The Free Atom

The free phosphorus or nitrogen atom has a quartet ground state. This means that there are three unpaired, spin-up electrons in the ground state (a closed-shell molecule with no unpaired electrons has a singlet ground state). For nitrogen, the valence electron configuration can be written as $(2s)^2(2p)^3$, while for P the valence configuration is $(3s)^2(3p)^3$. The valence orbital ionization energies (VOIE) for these levels are (approximately) -25 and -13 eV in the case of nitrogen, while for phosphorus, -19 and -10 eV, in keeping with the electronegativity values of 3.1 for N and 2.1 for P. Note that the electronegativity values for carbon (2.5) and hydrogen (2.2) fall in between those for N and P. Also remember that VOIE values correlate nicely with element electronegativity.

Single versus Triple bonds

bond	kJ/mol
N–N	159
N≡N	946
P–P	200
P≡P	490

The table gives typical values for the homolytic bond dissociation energy (BDE) of homonuclear single and triple bonds for nitrogen and phosphorus. A key observation is that while the N≡N triple bond (in the N_2 molecule) is almost twice as strong as the triple bond in the P_2 molecule, conversely, the single bond in the case of phosphorus, P–P, is stronger than the N–N single bond. The weak nature of the N–N single bond is attributed to lone pair (Pauli) repulsion, and this is a characteristic feature of bonds between very electronegative elements with lone pairs on adjacent atoms. The hydrazine molecule, H_2N–NH_2 is an example of a weak single bond for nitrogen, while hydrogen peroxide, HO–OH, provides an example for oxygen, and F_2 for fluorine.

From the table we also see that the BDE value for the N≡N bond is greater than the sum of three N–N single bond energies. On the contrary, the sum of three P–P single bond energies exceeds the value for the P≡P triple bond. This is in keeping with the observation that the only stable form of elemental nitrogen is as the diatomic N_2 molecule, while in the case of phosphorus, the only stable molecular form of the element is as the tetrahedral P_4 molecule (white phosphorus).

As to the thermodynamic stability of triple bonded systems of this type, the ΔH_f° values for P_2 and P≡N are respectively $+144$ and $+104$ kJ/mol, the positive values for heat of formation indicating instability with respect to the elements in their standard state.

Reactive if Generated

While P_2 is not stable, and to generate it from P_4 by heating requires temperatures close to 1100 K, evidence is building that the P_2 molecule is reactive if generated under milder conditions amenable to organic transformations. One way to generate P_2 close to 25 °C is to irradiate mixtures that contain P_4 using ultraviolet light. The P_2 molecule is thought to be an intermediate in the photochemical transformation of white phosphorus into red phosphorus. Carrying out UV irradiation of P_4 in the presence of organic 1,3-diene molecules both suppresses the formation of red phosphorus and represents a synthetic route to double Diels-Alder adducts of P_2 with the dienes. In such a process, both π bonds of the P_2 molecule are replaced with four P–C single bonds, the reactive P_2 molecule being an excellent Diels-Alder dienophile.

Comparing NH_3 with PH_3

Ammonia has $\angle(\text{H–N–H}) = 107°$, while the value for phosphine of $\angle(\text{H–P–H})$ is much smaller, close to $93°$. In turn, this means that the hybridization of the nitrogen lone pair in ammonia is close to sp^3, while that at the phosphorus in phosphine is closer to pure s in character. This is consistent with the low basicity and nucleophilicity of phosphine as compared with ammonia, since in the case of PH_3 the lone pair resides mostly in an energetically low-lying s atomic orbital.

Another key property that differentiates ammonia and phosphine is the ease of undergoing the "umbrella" inversion at the central atom. This is the motion that takes the initial C_{3v} structure along an excursion to a D_{3h} transition state, and along to a new C_{3v} geometry such that the molecule appears to have rotated by $180°$. In the case of ammonia, the energy barrier associated with reaching the D_{3h} transition state is small, only ca. 24.7 kJ/mol. When we recognize that in the D_{3h} transition state the central-atom lone pair resides in a pure p_z orbital, we see that ammonia does not resist putting nitrogen s character into its N–H bonds and housing its lone pair in a pure p orbital. On the contrary, PH_3 has a much higher barrier to inversion, approximately 155 kJ/mol. This means that the inversion frequency for NH_3 is greater than that for PH_3 by a factor of 4000! Clearly, the central phosphorus atom in PH_3 strongly *resists* putting s character into its P–H bonds and resists putting p character into its lone pair.

Bent's Rule

After examining a large number of structures of p-block element compounds, Bent formulated the following important rule: "s character concentrates in orbitals directed toward electropositive substituents". In demonstration of this concept, silylamines such as $N(SiMe_3)_3$ are planar at nitrogen, rather than pyramidal as in the case of ammonia. This maximizes the s-character in the bonds to the electropositive silicon substituents. Using the rule in reference to the comparison between NH_3 and PH_3, hydrogen (EN = 2.2) is *relatively* more electronegative with respect to P (EN = 2.1) than N (EN = 3.1) and thus the p-character maximizes in the P–H bonds of PH_3.

First Industrial Nitrogen Fixation

In 1903 the process used for fixing nitrogen industrially was the energy-intensive one that used an electric arc furnace to combine nitrogen directly with oxygen and water making nitric acid:

$$0.5N_2 + 1.25O_2 + 0.5H_2O \rightarrow HNO_3 \tag{1}$$

This process is thermodynamically downhill with $\Delta H°_{\text{rxn}} = -30.3$ kJ/mol, but the high kinetic barrier to the process is what demands great energy input to make the reaction take place at an appreciable rate. Indeed, it is fortunate for life on Earth that there is a high barrier to this reaction, otherwise our atmosphere would be devoid of oxygen and the world's oceans would consist of dilute aqueous nitric acid!

Modern HNO_3 Synthesis

The modern synthesis of nitric acid is based on the catalytic oxidation of NH_3, and therefore it relies on the Haber-Bosch ammonia synthesis process for nitrogen fixation. The process, developed by W. Ostwald (Nobel Prize, 1909), involves passing a mixture of gases (90% air, 10% NH_3) over a

hot Pt gauze catalyst with ca. 1 ms contact time (850 °C, 5 atm) to provide aqueous ammonia (60% NH_3) as the condensate product. The reaction runs at ca. 96% conversion of starting materials to the desired product, thus representing one the most efficient industrial catalytic reactions known.

The success of the catalytic reaction hinges on the selective oxidation of ammonia to NO (nitric oxide) in the first step:

$$NH_3 + 1.25O_2 \rightarrow NO + 1.5H_2O \tag{2}$$

The subsequent steps are likely facile as uncatalyzed reactions under the conditions of temperature and pressure that are used:

$$NO + 0.5O_2 \rightarrow NO_2 \tag{3}$$

$$NO_2 + 0.33H_2O \rightarrow 0.66HNO_3 + 0.33NO \tag{4}$$
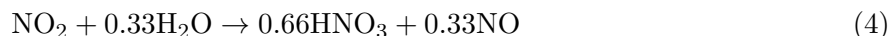
Multiplying the latter two steps by 1.5 and adding together the three steps gives the overall reaction:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O \tag{5}$$

This reaction is exothermic with $\Delta H^{\circ}_{\text{rxn}} = -412.6$ kJ/mol.

Nitrate versus Metaphosphate

The nitrate ion, $[NO_3]^-$ has D_{3h} symmetry and exists as a monomeric entity with delocalized π bonding. In contrast, metaphosphate exists either as cyclic oligomers such as trimetaphosphate $[PO_3]_3^{3-}$ and tetrametaphosphate, $[PO_3]_4^{4-}$, or as linear chain polymers whose structure is similar to the triphosphate chain found in ATP. In the metaphosphate structures (as in ATP) the geometry at phosphorus is tetrahedral, with each phosphorus surrounded by four oxygen atoms.

Nitrogen Oxides

Nitrogen forms a variety of interesting molecular oxides, some of which are simple examples of stable free radicals. Nitrous oxide (N_2O, laughing gas, point group $C_{\infty v}$) has a closed-shell singlet ground state and is isoelectronic with CO_2; like the latter it is kinetically quite unreactive. Nitric oxide (NO) in contrast has a doublet ground state (one unpaired electron in the π^* orbital manifold) and a bond order of 2.5; this molecule has great importance in biology for signal transduction and as a vasodilator. It is produced in biological systems by the enzyme nitric oxide synthase (NOS). Dinitrogen trioxide, N_2O_3, is a blue solid with C_s symmetry and a long N–O bond; upon warming it dissociates into gaseous NO and NO_2. The latter, nitrogen dioxide, a brown gas, is a doublet ground state radical having C_{2v} molecular symmetry. The nitrite ion (conjugate base of nitrous acid) is similar in structure (bent) but is closed-shell with a negative charge: $[NO_2]^-$. Dinitrogen tetroxide, N_2O_4, like ethylene has D_{2h} molecular symmetry and is the dimer of nitrogen dioxide, existing in the solid state or as a colorless liquid with a long N–N bond. Nitrogen oxides as pollutants are known collectively as NO_x or NOX.

Nitrogen Hydrides

Ammonia ($\Delta H_f^\circ = -46$ kJ/mol) as a liquid (b.p. $-33\,^\circ$C) is a strongly ionizing solvent that dissolves alkali metals to give blue solutions containing solvated electrons!

Hydrazine ($\Delta H_f^\circ = +50$ kJ/mol) is an unstable, fuming colorless liquid with a molecular dipole moment of 1.85 D (ruling out the C_{2v} conformer). It is prepared by the oxidation of ammonia with sodium hypochlorite (bleach):

$$2\mathrm{NH_3} + \mathrm{NaOCl} \rightarrow \mathrm{N_2H_4} + \mathrm{NaCl} + \mathrm{H_2O} \tag{6}$$
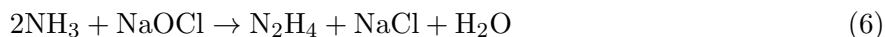
Hydrazine is used as rocket fuel and it burns rapidly and completely in air:

$$\mathrm{N_2H_4} + \mathrm{O_2} \rightarrow \mathrm{N_2} + 2\mathrm{H_2O} \tag{7}$$

The above combustion reaction is quite exothermic with $\Delta H_\mathrm{rxn}^\circ = -621.5$ kJ/mol.

Diazene, $\mathrm{N_2H_2}$, exists in *cis* or *trans* configurations both with an N=N double bond, and is not sufficiently stable for isolation ($\Delta H_f^\circ = +213$ kJ/mol) and even is difficult to observe due to its high reactivity and consequent transient nature.

Hydrazoic azide ($\mathrm{HN_3}$, hydrogen azide) is a very nitrogen-rich and unstable compound ($\Delta H_f^\circ = +269.5$kJ/mol), being also a poisonous and explosive gas. Curtius described its preparation in 1890 via reaction of hydrazine with nitrous acid:

$$\mathrm{N_2H_4} + \mathrm{HONO} \rightarrow \mathrm{HN_3} + 2\mathrm{H_2O} \tag{8}$$