

## 12.6: Group VA Elements

Although all the elements in this group form compounds in which their oxidation state of +5 equals the group number, their other properties vary considerably. Nitrogen is clearly nonmetallic and consists of diatomic triply-bonded  $N_2$  molecules.

Phosphorus, also a nonmetal, exists as tetrahedral  $P_4$  molecules (Figure 12.6.1a) in the vapor and the white allotropic form of the solid. On standing, white phosphorus slowly changes to the red allotrope, whose structure is shown in Figure 12.6.1c. The most stable form of the element is black phosphorus, which has a layer structure (Figure 12.6.1b). Black phosphorus can be made by heating the white form with a mercury catalyst for 8 days at 220 to 370°C.

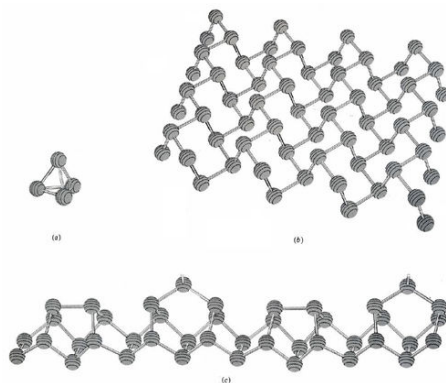


Figure 12.6.1 Allotropic forms of phosphorus. (a)  $P_4$  molecule of phosphorus vapor and solid white phosphorus; (b) layer structure of black phosphorus; (c) chain (polymeric) structure of red phosphorus. Note that in all structures each phosphorus atom forms three bonds.

Arsenic is a semimetal and consists of  $As_4$  molecules in the gas phase. When  $As_4(g)$  is condensed to a solid, three allotropes may form. The most stable of these is metallic arsenic, in which each arsenic atom has three nearest neighbors, with three more arsenic atoms somewhat farther away.

Antimony, also a semimetal, has two allotropes, the more stable one being metallic, like arsenic. In the case of bismuth, only the metallic form occurs. Note that for all the group VA elements the  $8 - N$  rule is followed. The number of bonds or nearest neighbors for each atom is 8 minus the group number in  $N \equiv N$ ,  $P_4$ , and even in the metallic forms of As, Sb, and Bi. The table summarizes the atomic properties of the group VA elements. Overall, the trends are what we would expect, based on our experience with previous groups. These elements exhibit a much wider variety of oxidation states, however, especially in the case of nitrogen. This element forms compounds in which it has every possible oxidation number from  $-3$  (the group number minus 8) to  $+5$  (the group number). As in previous groups, the oxidation state in which the  $ns^2$  pair of electrons is not used for bonding becomes more prominent toward the bottom of the periodic table. There are a few compounds,  $Bi(NO_3)_3$ , for example, in which discrete  $Bi^{3+}$  ions are present.

Table 12.6.1 : Properties of the Group VA Elements.

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm	
				Covalent	Ionic (Charge)
Nitrogen	N	$[He]2s^2 2p^3$	+5, +3, -3	70	(3-)171
Phosphorus	P	$[Ne]3s^2 3p^3$	+5, +3, -3	110	-
Arsenic	As	$[Ar]4s^2 3d^{10} 4p^3$	+5, +3	121	-
Antimony	Sb	$[Kr]5s^2 4d^{10} 5p^3$	+5, +3	141	-
Bismuth	Bi	$[Xe]6s^2 4f^{14} 5d^{10} 6p^3$	+5, +3	146	(3+)108

Symbol	Ionization Energy/MJ mol <sup>-1</sup>					Density/ g cm <sup>-3</sup>	Electro- negativity	Melting Point (in °C)
	First	Second	Third	Fourth	Fifth			
N	1.407	2.862	4.585	7.482	9.452	$1.25 \times 10^{-3}$	3.0	-210

Symbol	Ionization Energy/MJ mol <sup>-1</sup>					Density/ g cm <sup>-3</sup>	Electro- negativity	Melting Point (in °C)
P	1.018	1.909	2.918	4.963	6.280	1.82	2.1	44
As	0.953	1.804	2.742	4.843	6.049	5.72	2.0	817
Sb	0.840	1.601	2.450	4.271	5.403	6.69	1.9	631
Bi	0.710	1.616	2.472	4.380	5.417	9.80	1.9	271

The most important compounds of the group VA elements are those of nitrogen and phosphorus. Both elements are essential to all living organisms, and both are progressively removed from soil when plants are cultivated and crops harvested. According to Liebig's law of the minimum, an insufficient supply of either element can limit plant growth and reduce crop yields, and so these elements are important components of fertilizer. More recently both elements have been implicated in several kinds of pollution problems. As we discuss the properties of nitrogen and phosphorus compounds, their effects on food production and environmental degradation will also be discussed.

## Nitrogen

The importance of nitrogen fertilizer was first recognized over a century ago. By the late 1800s the only major ore of nitrogen, Chile saltpeter, NaNO<sub>3</sub>, was being mined in Chile and shipped to Europe for application to agricultural land, but the supply was obviously limited. Most nitrogen at the earth's surface is in the form of N<sub>2</sub>(g), which makes up 78 percent of the atmosphere by volume (or by amount of substance). Therefore chemists began to look for ways of obtaining nitrogen compounds directly from the atmosphere. Any process which does this is called **nitrogen fixation**.

Nitrogen fixation can occur naturally when an electrical discharge (lightning) heats air to a high temperature. The following reaction occurs:



The nitrogen monoxide (nitric oxide) formed can react further at ordinary temperatures, producing the brown gas, nitrogen dioxide:



The Lewis diagrams for these and other important nitrogen compounds are shown in Figure 12.6.2.

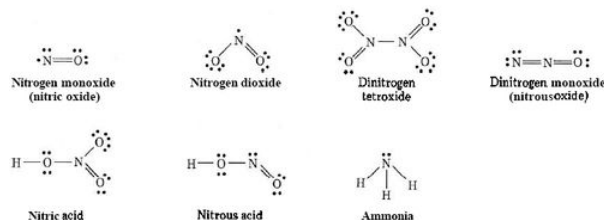
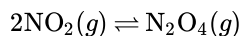


Figure 12.6.2: Lewis diagrams for important nitrogen compounds.

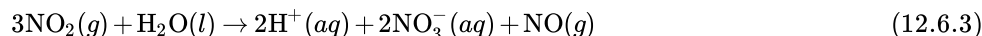
From the figure you can see that both NO and NO<sub>2</sub> have an odd number of electrons and violate the octet rule. In such a case it is common for two molecules to combine (dimerize) by pairing their odd electrons. In the case of NO<sub>2</sub>, dimerization occurs below room temperature, producing colorless dinitrogen tetroxide:



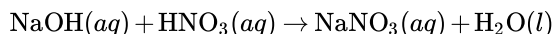
At room temperature, however, the NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> are in equilibrium, as evidenced by the brown color of the mixture. NO dimerizes only at very low temperatures in the solid state.

The first industrial nitrogen fixation was done by mimicking nature.

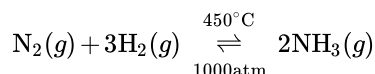
Reaction 12.6.1 was carried out in a plant near Niagara Falls, where hydroelectric generation provided inexpensive power to support an electric arc. NO was further oxidized to NO<sub>2</sub> which was dissolved in H<sub>2</sub>O to convert it to nitric acid, HNO<sub>3</sub>:



Note that  $\text{NO}_2$  is not the acid anhydride of  $\text{HNO}_3$ . This reaction involves, dis-proportionation of  $\text{NO}_2$  (which contains N in the +4 oxidation state) to form  $\text{HNO}_3$  in the +5 state and  $\text{NO}$  (N in the +2 state). The  $\text{NO}$  can be recycled by reoxidizing it to  $\text{NO}_2$ , and so it was not wasted. The  $\text{HNO}_3$  produced in Equation (12.5) was neutralized with  $\text{NaOH}$  to make a substitute for Chile saltpeter:

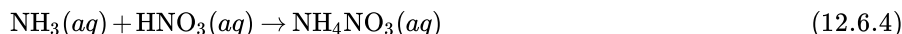


Fixation of nitrogen by the electric-arc process used a great deal of energy and was rather expensive. Other methods were designed to replace it, and the most successful of these is the **Haber process**, which is the major one used today. Nitrogen is reacted with hydrogen at a high temperature and extremely high pressure over a catalyst consisting of iron and aluminum oxide:

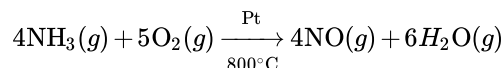


The ammonia produced by the Haber process is used directly as a fertilizer. It can be liquefied under pressure and injected through special nozzles about a foot under the soil surface. This prevents loss of gaseous ammonia which would otherwise irritate the nose, throat, and lungs of anyone near a fertilized field. You are probably familiar with the odor of ammonia since it is the most common weak base encountered in the chemical laboratory.

Prior to the recent development of underground injection techniques, most ammonia was converted to ammonium nitrate for fertilizer use:

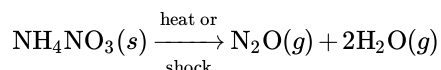


Except for ammonia, ammonium nitrate contains a greater mass fraction of nitrogen than any other compound of comparable cost. Ammonium nitrate manufacture requires that half the ammonia produced in the Haber process be converted to nitric acid. The first step is oxidation of ammonia over a catalyst of platinum metal:



This is called the Ostwald process. It is followed by Eqs. 12.6.2 and 12.6.3, yielding nitric acid, which can be combined with ammonia (Equation 12.6.4).

Nitric acid and nitrates have commercial applications other than fertilizer production. Because  $\text{NO}_3^-$  is a strong oxidizing agent, it reacts vigorously with substances whose elements are in low oxidation states. One example of this is black powder, which consists of charcoal (carbon), sulfur, and potassium nitrate,  $\text{KNO}_3$  (saltpeter or nitre). During the American revolution, for example, both armies had numerous persons whose job was to find caves in which the relatively soluble  $\text{KNO}_3$  had been deposited as water evaporated. A second example is nitroglycerin which contains carbon and hydrogen in low oxidation states as well as nitrate. Still another example of an explosive nitrate is  $\text{NH}_4\text{NO}_3$ , which contains nitrogen in its maximum and minimum oxidation state.  $\text{NH}_4\text{NO}_3$  decomposes as follows:

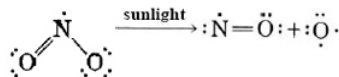


$$\Delta H_m = -37 \text{ kJ mol}^{-1}$$

The reaction is exothermic and produces 3 mol of gaseous products for every mole of solid reactant. This causes a tremendous increase in pressure, and, if the reaction is rapid, an explosion.

The compound dinitrogen monoxide (nitrous oxide or laughing gas), produced by decomposition of  $\text{NH}_4\text{NO}_3$ , is a third important oxide of nitrogen (in addition to  $\text{NO}$  and  $\text{NO}_2$ ).  $\text{N}_2\text{O}$  is produced during microbial decomposition of organic matter containing nitrogen. Because it is quite unreactive, it is the second most-concentrated nitrogen-containing substance in the atmosphere (after  $\text{N}_2$ ). It is used commercially as an anesthetic, is mildly intoxicating, and is poisonous in large doses.

The other two important oxides of nitrogen,  $\text{NO}$  and  $\text{NO}_2$ , play a major role in an air-pollution problem known as **photochemical smog** (or Los Angeles smog).  $\text{NO}$  is formed by Equation 12.6.1 in automobile engines and other high-temperature combustion processes. At normal temperatures  $\text{NO}$  is oxidized to  $\text{NO}_2$  (Equation 12.6.2). Both these oxides are free radicals and are rather reactive. Moreover, brown-colored  $\text{NO}_2$  absorbs sunlight, and the energy of the absorbed photons breaks a nitrogen-oxygen bond:

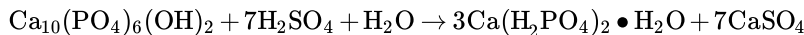


The oxygen atoms produced are highly reactive. They combine with hydrocarbon molecules (from evaporated or unburned gasoline) to form aldehydes, ketones, and a number of other compounds which form an almost fog-like cloud and irritate the eyes, throat, and lungs. Photochemical smog is especially bad in cities like Los Angeles and Denver which have lots of sunshine and automobile traffic, but its effects have been observed in every large city in the United States.

## Phosphorus

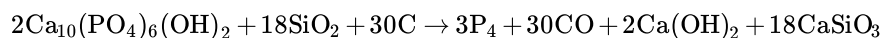
As in the case of carbon and silicon, there are major differences between the chemistries of nitrogen and phosphorus. The concentrations of phosphorus compounds in the earth's atmosphere are so small as to be negligible, but phosphorus is more abundant than nitrogen in the solid crust. Here it is found as phosphate rock, which is mainly hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , or fluorapatite,  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ . (These are the same substances involved in the discussion of dental decay in the section on group IVA elements.)

Phosphate rock is quite insoluble, and hence its phosphate ions cannot be assimilated by plants. Production of phosphate fertilizer requires treatment of apatite acid. This protonates the  $\text{PO}_4^{3-}$  ions, converting them to  $\text{H}_2\text{PO}_4^-$ , whose calcium salt is much more soluble:

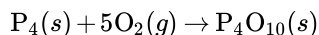


The compound  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  is known as superphosphate, and  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  is called triple superphosphate.

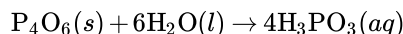
The phosphoric acid,  $\text{H}_3\text{PO}_4$ , used to make triple superphosphate is also obtained from phosphate rock. The first step is a reduction with carbon (coke) and silicon dioxide in an electric furnace:



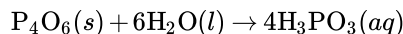
The phosphorus obtained this way is then oxidized to phosphorus pentoxide:



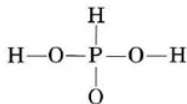
(The name phosphorus pentoxide for  $\text{P}_4\text{O}_{10}$  comes from the empirical formula  $\text{P}_2\text{O}_5$  of this compound.) Phosphorus pentoxide is the acid anhydride of phosphoric acid:



Although not a very strong acid, phosphoric acid is triprotic. Therefore, 1 mol of this acid can transfer 3 mol of protons to a strong base. There is another oxide of phosphorus,  $\text{P}_4\text{O}_6$ , which involves the +3 oxidation state, corresponding to use of the  $3p^3$ , but not the  $3s^2$ , electrons for bonding.  $\text{P}_4\text{O}_6$  is the acid anhydride of phosphorous acid,  $\text{H}_3\text{PO}_3$ :

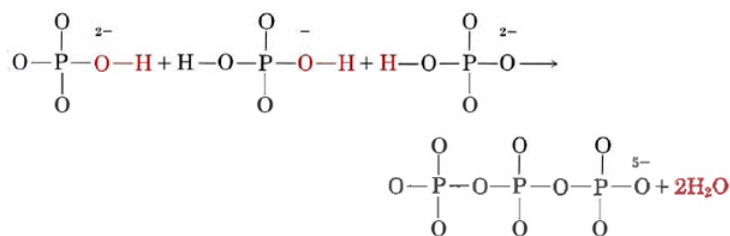


Phosphorous acid is quite weak, and, contrary to what its formula might suggest, can only donate two protons. This is apparently because its Lewis structure is

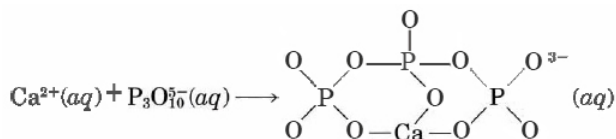


Only the two protons bonded to highly electronegative oxygen atoms are expected to be acidic.

Another major commercial use of phosphates is in laundry detergents. The problem of precipitation of soap by hard-water ions such as  $\text{Ca}^{2+}$  was mentioned in the section on alkaline earth metals. This can be prevented, and the cleaning power of synthetic detergents can be improved, by adding phosphates. The compound usually used is sodium tripolyphosphate, whose anion is a condensation polymer of hydrogen phosphate and dihydrogen phosphate ions:



The tripolyphosphate ion has numerous O atoms whose lone pairs of electrons can form coordinate covalent bonds to metal ions like  $\text{Ca}^{2+}$ :



The  $\text{Ca}^{2+}$  ions are effectively removed from solution (they are said to be **sequestered**) because they are bonded to the tripolyphosphate ion. Consequently  $\text{Ca}^{2+}(\text{aq})$  is not available to precipitate soap or detergent molecules.

The use of phosphates in detergents is responsible in part for an environmental problem known as **accelerated eutrophication**, or premature, aging of bodies of water. Over a period of many thousands of years, a lake or other body of water will slowly accumulate essential nutrient elements such as nitrogen or phosphorus because their compounds dissolve in streams that feed the lake. As the water becomes richer in nutrients, more plants and microorganisms can grow. Some of the organic matter which remains when these organisms die precipitates to the bottom of the lake and is not decomposed. Eventually the lake fills up with debris, becoming a swamp, and finally dry land.

This process of eutrophication can be greatly accelerated by human input of nutrients such as nitrogen or phosphorus fertilizers, or phosphates from detergents. Since reduction in the use of detergent phosphates would appear to have the least negative effects—people's clothes might not look as clean—many have suggested that prohibiting or limiting phosphate content is the way to solve the problem. Many states have passed laws implementing such limitations or bans.

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