

## Chapter 15

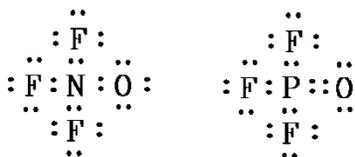
### THE GROUP 15 ELEMENTS

#### Exercises

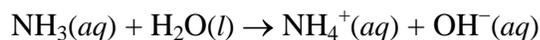
- 15.2 (a)  $\text{NH}_4\text{NO}_2(aq) \rightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(l)$   
(b)  $(\text{NH}_4)_2\text{SO}_4(aq) + 2 \text{NaOH}(aq) \rightarrow \text{Na}_2\text{SO}_4(aq) + 2 \text{NH}_3(g) + 2 \text{H}_2\text{O}(l)$   
(c)  $3 \text{NH}_3(g) + \text{H}_3\text{PO}_4(aq) \rightarrow (\text{NH}_4)_3\text{PO}_4(aq)$   
(d)  $2 \text{AgN}_3(s) \rightarrow 2 \text{Ag}(s) + 3 \text{N}_2(g)$   
(e)  $\text{NO}(g) + \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_3(l)$   
(f)  $\text{Pb}(\text{NO}_3)_2(s) \rightarrow \text{PbO}(s) + 2 \text{NO}_2(g) + \frac{1}{2} \text{O}_2(g)$   
(g)  $\text{P}_4(s) + 5 \text{O}_2(g) \rightarrow \text{P}_4\text{O}_{10}(s)$   
(h)  $\text{Ca}_3\text{P}_2(s) + 6 \text{H}_2\text{O}(l) \rightarrow 3 \text{Ca}(\text{OH})_2(aq) + 2 \text{PH}_3(g)$   
(i)  $\text{N}_2\text{H}_4(aq) + \text{HCl}(aq) \rightarrow \text{N}_2\text{H}_5^+(aq) + \text{Cl}^-(aq)$   
 $\text{N}_2\text{H}_5^+(aq) + \text{HCl}(aq) \rightarrow \text{N}_2\text{H}_6^{2+}(aq) + \text{Cl}^-(aq)$

15.4 Unlike the other members of the group, nitrogen readily forms multiple bonds. As well, a nitrogen atom forms a maximum of four bonds, while atoms of other members of the group form compounds with up to six bonds. Finally, nitrogen has a much higher electronegativity than the other Group 15 elements, accounting for different reaction products in some cases and a very basic hydride, ammonia.

15.6 The central nitrogen atom is limited to four electron pairs in its outer electron set; hence the oxygen atom must be bonded as a coordinate covalent bond (or as a Lewis acid/base addition). Phosphorus can exceed the octet, and the oxygen atom forms a double bond with the phosphorus atom.

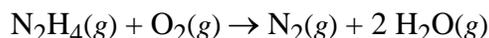


- 15.8 The terminology is inappropriate, for when ammonia dissolves in water, most of the ammonia is present as hydrated ammonia molecules; very little is there as ammonium and hydroxide ions. As well, the term implies that “ammonium hydroxide” is an actual isolable compound, which is not the case.



- 15.10 It is surprising that high temperatures are used because the reaction is exothermic. However, the overriding consideration must be the necessity for a rapid attainment of equilibrium (overcoming a high activation energy) rather than the optimum position of equilibrium.

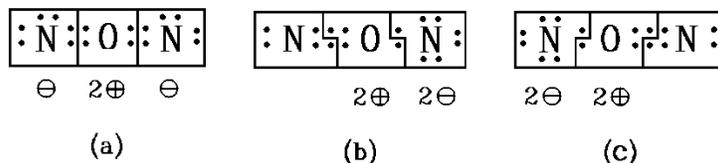
- 15.12 The chemical reaction is



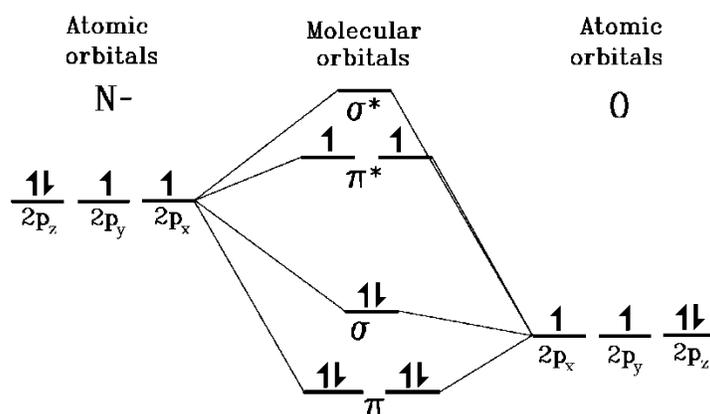
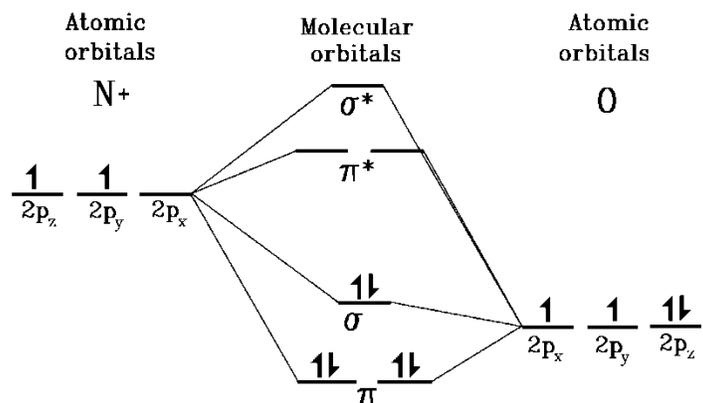
Using bond energy values from Appendix 3:

Bonds broken:	4(N–H)	= 4(386) kJ	= 1544 kJ
	1(N–N)	= 1(247) kJ	= 247 kJ
	1(O=O)	= 1(494) kJ	= 494 kJ
		Total	= 2285 kJ
Bonds formed:	1(N≡N)	= 1(942) kJ	= 942 kJ
	4(O–H)	= 4(459) kJ	= 1836 kJ
		Total	= 2778 kJ
Net energy change	= (2285 – 2778) kJ = +493 kJ		

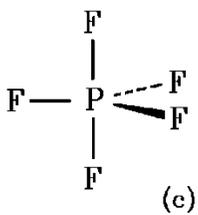
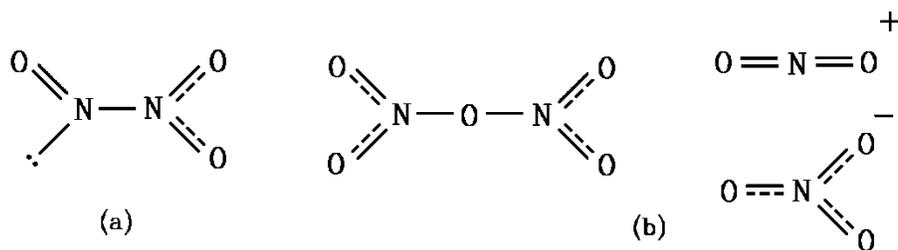
- 15.14 The three formal charge structures below are among the more reasonable, but even these have higher formal charges than either of the N–N–O bonding arrangements shown in Figure 15.11. Thus the asymmetric structure is preferred to minimize charge.



15.16  $\text{NO}^+$  has a bond order of three, and  $\text{NO}^-$  has a bond order of two:

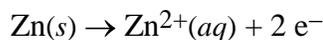
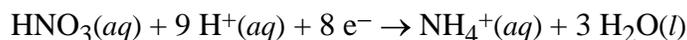


15.18

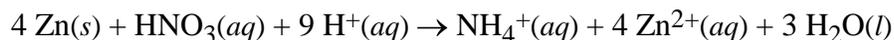


- 15.20 (a) Nitric acid is a colorless, oily liquid when pure. It is miscible with water to give a very acidic solution.
- (b) Ammonia is a colorless, basic gas with a characteristic odor. It is very soluble in water.

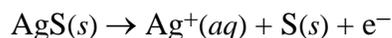
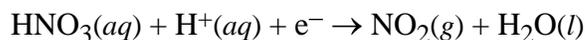
- 15.22 (a) Half-reactions:



Overall reaction:



(b) Half-reactions:

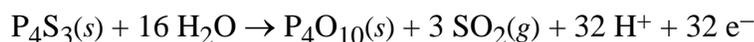
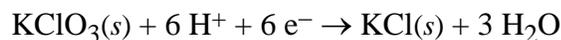


Overall reaction:



- 15.24 Both ammonia and phosphine are colorless gases; ammonia is a very basic gas, whereas phosphine is close to neutral.

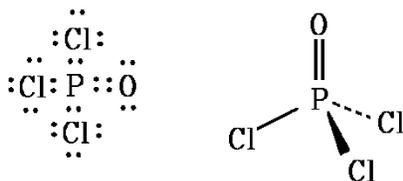
- 15.26 We can use “H<sub>2</sub>O” and “H<sup>+</sup>” to balance the half-reactions even though there are none present in the reaction system as long as the species are eliminated when the overall equation is constructed:



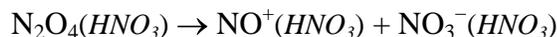
The overall reaction is



- 15.28 The shape of the molecule is tetrahedral (see the structures). The hybridization is likely to be  $sp^3$ . The short P–O bond can be explained in terms of a multiple-bond component, a  $\pi$  bond involving a filled oxygen orbital and an empty phosphorus orbital.



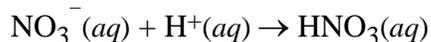
- 15.30 The species would most likely be  $\text{NO}^+$  and  $\text{NO}_3^-$  ( $\text{NO}_2^+$  and  $\text{NO}_2^-$  would be theoretically possible, but the nitrite ion is not as stable as the nitrate ion);



- 15.32 One possible answer is that the atoms bonded to the arsenic are increasing in size, hence forcing the bond angle to be greater than the pure  $p$  angle of  $90^\circ$ . Alternatively, one can say that the bond to the more electronegative fluorine has a greater  $p$  character than that with chlorine.

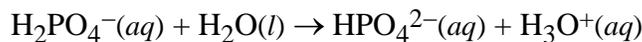
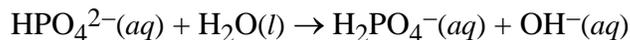
- 15.34  $\text{NO}^+$  and  $\text{CN}^-$  are the most obvious choices.

- 15.36 From the Frost diagram, the nitrate ion is a quite thermodynamically stable species (as is the ammonium ion). In acid solution, there would be an equilibrium, forming some nitric acid:



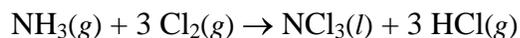
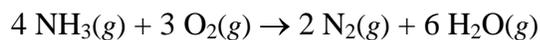
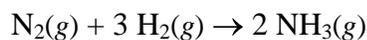
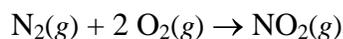
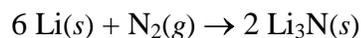
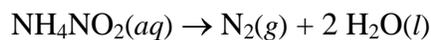
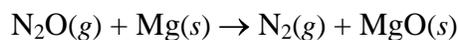
Nitric acid is very strongly oxidizing, so it would more readily oxidize the ammonium ion, at least according to thermodynamic principles.

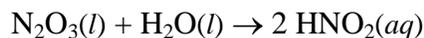
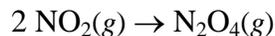
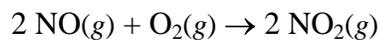
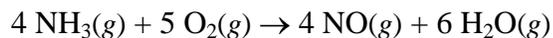
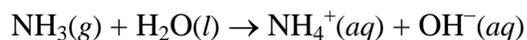
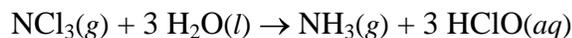
- 15.38 The equilibria are



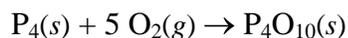
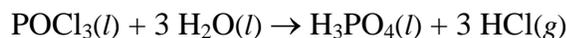
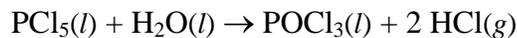
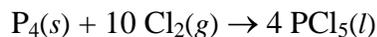
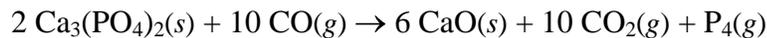
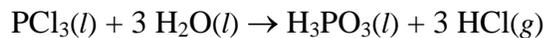
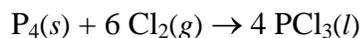
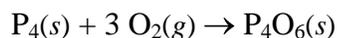
- 15.40  $\text{V}_2\text{O}_7^{2-}$ . This is on the basis of the ( $n$ ) and ( $n+10$ ) relationship, that there should be a similarity between vanadium (Group 5) and phosphorus (Group 15).

- 15.42 Nitrogen:



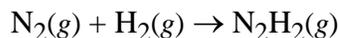


### Phosphorus:



## Beyond the Basics

15.44 The first step is



Using bond energy values from the Appendix:

Bonds broken:	(N≡N)		= 942 kJ
	(H–H)		= 432 kJ
		Total	= 1374 kJ
Bonds formed:	(N=N)		= 418 kJ
	2(N–H)	= 2(386) kJ	= 772 kJ
		Total	= 1190 kJ

$$\text{Net energy change} = +1374 \text{ kJ} - 1190 \text{ kJ} = +184 \text{ kJ}$$

The second step is

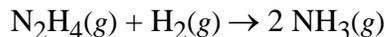


Using bond energy values from the Appendix:

Bonds broken:	(N=N)		= 418 kJ
	2(N-H)	= 2(386) kJ	= 772 kJ
	(H-H)		= 432 kJ
		Total	= 1622 kJ
Bonds formed:	(N-N)		= 247 kJ
	4(N-H)	= 4(386) kJ	= 1544 kJ
		Total	= 1791 kJ

$$\text{Net energy change} = +1622 \text{ kJ} - 1791 \text{ kJ} = -169 \text{ kJ}$$

The third step is



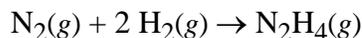
Using bond energy values from the Appendix:

Bonds broken:	(N-N)		= 247 kJ
	4(N-H)	= 4(386) kJ	= 1544 kJ
	(H-H)		= 432 kJ
		Total	= 2223 kJ
Bonds formed:	6(N-H)	= 6(386) kJ	= 2316 kJ
		Total	= 2316 kJ

$$\text{Net energy change} = +2223 \text{ kJ} - 2316 \text{ kJ} = -93 \text{ kJ}$$

The major weakness is the first step. It is significantly endothermic, and as a result of the decreasing number of gas molecules, there is an entropy decrease. This reaction must be nonspontaneous.

An alternative would be the combination of the first two steps. Such a three-body collision would be rare, explaining the slow rate of reaction.



For this combined step, using bond energy values from the Appendix:

Bonds broken:	(N≡N)		= 942 kJ
	2(H-H)	=2(432 kJ)	= 864 kJ
		Total	= 1806 kJ
Bonds formed:	(N-N)		= 247 kJ
	4(N-H)	= 4(386) kJ	= 1544 kJ
		Total	= 1791 kJ

$$\text{Net energy change} = +1806 \text{ kJ} - 1791 \text{ kJ} = +15 \text{ kJ}$$

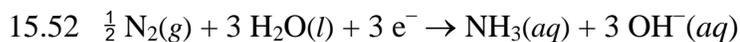
This is still very slightly endothermic on the basis of bond energy values. However, taking into account the approximate values of bond energies, the error value is sufficiently large that the reaction could be spontaneous. In fact, the sum of these bond energies gives an enthalpy of formation value of  $-78 \text{ kJ}$ , when in reality the value is  $-46 \text{ kJ}$ —illustrating the inherent errors of the average bond energy method.



because chlorine is more electronegative than phosphorus.

15.48 Phosphorus trichloride is a liquid at room temperature and it can act as a solvent for the reaction, whereas the other route involves the combination of two solid compounds. In addition, phosphorus trichloride is an important industrial reagent and is obtainable commercially.

15.50 When bonding through the oxygen, the nitrite ion should be hard; when bonding through the nitrogen atom, it should be more borderline.

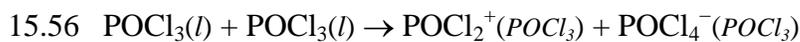


$$\Delta G^\circ = [(-26.5) + 3(-157) - 3(-237)] \text{ kJ}\cdot\text{mol}^{-1} = +214 \text{ kJ}\cdot\text{mol}^{-1}$$

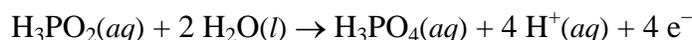
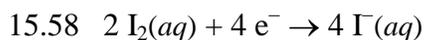
$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{+214 \times 10^3 \text{ J}\cdot\text{mol}^{-1}}{3 \times (9.65 \times 10^4 \text{ J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1})} = -0.739 \text{ V}$$

15.54 When a chlorine atom is lost from nitrogen trichloride, the remaining fragment will still contain two N-Cl single bonds. When the chlorine is lost from NOCl, the nitrogen-oxygen bond order in the nitrogen monoxide formed will be  $2\frac{1}{2}$  (see molecular orbital diagram) compared to 2 for

Cl–N=O. Thus the energy input to break the N–Cl bond is reduced by the energy released as the N–O bond strengthens.

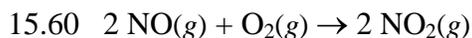


$\text{POCl}_2^+$  would be the acid, and  $\text{POCl}_4^-$  the base.

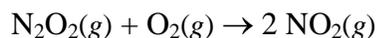
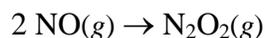


Because the phosphorus in phosphoric acid is in the +5 oxidation state, then the phosphorus in in phosphinic acid must be in the  $(+5 - 4 =) +1$  oxidation state.

By comparison, the oxidation state of phosphorus in phosphonic acid,  $\text{H}_3\text{PO}_3$ , would be +3.



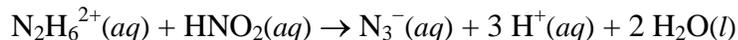
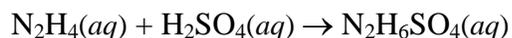
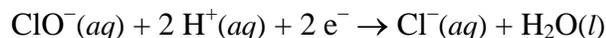
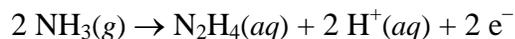
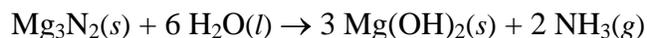
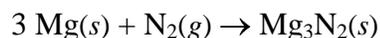
Three-body collision reactions are slow, but there is a two-step reaction sequence that can be proposed that would also have a very high dependence upon nitrogen oxide concentration. In Section 15.10, we mention that at low temperatures, nitrogen monoxide forms a dimer,  $\text{N}_2\text{O}_2$ . It is possible that the reaction proceeds by the following steps:

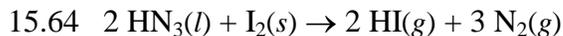
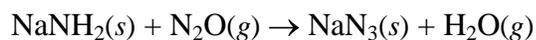


This sequence would explain the slowness at low nitrogen monoxide concentrations in that two NO molecules must collide for the reaction to be initiated. Further, a dioxygen molecule must impact the dimer before it dissociates back to nitrogen monoxide.

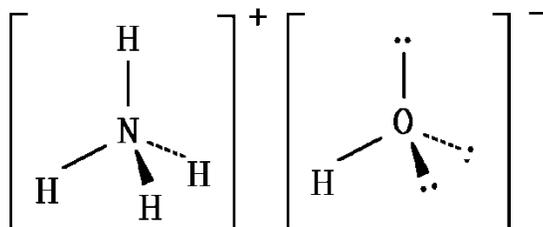
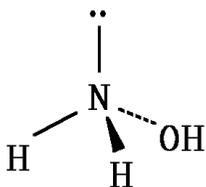
15.62 [A] Magnesium nitride; [B] magnesium hydroxide; [C] ammonia; [D] hydrazine; [E] hydrazinium sulfate; [F] ammonium azide; [G] sodium amide;

[H] sodium azide.

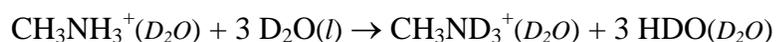




15.66  $\text{NH}_2\text{OH}$  is a simple covalently bonded molecule; ammonium hydroxide consists of separate ammonium and hydroxide ions.



15.68 Only the hydrogen atoms attached to the ammonium unit are replaceable:



The asymmetric structure of dinitrogen oxide,  $\text{N}\equiv\text{N}-\text{O}$ , enables the oxygen atom to react with the magnesium, leaving the  $\text{N}\equiv\text{N}$  unit intact.

Had the oxygen atom been in the center of the molecule, there would not have been a simple reaction pathway.

15.72 Nitramide:

