

nitrogen through the noble gases, four groups that get less reactive from the top and more reluctant from the right

Group 15: the nitrogen family *

N_2 is inert

a $N \equiv N$ triple bond, very high bond enthalpy (~ 941 kJ/mol), so N_2 needs real heat or a catalyst to react at all

Oxidation states

N ranges from -3 (NH_3) to $+5$ (HNO_3), the widest spread in the group; heavier members lean toward $+3$ and $+5$

Down the group

metallic character rises (N, P non-metal; As, Sb metalloid; Bi metal), and hydride stability/basicity falls

Ammonia: structure and manufacture

- N is sp^3 hybridised with one lone pair, giving a pyramidal shape; the lone pair's extra repulsion squeezes the H-N-H angle to about 107° , below the tetrahedral 109.5°
- Haber process: $N_2 + 3H_2 \rightleftharpoons 2NH_3$, run over an iron catalyst (with a molybdenum promoter) at roughly 200 atm and 700 K
- the lone pair makes NH_3 a Lewis base: it accepts a proton readily (NH_4^+) and forms coordinate bonds to metal ions

Nitric acid and phosphorus allotropes *

- Ostwald process continues: $2NO + O_2 \rightarrow 2NO_2$, then $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$, the leftover NO is recycled
- aqua regia is concentrated HNO_3 and concentrated HCl in a 1:3 ratio by volume; it dissolves even gold and platinum, metals neither acid touches alone
- white phosphorus is P_4 (tetrahedral), waxy, poisonous, glows in the dark, and is stored under water because it catches fire in air on its own
- red phosphorus is a polymeric chain of linked P_4 units, far less reactive and not poisonous; black phosphorus is the thermodynamically most stable form

Two industrial gas-phase reactions of nitrogen compounds



Haber process: reversible, so the ammonia is drawn off before the mixture can equilibrate back

Ostwald process, step one: catalytic oxidation of ammonia is what starts nitric acid manufacture

PCl_3 and PCl_5 : same element, two shapes

- PCl_3 : P is sp^3 hybridised with one lone pair, so it is pyramidal, the same shape family as NH_3
- PCl_5 as a gas or liquid: sp^3d hybridised, trigonal bipyramidal, with the three equatorial P-Cl bonds shorter than the two axial ones
- PCl_5 as a solid: it exists ionically as $[PCl_4]^+[PCl_6]^-$, a tetrahedral cation paired with an octahedral anion, not as neutral PCl_5 molecules