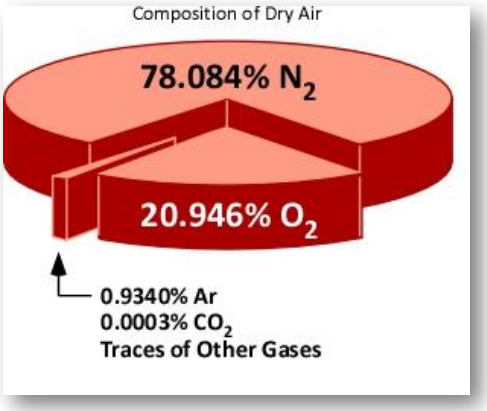
Lecture 6

Group 15 (5A)

Nitrogen Family

Pnicogens Or Pnictogen



Electronic configuration of Nitrogen group

$_{7}N$	$1s^2 2s^2 2p^3$	[He] $2s^2 2p^3$
$_{15}P$	$1s^2 2s^2 2p^6 3s^2 3p^3$	[Ne] $3s^2 3p^3$
$_{33}As$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$	[Ar] $4s^2 4p^3$
$_{51}Sb$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^3$	[Kr] $5s^2 5p^3$
$_{83}Bi$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^3$	[Xe] $6s^2 6p^3$

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Group 5A

- **Valence-shell configuration: $ns^2\ np^3$**
- **Exhibits varied chemical properties.**
  1. **N and P are nonmetals;**
  2. **As and Sb are metalloids;**
  3. **Bi is a metal (the heaviest non-radioactive element)**

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Atomic and Physical Properties of Group 15 Elements

Property		N	P	As	Sb	Bi
Atomic number		7	15	33	51	83
Atomic mass/g mol^{-1}		14.01	30.97	74.92	121.75	208.98
Electronic configuration		$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10} 4s^2 4p^3$	$[Kr]4d^{10} 5s^2 5p^3$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$
Ionisation enthalpy ($\Delta_i H$/(kJ mol^{-1}))	I	1402	1012	947	834	703
	II	2856	1903	1798	1595	1610
	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9
Covalent radius/pm[a]		70	110	121	141	148
Ionic radius/pm		171[b]	212[b]	222[b]	76[c]	103[c]
Melting point/K		63*	317[d]	1089[e]	904	544
Boiling point/K		77.2*	554[d]	888[f]	1860	1837
Density/[g cm^{-3}(298 K)]		0.879[g]	1.823	5.778[h]	6.697	9.808

Electronic Configuration.

- The valence shell electronic configuration of these elements is ns^2np^3

Atomic and Ionic Radii.

- Covalent and ionic (in a particular state) radii **increase** in size down the group.
- There is a considerable increase in **covalent** radius from **N to P**
- However, from **As to Bi** only a small increase in covalent radius is observed. This is due to the presence of completely filled ***d***- and/or ***f*** orbitals in heavier members.

Physical Properties

- All the elements of this group are polyatomic
- Dinitrogen is a diatomic gas while all others are solids.
- Metallic character **increases down** the group.
- Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids and bismuth is a metal.

  Due to:

  (i) decrease in ionization enthalpy
  (ii) increase in atomic size.

- The boiling points, in general, increase from top to bottom in the group but the melting point increases up to arsenic and then decreases up to bismuth
- Except nitrogen, all the elements show **allotropy**

Some Exceptional

- Considerable increase in covalent radius from nitrogen to phosphorus but only a small increase from arsenic to bismuth, This is due to completely filled d and f orbital's in heavier members.
- The ionization energy of group **15** elements is much greater than the group **14** elements in corresponding period, this is due to extra stability of half filled p orbitals electronic configuration and small size.

Anomalous properties of nitrogen

Nitrogen differs from the rest of the members of its group due to it's:

small size,

high electronegativity,

high ionization enthalpy and,

non availability of d-orbital's.

It has an ability to form pπ-pπ bonds with itself and hence it is inert at room temperature. Other elements if its group are singly bonded.

Physical properties of dinitrogen (N_2)

- Colourless, odourless, tasteless, non toxic gas
- Low molecular mass, low intermolecular forces
- Two stable isotopes (N-14, N-15).
- Low solubility in water , low freezing and boiling point
- Inert at room temperature due to high bond dissociation enthalpy

Chemical properties of dinitrogen

- Combination with metals:
  $6\ Li + N_2 \rightarrow 2\ Li_3N$
- Combines with hydrogen (H_2):(Haber's process)
  $N_2 + 3\ H_2 \rightarrow 2\ NH_3$ $(\Delta H = -92.4\ kJ \cdot mol^{-1})$
- Formation of nitric oxide (NO)
  $N_2 + O_2 \rightarrow 2\ NO$

Uses of dinitrogen

- Manufacture of ammonia.
- Provide an inert atmosphere in industries.
- Used as a refrigerants.

Nitrogen Fixation

- The process of transforming N_2 to other nitrogen–containing compounds.
- Atmospheric fixation (can occurs naturally)

$N_2(g) + O_2(g) \rightarrow 2NO(g)$; $\Delta H^o = 180$ kJ

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; $\Delta H^o = -112$ kJ

$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$;

$\Delta H^o = -140$ kJ

Industrial Nitrogen Fixation

- Industrial Fixation (the Haber Process):

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta H° = -92 \text{ kJ}$$

- Most NH_3 are converted to:
  1. Fertilizers (~70%)
  2. Nitric acid, HNO_3 (~20%)
  3. Hydrazine, N_2H_4, and monomers for various plastics and nylons.

Main Compounds of the Nitrogen

Hydride

- NH_3
- N_2H_4, NH_2OH
- Ammonium salts

Oxides

- NO
- NO_2

Oxyacid and its salts

- Nitrous acid and nitrite
- Nitric acid and nitrate

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Hydrides of Nitrogen

Ammonia, NH_3 (most important hydride)

- Production of fertilizers (NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_3PO_4$, and $CO(NH_2)_2$), HNO_3, and N_2H_4

Hydrazine, N_2H_4

- manufacture of plastics, agricultural pesticides;

Monomethylhydrazine, $CH_3N_2H_3$

- Rocket fuels

Oxides of Nitrogen

In its oxides nitrogen has oxidation states ranging from +1 to +5.

1. N_2O (+1)
2. NO (+2)
3. N_2O_3 & HNO_2 (+3)
4. NO_2 (+4)
5. N_2O_5 & HNO_3 (+5)

- In other compounds, nitrogen could have oxidation states of -1 to -3.
- NH_2OH (-1), N_2H_4 (-2), and NH_3 (-3)

Oxides of Group 5A Elements

- **Nitrogen: N_2O, NO, N_2O_3, NO_2, N_2O_4, N_2O_5;**
- **Phosphorus: P_4O_6 & P_4O_{10};**
- **Arsenic: As_2O_3 (As_4O_6) & As_2O_5;**
- **Antimony: Sb_2O_3 & Sb_2O_5**
- **Bismuth: Bi_2O_3 & Bi_2O_5**

Chlorides of Group 5A Elements

- Nitrogen: **only** NCl_3;
- Phosphorus: PCl_3 and PCl_5;
- Arsenic: $AsCl_3$ and $AsCl_5$;
- Antimony: $SbCl_3$ and $SbCl_5$;
- Bismuth: $BiCl_3$
- All are molecular compounds.

Reactivity towards hydrogen

- All the elements of Group 15 form hydrides of the type EH_3

$$N_2(g) + 3H_2(g)\ (773\ k) \Longrightarrow 2NH_3(g);\ \Delta H = -46.1\ kJmol^{-1}$$

$$P_4 + 6H_2\ (heat, p) \Longrightarrow 4PH_3$$

- The stability of hydrides decreases from NH_3 to BiH_3.
- The reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides.
- Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

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Reactivity towards oxygen

- All these elements form two types of oxides:
  E_2O_3 and E_2O_5
- The oxide in the **higher oxidation** state of the element is **more acidic** than that of lower oxidation state.
- Their acidic character decreases down the group.
- The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic.

$$N_{2\,(g)} + O_{2\,(g)} \text{ (heat)} \rightarrow 2NO\ (g)$$

$$P_4 + 5O_2\ (\text{heat}) \rightarrow 2P_4O_{10}$$

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Reactivity towards halogens

- These elements react to form two series of halides:
  EX_3 and EX_5
- Nitrogen does not form **pentahalide**.
- Pentahalides are more covalent than trihalides.
- All the trihalides of these elements except those of nitrogen are stable.
- In case of nitrogen, only **NF_3** is known to be stable.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

$$3PCl_5 + 2P \rightarrow 5PCl_3$$

$$3PCl_5 + P_2O_5 \rightarrow 5POCl_3$$

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Ammonia

Preparation:

- *By Haber's process*

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3 \quad (\Delta H = -92.4\ kJ \cdot mol^{-1})$$

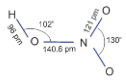
- *From ammonium salts*

$$Ca(OH)_{2(s)} + 2NH_4Cl_{(s)} \rightarrow CaCl_{2(s)} + 2H_2O_{(l)} + 2NH_{3(g)}$$

- *From decay of organic matter*

$$NH_2CONH_2\ 2H_2O \rightarrow (NH_4)_2\ CO_3 \rightarrow 2\ NH_3 + 4H_2O + CO_2$$

Nitric acid



In the laboratory, nitric acid is prepared by heating KNO_3 or NaNO3 and concentrated H_2SO_4 in a glass retort:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

On a large scale it is prepared mainly by Ostwald's process. This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.

$$4NH_3(g) + \underset{\text{(from air)}}{5O_2(g)} \xrightarrow[500\,K,\ 9\,bar]{Pt\ /\ Rh\ gauge\ catalyst} 4NO(g) + 6H_2O(g)$$

Nitric oxide thus formed combines with oxygen giving NO_2.

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

Nitrogen dioxide so formed, dissolves in water to give HNO_3.

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

Nitric acid

- In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

- Concentrated nitric acid is a strong oxidizing agent and attacks most metals except noble metals such as gold and platinum.

$$8HNO_3\ (dilute) + 3Cu \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$4Sn + 10HNO_3 \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Nitric acid as an oxidizing agent

1. **Reaction with elements less electropositive than hydrogen**

Concentrated HNO_3

$Cu + 4\ HNO_3 \rightarrow Cu(NO_3)_2 + 2\ NO_2 + 2\ H_2O$

Dilute HNO_3

$8\ HNO_3 + 3\ Cu \rightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$

2. **Reaction with elements more electropositive than hydrogen**

Concentrated HNO_3

$4\ Zn + 10\ HNO_3\ (dilute) \rightarrow 4\ Zn(NO_3)2 + N_2O + 5\ H_2O$

Dilute HNO_3

$Zn + 4\ HNO_3\ (Conc) \rightarrow Zn(NO_3)_2 + 2\ NO_2 + 2\ H_2O$

3. **Some metals donot dissolve in concentration nitric acid because of formation of passive film of oxide of surface.**

Brown Ring Test

- test for nitrates depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown coloured complex.

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

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

(brown)

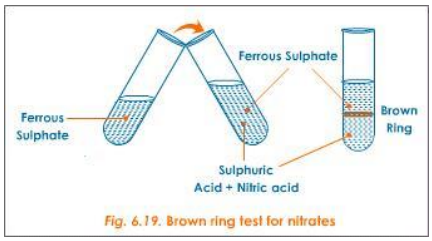
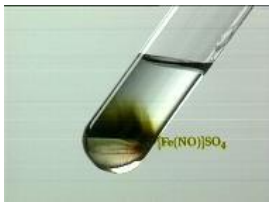


Fig. 6.19. Brown ring test for nitrates



Phosphine

Phosphine is prepared by the reaction of **calcium phosphide** with water or dilute **HCl**

$$Ca_3P_2 + 6\,H_2O \rightarrow 3\,Ca(OH)_2 + 2\,PH_3$$

$$Ca_3P_2 + 6\,HCl \rightarrow 3\,CaCl_2 + 2\,PH_3$$

In the laboratory, it is prepared by heating white phosphorus with **conc. NaOH** solution in an inert atmosphere of CO2.

$$P_4 + 3\,NaOH + 3H_2O \rightarrow PH_3 + 3\,KH_2PO_4$$

$$PH_4I + KOH \rightarrow KI + H_2O + PH_3$$

(phosphonium iodide)

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Properties of phosphine

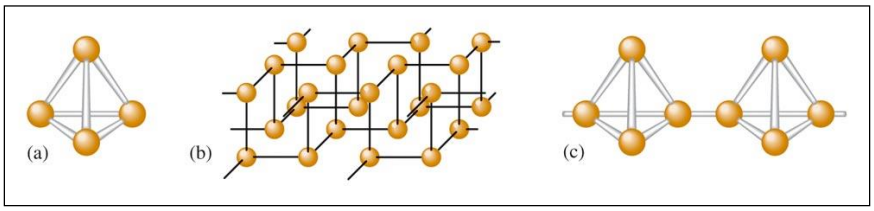
- Colourless gas with rotten fish smell.
- Highly poisonous.
- It explodes in contact with traces of oxidizing agents like HNO_3 .
- It is slightly soluble in water.
- It is weakly basic

$$PH_3 + HBr \rightarrow PH_4Br$$

Uses:

- Used in Holme's signals
- Also used in smoke screens.

Allotropes of Phosphorus



(a) White Phosphorus
(b) Black Phosphorus
(c) Red Phosphorus

Oxides of Phosphorus

Reaction of white phosphorus with oxygen:

1. $P_4(s) + 3O_2(g) \rightarrow P_4O_6(l)$; **(o.s. of P = +3)**
2. $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$; **(o.s. of P = +5)**

Reactions of phosphorus oxides with water:

1. $P_4O_6(l) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$;
2. $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$;