

Chapter 15

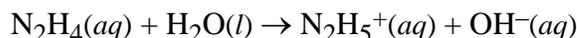
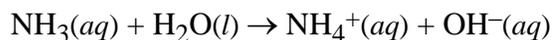
THE GROUP 15 ELEMENTS

Exercises

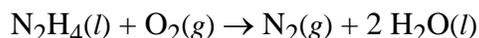
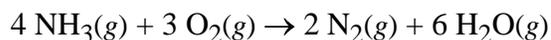
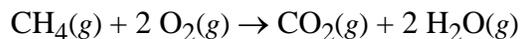
- 15.1 (a) $\text{AsCl}_3(l) + 3 \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{AsO}_3(aq) + 3 \text{HCl}(g)$
(b) $3 \text{Mg}(s) + \text{N}_2(g) \rightarrow \text{Mg}_3\text{N}_2(s)$
(c) $\text{NH}_3(g) + 3 \text{Cl}_2(g) \rightarrow \text{NCl}_3(l) + 3 \text{HCl}(g)$
(d) $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3 \text{H}_2(g)$
(e) $\text{N}_2\text{H}_4(l) + \text{O}_2(g) \rightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(g)$
(f) $\text{NH}_4\text{NO}_3(aq) \rightarrow \text{N}_2\text{O}(g) + 2 \text{H}_2\text{O}(l)$
(g) $2 \text{NaOH}(aq) + \text{N}_2\text{O}_3(aq) \rightarrow 2 \text{NaNO}_2(aq) + \text{H}_2\text{O}(l)$
(h) $2 \text{NaNO}_3(s) \rightarrow 2 \text{NaNO}_2(s) + \text{O}_2(g)$
(i) $\text{P}_4\text{O}_{10}(g) + \text{C}(s) \rightarrow \text{P}_4(g) + 10 \text{CO}(g)$

15.3 Arsenic has both metallic and nonmetallic allotropes; its oxides are amphoteric, while its chemistry mostly resembles nonmetallic phosphorus.

15.5 The first point of contrast is the difference in boiling points: the nonpolar hydrocarbons have very low boiling points, while the hydrogen-bonding hydrides of nitrogen have much higher boiling points. Following from this, they have different acid-base properties, both hydrides of carbon being neutral while those of nitrogen are basic:



The most obvious difference is in their combustions, both hydrocarbons producing carbon dioxide while the nitrogen hydrides produce nitrogen gas:



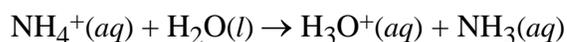
15.7 (a) Nitrogen has a very strong nitrogen-nitrogen triple bond; hence any reaction that produces dinitrogen will have a strongly negative enthalpy contribution even before the other terms in the energy cycle are included.

Also, being a gas, its formation will contribute a positive factor to the entropy change.

(b) Though dinitrogen is often the thermodynamically preferred product, kinetic factors (that is, comparative activation energies) can lead to other products.

15.9 Air contains about 1 percent argon. Thus as the unreacted gases are recycled and additional air is added, the argon proportion will continuously increase. One possibility would be to cool the mixture and have the argon condense out, since it has a boiling point higher than dinitrogen or dihydrogen. However, the energy requirements for this procedure would probably be prohibitive. Alternatively, the used gases could be periodically siphoned off and the dihydrogen burned as an energy source.

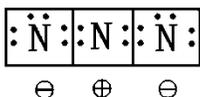
15.11 Though the ammonium ion is very similar to an alkali metal ion in terms of charge density (thus stabilizing large, low-charge anions) and compound solubility, it has two major differences. First, a solution of the ion is acidic, not neutral, due to the following equilibrium:



Second, its compounds are all very thermally unstable, unlike those of the alkali metal ions, and the products are quite dissimilar. For example, ammonium nitrate decomposes on gentle heating to give dinitrogen oxide and water, while sodium nitrate upon very strong heating forms sodium nitrite and dioxygen:



15.13 The least formal charge is provided by the following representation of two double bonds:



15.15 The chemical equation is



$$\text{Mole of NaN}_3 = 7.7 \times 10^{-2} \text{ mol}$$

$$\text{Mole of N}_2 = 0.11(5) \text{ mol}$$

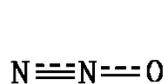
$$\text{Volume of gas} = nRT/P$$

$$= (0.115 \text{ mol})(8.31 \text{ kPa}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298\text{K})/(102 \text{ kPa})$$

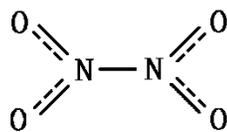
$$= 2.8 \text{ L}$$

15.17 It is ammonia that has the “anomalous” boiling point as a result of the strong hydrogen bonds between neighboring ammonia molecules.

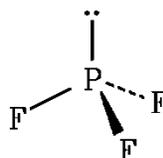
15.19 The shapes are:



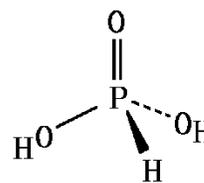
(a)



(b)

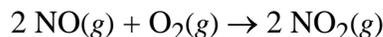


(c)



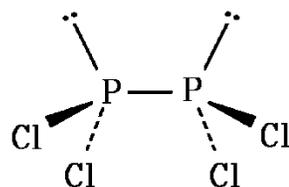
(d)

15.21 The reaction



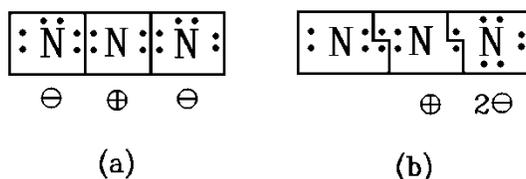
is performed under high pressure because the reaction direction is favored that will result in the lesser moles of gas. A low temperature will increase the yield, as the forward process is exothermic. Both conclusions are in accordance with Le Chatelier's principle.

15.23 White phosphorus is a very reactive, white, waxy substance that consists of P_4 molecules, shown in (a), while red phosphorus is a red powdery solid that consists of long polymer chains of linked P_4 units, shown in (b). White phosphorus burns in contact with the oxygen in air, while red is air-stable. The white allotrope melts in hot water and is very soluble in nonpolar solvents, while the red allotrope is high melting and is insoluble in all solvents.

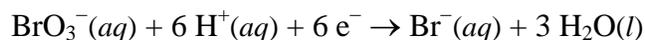
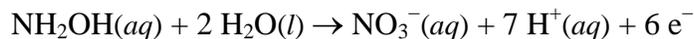


15.31 The bromine atom is probably too large for six of them to be accommodated around a phosphorus atom.

15.33 In hydrogen azide, formal charge arguments would give an equal weighting to the double-double and single-triple nitrogen-nitrogen bonds. As can be seen from figure (a), for the azide ion, the double-double nitrogen-nitrogen bond is strongly preferred.



15.35 Half reactions:



Overall reaction:



15.37 $\text{NOF}(g) + \text{SbF}_5(l) \rightarrow \text{NO}^+(\text{SbF}_5) + \text{SbF}_6^-(\text{SbF}_5)$

15.39 $\text{H}_2\text{S}_2\text{O}_7$ and $\text{H}_6\text{Si}_2\text{O}_7$.

15.41 (a) Rapid algae growth leading to a depletion of dissolved dioxygen in lakes and rivers.

(b) Mutually beneficial relationship between two organisms.

(c) Use of a chemical compound to combat disease.

(d) Geological name of calcium hydroxide phosphate that is the bone material.

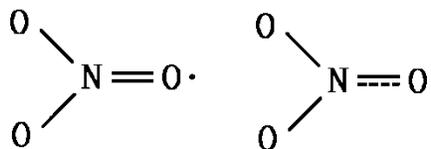
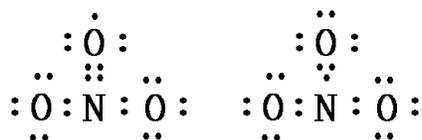
Beyond the Basics

15.43 The initial products are PH_4^+ and Cl^- (analogous to ammonia). The chloride ion then reacts with the electron-pair acceptor BCl_3 to give BCl_4^- .

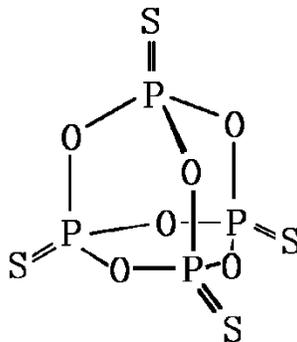


In the first reaction, phosphine is the Lewis base, hydrogen chloride the Lewis acid. In the second reaction, it is the chloride ion that is the base; boron trichloride is the acid.

15.45 There are two alternatives, one with the single electron in a bond, the other with it on the double-bonded oxygen. In both cases, the bond angles should all be 120° . The average bond order would be 1.33 in the first case and 1.17 in the other.



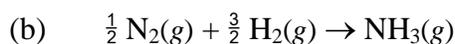
15.47 The most obvious structure would be that in which the four terminal oxygen atoms in P_4O_{10} are replaced by sulfur atoms.



15.49 The bonding between sodium and azide ions is likely to be predominantly ionic whereas that in the heavy metal azides (Fajan's rules) will be more covalent. It is the covalently bonded species, like hydrogen azide, that are more of an explosion hazard.

$$15.51 \quad (a) \quad \ln K = -\frac{\Delta G^\circ}{RT} = -\frac{-16 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K}} = +6.5$$

$$K = 6 \times 10^2$$



$$\Delta H^\circ = -46 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S^\circ = [(+193) - \frac{1}{2}(+192) - \frac{3}{2}(+131)] \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$= -100 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

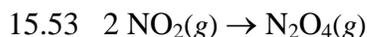
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -46 \text{ kJ} \cdot \text{mol}^{-1} - (775 \text{ K})(-0.100 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$$

$$= +32 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln K = -\frac{+32 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 775 \text{ K}} = -5.0$$

$$K = 7 \times 10^{-3}$$

(c) The rate of the reaction is as important as the yield. By performing the reaction at a higher temperature, equilibrium is attained much more rapidly.



$$\Delta H^\circ = [(+9) - 2(+33)] \text{ kJ} \cdot \text{mol}^{-1} = -57 \text{ kJ} \cdot \text{mol}^{-1}$$

Thus the N–N bond energy must be approximately $57 \text{ kJ} \cdot \text{mol}^{-1}$, assuming that the N–O bond strength remains the same.

15.55 The easiest way of solving the problem is to use the Henderson-Hasselbach equation that you should recall from your general chemistry courses:

$$pH = pK_a + \log_{10} \frac{[\text{base}]}{[\text{acid}]}$$

Let x = concentration of acid ion; then $(0.10 - x)$ = concentration of base ion.

$$6.80 = 7.21 + \log \frac{(0.10 - x)}{x}$$

$$x = [\text{acid}] = 0.072 \text{ mol}\cdot\text{L}^{-1}, [\text{base}] = 0.028 \text{ mol}\cdot\text{L}^{-1}$$

$$\text{Mass Na}_2\text{HPO}_4 = 4.0 \text{ g}, \text{ mass NaH}_2\text{PO}_4 = 8.6 \text{ g}$$

15.57 The comparable bond energies ($\text{kJ}\cdot\text{mol}^{-1}$) are shown below:

P–Cl	326	Cl–Cl	240
P–F	490	F–F	155

Assuming that the P–Cl bond has about the same energy in PCl_5 and PCl_3 , the dissociation energy is

$$[240 - 2(326)] \text{ kJ}\cdot\text{mol}^{-1} = 412 \text{ kJ}\cdot\text{mol}^{-1},$$

a significant amount of energy, but entropy will favor decomposition at high enough temperatures.

For the decomposition of PF_5 , the energy change will be

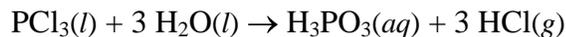
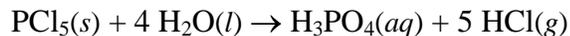
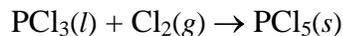
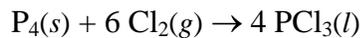
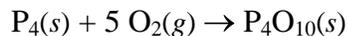
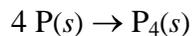
$$[155 - 2(490)] \text{ kJ}\cdot\text{mol}^{-1} = 825 \text{ kJ}\cdot\text{mol}^{-1}.$$

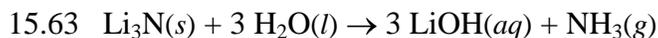
This much higher value results from fluorine bonds to other elements being stronger than those of chlorine to the same element, and the weakness of the F–F bond compared to the Cl–Cl bond.

15.59 $[\text{NF}_4]^+\text{F}^-$ — tetrafluoroammonium fluoride.

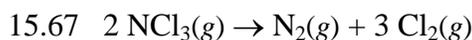
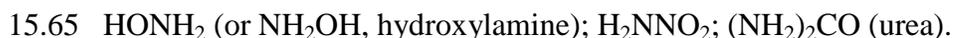
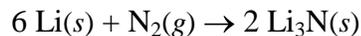
15.61 [A] Red phosphorus; [B] white phosphorus; [C] tetraphosphorus decaoxide;

[D] phosphoric acid; [E] phosphorus trichloride; [F] phosphorus pentachloride; [G] phosphorous/phosphonic acid.





This would be uneconomical, as one would need to produce lithium metal first, a highly energy-intensive electrolytic process, in order to synthesize the lithium nitride:



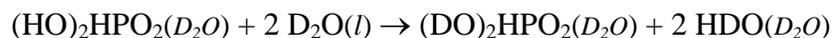
Using bond energy values from the Appendix:

Bonds broken:	$6(\text{N}-\text{Cl})$	$= 6(192 \text{ kJ})$	$= 1152 \text{ kJ}$
		Total	$= 1152 \text{ kJ}$
Bonds formed:	$(\text{N}\equiv\text{N})$		$= 942 \text{ kJ}$
	$3(\text{Cl}-\text{Cl})$	$= 3(240) \text{ kJ}$	$= 720 \text{ kJ}$
		Total	$= 1662 \text{ kJ}$

$$\text{Net energy change} = +1152 \text{ kJ} - 1662 \text{ kJ} = -510 \text{ kJ}$$

The reaction is highly exothermic due primarily to the strength of the nitrogen-nitrogen triple bond.

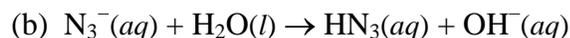
15.69 Only two hydrogens are replaced because the structure contains only two hydroxyl groups. The hydrogen bonded to the phosphorus is not labile and cannot be replaced.



15.71 NO_2^+ and CNO^- are isoelectronic with the azide ion.

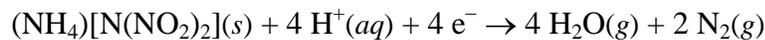
15.73 A very large low-charge anion – such as the hexafluoroosmate ion, $[\text{OsF}_6]^-$ ion – might stabilize the pentanitrogen cation.

15.75 (a) Silver(I) or lead(II) or mercury(I).

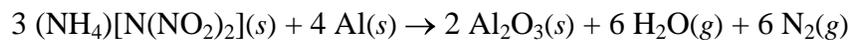


(c) The azide ion will decompose on heating to give nitrogen gas.

15.77 We can write half-reactions as if the reaction took place in solution, provided that when the final balanced equation is derived, the hydrogen ions and electrons “cancel out.”



Balanced equation:



Reasons for its exothermicity:

- (a) the formation of dinitrogen, with its strong triple bond;
- (b) the formation of water with strong (O–H) bonds;
- (c) the formation of aluminum oxide with the very high lattice energy

It would be a good propellant because of the large volume of gas produced per mole of ADN.

15.79 Zinc and sulfuric acid are added to the sample, which we will assume contains the arsenate ion:



The hydrogen gas reduces the arsenate ion to arsine:



The released arsine gas is then passed through a hot tube where it decomposes to give a metallic-looking deposit of arsenic:

