The p-Block Elements

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.

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

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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