

Chapter 8

Group 15: The Pnictogens

8.1 The Group 15 Elements: The Pnictogens¹

8.1.1 The elements

The Group 15 elements have a particular name *pnictogens*. Despite the modern IUPAC notation, the Group 15 elements are still referred to as Group V elements in particular by the semiconductor industry. Table 8.1 lists the derivation of the names of the Group 15 elements.

Element	Symbol	Name
Nitrogen	N	Latin <i>nitrogenium</i> , where <i>nitrum</i> (derived from Greek <i>nitron</i>) means <i>saltpetre</i>
Phosphorus	P	From the Greek <i>phosphoros</i> meaning <i>bringer of light</i>
Arsenic	As	Derived from Syriac <i>zarniqa</i> and Persian <i>zarnikh</i> , meaning <i>yellow orpiment</i>
Antimony	Sb	Greek <i>anti</i> and <i>monos</i> meaning <i>not alone</i> . The symbol Sb from Latin <i>stibium</i>
Bismuth	Bi	New Latin <i>bisemutum</i> from German <i>Wismuth</i> , meaning <i>white mass</i>

Table 8.1: Derivation of the names of each of the Group 15 (V) elements.

NOTE: According to the Oxford English Dictionary, the correct spelling of the element is phosphorus. The word phosphorous is the adjectival form of the P^{3+} valence. In the same way that sulfur forms sulfurous and sulfuric compounds, phosphorus forms phosphorous compounds (e.g., phosphorous acid) and P^{5+} valency phosphoric compounds (e.g., phosphoric acids and phosphates).

8.1.1.1 Discovery

8.1.1.1.1 Nitrogen

Nitrogen was discovered by Rutherford (Figure 8.1) in 1772. He called it *noxious air* or *fixed air* because there it had been known since the late 18th century that there was a fraction of air that did not support combustion. Nitrogen was also studied by Scheele (Figure 8.2), Cavendish (Figure 8.3), and Priestley (Figure 8.4), who referred to it as *burnt air* or *phlogisticated air*.

¹This content is available online at <<http://cnx.org/content/m34992/1.1/>>.



Figure 8.1: Scottish chemist and physician Daniel Rutherford (1749 - 1819).



Carl Wilhelm Scheele.

Figure 8.2: Swedish chemist Carl Wilhelm Scheele (1742 – 1786). Isaac Asimov called him "hard-luck Scheele" because he made a number of chemical discoveries before others who are generally given the credit.



Figure 8.3: British scientist Henry Cavendish FRS (1731 - 1810).



Figure 8.4: Portrait (by Ellen Sharples) of British clergyman natural philosopher, educator, and political theorist Joseph Priestley (1733 - 1804).

8.1.1.1.2 Phosphorus

German alchemist Hennig Brand (Figure 8.5) was experimenting with urine (which contains dissolved phosphates) in 1669. While attempting to create the fabled philosopher's stone (the legendary alchemical sub-

stance capable of turning base metals, such as lead, into gold) by the distillation of salts from urine, he produced a white material that glowed in the dark and burned with a brilliant light. He gave the substance the name *phosphorus mirabilis* (*miraculous bearer of light*). His process involved letting the urine stand for days then boiling it down to a paste which led to a white waxy substance, white phosphorus.



Figure 8.5: The discovery of phosphorus by German merchant and alchemist Hennig Brand (1630 - 1710) as depicted by Joseph Wright (with significant artistic license with regard to the brightness of the chemiluminescence).

Brand sold the recipe for 200 thaler (a silver coin from whose name the dollar is derived) to D Krafft who toured much of Europe showing it. During his journeys he met Robert Boyle (Figure 8.6) who without learning the details of the synthesis recreated and improved it by using sand in the reduction of the phosphate, (8.1).

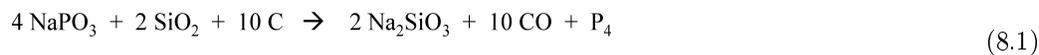




Figure 8.6: British natural philosopher, chemist, physicist, and inventor Robert Boyle (1627 - 1691).

8.1.1.1.3 Arsenic

Arsenic sulfides and oxides were known since ancient times. Zosimos (ca. 300 AD) describes roasting *sandarach* (realgar, $\alpha\text{-As}_4\text{S}_4$) to obtain cloud of arsenious oxide (As_2O_3) that he reduced to metallic arsenic (Figure 8.7).

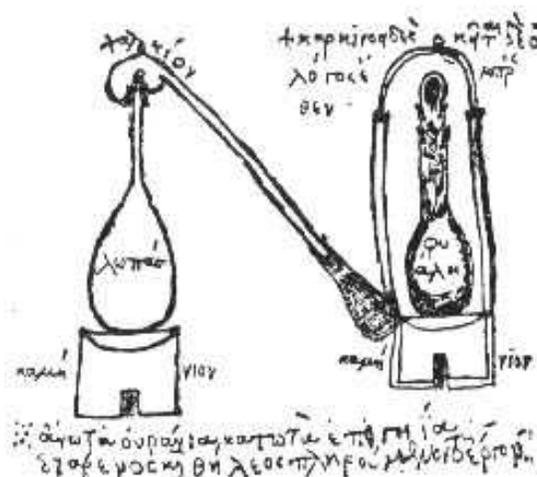


Figure 8.7: The distillation apparatus of Zosimos.

8.1.1.1.4 Antimony

Antimony(III) sulfide, Sb_2S_3 was known as early as 3000 BC. Pastes of Sb_2S_3 powder in fat were used as eye cosmetics in the Middle East. An artifact made of antimony dating to about 3000 BC was found at Tello (part of present-day Iraq), and copper objects plated with antimony from 2500 - 2200 BC have been found in Egypt. The first European description of a procedure for isolating antimony is in the book *De la pirotechnia* by Vannoccio Biringuccio (1480 - 1539).

8.1.1.1.5 Bismuth

Since bismuth was known in ancient times, no one person is credited with its discovery. However, the French chemist Claude François Geoffroy (1729 - 1753) demonstrated in 1753 that this metal is distinct from lead and tin.

8.1.1.2 Abundance

The abundance of the Group 15 elements is given in Table 8.2.

Element	Terrestrial abundance (ppm)
N	25 (Earth's crust), 5 (soil), 0.5 (sea water), 78×10^4 (atmosphere)
P	1000 (Earth's crust), 0.65 (soil), 60×10^{-3} (sea water), trace (atmosphere)
As	1.5 (Earth's crust), 10 (soil), 16×10^{-3} (sea water), trace (atmosphere)
Sb	0.2 (Earth's crust), 1 (soil), 0.3×10^{-3} (sea water)
Bi	48×10^{-3} (Earth's crust), 0.25 (soil), 400×10^{-6} (sea water)

Table 8.2: Abundance of the Group 15 elements.

8.1.1.3 Isotopes

The naturally abundant isotopes of the Group 15 elements are listed in Table 8.3.

Isotope	Natural abundance (%)
Nitrogen-14	99.634
Nitrogen-15	0.0366
Phosphorus-31	100
Arsenic-75	100
Antimony-121	57.36
Antimony-123	42.64
Bismuth-209	100%

Table 8.3: Abundance of the non-synthetic isotopes of the Group 15 elements.

Two radioactive isotopes of phosphorus (^{32}P and ^{33}P) have half-lives that make them useful for scientific experiments (14.262 and 25.34 days, respectively). ^{32}P is a β -emitter (1.71 MeV) and is used to produce radiolabeled DNA and RNA probes. Due to the high energy of the β particles which can penetrate skin and corneas, and because any ^{32}P ingested, inhaled, or absorbed is incorporated into bone and nucleic acids

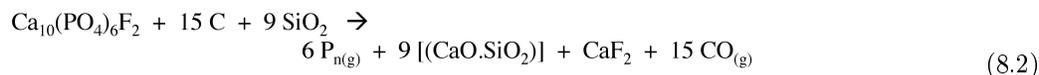
extreme care needs to be taken in handling. The lower energy β particles emitted from ^{33}P (0.25 MeV) make it useful for applications such as DNA sequencing.

While bismuth is traditionally regarded as the element with the heaviest stable isotope, ^{209}Bi , it had long been suspected to be unstable on theoretical grounds. In 2003 researchers at the Institut d'Astrophysique Spatiale in Orsay, France, measured the alpha emission half-life of ^{209}Bi to be 1.9×10^{19} years, over a billion times longer than the current estimated age of the universe!

8.1.2 Industrial production of the elements

Nitrogen is the largest constituent of the Earth's atmosphere (78.082% by volume, 75.3% by weight). It is created by fusion processes in stars, and is estimated to be the 7th most abundant element by mass in the universe. Industrial gas produced is by the fractional distillation of liquid air, or by mechanical means using gaseous air (i.e., pressurized reverse osmosis membrane or pressure swing adsorption). Commercial nitrogen is often a byproduct of air processing for industrial concentration of oxygen for steelmaking, etc.

White phosphorus was originally made commercially for the match industry in the 19th century, by distilling off phosphorus vapor from precipitated phosphates, mixed with ground coal or charcoal, (8.2). The precipitated phosphates were made from ground-up bones that had been de-greased and treated with strong acids. This process is, however, obsolete due to the submerged-arc furnace for phosphorus production was introduced to reduce phosphate rock. Calcium phosphate (phosphate rock) is heated to 1200 - 1500 °C with SiO_2 and coke (impure carbon) to produce vaporized tetraphosphorus, P_4 .



8.1.2.1 Physical properties

The physical properties of the Group 15 elements (Table 8.4) encompasses a gas (N_2), a non-metallic solid (P_4), metalloids (As and Sb), and a metal (Bi).

Element	Mp (°C)	Bp (°C)	Density (g/cm ³)
N	-210.00	-195.79	1.251 g/L (0 °C @ 101.325 kPa)
P	44.2 (white), 610 (black)	280.5 (white), 416 - 590 (sub., red), 620 (sub, violet)	1.823 (white), 2.2 - 2.34 (red), 2.36 (violet), 2.69 (black)
As	817	615 (sub.)	5.727
Sb	630.63	1587	6.697 (solid), 6.53 (liquid)
Bi	271.5	1564	9.78 (solid), 10.05 (liquid)

Table 8.4: Selected physical properties of the Group 15 elements.

8.1.2.2 Vapor phase

Nitrogen forms a dimer in the vapor phase with a triple bond (Figure 8.8). In the vapor phase above 800 °C tetraphosphorus (P_4) is partially dissociated to P_2 .

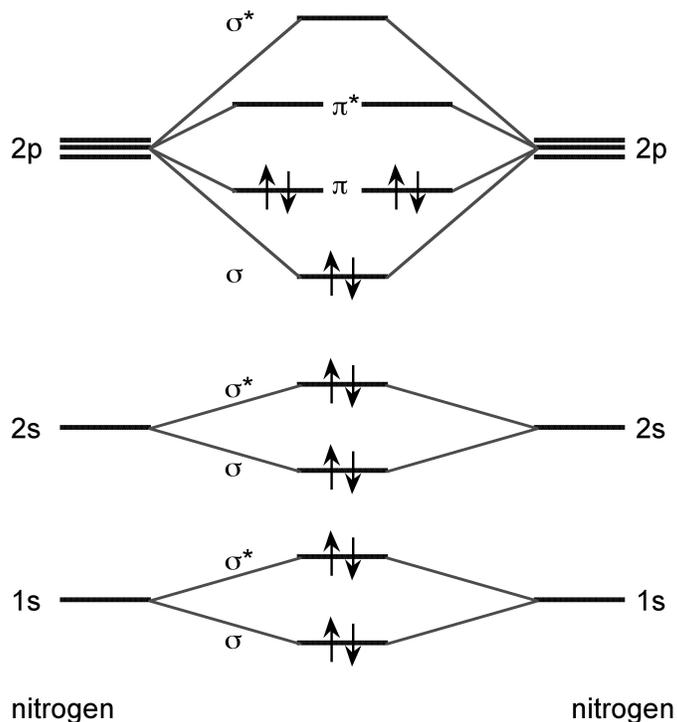


Figure 8.8: Molecular orbital diagram for the formation of N_2 .

8.1.2.3 Solid state

Phosphorus forms a number of allotropes with very different properties (Figure 8.9). Red phosphorus is an intermediate phase between the white and violet forms. Scarlet phosphorus is obtained by allowing a solution of white phosphorus in carbon disulfide to evaporate in sunlight. Black phosphorus is formed by heating white phosphorus under high pressures (ca. 12,000 atmospheres).



Figure 8.9: Images of (left to right) white, red, violet and black allotropes of phosphorus.

White phosphorus has two forms, low-temperature β form and high-temperature α form; both of which contain the P_4 tetrahedron (Figure 8.10). White phosphorus is the least stable, the most reactive, most volatile, less dense, and most toxic of the allotropes.

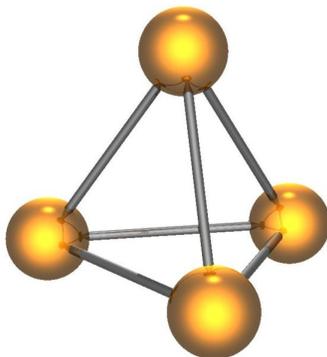


Figure 8.10: The structure of the P_4 molecule in white phosphorus.

The structural relationship between white and red phosphorus involves breaking one of the P-P bonds in the P_4 unit and forming a bond with a neighboring tetrahedron to give a chain structure (Figure 8.11). Red phosphorus is formed by heating white phosphorus to 250 °C or by exposing white phosphorus to sunlight. Actually red phosphorus is not a single allotrope, but rather an intermediate phase between the white and violet phosphorus, and most of its properties have a range of values (Table 8.4).

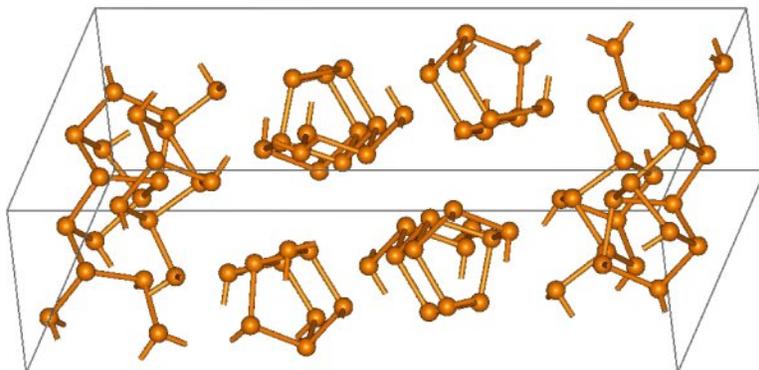


Figure 8.11: Crystal unit cell of red phosphorus.

Violet phosphorus (Figure 8.12) is the thermodynamic stable form of phosphorus that is produced by heating red phosphorus above 550 °C. Due to the synthesis being developed by Johann Hittorf (Figure 8.13) it is sometimes known as *Hittorf's phosphorus*.

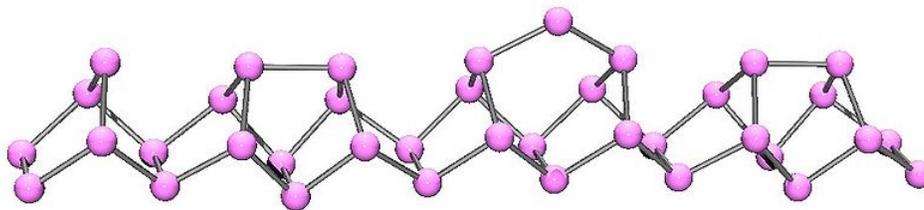


Figure 8.12: Structure of violet (Hittorf's) phosphorus.



Figure 8.13: German physicist Johann Wilhelm Hittorf (1824 - 1914).

Black phosphorus is the least reactive allotrope and the thermodynamic stable form below 550 °C. It is also known as β -metallic phosphorus and has a structure somewhat resembling that of graphite (Figure 8.14).

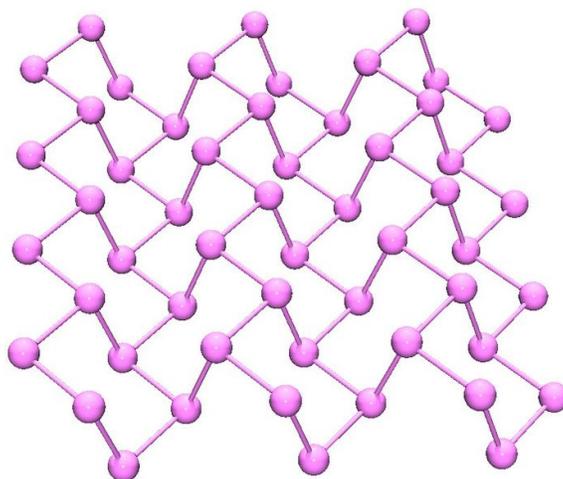


Figure 8.14: Crystal structure of black phosphorus.

In a similar manner to phosphorus, arsenic has several allotropes some of which are structurally related to those of phosphorus. Grey arsenic has a structure similar to black phosphorus (Figure 8.14). Yellow arsenic (As_4) is soft and waxy with a structure similar to that of P_4 (Figure 8.10). Finally, black arsenic is similar in structure to red phosphorus (Figure 8.11). Antimony and bismuth are both traditional metals and have trigonal hexagonal structures ($a = 4.299$, $c = 11.25$ Å, and $a = 4.537$, $c = 11.838$ Å, respectively).

8.1.3 Bibliography

- V. Biringuccio, *The Pirotechnia of Vannoccio Biringuccio: The Classic Sixteenth-Century Treatise on Metals and Metallurgy*, Dover Publications (1990).

8.2 Reaction Chemistry of Nitrogen²

Despite nitrogen being the inert component of the Earth's atmosphere, dinitrogen undergoes a range of reactions, although it only reacts with a few reagents under standard temperature and pressure. Nitrogen reacts with oxygen in an electric arc, (8.3), both in the laboratory and within lightning strikes.



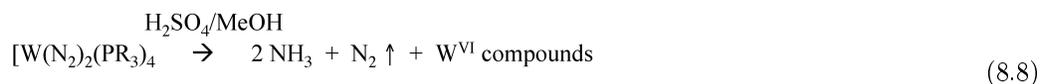
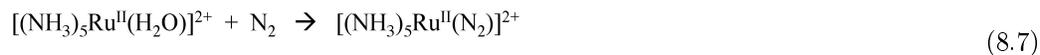
The synthesis of ammonia is accomplished by the Harber process, using an iron oxide (Fe_3O_4) catalyst, (8.4), at about 500 °C and 200 atmospheres pressure.



Nitrogen reacts with lithium metal at room temperature to form the nitride, (8.5). Magnesium also burns in nitrogen, forming magnesium nitride, (8.6).



Nitrogen forms complexes with transition metals yielding nitrido complexes, (8.7). Under some conditions these complexes react to give ammonia, (8.8), and as such may give a hint to the action of nitrogenase in which molybdenum in the active site.



8.3 Hydrides

8.3.1 Trihydrides of the Group 15 Elements³

All five of the Group 15 elements form hydrides of the formula EH_3 . Table 8.5 lists the IUPAC names along with those in more common usage.

²This content is available online at <<http://cnx.org/content/m35169/1.1/>>.

³This content is available online at <<http://cnx.org/content/m32951/1.1/>>.

Compound	Traditional name	IUPAC name
NH ₃	Ammonia	Azane
PH ₃	Phosphine	Phosphane
AsH ₃	Arsine	Arsane
SbH ₃	Stibine	Stibane
BiH ₃	Bismuthine	Bismuthane

Table 8.5: Traditional and IUPAC (International Union of Pure and Applied Chemistry) names for the Group 15 hydrides.

The boiling point and melting point increase increases going down the Group (Table 8.6) with increased molecular mass, with the exception of NH₃ whose anomalously high melting and boiling points (Figure 8.15) are a consequence of strong N-H···H hydrogen bonding. A similar (and stronger) effect is observed for the Group 16 hydrides (H₂E).

Compound	Mp (°C)	Bp (°C)	ΔH_f (kJ/mol)	E-H bond energy (kJ/mol)	H-E-H bond angle (°)
NH ₃	-77.7	-33.35	-46.2	391	107
PH ₃	-133	-87.7	9.3	322	93.5
AsH ₃	-116.3	-55	172.2	247	92
SbH ₃	-88	-17.1	142.8	255	91.5

Table 8.6: Selected physical properties of Group 15 hydrides.

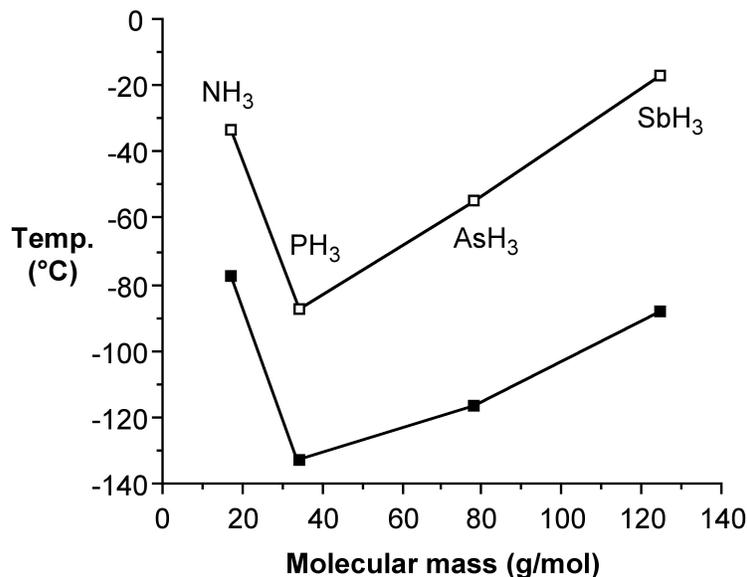


Figure 8.15: Plot of melting and boiling points of EH_3 ($\text{E} = \text{N}, \text{P}, \text{As},$ and Sb) as a function of molecular mass.

The E-H bond strengths decrease down the group and this correlates with the overall stability of each compound (Table 8.6). The H-E-H bond angles (Table 8.6) also decrease down the Group. The H-E-H bond angle is expected to be a tetrahedral ideal of 109.5° , but since lone pairs repel more than bonding pairs, the actual angle would be expected to be slightly smaller. Two possible explanations are possible for the difference between NH_3 and the other hydrides.

1. The N-H bond is short (1.015 \AA) compared to the heavier analogs, and nitrogen is more electronegative than hydrogen, so the bonding pair will reside closer to the central atom and the bonding pairs will repel each other opening the H-N-H angle more than observed for PH_3 , etc.
2. The accessibility of the $2s$ and $2p$ orbitals on nitrogen allows for hybridization and the orbitals associated with N-H bonding in NH_3 are therefore close to sp^3 in character, resulting in a close to tetrahedral geometry. In contrast, hybridization of the ns and np orbitals for P, As, etc., is less accessible, and as a consequence the orbitals associated with P-H bonding in PH_3 are closer to p in character resulting in almost 90° H-P-H angle. The lower down the Group the central atom the less hybridization that occurs and the closer to pure p-character the orbitals on E associated with the E-H bond.

8.3.2 Ammonia⁴

Ammonia (NH_3) is a colorless, pungent gas (bp = -33.5°C) whose odor can be detected at concentrations as low 20 – 50 ppm. Its high boiling point relative to its heavier congeners is indicative of the formation of strong hydrogen bonding. The strong hydrogen bonding also results in a high heat of vaporization (23.35 kJ/mol) and thus ammonia can be conveniently used as a liquid at room temperature despite its low boiling point.

⁴This content is available online at <http://cnx.org/content/m32956/1.5/>.

WARNING: Ammonia solution causes burns and irritation to the eyes and skin. The vapor causes severe irritation to the respiratory system. If swallowed the solution causes severe internal damage.

8.3.2.1 Synthesis

Ammonia is manufactured on the industrial scale by the Haber process using the direct reaction of nitrogen with hydrogen at high pressure ($10^2 - 10^3$ atm) and high temperature ($400 - 550$ °C) over a catalyst (e.g., α -iron), (8.9).



On the smaller scale ammonia is prepared by the reaction of an ammonium salt with a base, (8.10), or hydrolysis of a nitride, (8.11). The latter is a convenient route to ND_3 by the use of D_2O .



8.3.2.2 Structure

The nitrogen in ammonia adopts sp^3 hybridization, and ammonia has an umbrella structure (Figure 8.16) due to the stereochemically active lone pair.

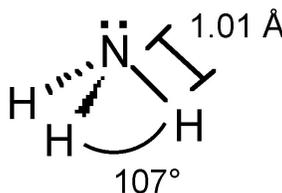


Figure 8.16: The structure of ammonia.

The barrier to inversion of the umbrella is very low ($E_a = 24$ kJ/mol) and the inversion occurs 100's of times a second, (8.12). As a consequence it is not possible to isolate chiral amines in the same manner that is possible for phosphines.



In a similar manner to water, (8.13), ammonia is a self-ionizing, (8.13); however, the equilibrium constant ($K = 10^{-33}$) is much lower than water ($K = 10^{-14}$). The lower dielectric constant of ammonia (16.5 @ 20 °C)

as compared to water (80.4 @ 20 °C) means that ammonia is not as good as water as a solvent for ionic compounds, but is better for covalent organic compounds.



8.3.2.3 Reactions

The similarity of ammonia and water means that the two compounds are miscible. In fact, ammonia forms a series of solid hydrates, analogous to ice in which hydrogen bonding defines the structures (Figure 8.17). Several hydrates of ammonia are known, including: $\text{NH}_3 \cdot 2\text{H}_2\text{O}$ (ammonia dihydrate, ADH), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (ammonia monohydrate, AMH), and $2\text{NH}_3 \cdot 2\text{H}_2\text{O}$ (ammonia hemihydrate, AHH).

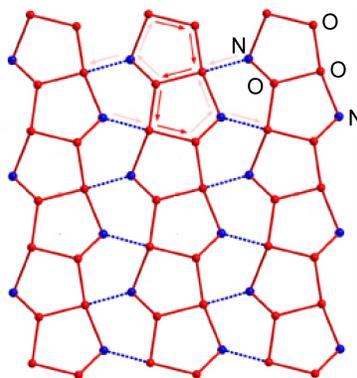


Figure 8.17: The crystal structure of ammonia monohydrate (ANH-II) with hydrogen atoms omitted. Adapted from A. D. Fortes, E. Suard, M. -H. Lemée-Cailleau, C. J. Pickard, and R. J. Needs, *J. Am. Chem. Soc.*, 2009, **131**, 13508. Copyright: American Chemical Society (2009).

It should be noted that these hydrates do not contain discrete NH_4^+ or OH^- ions, indicating that ammonium hydroxide does not exist as a discrete species despite the common usage of the name. In aqueous solution, ammonia is a weak base ($\text{pK}_b = 4.75$), (8.15).



NOTE: Ammonia solutions commonly used in the laboratory is a 35% solution in water. In warm weather the solution develops pressure and the cap must be released with care. The 25% solution sold commercially (for home use) is free from this problem.

Ammonia is a Lewis base and readily forms Lewis acid-base complexes with both transition metals, (8.16), and main group metals (Figure 8.18).

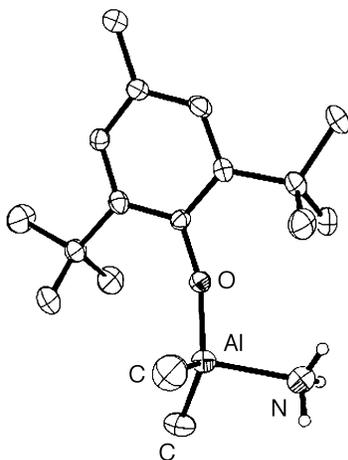
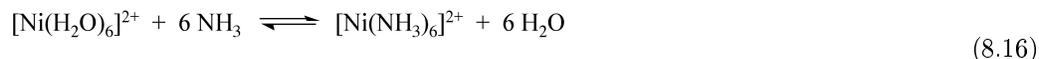
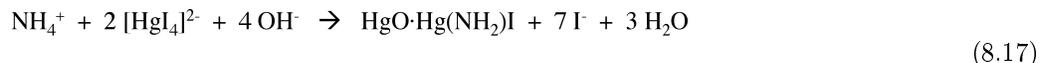


Figure 8.18: The molecular structure of $\text{AlMe}_2(\text{BHT})\text{NH}_3$. Hydrogen atoms, except those attached to nitrogen, are omitted for clarity. Adapted from M. D. Healy, J. T. Leman, and A. R. Barron, *J. Am. Chem. Soc.*, 1991, **113**, 2776. Copyright: American Chemical Society.

The formation of stable ammonia complexes is the basis of a simple but effective method of detection: Nessler's reagent, (8.17). Using a 0.09 mol/L solution of potassium tetraiodomercurate(II), $\text{K}_2[\text{HgI}_4]$, in 2.5 mol/L potassium hydroxide. A yellow coloration indicates the presence of ammonia: at higher concentrations, a brown precipitate may form. The sensitivity as a spot test is about $0.3 \mu\text{g NH}_3$ in $2 \mu\text{L}$.



Ammonia forms a blue solution with Group 1 metals. As an example, the dissolution of sodium in liquid ammonia results in the formation of solvated Na^+ cations and electrons, (8.18) where $\text{solv} = \text{NH}_3$. The solvated electrons are stable in liquid ammonia and form a complex: $[\text{e}^-(\text{NH}_3)_6]$.



It is this solvated electron that gives the strong reducing properties of the solution as well as the characteristic signal in the ESR spectrum associated with a single unpaired electron. The blue color of the solution is often ascribed to these solvated electrons; however, their absorption is in the far infra-red region of the spectrum. A second species, $\text{Na}^-(\text{solv})$, is actually responsible for the blue color of the solution.



The reaction of ammonia with oxygen is highly favored, (8.20), and the flammability limit of ammonia is 16 – 25 vol%. If the reaction is carried out in the presence of a catalyst (Pt or Pd) the reaction can be limited

to the formation of nitric oxide (NO), (8.21).



8.3.2.4 Ammonium salts

The ammonium cation (NH_4^+) behaves in a similar manner to the Group 1 metal ions. The solubility and structure of ammonium salts particularly resembles those of potassium and rubidium because of their relative size (Table 8.7). One difference is that ammonium salts often decompose upon heating, (8.22).



Cation	Ionic radius (Å)
K^+	1.33
NH_4^+	1.43
Rb^+	1.47

Table 8.7: Ionic radius of the ammonium ion compared to those of potassium and rubidium.

The decomposition of ammonium salts of oxidizing acids can often be violent to highly explosive, and they should be treated with care. For example, while ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, decomposes to give a volcano (Figure 8.19), ammonium permanganate, $\text{NH}_4[\text{MnO}_4]$, is friction sensitive and explodes at 60 °C. Ammonium nitrate, $\text{NH}_4[\text{NO}_3]$, can cause fire if contacted with a combustible material and is a common ingredient in explosives since it acts as the oxygen source due to its positive oxygen balance, i.e., the compound liberates oxygen surplus to its own needs upon decomposition, (8.23).



Figure 8.19: A laboratory demonstration of an ammonium dichromate volcano.

8.3.2.5 Bibliography

- A. R. Barron, *The Detonator*, 2009, **36**, 60.
- A. D. Fortes, E. Suard, M. -H. Lemée-Cailleau, C. J. Pickard, and R. J. Needs, *J. Am. Chem. Soc.*, 2009, **131**, 13508.
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8.3.3 Liquid Ammonia as a Solvent⁵

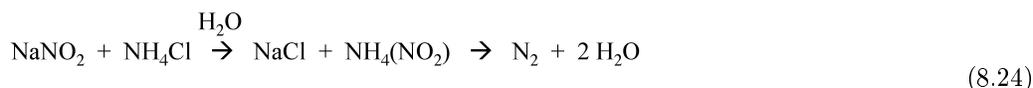
Ammonia has a reasonable liquid range (-77 to -33 °C), and as such it can be readily liquefied with dry ice (solid CO₂, T_{sub} = -78.5 °C), and handled in a thermos flask. Ammonia's high boiling point relative to its heavier congeners is indicative of the formation of strong hydrogen bonding, which also results in a high heat of vaporization (23.35 kJ/mol). As a consequence ammonia can be conveniently used as a liquid at room temperature despite its low boiling point.

Liquid ammonia is a good solvent for organic molecules (e.g., esters, amines, benzene, and alcohols). It is a better solvent for organic compounds than water, but a worse solvent for inorganic compounds. The solubility of inorganic salts is highly dependant on the identity of the counter ion (Table 8.8).

Soluble in liquid NH ₃	Generally insoluble in liquid NH ₃
SCN ⁻ , I ⁻ , NH ₄ ⁺ , NO ₃ ⁻ , NO ₂ ⁻ , ClO ₄ ⁻	F ⁻ , Cl ⁻ , Br ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ , O ²⁻ , OH ⁻ , S ²⁻

Table 8.8: General solubility of inorganic salts in liquid ammonia as a function of the counter ion.

The difference in solubility of inorganic salts in ammonia as compared to water, as well as the lower temperature of liquid ammonia, can be used to good advantage in the isolation of unstable compounds. For example, the attempted synthesis of ammonium nitrate by the reaction of sodium nitrate and ammonium chloride in water results in the formation of nitrogen and water due to the decomposition of the nitrate, (8.24). By contrast, if the reaction is carried out in liquid ammonia, the sodium chloride side product is insoluble and the ammonium nitrate may be isolated as a white solid after filtration and evaporation below its decomposition temperature of 0 °C, (8.25).



8.3.3.1 Ammoniation

Ammoniation is defined as a reaction in which ammonia is added to other molecules or ions by covalent bond formation utilizing the unshared pair of electrons on the nitrogen atom, or through ion-dipole electrostatic interactions. In simple terms the resulting *ammine* complex is formed when the ammonia is acting as a

⁵This content is available online at <<http://cnx.org/content/m33060/1.2/>>.

Lewis base to a Lewis acid, (8.26) and (8.27), or as a ligand to a cation, e.g., $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$, and $[\text{Co}(\text{NH}_3)_6]^{3+}$.



8.3.3.2 Ammonolysis

Ammonolysis with ammonia is an analogous reaction to hydrolysis with water, i.e., a dissociation reaction of the ammonia molecule producing H^+ and an NH_2^- species. Ammonolysis reactions occur with inorganic halides, (8.28) and (8.29), and organometallic compounds, (8.30). In both cases the NH_2^- moiety forms a substituent or ligand.

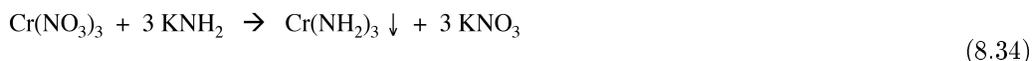


The reaction of esters, (8.31), and aryl halides, (8.32), are also examples of ammonolysis reactions.



8.3.3.3 Homoleptic amides

A homoleptic compound is a *compound with all the ligands being identical*, e.g., $\text{M}(\text{NH}_2)_n$. A general route to homoleptic amide compounds is accomplished by the reaction of a salt of the desired metal that is soluble in liquid ammonia (Table 8.8) with a soluble Group 1 amide. The solubility of the Group 1 amides is given in Table 8.9. Since all amides (except those of the Group 1 metals) are insoluble in liquid ammonia, the resulting amide may be readily isolated, e.g., (8.33) and (8.34).



Amide	Solubility in liquid ammonia
LiNH ₂	Sparingly soluble
NaNH ₂	Sparingly soluble
KNH ₂	Soluble
RbNH ₂	Soluble
CsNH ₂	Soluble

Table 8.9: Solubility of Group amides in liquid ammonia.

8.3.3.4 Redox reactions

Ammonia is poor as an oxidant since it is relatively easily oxidized, e.g., (8.35) and (8.36). Thus, if it is necessary to perform an oxidation reaction ammonia is not a suitable solvent; however, it is a good solvent for reduction reactions.



Liquid ammonia will dissolve Group 1 (alkali) metals and other electropositive metals such as calcium, strontium, barium, magnesium, aluminum, europium, and ytterbium. At low concentrations (ca. 0.06 mol/L), deep blue solutions are formed: these contain metal cations and solvated electrons, (8.37). The solvated electrons are stable in liquid ammonia and form a complex: $[\text{e}^-(\text{NH}_3)_6]$.



The solvated electrons provide a suitable and powerful reducing agent for a range of reactions that are not ordinarily accomplished, e.g., (8.38) and (8.39).



8.3.4 Ammonia: From Uses in Agriculture and Beer Production to Prolonging the First World War⁶

One of the cornerstones of the industrial expansion in Germany between 1870 and 1910 (when the population grew from 41 million to 66 million) was the chemicals industry. In particular companies such as Badische Anilin und Soda Fabrik (Baden Aniline and Soda Factory or BASF) had developed their business on the formation of synthetic dyes derived from the chemicals in coal tar.

Coal tar was formed as a by-product of the gasification of coal. A key ingredient of coal tar is naphtha (Table 8.10) that was used by the rubber industry; however, the remainder was disposed off. It was not long before chemists started to investigate the constituents present in coal tar. One of the first discoveries

⁶This content is available online at <<http://cnx.org/content/m33048/1.3/>>.

was by a chemistry student at the Royal College of Chemistry (now Imperial College) in London, William Perkin (Figure 8.20), who isolated the first synthetic dye: mauveine (Figure 8.21). This discovery led to an explosion in the chemical industry based on the extraction of compounds from coal tar, which was an essentially free waste product from every gasworks. Nowhere was this research more commercially driven than in Germany.

Property	Typical value
Molecular weight	100 - 215 g/mol
Specific gravity	0.75 - 0.85 g/cm ³
Boiling point	160 - 220 °C
Vapor pressure	5 mmHg
Solubility in water	Insoluble

Table 8.10: The typical physical properties of naphtha.

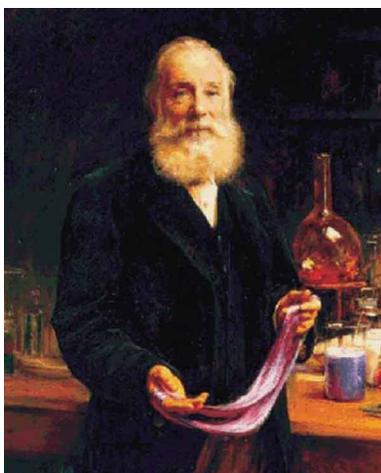


Figure 8.20: A portrait of English chemist Sir William Perkin (1838 - 1907) holding a sample of cloth dyed with his discovery, mauveine, which is often called *Perkin's purple*.

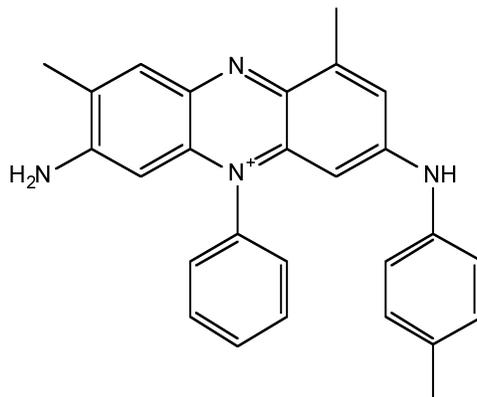


Figure 8.21: The structure of mauveine-B.

The rapid increase in the German population also put a strain on the country's food resources. What compounded this issue was that the aristocratic Junker families of East Prussia who owned much of the land in what was known as *Germany's breadbasket*. Junkers grew rye on their estates because the soil was too light for wheat, and since rye was fertilized with potash (potassium oxide, K_2O) of which Germany had vast resources. However, in 1870 grain from the US was becoming cheaper and thus competitive with German rye. To protect their profits the Junkers demanded both subsidies for the export of rye and tariffs for the import of wheat. The result of this was that all the German rye was leaving the country and there was not enough wheat being produced to satisfy the needs of the local population. Sufficient wheat could be grown in Germany if a suitable fertilizer was available.

Sodium nitrate ($NaNO_3$), also known as *Chile saltpeter*, was the most common fertilizer. Unfortunately, by 1900 the deposits looked to be depleted and an alternative was needed. The alternative was found as a component in coal tar. It was known that one of the chemicals that caused the *stink* associated with coal gas and coal tar was ammonia (NH_3). Chemist George Fownes (Figure 8.22) had suggested that ammonia be turned into a salt and used as a fertilizer. Unfortunately, the amount of ammonia that could be separated from coal tar was still insufficient, so if ammonia could be made on a large enough scale, then large-scale manufacture of a fertilizer could be realized.



Figure 8.22: British chemist George Fownes, FRS (1815 – 1849).

In 1909 Fritz Haber (Figure 8.23) presented a method of ammonia synthesis to BASF. His work in collaboration with Carl Bosch (Figure 8.24) resulted in the process known as the Haber-Bosch process in which nitrogen and hydrogen are mixed at high temperature (600 °C) under pressure (200 atm) over an osmium catalyst, (8.40).

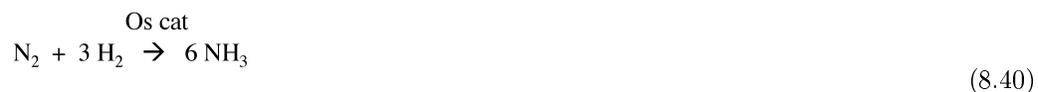




Figure 8.23: German chemists Fritz Haber (1868 –1934) who received the Nobel Prize in Chemistry in 1918 for his development for synthesizing ammonia.



Figure 8.24: German chemist Carl Bosch (1874 –1940) who received the Nobel Prize in Chemistry in 1931 for his work in high-pressure chemistry.

It is interesting to note that the realization of the Haber-Bosch process required not only high-pressure vessels to be constructed by the steel industry, but also the liquid forms of nitrogen and hydrogen. As it turned out ammonia was a necessary component for enabling the production of liquid nitrogen and hydrogen, and involved a false hypothesis of what caused malaria, which led to a desire to keep drinks cold.

Long before it was understood the real cause of malaria, John Gorrie (Figure 8.25), a doctor working in Apalachicola on the Gulf Coast of Florida, was obsessed with finding a cure for malaria. The term *malaria* originated from Medieval Italian: *mala aria* (bad air), and it was associated with swamps and marshlands. Gorrie noticed that malaria was connected to hot humid weather so he began hanging bowl of ice in wards and circulating the air with a fan. However, ice was cut from frozen lakes and rivers in the North East of the US, stored and then shipped all over the world, and Apalachicola was so small that ice was seldom delivered. Gorrie started looking into methods of making ice. It was well known that when a compressed gas expands it takes heat from its surroundings. Gorrie made a steam engine that compressed air in a piston, which when the piston retracted the air cooled. On the next compression stroke the cold air was pushed out across a brine solution (saturated aqueous NaCl) cooling it. When he brought water in contact with the cold brine, it froze creating the first man made ice. On 14 July 1850 Gorrie produced ice for the French Consul to cool the champagne for the celebration of Bastille Day. Just before he died, Gorrie suggested that his (by then) Patented process could be used for cooling food for transport, and it was this application that was used extensively by British merchants to bring meat from Australia to Britain. However, in Germany, Gorrie's invention was more useful for beer.



Figure 8.25: Portrait of American physician and scientist John Gorrie (1803 –1855) is considered the father of refrigeration and air conditioning.

Whereas the British traditionally brewed beer in which the yeast ferments on the surface (*top fermentation*) at a temperature of 60 – 70 °F, in Germany beer was made using *bottom fermentation*. This style of fermentation requires a temperature just above freezing. Traditionally, cold cellars were used to store the fermenting beer, and it is from here the name lager is derived from the German verb *lagern*: to store. There had been a law in Germany preventing brewing in the summer, but with Gorrie's process the possibility was

to be able to brew beer all year. Carl von Linde (Figure 8.26) was asked to develop a refrigeration system. He used ammonia instead of air in Gorrie's system, and in 1879 he set up a company to commercialize his ideas. The success of his refrigerator was such that by 1891 there were over 12,000 fridges being used, and more importantly there was now a convenient method of liquefying gases such as hydrogen and nitrogen; both of which were needed for the Haber-Bosch process.

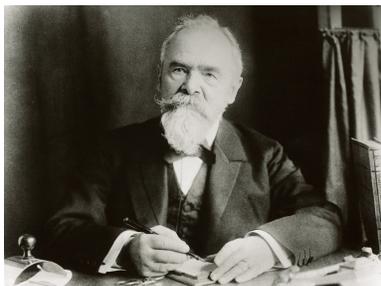
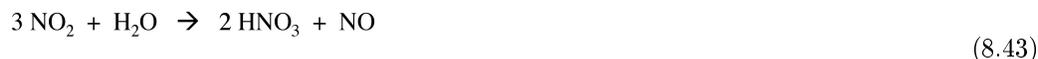


Figure 8.26: German engineer Carl Paul Gottfried von Linde (1842 - 1934).

As a consequence of the use of ammonia as a refrigerant, it was possible to prepare ammonia on a large industrial scale. Ammonia prepared by the Haber-Bosch process can be converted to nitric acid by the Ostwald process developed by Wilhelm Ostwald (Figure 8.27). Treatment of ammonia with air over a platinum catalyst yields initially nitric oxide, (8.41), and subsequently to nitrogen dioxide, (8.42), which dissolves in water to give nitric acid, (8.43).



Addition of soda (sodium hydroxide, NaOH) to nitric acid results in the formation of sodium nitrate, (8.44), which was the same fertilizer produced from the deposits in Chile.



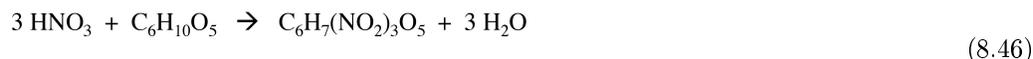


Figure 8.27: German chemist Friedrich Wilhelm Ostwald (1853 – 1932) received the Nobel Prize in 1909 for his work on catalysis.

Unfortunately, for the Haber-Bosch and Ostwald processes, an even cheaper form of fertilizer was synthesized around the same time using calcium carbide to prepare calcium cyanamide (CaCN_2), (8.45). As a consequence, the Haber-Bosch process was forgotten until the outbreak of the First World War in 1914.



Within weeks of the outbreak Germany realized it had only enough explosives for about a year of conflict. This was because the main source of explosives, sodium nitrate was the same source that gave fertilizer, i.e., Chile. Realizing this, the Royal Navy effectively blockaded the supply lines. If Germany did not find another source of Great War would have been over early in 1916, however, it was remembered that the Haber-Bosch process in combination with the Ostwald processes would allow the synthesis of nitric acid, which when mixed with cotton, made nitrocellulose (Figure 8.28), also known as gun cotton, an explosive, (8.46).



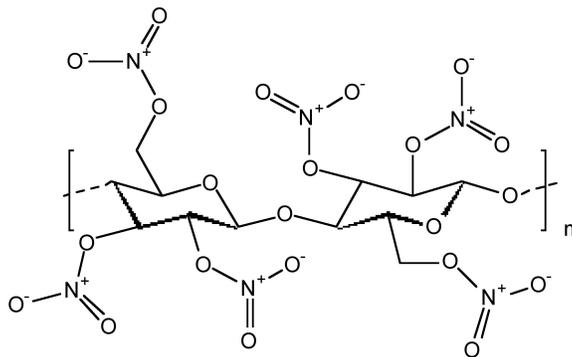


Figure 8.28: The structure of nitrocellulose.

As a result of the industrial synthesis of ammonia Germany was able to manufacture sufficient explosives to fight until 11 November 1918, by which time almost 10 million were dead, almost 7 million missing, and over 21 million were wounded (Figure 8.29).



Figure 8.29: The Douaumont Ossuary cemetery and World War I memorial in Verdun, France.

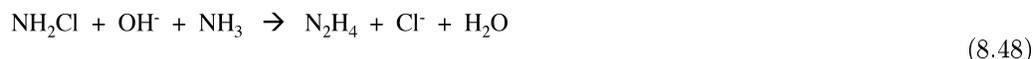
8.3.5 Hydrazine⁷

Hydrazine (N_2H_4) is a colorless liquid with an odor similar to ammonia. Hydrazine has physical properties very close to water, with a melting point of $2\text{ }^\circ\text{C}$ and a boiling point of $114\text{ }^\circ\text{C}$. The similarity in its chemistry to water is as a result of strong intermolecular hydrogen bonding.

WARNING: Hydrazine is highly toxic and dangerously unstable, and is usually handled as aqueous solution for safety reasons. Even so, hydrazine hydrate causes severe burns on the skin and eyes. Contact with transition metals, their oxides (e.g., rust), or salts cause catalytic decomposition and possible ignition of evolved hydrogen. Reactions with oxidants are violent.

8.3.5.1 Synthesis

Hydrazine is manufactured on the industrial scale by the Olin Raschig process using the reaction of a sodium hypochlorite solution with ammonia at $5\text{ }^\circ\text{C}$ to form chloramine (NH_2Cl) and sodium hydroxide, (8.47). The chloramines solution is then reacted with ammonia under pressure at $130\text{ }^\circ\text{C}$, (8.48). Ammonia is used in a 33 fold excess.



If transition metals are present then decomposition occurs, (8.49), and therefore, ethylenediaminetetraacetic acid (EDTA, Figure 8.30) is added to complex the transition metal ions. The as produced hydrazine solution can be concentrated by distillation to give a 65% solution. Anhydrous hydrazine is formed by the distillation from NaOH.

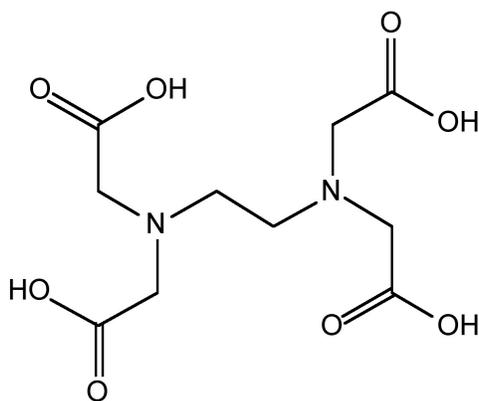
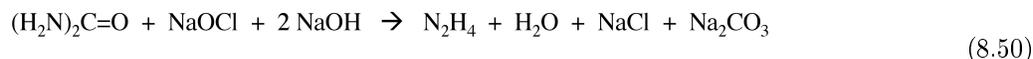


Figure 8.30: The structure of ethylenediaminetetraacetic acid (EDTA).

⁷This content is available online at <<http://cnx.org/content/m33041/1.2/>>.

Alternative routes to hydrazine include the oxidation of urea with sodium hypochlorite, (8.50), and the reaction of ammonia and hydrogen peroxide, (8.51).



8.3.5.2 Structure

The nitrogen atoms in hydrazine adopt sp^3 hybridization (Figure 8.31a), and molecule adopts a *gauche* conformation in the vapor, liquid and solid states (Figure 8.31b).

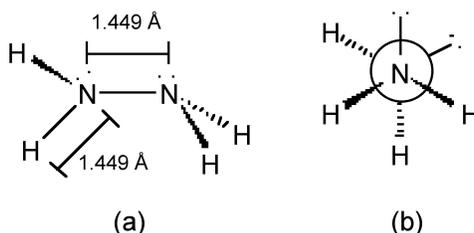


Figure 8.31: The structure of hydrazine.

In a similar manner to ammonia, (8.52), hydrazine is a self-ionizing, (8.53). While there is a wide range of salts of the N_2H_5^+ cation, only the sodium and potassium salts of N_2H_3^- are stable.



8.3.5.3 Reaction chemistry and uses

Hydrazine is polar, highly ionizing, and forms stable hydrogen bonds, and its resemblance to water is reflected in the formation of aqueous solutions and hydrates. In the solid state the monohydrate is formed, i.e., $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. In solution hydrazine acts as a base to form the hydrazinium ion, (8.54) where $K_b = 8.5 \times 10^{-7}$. The presence of a second Lewis base site means that hydrazine can be protonated twice to form the hydrazonium ion, (8.55) where $K_b = 8.9 \times 10^{-16}$. Salts of the cation N_2H_5^+ are stable in water; however, the salts of the dication are less stable.



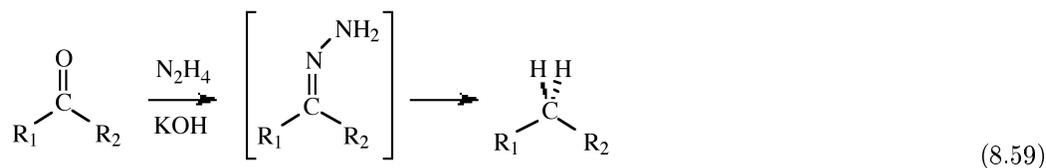
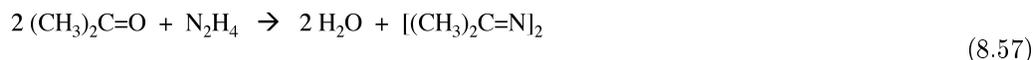


The reaction of hydrazine with oxygen is highly favored, (8.56), and the explosive limit is 1.8 – 100 vol%.



Hydrazine is useful in a number of organic reactions for the synthesis of a wide range of compounds used in pharmaceuticals, textile dyes, and in photography, including:

- Hydrazone formation, (8.57) and (8.58).
- Alkyl-substituted hydrazine synthesis via direct alkylation with alkyl halides.
- Reaction with 2-cyanopyridines to form amide hydrazides, which can be converted using 1,2-diketones into triazines.
- Use in the Wolff-Kishner reduction that transforms the carbonyl group of a ketone or aldehyde into a methylene (or methyl) group via a hydrazone intermediate, (8.59).
- As a building block for the preparation of many heterocyclic compounds via condensation with a range of difunctional electrophiles.
- Cleavage N-alkylated phthalimide derivatives.
- As a convenient reductant because the by-products are typically nitrogen gas and water.



8.3.5.3.1 Messerschmitt Me 163 Komet

Designed by Alexander Lippisch (Figure 8.32), the Messerschmitt Me 163B Komet (Figure 8.33) was the first rocket-powered fighter plane. With a top speed of around 596 mph (Mach 0.83) and a service ceiling of 40,000 ft, the Komet's performance of the Me 163B far exceeded that of contemporary piston engine fighters. However, despite its impressive performance, it was only produced in limited numbers (*ca.* 370 as compared to the 1,430 built of its jet powered compatriot the Me 262) and was not an effective combat airplane.



Figure 8.32: German pioneer of aerodynamics Alexander Martin Lippisch (1894 – 1976).



Figure 8.33: The Messerschmitt Me 163B-1.

The Komet was powered by the HWK 109-509 *hot engine* (Figure 8.34) that used a mixture of a fuel and an oxidizer. The fuel was a mixture of hydrazine hydrate (30%), methanol (57%), and water (13%) that was designated by the code name, *C-Stoff*, that burned with the oxygen-rich exhaust from hydrogen peroxide (*T-Stoff*) used as the oxidizer. The *C-Stoff* was stored in a glass tank on the plane, while the *T-Stoff* was stored in an aluminum container. An oxidizing agent cocktail of CaMnO_4 and/or K_2CrO_4 was added to the *T-Stoff* generating steam and high temperatures, this in turn reacted violently with the *C-Stoff*. The flow of reagents was controlled by two pumps, to regulate the rate of combustion and thereby the amount of thrust. The violent combustion process resulted in the formation of water, carbon dioxide and nitrogen, and a huge amount of heat sending out a superheated stream of steam, nitrogen and air that was drawn in through the

hole in the mantle of the engine, thus providing a forward thrust of approximately 3,800 lbf. Because of the potential hazards of mixing the fuels, they were stored at least $1/2$ mile apart, and the plane was washed with water between fueling steps and after missions.

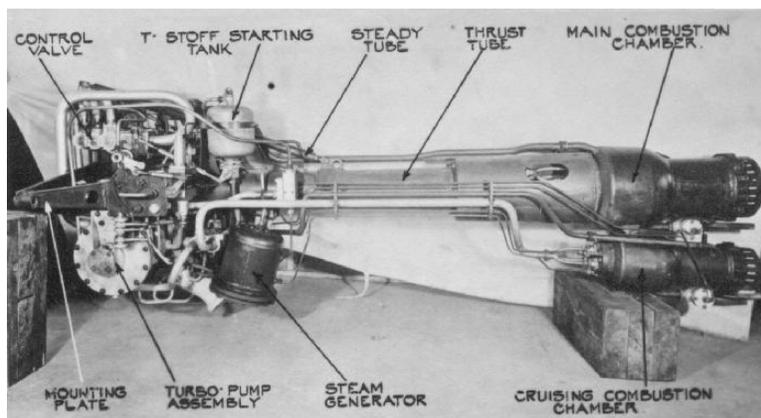


Figure 8.34: A photograph taken by Professor A. D. Baxter of the HWK 109-509 *hot engine*.

8.3.6 Phosphine and Arsine⁸

Because of their use in metal organic chemical vapor deposition (MOCVD) of 13-15 (III-V) semiconductor compounds phosphine (PH_3) and arsine (AsH_3) are prepared on an industrial scale.

8.3.6.1 Synthesis

Phosphine (PH_3) is prepared by the reaction of elemental phosphorus (P_4) with water, (8.60). Ultra pure phosphine that is used by the electronics industry is prepared by the thermal disproportionation of phosphorous acid, (8.61).



Arsine can be prepared by the reduction of the chloride, (8.62) or (8.63). The corresponding syntheses can also be used for stibine and bismuthine.



The hydrolysis of calcium phosphide or arsenide can also generate the trihydrides.

⁸This content is available online at <<http://cnx.org/content/m33043/1.5/>>.

8.3.6.2 Structure

The phosphorus in phosphine adopts sp^3 hybridization, and thus phosphine has an umbrella structure (Figure 8.35a) due to the stereochemically active lone pair. The barrier to inversion of the umbrella ($E_a = 155$ kJ/mol) is much higher than that in ammonia ($E_a = 24$ kJ/mol). Putting this difference in context, ammonia's inversion rate is 10^{11} while that of phosphine is 10^3 . As a consequence it is possible to isolate chiral organophosphines (PRR'R''). Arsine adopts the analogous structure (Figure 8.35b).

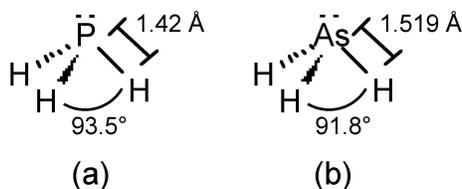


Figure 8.35: The structures of (a) phosphine and (b) arsine.

8.3.6.3 Reactions

Phosphine is only slightly soluble in water (31.2 mg/100 mL) but it is readily soluble in non-polar solvents. Phosphine acts as neither an acid nor a base in water; however, proton exchange proceeds via the phosphonium ion (PH_4^+) in acidic solutions and via PH_2^- at high pH, with equilibrium constants $K_b = 4 \times 10^{-28}$ and $K_a = 41.6 \times 10^{-29}$, respectively.

Arsine has similar solubility in water to that of phosphine (i.e., 70 mg/100 mL), and AsH_3 is generally considered non-basic, but it can be protonated by superacids to give isolable salts of AsH_4^+ . Arsine is readily oxidized in air, (8.64).



Arsine will react violently in presence of strong oxidizing agents, such as potassium permanganate, sodium hypochlorite or nitric acid. Arsine decomposes to its constituent elements upon heating to 250 - 300 °C.

8.3.6.3.1 Gutzeit test

The Gutzeit test is the characteristic test for arsenic and involves the reaction of arsine with Ag^+ . Arsine is generated by reduction of aqueous arsenic compounds, typically arsenites, with Zn in the presence of H_2SO_4 . The evolved gaseous AsH_3 is then exposed to silver nitrate either as powder or as a solution. With solid AgNO_3 , AsH_3 reacts to produce yellow Ag_4AsNO_3 , while with a solution of AgNO_3 black Ag_3As is formed.

8.3.6.4 Hazards

Pure phosphine is odorless, but technical grade phosphine has a highly unpleasant odor like garlic or rotting fish, due to the presence of substituted phosphine and diphosphine (P_2H_4). The presence of P_2H_4 also causes spontaneous combustion in air. Phosphine is highly toxic; symptoms include pain in the chest, a sensation of coldness, vertigo, shortness of breath, and at higher concentrations lung damage, convulsions and death. The recommended limit (RL) is 0.3 ppm.

Arsine is a colorless odorless gas that is highly toxic by inhalation. Owing to oxidation by air it is possible to smell a slight, garlic-like scent when arsine is present at about 0.5 ppm. Arsine attacks hemoglobin in the red blood cells, causing them to be destroyed by the body. Further damage is caused to the kidney and liver. Exposure to arsine concentrations of 250 ppm is rapidly fatal: concentrations of 25 – 30 ppm are fatal for 30 min exposure, and concentrations of 10 ppm can be fatal at longer exposure times. Symptoms of poisoning appear after exposure to concentrations of 0.5 ppm and the recommended limit (RL) is as low as 0.05 ppm.

8.3.6.5 Bibliography

- R. Minkwitz, A. Kornath, W. Sawodny, and H. Härtner, *Z. Anorg. Allg. Chem.*, 1994, **620**, 753.

8.4 Oxides and Oxoacids

8.4.1 Oxides of Nitrogen⁹

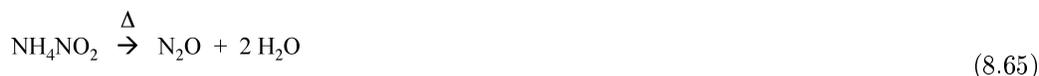
A summary of the physical properties of the oxides of nitrogen is given in Table 8.11.

Oxide	Formula	Mp (°C)	Bp (°C)
Nitrous oxide	N ₂ O	-90.8	-88.5
Nitric oxide	NO	-163.6	-161.8
Dinitrogen trioxide	N ₂ O ₃	-100.6	3.5 (dec.)
Nitrogen dioxide (dinitrogen tetroxide)	NO ₂ /N ₂ O ₄	-11.2 (NO ₂)	21.2 (N ₂ O ₄)
Nitrogen pentoxide	N ₂ O ₅	30	47

Table 8.11: Physical properties of the oxides of nitrogen.

8.4.1.1 Nitrous oxide

Gaseous nitrous oxide (N₂O) is prepared by the careful thermal decomposition of ammonium nitrate (NH₄NO₂), (8.65). Nitrous oxide is a linear molecule (Figure 8.36a) that is isoelectronic (and isostructural) with carbon dioxide. Despite its use as a power enhancement for automobiles, nitrous oxide is actually not very reactive and a major use is as an aerosol propellant.



⁹This content is available online at <<http://cnx.org/content/m35076/1.1/>>.

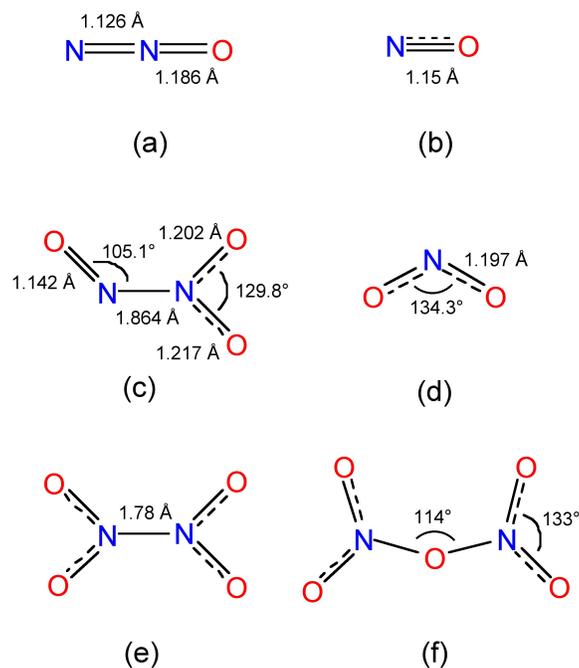


Figure 8.36: Structures of (a) nitrous oxide, (b) nitric oxide, (c) dinitrogen trioxide, (d) nitrogen dioxide, (e) nitrogen tetroxide, and (f) nitrogen pentoxide.

8.4.1.1.1 Nitrous oxide as an anesthetic drug

Nitrous oxide is known as "laughing gas" due to the euphoric effects of inhaling it, a property that has led to its recreational use as a hallucinogen. However, it is as an anesthetic that it has a legitimate application.

The first use of nitrous oxide as an anesthetic drug was when dentist Horace Wells (Figure 8.37) with assistance by Gardner Quincy Colton (Figure 8.38) and John Mankey Riggs (Figure 8.39), demonstrated insensitivity to pain from a dental extraction in December 1844. Wells subsequently treated 12-15 patients, and according to his own record it only failed as an anesthetic in two cases. In spite of these results, the method was not immediately adopted, probably because during his first public demonstration was only partly successful.



Figure 8.37: American dentist Horace Wells (1815 - 1848).



Figure 8.38: American showman, lecturer, and former medical student Gardner Quincy Colton (1814 - 1898).



Figure 8.39: John Mankey Riggs (1811 - 1885) was the leading authority on periodontal disease in the United States, to the point that periodontal disease was known as *Riggs disease*.

The method did not come into general use until 1863, when Colton successfully used it for more than 25,000 patients. As such, the usage of nitrous oxide rapidly became the preferred anesthetic method in dentistry. Because the gas is mild enough to keep a patient in a conscious and conversational state, and yet in most cases strong enough to suppress the pain caused by dental work, it remains the preferred gas anesthetic in today's dentistry.

8.4.1.1.2 Nitrous: the secret to more power.

In motorsports, nitrous oxide (often referred to as *nitrous* or *NOS*) allows the engine to burn more fuel, resulting in a more powerful combustion, and hence greater horsepower. The gas itself is not flammable, but it delivers more oxygen (33%) than atmospheric air (21%) by breaking down at elevated temperatures. When N_2O breaks down during fuel combustion, the decomposition of nitrous is exothermic, contributing to the overall power increase.

Nitrous oxide is stored as a compressed liquid (Figure 8.40); the evaporation and expansion of liquid nitrous oxide in the intake manifold causes a large drop in intake charge temperature, resulting in a denser charge, further allowing more air/fuel mixture to enter the cylinder. Nitrous oxide is sometimes injected into (or prior to) the intake manifold, whereas other systems directly inject right before the cylinder (direct port injection) to increase power.



Figure 8.40: A typical NOS system for automotive use.

One of the major problems of using nitrous oxide in a reciprocating engine is that it can produce enough power to damage or destroy the engine. Very large power increases are possible, and if the mechanical structure of the engine is not properly reinforced, the engine may be severely damaged or destroyed during this kind of operation.

WARNING: Automotive-grade liquid nitrous oxide differs slightly from medical-grade nitrous oxide in that a small amount of sulfur is added to prevent substance abuse.

8.4.1.2 Nitric oxide

Nitric oxide (NO) is formed by the high temperature oxidation of nitrogen, (8.66), or the platinum catalyzed oxidation of ammonia at 800 °C, (8.67).



Nitric oxide (Figure 8.36b) is electronically equivalent to dinitrogen (N_2) plus an electron, and as a consequence it is paramagnetic with one unpaired electron. The location of the unpaired electron in the π^* orbital (Figure 8.41a) results in a bond order of 2.5 rather than the triple bond observed for N_2 (Figure 8.41b). The N-O distance of 1.15 Å is intermediate between the triple bond distance in NO^+ (1.06 Å) and the typical double bond distance (ca. 1.20 Å). Furthermore, because of the location of the electron it is easy to oxidize nitric oxide to the nitrosonium ion (NO^+), (8.68).



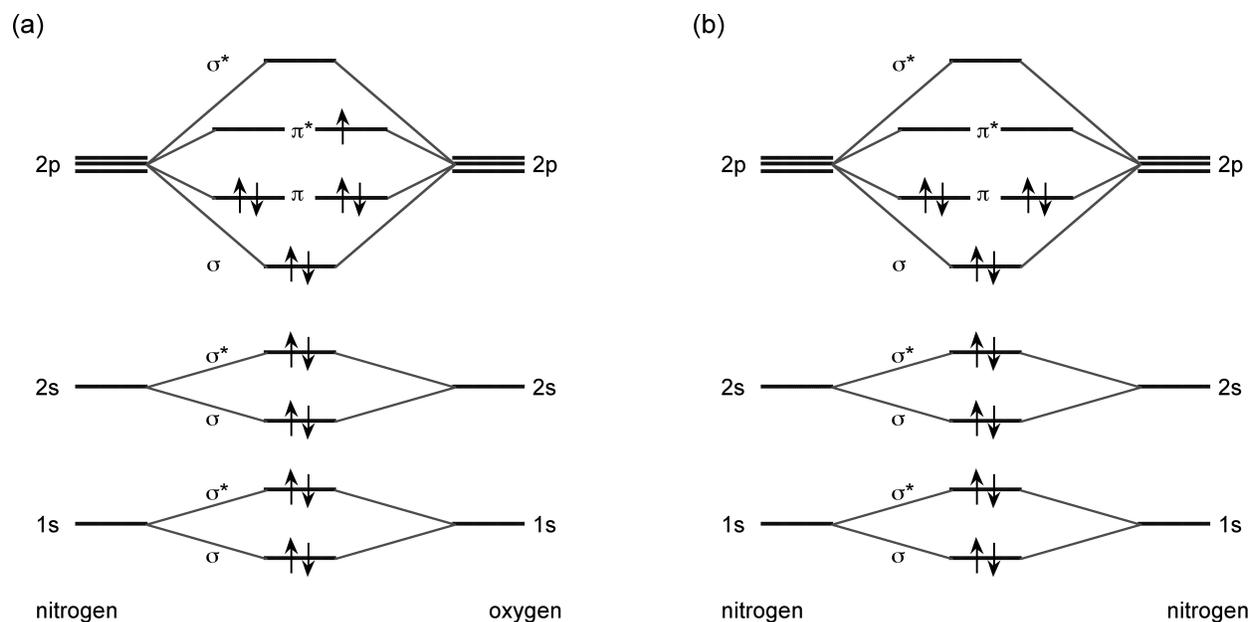


Figure 8.41: Molecular orbital diagrams for (a) nitric oxide and (b) dinitrogen.

Nitric oxide is unstable to heat, (8.70), and oxidation, (8.69). It will also react with halogens to form the nitrosyl halides, XNO.



8.4.1.3 Dinitrogen trioxide

Dinitrogen trioxide (N_2O_3) is formed from the stoichiometric reaction between NO and O_2 or NO and N_2O_4 . Dinitrogen trioxide has an intense blue color in the liquid phase and a pale blue color in the solid state. Thermal dissociation of N_2O_3 , (8.71), occurs above -30°C , and some self-ionization of the pure liquid is observed, (8.72). The asymmetric structure of N_2O_3 (Figure 8.36c) results in a polar molecule (Figure 8.42).



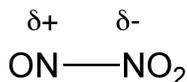


Figure 8.42: The polarization of the N-N bond in dinitrogen trioxide.

8.4.1.4 Nitrogen dioxide (and tetroxide)

Formed from the oxidation of nitric oxide, (8.73), brown nitrogen dioxide is actually in equilibrium with its colorless dimeric form, nitrogen tetroxide (N_2O_4), (8.74).



Nitrogen dioxide (Figure 8.36d) is electronically equivalent to the nitrate anion (NO_2^-) less one electron, and as such it is paramagnetic with one unpaired electron. The location of the unpaired electron in a nitrogen sp^2 orbital, and a consequently it forms a dimer through a N-N bond (Figure 8.36e). Furthermore, it is easy to oxidize nitrogen dioxide to the nitronium ion (NO_2^+), (8.75).



Nitrogen dioxide dissolves in water to form a mixture of nitric and nitrous acids, (8.76). Nitrogen dioxide acts as an oxidizing agent with the formation of nitrate anion, (8.77).



The most common structural form of N_2O_4 (Figure 8.36e) is planar with a long N-N bond (1.78 Å) that is significantly longer than observed in hydrazine (1.47 Å). Rationalization of this structural effect is obtained from a consideration of the molecular orbitals, which show that the electrons in the σ -bond are actually delocalized over the whole molecule. The rotation about the N-N bond is 9.6 kJ/mol.

8.4.1.5 Nitrogen pentoxide

The dehydration of nitric acid, with P_2O_5 , yields nitrogen pentoxide, (8.78), which is an unstable solid at room temperature (Table 8.11). In the solid state nitrogen pentoxide is actually nitronium nitrate ($\text{NO}_2^+\text{NO}_3^-$), however, in the vapor phase it exists as a molecular species (Figure 8.36f) with a bent N-O-N unit. Nitrogen pentoxide is a very powerful nitrating and oxidation agent.



8.4.1.6 Nitrogen oxides as precursors to smog and acid rain

Nitrogen oxides (NO_x) emissions are estimated to be in the range of 25 - 100 megatonnes of nitrogen per year. Natural sources are thought to make up approximately $\frac{1}{3}$ of the total. The generations of NO_x (primarily a mixture of NO_2 and NO) is the main source of smog and a significant contribution to atmospheric pollution; however, NO_x is also responsible for much of the acidity in acid rain.

8.4.1.6.1 Atmospheric reactions leading to acid rain

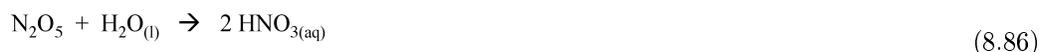
In the dry atmosphere, nitric oxide reacts is oxidized rapidly in sunlight by ozone, (8.79). The nitrogen dioxide reacts with the hydroxide radical, formed by the photochemical decomposition of ozone, (8.80) and (8.81), in the presence of a non-reactive gas molecule such as nitrogen to form nitric acid vapor, (8.82). The conversion rate for NO_x to HNO_3 is approximately ten times faster than the equivalent reaction for sulfur dioxide. For example, conversion is essentially complete for a NO_x plume by the time it transverses the North Sea from the UK to Scandinavia.



At night, conversion takes place via the formation of a nitrate radical, (8.83), which subsequently photochemically unstable under sunlight forming nitrogen pentoxide, (8.84), that reacts with water on the surface of aerosol particles to form nitric acid, (8.85).



Both NO and NO_2 are only slightly soluble in water and it is therefore more probable that the nitric acid content of rain is more likely due to the dissolution of nitric acid vapor into raindrops, (8.86), rather than a separate reaction.



8.4.2 Oxoacids of Nitrogen¹⁰

8.4.2.1 Nitrous acid

In the gas phase nitrous acid can be made by the following reaction:



¹⁰This content is available online at <<http://cnx.org/content/m35056/1.1/>>.

The gas phase structure as determined by IR spectroscopy is shown in Figure 8.43a, in which the nitrogen is planar with sp^2 hybridization.

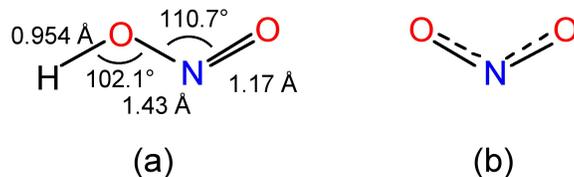
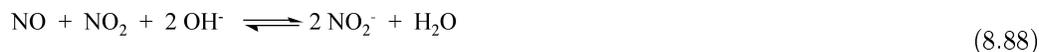


Figure 8.43

In basic aqueous solution the same reaction results in the formation of the nitrite ion, (8.88), which can be precipitated as the Ba^{2+} salt. After separation the addition to sulfuric acid yields a solution of nitrous acid. However, it is not possible to concentrate by heating since decomposition occurs, (8.89).



Nitrous acid is a fairly weak acid in water ($pK = 5.22$); however, many salts are known of the nitrite ion, NO_2^- (Figure 8.43b). Complexes of the nitrite ion can be monodentate with bonding via nitrogen (nitro) or an oxygen (nitrito). Both isomers can be isolated in the case of an inert metal, i.e., substitutionally inert d^6 octahedral complexes (Figure 8.44). Bidentate and bridging modes of coordination are also known for the nitrite anion (Figure 8.45).

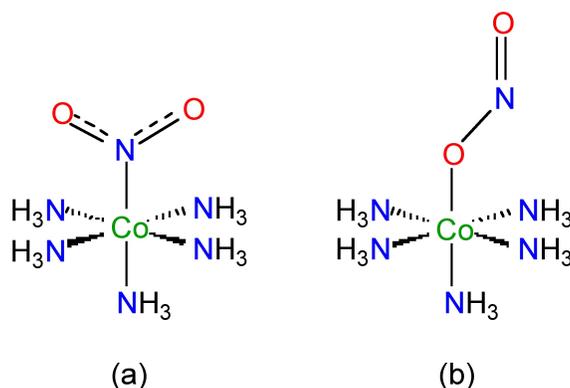


Figure 8.44: Structures of (a) orange nitro and (b) pink nitrito isomers of $[Co^{III}(NH_3)_5(NO_2)]^{2+}$.

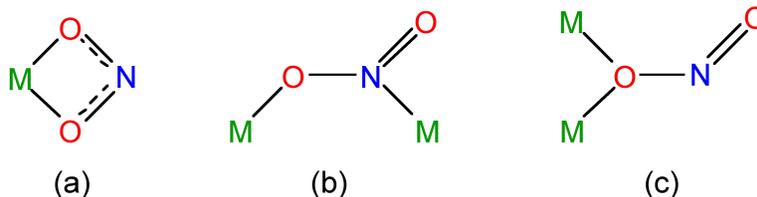
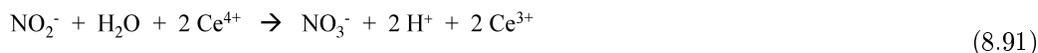


Figure 8.45: Bidentate (a) and bridging (b and c) modes of coordination of the nitrite anion.

Nitrite can act as either an oxidizing agent, (8.90), or a reducing agent, (8.91).



The most important use of nitrous acid is in the diazotization reactions in which nitrous acid is generated by acidifying nitrite solution.

8.4.2.2 Nitric acid

Nitric acid (HNO_3), also known as *aqua fortis* and *spirit of nitre*, is made by the dissolution of nitrogen dioxide in water, (8.92). Nitric acid can be concentrated by distillation from concentrated sulfuric acid.



The structure of HNO_3 in the gas phase is planar at the sp^2 nitrogen (Figure 8.46a).

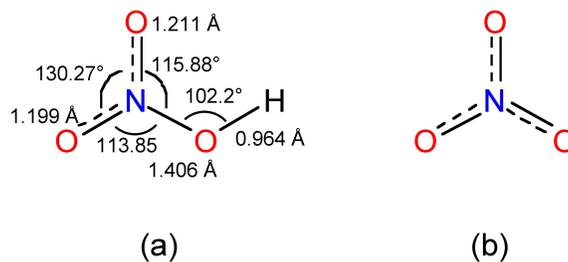


Figure 8.46: The structures of (a) nitric acid and (b) the nitrate anion.

Pure 100% nitric acid is a very corrosive liquid that is strongly acidic and protonates and dissolves organic species. In the liquid phase it is slightly dissociated, (8.93). It is also a powerful oxidizing agent, converting non-metal elements to either the oxide or oxoacid. In contrast with metals it forms either salts or complexes in which the metal is in its highest oxidation state. It is unstable and decomposes upon heating or photolysis.



The pure acid has the highest self ionization of pure liquid acids, (8.94). However, the loss of water results, (8.95), such that the overall reaction can be described by (8.96).



The common concentration of nitric acid is 70%. While the pure acid is colorless, samples often take on a yellow color due to the photochemical decomposition of nitric acid to give brown NO_2 .



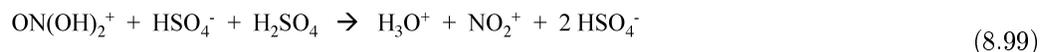
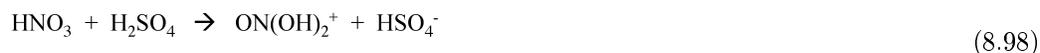
NOTE: The term the “acid test” is derived from the medieval practice of debasing of gold and silver currencies (often by the Monarchs who issued them) by debasing with copper. With ducats (Milan), livres (France), florins (Florence), maravedies (Spain) and bezants (Constantinople) in widespread use, and each with a nominal gold or silver content, it was important for a merchant to be able verify the worth of any particular coin. If a drop of dilute nitric acid was placed onto a silver coin adulterated with copper, it turned green, due to the formation of copper(II) nitrate. Conversely, if a gold coin reacted in any way with the nitric acid it was not pure. In both cases the coins failed the “acid test”.

Aqua regia (so called because it dissolves gold) is a mixture of 70% nitric acid and hydrochloric acid in a 1:3 ratio. *Aqua regia* is a very powerful oxidizing agent (it contains Cl_2) and stabilizes some metals as their chloro complexes (Table 8.12). If HF is added in place of HCl, tantalum may be dissolved with the formation of $[\text{TaF}_2]^-$.

Metal	Chloride salt formed
Au	$[\text{AuCl}_4]^-$
Pt	$[\text{PtCl}_6]^{2-}$

Table 8.12: Metal chloride salts formed by the dissolution of metals in *aqua regia*.

Fuming nitric acid (100% nitric) is exceedingly corrosive and should not be used. In 100% sulfuric acid, nitric acid acts as a base and gets protonated, (8.98) and (8.99), and acts as a powerful nitrating agent.



In water dilute nitric acid is fully ionized, (8.100).



The nitrate ion is planar (Figure 8.46b) and forms many salts and complexes. The nitrate anion is most commonly a monodentate ligand, but can also be a bidentate ligand (Figure 8.47a) or a bridging ligand (Figure 8.47b and c).

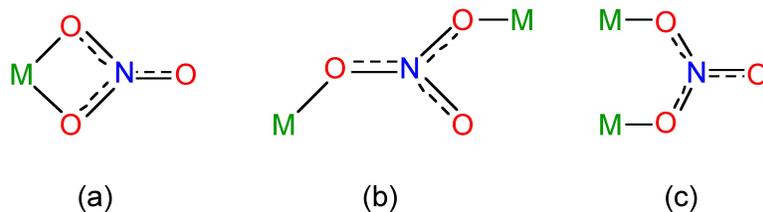


Figure 8.47: Coordination modes of the nitrate anion.

8.4.3 Phosphorous Oxides¹¹

8.4.3.1 Phosphorous trioxide

The stoichiometric oxidation of white phosphorus yields phosphorous trioxide, (8.101).



Several structural forms of phosphorous trioxide are known, but P_4O_6 is a stable molecule structure (Figure 8.48), while the rest are polymers.

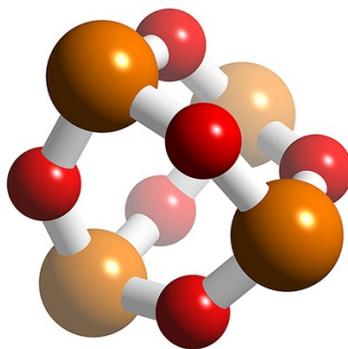


Figure 8.48: The structure of P_4O_6 . Phosphorus atoms are represented by the large spheres, and oxygen atoms by the small spheres (Copyright: Karl Harrison, 2005).

8.4.3.2 Phosphorous pentoxide

The reaction of white phosphorus with excess oxygen (or the oxidation of phosphorous trioxide) yields phosphorous pentoxide, (8.102).



¹¹This content is available online at <<http://cnx.org/content/m35000/1.1/>>.

The structure of hexagonal phosphorous pentoxide is actually that of the dimeric form, P_4O_{10} , and is based upon the structure of P_4O_6 , but with $P=O$ units instead of lone pairs (Figure 8.49). The structure is maintained in the vapor phase; however, other crystalline and glassy forms comprise of a sheet-like structure (Figure 8.50).

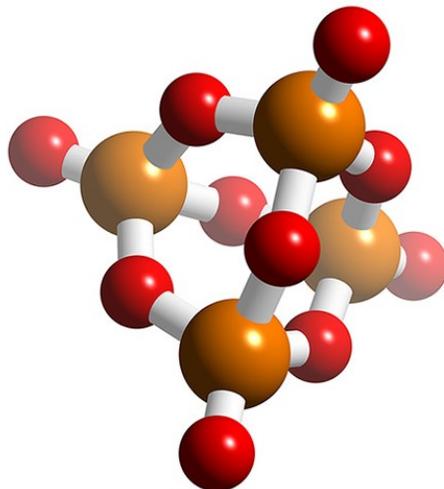


Figure 8.49: The structure of hexagonal P_4O_{10} . Phosphorus atoms are represented by the large spheres, and oxygen atoms by the small spheres (Copyright: Karl Harrison, 2005).

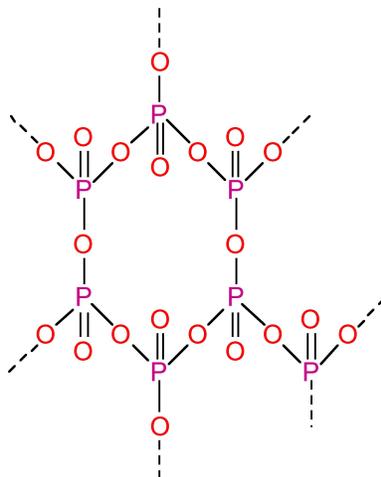


Figure 8.50: The structure of a sheet in glassy P_4O_{10} .

Phosphorous pentoxide is an excellent drying agent below 100 °C. It reacts with water to form various phosphoric acids, and it will extract water from other 'drying agents', e.g., (8.103) and (8.104). Phosphorous pentoxide will dehydrate amides to give nitriles, (8.105).



8.4.4 Oxoacids of Phosphorus¹²

Phosphorous pentoxide (P_2O_5) is an excellent drying agent, and its action is a result of the formation of a range of oxoacids.

8.4.4.1 Hypophosphorous acid

Hypophosphorous acid, H_3PO_2 , is easily prepared pure by the reaction of white phosphorous with base, followed by acidification, (8.106). The pure acid is a solid (Mp = 27 °C) and very soluble in water.



The structure of H_3PO_2 is determined by X-ray crystallography to be tetrahedral with two hydride ligands and a hydroxide (Figure 8.51a). The presence of two hydrides is confirmed by NMR spectroscopy. The ^1H NMR resonance shows an OH line and a doublet from the P-H with a large one-bond coupling constant to the ^{31}P nucleus. The non-decoupled ^{31}P NMR spectrum shows a triplet ($\delta = 13$ ppm, $J_{\text{P-H}} = 530$ Hz) due to the two hydrides.

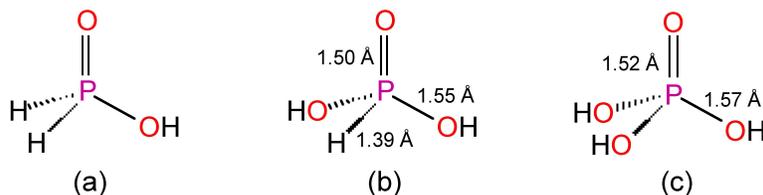
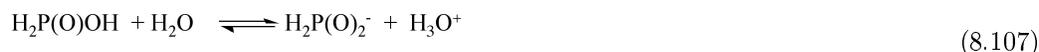


Figure 8.51: Oxoacids of phosphorous: (a) hypophosphorous acid, (b), phosphorous acid, and (c) phosphoric acid.

¹²This content is available online at <<http://cnx.org/content/m35001/1.1/>>.

In water hypophosphorous acid is a monobasic acid ($pK = 1.2$), (8.107), and it forms a wide range of salts. It is also a powerful reducing agent, but its reaction kinetics is slow.



8.4.4.2 Phosphorous acid

The reaction of P_4O_6 or PCl_3 with water yields phosphorous acid, H_3PO_3 ; which like hypophosphorous acid is a solid ($M_p = 70.1\text{ }^\circ\text{C}$) and very soluble in water. The structure is shown by X-ray crystallography to be comprised of a tetrahedral phosphorus with one hydride and two hydroxides (Figure 8.51b). ^{31}P NMR spectroscopy demonstrates the presence of a single hydride by the presence of a doublet as a consequence of the phosphorous center being split by a single hydride ($\delta = 4\text{ ppm}$, $J_{\text{P-H}} = 700\text{ Hz}$). The ^1H NMR spectrum shows a doublet for the hydride and a single resonance of twice the intensity for the hydroxide.

As expected, in water phosphorous acid is dibasic, (8.108). The acid (and the anions) are strong reducing agents, yielding phosphoric acid. They actually react very slowly, and it is thought that this may be due to the reaction being in the tautomeric form, P(OH)_3 . Although this has not been isolated, the trialkyl derivatives exist in both forms, i.e., esters of phosphoric acids (Figure 8.52a) and trialkyl phosphates (Figure 8.52b).

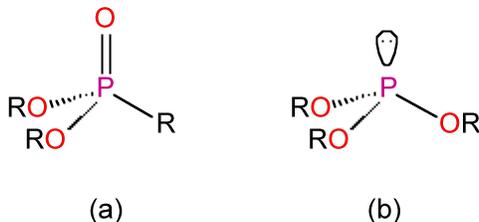
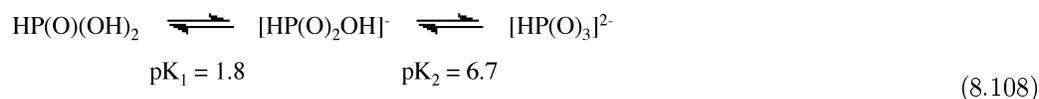


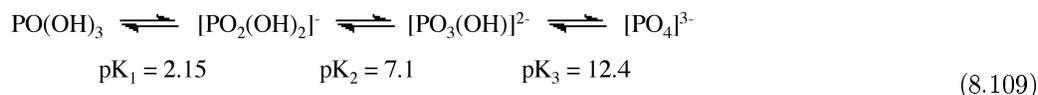
Figure 8.52: Structures of two tautomeric forms; (a) an ester of phosphoric acid and (b) a trialkyl phosphate.

8.4.4.3 Ortho phosphoric acid

Orthophosphoric acid (H_3PO_4) is the most common oxoacid of phosphorus (Figure 8.51c). The term acid phosphoric acid is commonly used. It is made from the reaction of phosphates with sulfuric acid (H_2SO_4), or from the hydrolysis of P_4O_{10} . The pure acid is a colorless crystalline solid ($M_p = 42.35\text{ }^\circ\text{C}$) with extensive hydrogen bonding. The inter-phosphoric acid hydrogen bonding is partially maintained in aqueous solutions above 50% solutions.

Phosphoric acid is very stable and shows no oxidation chemistry below $350\text{ }^\circ\text{C}$. As expected, phosphoric acid is tribasic, (8.109). The anions H_2PO_4^- and HPO_4^{2-} have particular names, dihydrogen phosphate and

monohydrogen phosphate, respectively.

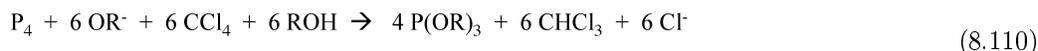


Many salts of are known for all three anions; those with phosphate (PO_4^{2-}) are often insoluble in water. Many coordination complexes are known, especially with M^{3+} and M^{4+} ions.

8.4.4.3.1 Phosphorous esters

The alkyl and aryl homologs of phosphoric acid (i.e., the phosphate triester $\text{O}=\text{P}(\text{OR})_3$) are prepared by the reaction of P_4O_{10} with the appropriate alcohol. The triesters are good solvents and Lewis basic ligands with coordination via the oxide moiety. The diesters and monoesters can also be made, and they are important in biochemical processes.

Phosphite triesters, $\text{P}(\text{OR})_3$, may be made by the reaction of PCl_3 with alcohols or phenols in the presence of an organic base as the acceptor for the HCl formed. Alternatively, they can be prepared directly from white phosphorous, (8.110).



Phosphite triesters are readily oxidized to the appropriate phosphate triester, (8.111). They also react with alkyl halides to form the dialkyl phosphonate via the Michaelis-Arbusov reaction, (8.112).



8.4.4.3.2 Polyphosphates

Polyphosphates contain the PO_4 unit, and the simplest example (pyrophosphate or diphosphate, Figure 8.53a) can be considered as condensation products of monohydrogen phosphate, (8.113). Longer chains can be formed, e.g., the triphosphate $\text{P}_3\text{O}_{10}^{5-}$ (Figure 8.53b). The formation and reverse (hydrolysis) reaction are slow, but are readily catalyzed, e.g., by enzymes.

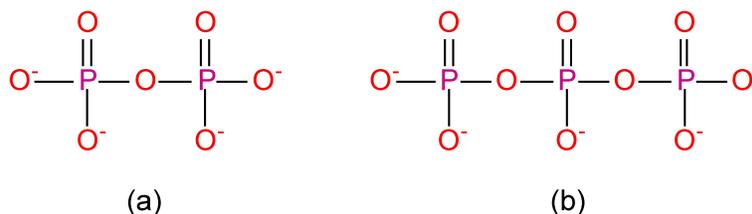
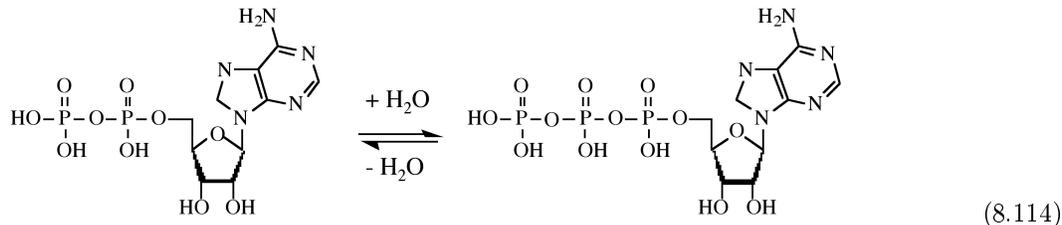


Figure 8.53: The structures of the (a) diphosphate and (b) triphosphate anions.

The monoesters of the diphosphate and triphosphate are very important in biological processes. In particular the conversion of the triphosphate ATP (adenosine triphosphate) to the diphosphate ADP (adenosine diphosphate) by the transfer of a phosphate group, (8.114), is important in the energetics of biological reactions.



8.4.4.3.3 Cyclic polyphosphates

Also known as meta phosphates, cyclic phosphates are also made from fused PO_4 units. The simplest, $\text{P}_3\text{O}_9^{3-}$, is shown in Figure 8.54. Slow addition of water to P_4O_{10} results in the formation of the tetrameric polyphosphate, $\text{P}_4\text{O}_{12}^{4-}$ (Figure 8.55), which is known as *calgon* due to its ability to complex Ca^{2+} as well as other metals.

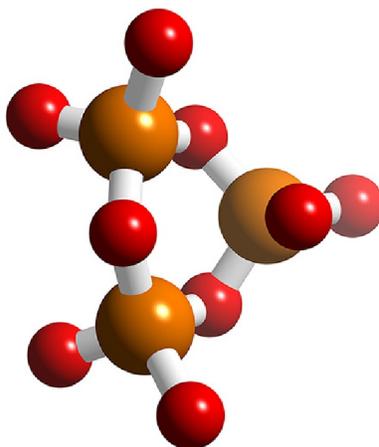


Figure 8.54: The structure of $\text{P}_3\text{O}_9^{3-}$. Phosphorus atoms are represented by the large spheres, and oxygen atoms by the small spheres (Copyright: Karl Harrison, 2005).

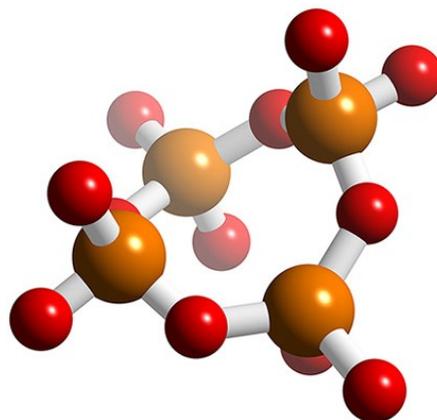
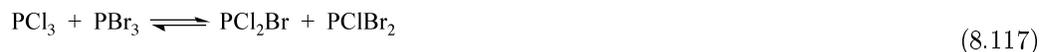


Figure 8.55: The structure of $P_4O_{12}^{4-}$ *calgon*. Phosphorus atoms are represented by the large spheres, and oxygen atoms by the small spheres (Copyright: Karl Harrison, 2005).

8.5 Halides of Phosphorous¹³

8.5.1 Phosphorous trihalides

Phosphorous trihalides, PX_3 , are produced from the direct reaction of phosphorous with the appropriate halogen, (8.115). The fluoride is readily made from the halide exchange reaction of PCl_3 with fluoride salts, (8.116). Mixed trihalides are formed by halide exchange, (8.117).



A summary of the physical properties of the phosphorous trihalides is given in Table 8.13. All the compounds have a pyramidal structure in the vapor phase and in solution.

Compound	Mp ($^{\circ}C$)	Bp ($^{\circ}C$)	P-X (\AA)	X-P-X ($^{\circ}$)
PF_3	-151.5	-101.8	1.56	96.3
PCl_3	-93.6	76.1	2.04	100
PBr_3	-41.5	173.2	2.22	101
PI_3	61.2	200 (dec.)	2.43	102

¹³This content is available online at <<http://cnx.org/content/m35020/1.1/>>.

Table 8.13: Selected physical properties of the phosphorous trihalides.

The phosphorous trihalides hydrolyze to phosphoric acid, (8.118), and undergo alcoholysis to form the trialkyl phosphite derivative, (8.119). Phosphorous trifluoride is only slowly hydrolyzed by water, but reacts readily with alkaline solutions. In contrast, phosphorous triiodide is an unstable red solid that reacts violently with water. Phosphorous trichloride in particular is an excellent synthon for most trialkyl phosphines, (8.120).



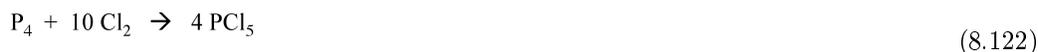
As with other P(III) compounds such as trialkyl phosphines, phosphorous trihalides can be oxidized to the analogous phosphene oxide, e.g., (8.121).



Phosphorous trihalides form Lewis acid-base complexes with main group metals, but the bonding to d^n ($n \neq 0$) transition metals occurs in the same manner to that of trialkyl phosphine, i.e., with $d\pi$ - $p\pi$ back donation. In fact one of the first examples of complexation of phosphorous to a low oxidation metal was the formation of PF_3 complexes with Fe-porphyrin.

8.5.2 Phosphorous pentahalides

The reaction of white phosphorous with excess halogen yields the pentahalides, (8.122). However, the pentafluoride is best prepared by halide exchange, (8.123).



The pentaiodide is unknown, however, selected physical properties are given for the others in Table 8.14.

Compound	Mp (°C)	Bp (°C)
PF_5	-93.78	-84.5
PCl_5	166.8	160 (subl.)
PBr_5	100	106.0

Table 8.14: Selected physical properties of phosphorous pentahalides.

The structures of the phosphorous pentahalides are all trigonal bipyramidal in the gas phase (Figure 8.56). Phosphorous pentafluoride maintains the trigonal bipyramidal structure in solid state, but the chloride and bromide are ionic solids, $[\text{PCl}_4]^+[\text{PCl}_6]^-$ and $[\text{PBr}_4]^+\text{Br}^-$ (Figure 8.57), respectively. The tetrahedral $[\text{PCl}_4]^+$ ion is also formed with the reaction of PCl_5 with other chloride ion acceptors, (8.124) and (8.125).



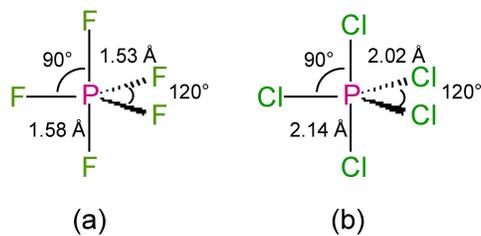


Figure 8.56: The structures of (a) PF_5 and (b) PCl_5 .

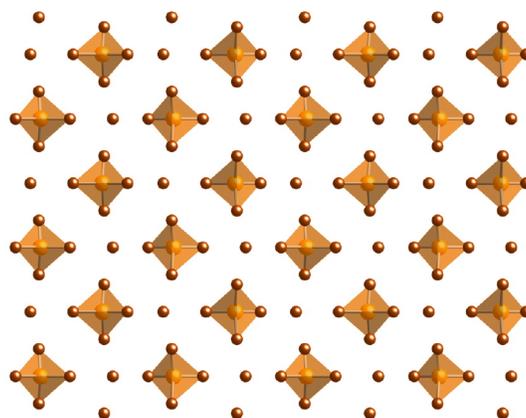


Figure 8.57: The crystal structure of phosphorous pentabromide.

All of the pentahalides undergo thermal decomposition, (8.126).



Careful hydrolysis of the pentahalides yields the oxide of the appropriate trihalide, (8.127), while excess hydrolysis yields phosphoric acid, (8.128).



