Group V

The elements of Group V are:

	symbol	electron configuration
nitrogen	N	$[He]2s^2 2p^3$
phosphorus	P	$[Ne]3s^2 3p^3$
arsenic	As	$[Ar]3d^{10} 4s^2 4p^3$
antimony	Sb	$[Kr]4d^{10} 5s^2 5p^3$
bismuth	Bi	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$

The most important members of this Group are nitrogen and phosphorus. The other elements will mostly not be considered here.

Appearance

The appearance of the Group V elements varies widely. Nitrogen is a colourless, odourless gas; phosphorus exists in white, red and black solid forms; arsenic is found in yellow and grey solid forms; antimony is found in a metallic or amorphous grey form; and finally bismuth is a white, crystalline, brittle metal. These appearances reflect the changing nature of the elements as the Group is descended, from non-metal to metal.

General Reactivity

The elements of Group V show a marked trend towards metallic character on descending the Group. This trend is reflected both in their structures and in their chemical properties, as for example in the oxides which become increasingly basic.

Occurrence

Nitrogen is found in the atmosphere, and makes up 78% of the air by volume. Phosphorus is not found free in nature, but occurs in several minerals and ores such as phosphate rock. The other elements are all found in the elemental form in the earth’s crust, but more frequently as minerals.

Physical Properties

The physical properties of this Group vary widely as nitrogen is a gas, and the other elements are solids of increasingly metallic character.

Nitrogen exists as the diatomic molecule N_2. It is a colourless, odourless gas, which condenses to a colourless liquid at 77K. The strength of the bond and the short bond length provide evidence for the bond between the N atoms being a triple bond.

Phosphorus has at least 2 allotropes, red and white phosphorus. White phosphorus is a solid composed of covalent tetrahedral P_4 molecules, and red phosphorus is an amorphous solid which has an extended covalent structure.

The covalent radii of the atoms increase on descending the Group. However, the N atom is anomalously small and so it can multiple-bond to other N, C and O atoms.

Chemical Properties

Both nitrogen and phosphorus exist in oxidation states +3 and +5 in their compounds. Nitrogen is very unreactive, mainly because its bond enthalpy is very high (944 kJ mol^{-1}). The only element to react with nitrogen at room temperature is lithium, to form the nitride Li_3N. Magnesium also reacts directly, but only when ignited. Some micro-organisms, however, have developed a mechanism for reacting directly with nitrogen gas and building it into protein - this is called nitrogen fixation, and is an important early step in the food chain.

Phosphorus is more reactive than nitrogen. It reacts with metals to form phosphides, with sulphur to form sulphides, with halogens to form halides, and ignites in air to form oxides. It also reacts with both alkalis and concentrated nitric acid.

Oxides

There are 5 oxides of nitrogen, with N ranging in oxidation number from +1 to +5; N_2O, NO, N_2O_3, NO_2, N_2O_5. There are also 2 important oxoacids of nitrogen - nitric (III) acid (nitrous acid) HONO, and nitric (V) acid (nitric acid) HNO_3. Nitric acid is highly reactive, and behaves as an oxidising agent and a nitrating agent as well as an acid.

There are many oxoacids of phosphorus, the most important being phosphoric acid $(HO)_3PO$. This is produced on a large scale commercially as it is used in the manufacture of fertilisers.

Halides

The nitrogen halides $N(hal)_3$ all have covalent, pyramidal structures. More important are the 2 series of phosphorus halides, $P(hal)_3$ and $P(hal)_5$

Compounds with hydrogen

The most important of these is ammonia, NH_3. During the industrial synthesis of ammonia the inert nitrogen obtained from the air is made into a reactive compound, ammonia, thus making atmospheric nitrogen available for many reactions. Ammonia is a reducing agent, but can be reduced by stronger reducing agents such as sodium metal. Ammonia is also a Lewis base, as it has a lone pair of electrons.

Phosphine, PH_3, is also a Lewis base but is less soluble in water than ammonia because it does not form hydrogen bonds.

Oxidation States and Ionisation Energies

The elements of this Group have the general electron configuration ns^2np^3. They all exhibit an expected oxidation state of +3 arising from the 3 unpaired p electrons, but also an oxidation state of +5. In all the elements except N this is made possible by promotion of an s electron to an available d orbital. Nitrogen is remarkable for its wide range of oxidation states ranging from -3 to +5.

In this Group the first 5 ionisation energies are relatively low, reflecting the removal of the 2 s and 3 p electrons. There is a larger increase between the 5th and 6th ionisation energies as an electron is removed from the inner, filled quantum shell.

Industrial Information

For industrial use nitrogen is obtained by tractional distillation of the air. It is used for the manufacture of ammonia by the Haber-Bosch Process:

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

A catalyst of finely-divided iron is required for this equilibrium reaction. The mixture is heated to 450°C at 250 atm of pressure. The yield of ammonia is increased by working at high pressure, but this adds to the cost of the plant, and a compromise between cost and yield is needed. The reaction is exothermic so the yield of ammonia is increased by low temperatures, but this slows up the reaction so again a compromise is needed. At the temperatures and pressures used in practice about 15% conversion is attained. The ammonia is condensed and removed from the plant and the unreacted gases are recirculated.

Ammonia has numerous uses - approximately 100 megatonnes are produced worldwide each year. It is used as a fertiliser both directly and after conversion to other fertilisers such as ammonium nitrate. It is also a raw material for nitric acid manufacture and for the production of nylon.

Gaseous nitrogen is used to provide an inert atmosphere for reactions which cannot be carried out in oxygen. It is also used as a carrier gas in liquid-gas chromatography. Phosphorus is used in match-heads and on safety match boxes.

Further Information

For further information look up the individual elements.

Data

	Atomic Number	Relative Atomic Mass	Melting Point/K	Density/kg m^{-3}
N	7	14.007	63.29	1.2506
P	15	30.974	317.3	1820 (white)
As	33	74.92	1090	5780
Sb	51	121.75	903.89	6691
Bi	83	208.98	544.5	9747

Ionisation Energies/kJ mol^{-1}

	1st	2nd	3rd	4th	5th	6th
N	1402.3	2856.1	4578	7474.9	9440	53265.6
P	1011.7	1903.2	2912	4956	6273	21268
As	947.0	1798	2735	4837	6042	12305
Sb	833.7	1794	2443	4260	5400	10400
Bi	703.2	1610	2466	4372	5400	8520

	Atomic Radius/nm	Covalent Radius/nm	Ionic Radius/nm
N	0.0549	0.070	
P	0.1105	0.110	
As	0.1245	0.121	
Sb	0.145	0.141	
Bi	0.154	0.146	0.117 (Bi^{3+})