Chemistry Study Materials for Class 12
(NCERT Based Notes of Chapter – 7)

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The p-Block Elements

The elements in which the last electron enters in the valence p-sub shell are called the p-block elements. They include elements of the groups 13 to 18. Their general outer electronic configuration is ns^2np^{1-6} (except He which has $1s^2$ configuration).They includes metals, non-metals and metalloids.

Group 15 Elements

Group 15 includes nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). As we go down the group, the metallic character increases. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a typical metal. The valence shell electronic configuration of these elements is ns^2np^3. The *s* orbital in these elements is completely filled and *p* orbitals are half-filled, making their electronic configuration extra stable.

Covalent and ionic radii increase 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* or *f* orbitals in heavier members. Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled *p* orbitals and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements.

Oxidation states and trends in chemical reactivity

The common oxidation states of these elements are –3, +3 and +5. The tendencies to exhibit –3 oxidation state decreases down the group due to increase in size and metallic character. The last member of the group, bismuth does not form any compound in –3 oxidation state. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group. Nitrogen exhibits + 1, + 2, and + 4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxoacids. Nitrogen is restricted to a maximum covalency of 4 since only four orbitals (one *s* and three *p*) are available for bonding.

Oxidation States

Elements:-	N	P	As	Sb	Bi
Atomic No.:-	**7**	**15**	**33**	**51**	**83**
	-3	**-3**	**-3**	**-3**	**--**
	+5	**+5**	**+5**	**+5**	**+5**
	+3	**+3**	**+3**	**+3**	**+ 3**
	+4	**+4**			
	+1	**+1**			

Notes:-1. Due to non-metallic (N and P) and metalloidic (As and Sb)nature N, P, As, Sb show negative oxidation state (-3)

2. Due to anomalous property "N" shows variables oxidation states.

3. Due to presence of vacant d- sub shell, non-metallic nature and more electronegative value "P" shows variables oxidation states.

4. Due to inert pair effect "As, Sb and Bi" show variables oxidation states.

Anomalous properties of nitrogen

Nitrogen differs from the rest of the members of this group due to its smaller size, high electro negativity, high ionisation enthalpy and non-availability of *d* orbitals. Some of the anomalous properties shown by nitrogen are:

1. Nitrogen has the ability to form ***p*π-*p*π multiple** bonds with itself and with other elements like C and O. Other elements of this group do not form *p*π-*p*π bonds.
2. Nitrogen exists as a diatomic molecule with a triple bond (one *s* and two *p*) between the two atoms. So its bond enthalpy is very high. While other elements of this group are poly atomic with single bonds.
3. The single N–N bond is weak. So the catenation tendency is weaker in nitrogen.
4. Due to the absence of *d* orbitals in its valence shell, the maximum covalency of nitrogen is four
5. N cannot form ***d*π–*p*π bond.** While Phosphorus and arsenic can form ***d*π–*d*π bond** with transition metals and with C and O.

Hydrides of Group 15 Elements

All the elements of Group 15 form hydrides of the type EH_3 (where E = N, P, As, Sb or Bi).

The hydrides show regular gradation in their properties. The bond dissociation enthalpy of E – H decreases from NH_3 to BiH_3. So the thermal stability decreases from NH_3 to BiH_3 and the reducing character increases.

Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Basicity decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. The melting point of these hydrides increases from top to bottom. This is due to increase in the atomic size of the central atom which increases the Vander Waal's force of attraction. NH_3 has the highest melting and boiling points due to inter molecular hydrogen bonding. All these hydrides have pyramidal geometry.

Q_1. Though nitrogen exhibits +5 oxidation states, it does not form pentahalides. Give reason.

Nitrogen with n = 2, has *s* and *p* orbitals only. It does not have *d* orbitals to expand its covalence beyond four. That is why it does not form pentahalides.

Q_2. PH_3 has lower boiling point than NH_3. Why?

Unlike NH_3, PH_3 molecules are not associated through inter molecular hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3.

Dinitrogen (N_2)

Preparation: Dinitrogen is produced commercially by the liquefaction and fractional distillation of air.In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4CI(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl\ (aq)$$

It can also be obtained by the thermal decomposition of ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

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

$$Ba(N_3)_2 \rightarrow Ba + 3N_2$$

Properties

Dinitrogen is inert at room temperature because of the high bond enthalpy of N≡ N bond. At higher temperatures, it directly combines with some metals to form ionic nitrides and with non-metals to form covalent nitrides.

$$6Li + N_2 \xrightarrow{Heat} 2Li_3N \qquad 3Mg + N_2 \xrightarrow{Heat} Mg_3N_2$$

It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia: $N_2 + 3H_2 \xrightarrow{Fe/\ 773K} 2NH_3$

Dinitrogen combines with dioxygen at very high temperature (at about 2000 K) to form nitric oxide $N_2 + O_2 \rightarrow 2\,NO$

Uses: 1. The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen (e.g., calcium cyanamide).

2. It also used to create an inert atmosphere in metallurgy.

3. Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

Ammonia

Preparation: In laboratory, ammonia is obtained by treating ammonium salts with caustic soda (NaOH) or slaked lime.

$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$$

On a large scale, ammonia is manufactured by Haber's process.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

In accordance with Le Chatelier's principle, high pressure of about 200 atm, a temperature of about 773 K and the catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 are employed to increase the rate of this reaction.

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