$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad K = 1.8 \times 10^5 \, moll^{-1}$$

NH_3 and NH_4OH both react with acids, forming ammonium salts. These salts resemble potassium salts in solubility and in their crystal structures. Like the Group 1 salts, ammonium salts are typically colourless. There are some differences. Ammonium salts are usually slightly acidic if they have been formed with strong acids such as HNO_3, HCl and H_2SO_4, since NH_4OH is only a weak base. Ammonium salts decompose quite readily on heating. If the anion is not particularly oxidizing (e.g. Cl^-, CO_3^{2-} or SO_4^{2-}) then ammonia is evolved:

$$NH_4Cl \xrightarrow{\text{heat}} NH_3 + HCl$$

$$(NH_4)_2SO_4 \xrightarrow{\text{heat}} 2NH_3 + H_2SO_4$$

If the anion is more oxidizing (e.g. NO_2^-, NO_3^-, $C1O_4^-$, $Cr_2O_7^{2-}$) then NH_4^+ is oxidized to N_2 or N_2O.

$$\overset{-III}{N}H_4\overset{III}{N}O_2 \xrightarrow{\text{heat}} \overset{0}{N}_2 + 2H_2O$$

$$\overset{-III}{N}H_4\overset{V}{N}O_3 \xrightarrow{\text{heat}} \overset{+I}{N}_2O + 2H_2O$$

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

NH_3 burns in dioxygen with a pale yellow flame:

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 3H_2O$$

The same reaction occurs in air, but the heat of reaction is insufficient to maintain combustion unless heat is supplied, for example in a gas flame. Certain mixtures of NH_3/O_2 and NH_3/air are explosive.

NH_3 is prepared in the laboratory by heating an ammonium salt with NaOH. This is a standard test in the laboratory for NH_4^+ compounds.

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$$

(b) Ammonium salts

Ammonium salts are all very soluble in water. They all react with NaOH, liberating NH_3. The NH_4^+ ion is tetrahedral.

NH_4Cl is well known. NH_4Cl is easily purified by sublimation. It can be recovered as a by-product from the Solvay process. It is used in 'dry batteries' of the Leclanche type. It is also used as a flux when tinning or soldering metals, since many metal oxides react with NH_4Cl, forming volatile chlorides, thus leaving a clean metal surface.

NH_4NO_3 is used in enormous amounts as a nitrogenous fertilizer. It is deliquescent. Because it can cause explosions it is often mixed with $CaCO_3$ or $(NH_4)_2SO_4$ to make it safe. It is also used as an explosive, since on strong heating (above 300°C), or with a detonator, very rapid decomposition occurs. The solid has almost zero volume and it produces seven volumes of gas : this causes the explosion:

$$2NH_4NO_3 \longrightarrow 2N_2 + 4H_2O$$

(c) Phosphine PH_3

Phosphine PH_3 is a colourless and extremely toxic gas, which smells slightly of garlic or bad fish. It is highly reactive. It can be formed either by hydrolysing metal phosphides such as Na_3P or Ca_3P_2 with water, or by hydrolysing white phosphorus with NaOH solution.

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

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$

PH_3, unlike NH_3, is not very soluble in water aqueous solutions are neutral. It is more soluble in CS_2 and other organic solvents. Phosphonium salts such as $[PH_4]^+Cl^-$ can be formed, but require PH_3 and anhydrous HCl (in contrast to the ready formation of NH_4X in aqueous solution). Pure PH_3 is stable in air, but it catches fire when heated to about 150°C.

$$PH_3 + 2O_2 \longrightarrow H_3PO_4$$

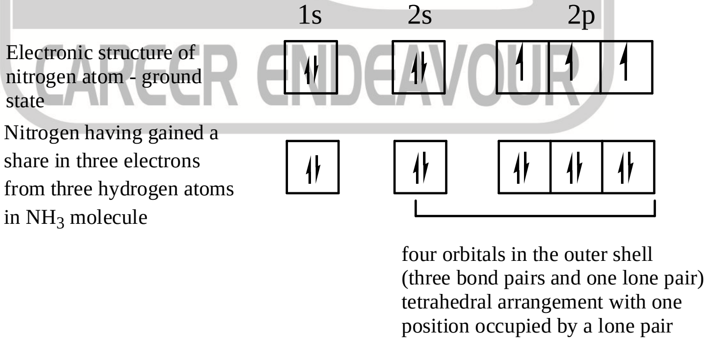
PH_3 frequently contains traces of diphosphine P_2H_6 which cause it to catch fire spontaneously.

(d) Arsine AsH_3, stibine SbH_3 and bismuthine BiH_3 :

The bond energy and the stability of the hydrides both decrease on descending the group. Consequently, arsine (AsH_3), stibine (SbH_3) and bismuthine (BiH_3) are only obtained in small amounts. AsH_3 and SbH_3 are both very poisonous gases. AsH_3, SbH_3 and BiH_3 can be prepared by hydrolysing binary metal compounds such as Zn_3As_2, Mg_3Sb_2 or Mg_3Bi_2 with water or dilute acid. AsH_3 and SbH_3 are formed in Marsh's test for As and Sb compounds. Before the use of instruments for analysis, this test was used as a forensic test. Practically all As or Sb compounds can be reduced with Zn and acid, forming AsH_3 or SbH_3. The gaseous hydrides are passed through a glass tube heated with a Bunsen burner. SbH_3 is less stable than AsH_3 hence it decomposes before passing through the flame, and gives a metallic mirror on the glass tube. AsH_3 is more stable, and requires stronger heating to make it decompose. Thus AsH_3 gives a mirror after the flame.

Structure and bonding in hydrides

The structure of ammonia may either be described as pyramidal, or tetrahedral with one position occupied by a lone pair. This shape is predicted using the VSEPR theory since there are four electron pairs in the outer shell. These comprise three bonding pairs and one lone pair. The repulsion between a lone pair and a bond pair of electrons always exceeds that between two bond pairs. Thus the bond angles are reduced from 109°27′ to 107°48′, and the regular tetrahedral shape is slightly distorted.



The hydrides PH_3, AsH_3 and SbH_3 would be expected to be similar. However, the bond pairs of electrons are much further away from the central atom than they are in NH_3. Thus the lone pair causes even greater distortion in PH_3, AsH_3 and SbH_3. The bond angle decreases to 91°18′. These bond angles suggest that in PH_3, AsH_3, SbH_3 and BiH_3 the orbitals used for bonding are close to pure *p* orbitals,

The melting and boiling points of the hydrides increase from PH_3 through AsH_3 to SbH_3. The values for NH_3 seem out of line with this trend one might have expected the boiling point of NH_3 to be –110°C or –120°C. The reason why NH_3 has a higher boiling point and is much less volatile than expected is that it is hydrogen bonded in the liquid state. The other hydrides do not form hydrogen bonds.