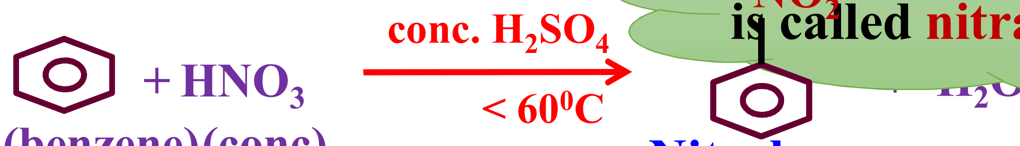
Tetrachloroaurate

$$Pt + 4[Cl] + 2HCl \longrightarrow H_2PtCl_6$$

Chloroplatinic acid

# Action of concentrated $HNO_3$

## With Benzene

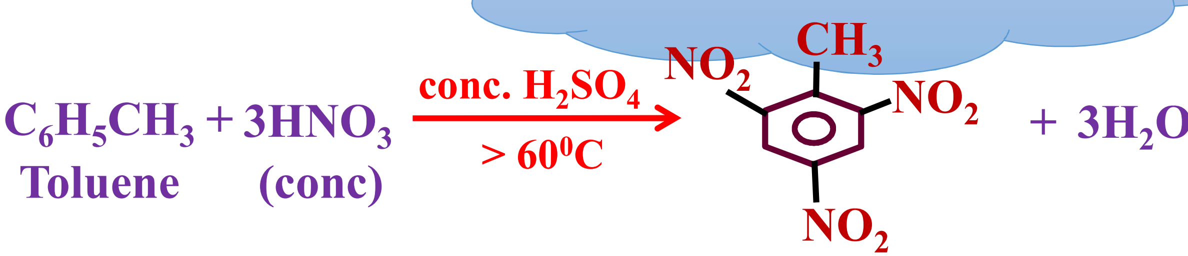



Nitrobenzene

Mixture of conc. $H_2SO_4$ + conc. $HNO_3$ is called **nitration mixture**

## With Toluene

Reaction is called **“Nitration”**

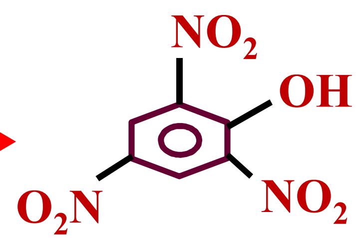



2, 4, 6 – trinitrotoluene

## Action of concentrated $HNO_3$

### With phenol

$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{(conc)}}{3HNO_3} \xrightarrow{\text{conc. } H_2SO_4}$$




$+ \; 3H_2O$

**2, 4, 6 – trinitrophenol**

- ➢ **2,4,6-trinitrophenol is called Picric acid ( explosive in nature)**

## Action of concentrated $HNO_3$

### With Cane sugar

$$\underset{\text{Cane Sugar}}{C_{12}H_{22}O_{11}} + 18(O) \xrightarrow[HNO_3]{\text{conc. } H_2SO_4} 6 \underset{\text{Oxalic acid}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}} + 5H_2O$$

MCQs

1. Aqua regia is a 1 : 3 mixture of ______ and ______.

a) HCl, $HNO_3$

b) $HNO_3$, HCl

c) $HNO_3$, $H_2SO_4$

d) $H_2SO_4$, $HNO_3$

2. Nitrating mixture is a mixture of ______ and ______.

a) conc. $H_2SO_4$, conc. HCl

b) conc. $H_2SO_4$, conc. $HNO_3$

c) conc. HCl, conc. $HNO_3$

d) None of these

3. **Brown ring test is done for ______ group**

a) $N_3^-$

b) $NH_4^+$

c) $NO_3^-$

d) All of these

**4. $C + 4\ HNO_3 \rightarrow A + 2H_2O + 4\ NO_2 \quad + C$ What is A?**

**a) $CO$**

**b) $CO_2$**

**c) $H_2CO_3$**

**d) None of these**

# TYPES OF NITROGEN OXIDE

## Dinitrogen oxide, $N_2O$ (Laughing Gas)

- It is also called nitrous oxide.
- It is stable and colorless gas.
- It has all electrons paired.
- Diamagnetic.

$$:\mathrm{N} \equiv \mathrm{N} \rightarrow \overset{..}{\underset{..}{\mathrm{O}}}: \leftrightarrow \overset{..}{\underset{..}{\mathrm{N}}} = \mathrm{N} = \overset{..}{\underset{..}{\mathrm{O}}}$$

## Nitric oxide (Nitrogen monoxide), NO :

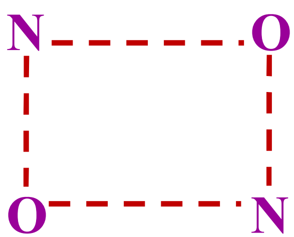
- **It is most stable oxide of nitrogen.**
- **‘N’ and ‘O’ together have 11 valence electrons.**
- **An odd electron molecule.**
- **Paramagnetic.**

## Nitric oxide (Nitrogen monoxide), NO :

➢ **It acts as an oxidising and reducing agent.**

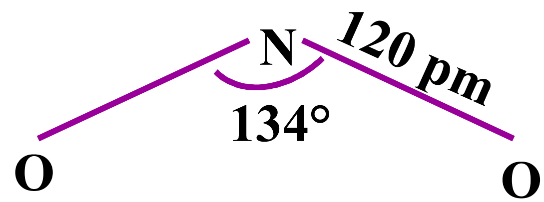
$$:\overset{-}{\ddot{N}} = \overset{+}{\dot{O}}: \leftrightarrow :\dot{N} = \ddot{O}:$$

(Ionic structure) (Covalent structure)



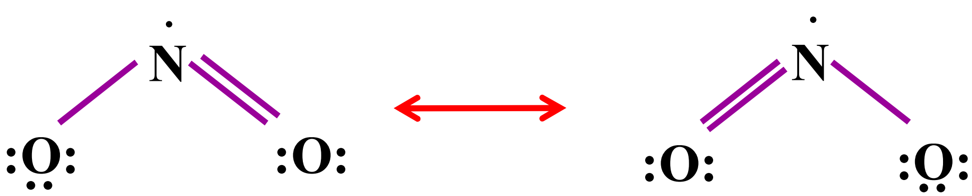

**Dimeric structure of NO**

## Nitrogen dioxide, $NO_2$




- It is an acidic oxide
- It is a reddish brown gas
- It is paramagnetic
- It is dimerizes to $N_2O_4$

$$2NO_2 \rightleftharpoons N_2O_4$$



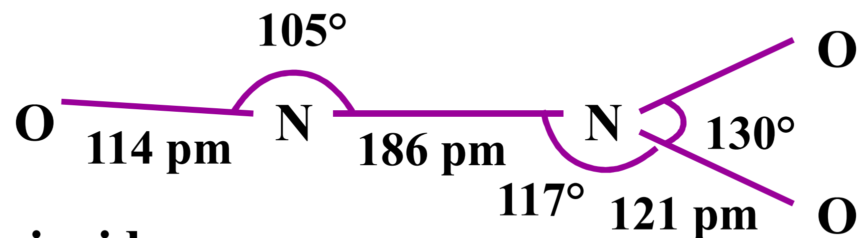
**Question**

**Why does $NO_2$ dimerise ?**

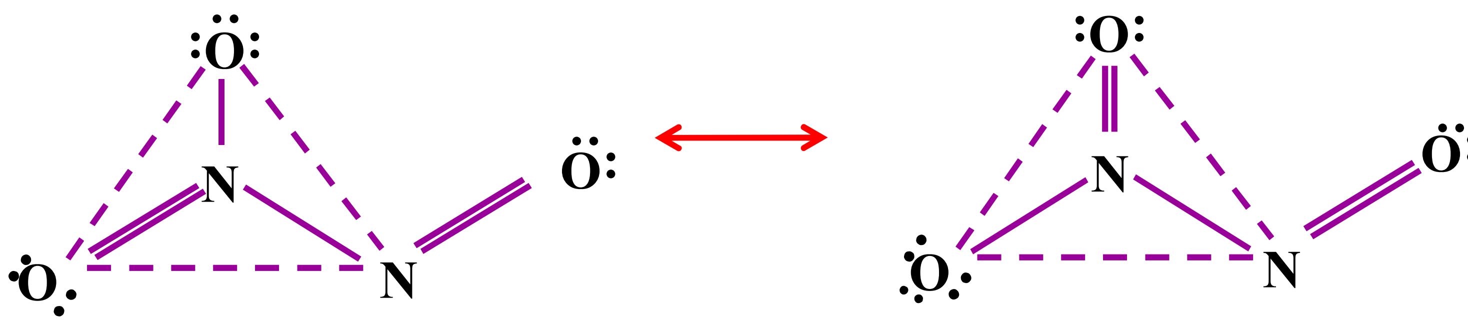
**Answer:**

**$NO_2$ contains odd number of valence electrons.**
**It behaves as a typical odd molecule.**
**On dimerisation , it is converted to stable $N_2O_4$ molecule with even number of electrons.**

## Dinitrogen trioxide $N_2O_3$

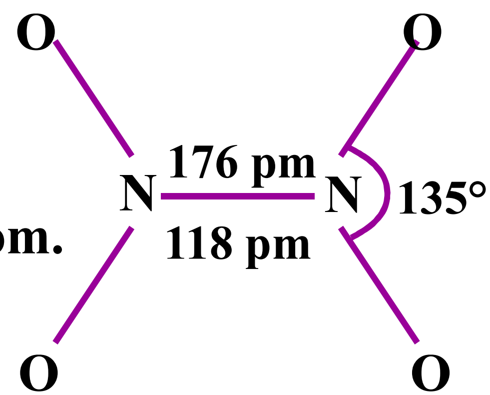


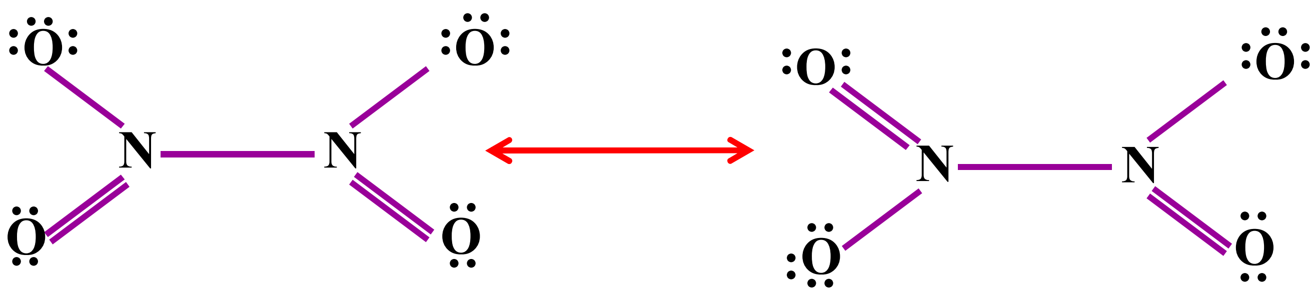

- It is an acidic oxide
- It is also known as nitrogen sesquioxide
- It is diamagnetic
- It's a planar molecule



## Dinitrogen tetroxide $N_2O_4$

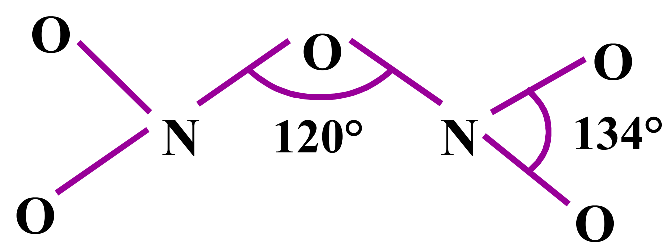
- It is an acidic oxide
- It has no unpaired electron on N atom.
- $\therefore$ It is diamagnetic
- It is a planar molecule

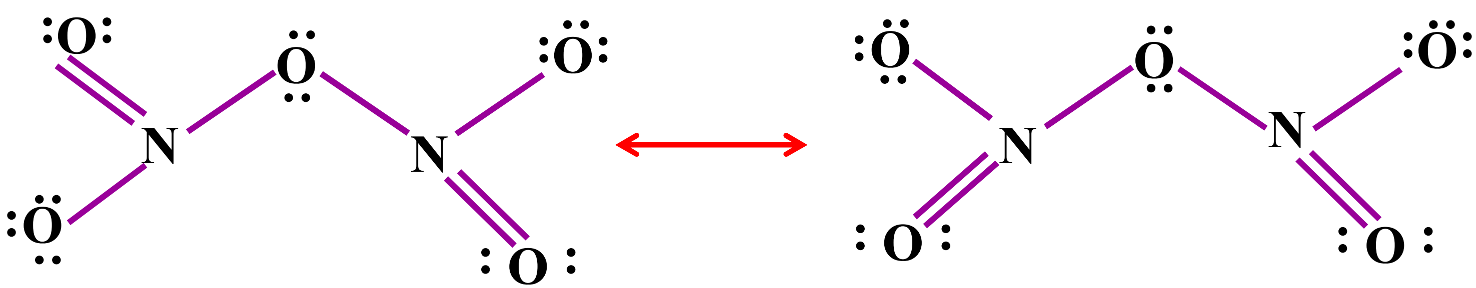


## Dinitrogen pentoxide $N_2O_5$

- It is an unstable acidic oxide.
- It is an excellent oxidizing agent.



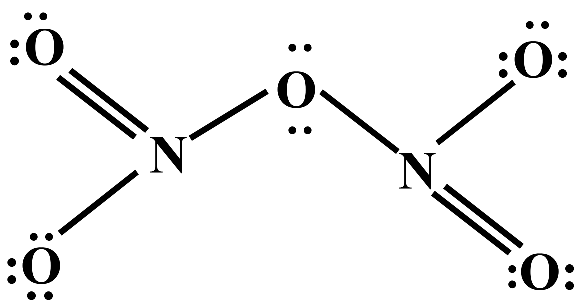



Question

**Q2. What is the covalency of nitrogen in $N_2O_5$?**

Answer:

**Structural formula of $N_2O_5$**



**Since, N atom has shared electron pair , the valence of N is 4**

# MCQs

**1. ______ is also called Laughing gas  or Laughing grites**

a) $NO_2$

b) $NO$

c) $N_2O_5$

d) $N_2O$

2. NO is…

a) Diamagnetic

b) Paramagnetic

c) Both a & b

d) None of these

3. $NO_2$ is reddish brown gas while $N_2O_4$ is ______.

a) Blackish gas

b) Brownish solid

c) Colorless gas or solid

d) Bluish gas or solid

4. $NO_2$ is ______ while $N_2O_4$ is diamagnetic.

a) Paramagnetic

b) Diamagnetic

c) Both a & b

d) None of these

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