Both $\text{NO}_4^{3-}$ and $\text{PO}_4^{3-}$ have 32 valence electrons so both have similar Lewis structures. From the Lewis structure for $\text{NO}_4^{3-}$, the central N atom has a tetrahedral arrangement of electron pairs. N is small. There is probably not enough room for all 4 oxygen atoms around N. P is larger, thus, $\text{PO}_4^{3-}$ is stable.

$\text{PO}_3^{-}$

$\text{PO}_3^{-}$ and $\text{NO}_3^{-}$ both have 24 valence electrons so both have similar Lewis structures. From the Lewis structure for $\text{PO}_3^{-}$, PO$_3^-$ has a trigonal arrangement of electron pairs about the central P atom (two single bonds and one double bond). P = O bonds are not particularly stable, while N = O bonds are stable. Thus, $\text{NO}_3^{-}$ is stable.

13. a. $8 \text{H}^+(\text{aq}) + 2 \text{NO}_3^-(\text{aq}) + 3 \text{Cu}(\text{s}) \rightarrow 3 \text{Cu}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l}) + 2 \text{NO}(\text{g})$

b. $\text{NH}_4\text{NO}_3(\text{s}) \xrightarrow{\text{Heat}} \text{N}_2\text{O}(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$

c. $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) + 2 \text{KOH}(\text{aq}) \rightarrow 2 \text{KNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$

15. $\text{NH}_3$: sp$^3$; $\text{N}_2\text{H}_4$: both Ns are sp$^3$; $\text{NH}_2\text{OH}$: sp$^3$; N$_2$: sp; N$_2\text{O}$: central N, sp

$\text{NO}$: sp$^2$; $\text{N}_2\text{O}_3$: both Ns are sp$^2$; $\text{NO}_2$: sp$^2$; $\text{HNO}_3$: sp$^2$

17. $27.37 \times 10^9 \text{ lb} \text{ NH}_3 \times \frac{1 \text{ kg}}{2.2046 \text{ lb}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} = 7.290 \times 10^{11} \text{ mol NH}_3$

$mol \text{ N}_2 = 7.290 \times 10^{11} \text{ mol NH}_3 \times \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} = 3.645 \times 10^{11} \text{ mol N}_2$; STP = 273.15 K and 1.000 atm

$V_{N_2} = \frac{nRT}{P} = \frac{3.645 \times 10^{11} \text{ mol} \times 0.08206 \text{ L atm} \times 273.15 \text{ K}}{1.000 \text{ atm}} = 8.170 \times 10^{12} \text{ L N}_2$

Since T and P are constant, then moles and volume are directly proportional to each other. From the balanced reaction, there is a 3:1 mol ratio between H$_2$ and N$_2$, so the volume of H$_2$ required is 3 times the volume of N$_2$ required.

$V_{H_2} = V_{N_2} \times \frac{3 \text{ mol H}_2}{1 \text{ mol N}_2} = 8.170 \times 10^{12} \text{ L} \times 3 = 2.451 \times 10^{13} \text{ L H}_2$

18. $P_{total} = 9.4 \times 10^4 \text{ Pa} \times \frac{1 \text{ atm}}{1.013 \times 10^5 \text{ Pa} \text{ atm}} \times 760 \text{ torr} = 710 \text{ torr}$

$P_{total} = P_{N_2O} + P_{H_2O}$, $P_{N_2O} = 710 \text{ torr} - 21 \text{ torr} = 690 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.91 \text{ atm}$

$2.6 \text{ g NH}_4\text{NO}_3 \times \frac{1 \text{ mol NH}_4\text{NO}_3}{80.05 \text{ g NH}_4\text{NO}_3} \times \frac{1 \text{ mol N}_2\text{O}}{1 \text{ mol NH}_4\text{NO}_3} = 3.2 \times 10^{-2} \text{ mol N}_2\text{O}$

$V_{N_2O} = \frac{nRT}{P} = \frac{3.2 \times 10^{-2} \text{ mol N}_2\text{O} \times 0.08206 \text{ L atm} \times 295 \text{ K}}{0.91 \text{ atm}} = 0.85 \text{ L}$
19. \[
\begin{align*}
\text{Bonds broken:} & & \\
1 \text{ N} - \text{ N} & (160. \text{ kJ/mol}) \\
4 \text{ N} - \text{ H} & (391 \text{ kJ/mol}) \\
2 \text{ F} - \text{ F} & (154 \text{ kJ/mol}) \\
\text{Bonds formed:} & & \\
4 \text{ H} - \text{ F} & (565 \text{ kJ/mol}) \\
1 \text{ N} = \text{ N} & (941 \text{ kJ/mol})
\end{align*}
\]
\[\Delta H = 160. + 4(391) + 2(154) - [4(565) + 941] = 2032 \text{ kJ} - 3201 \text{ kJ} = -1169 \text{ kJ}\]

21. \[\frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{NO}(g) \quad \Delta G^\circ = \Delta G_{f,NO}^\circ = 87 \text{ kJ/mol}; \quad \text{By definition, } \Delta G_{f}^\circ \text{ for a compound equals the free energy change that would accompany the formation of 1 mol of that compound from its elements in their standard states. NO (and some other oxides of nitrogen) have weaker bonds as compared to the triple bond of N}_2 \text{ and the double bond of O}_2. \quad \text{Because of this, NO (and some other oxides of nitrogen) have higher (positive) free energies as compared to the relatively stable N}_2 \text{ and O}_2 \text{ molecules.}\]

22. \[\Delta H^\circ = 2(90. \text{ kJ}) - [0 + 0] = 180. \text{ kJ}; \quad \Delta S^\circ = 2(211 \text{ J/K}) - [192 + 205] = 25 \text{ J/K}\]

\[\Delta G^\circ = 2(87 \text{ kJ}) - [0] = 174 \text{ kJ}\]

At the high temperatures in automobile engines, the reaction N\textsubscript{2} + O\textsubscript{2} \rightarrow 2 \text{NO} becomes spontaneous since the favorable \(\Delta S^\circ\) term will become dominate. In the atmosphere, even though 2 NO \rightarrow N\textsubscript{2} + O\textsubscript{2} is spontaneous at the cooler temperatures of the atmosphere, it doesn't occur because the rate is slow. Therefore, higher concentrations of NO are present in the atmosphere as compared to what is predicted by thermodynamics.

23. M.O model:

\[\text{NO}^+: (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2, \quad \text{Bond order} = \frac{8 - 2}{2} = 3, \quad 0 \text{ unpaired e}^- \text{ (diamagnetic)}\]

\[\text{NO}: (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^1, \quad \text{B.O. = 2.5, 1 unpaired e}^- \text{ (paramagnetic)}\]

\[\text{NO}^-: (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^2, \quad \text{B.O. = 2, 2 unpaired e}^- \text{ (paramagnetic)}\]

Lewis structures:

\[\text{NO}^+: \quad \left[ \begin{array}{c}
\vdots \\
\text{N} = \text{O}
\end{array} \right]^+\]

\[\text{NO}: \quad \left[ \begin{array}{c}
\vdots \\
\text{N} = \text{O}
\end{array} \right]\quad \left[ \begin{array}{c}
\vdots \\
\text{N} = \text{O}
\end{array} \right]\quad \left[ \begin{array}{c}
\vdots \\
\text{N} = \text{O}
\end{array} \right]\]

\[\text{NO}^-: \quad \left[ \begin{array}{c}
\vdots \\
\text{N} = \text{O}
\end{array} \right]^-
\]

The two models only give the same results for NO\textsuperscript{+} (a triple bond with no unpaired electrons). Lewis structure are not adequate for NO and NO\textsuperscript{-}. The M.O. model gives a better representation for all three species. For NO, Lewis structures are poor for odd electron species. For NO\textsuperscript{-}, both models predict a double bond but only the MO model correctly predicts that NO\textsuperscript{-} is paramagnetic.

25. a. H\textsubscript{3}PO\textsubscript{4} > H\textsubscript{3}PO\textsubscript{3}; The strongest acid has the most oxygen atoms.

b. H\textsubscript{3}PO\textsubscript{4} > H\textsubscript{2}PO\textsubscript{4} > HPO\textsubscript{4}\textsuperscript{2-}; Acid strength decreases as protons are removed.
27. To complete the Lewis structures, just add lone pairs to the terminal atoms to complete the octets. See part d for the Lewis structures (32 valence electrons).

a. Yes, both have 4 sets of electrons about the P. We would predict a tetrahedral structure for both.

b. The hybridization is sp^3 for each P since both structures are tetrahedral.

c. P has to use one of its d orbitals to form the π bond.

d. The formal charges for the O and P atoms are next to the atoms in the following Lewis structures. In both structures all Cl atoms have a formal charge of zero.

\[ \begin{align*}
\text{Cl} & \quad \text{Cl}^+ \\
: \quad \text{P} \quad \text{Cl}^+ \\
: & \quad \text{Cl} \\
\end{align*} \]

\[ \begin{align*}
\text{Cl} & \quad \text{Cl}^+ \\
\text{O}^+ \quad \text{Cl} \\
\text{O}^- \quad \text{Cl} \\
\text{Cl} \\
\end{align*} \]

The structure with the P = O bond is favored on the basis of formal charge since it has a zero formal charge for all atoms in the structure.

29. Production of antimony:

\[ 2 \text{Sb}_2\text{S}_3(s) + 9 \text{O}_2(g) \rightarrow 2 \text{Sb}_2\text{O}_3(s) + 6 \text{SO}_2(g); \quad 2 \text{Sb}_2\text{O}_3(s) + 3 \text{C}(s) \rightarrow 4 \text{Sb}(s) + 3 \text{CO}_2(g) \]

Production of bismuth:

\[ 2 \text{Bi}_2\text{S}_3(s) + 9 \text{O}_2(g) \rightarrow 2 \text{Bi}_2\text{O}_3(s) + 6 \text{SO}_2(g); \quad 2 \text{Bi}_2\text{O}_3(s) + 3 \text{C}(s) \rightarrow 4 \text{Bi}(s) + 3 \text{CO}_2(g) \]

31. \( \text{O} = \text{O} \rightarrow \text{O} = \text{O} + \text{O} \)

Break O – O bond: \( \Delta H = \frac{146 \text{kJ/mol}}{6.022 \times 10^{23} \text{mol}} \times 1 \text{mol} = 2.42 \times 10^{-19} \text{kJ} = 2.42 \times 10^{-19} \text{J} \)

A photon of light must contain at least \( 2.42 \times 10^{-19} \text{J} \) to break one O – O bond.

\[ E_{\text{photon}} = \frac{hc}{\lambda} \quad \lambda = \frac{hc}{E} \quad (6.626 \times 10^{-34} \text{ J s}) (2.998 \times 10^8 \text{ m/s}) = 8.21 \times 10^{-7} \text{ m} = 821 \text{ nm} \]

35. \( \text{SF}_5^- \) has 6 + 5(7) + 1 = 42 valence electrons.

\[
\begin{bmatrix}
\cdots & \cdots \\
\cdots & \cdots \\
\cdots & \cdots \\
\cdots & \cdots \\
\cdots & \cdots \\
\end{bmatrix}^-
\]

square pyramid
37. a. ClF₅, \(7 + 5(7) = 42\) e⁻  
   \[
   \text{Square pyramid; } d^2sp^3
   \]
   
   b. IF₅, \(7 + 3(7) = 28\) e⁻  
   \[
   \text{T-shaped; } dsp^3
   \]
   
   c. FBrO₂, \(7 + 7 + 2\) (6) = 26 e⁻  
   \[
   \text{Trigonal pyramid; } sp^3
   \]

39. The balanced half-reactions and the overall balanced reaction for this oxidation-reduction reaction are:

\[
\begin{align*}
2 \text{ e}^- + 2 \text{ H}^+ + \text{XeF}_2 & \rightarrow \text{Xe} + 2 \text{ HF} \\
\text{H}_2\text{O} + \text{BrO}_3^- & \rightarrow \text{BrO}_4^- + 2 \text{ H}^+ + 2 \text{ e}^-
\end{align*}
\]

\[
\text{H}_2\text{O(l)} + \text{BrO}_3^-(aq) + \text{XeF}_2(aq) \rightarrow \text{BrO}_4^-(aq) + \text{Xe(g)} + 2 \text{ HF(aq)}
\]

43. Xe has one more valence electron than I. Thus, the isoelectric species will have I plus one extra electron substituted for Xe, giving a species with a net minus one charge.

a. IO₄⁻  
   b. IO₃⁻  
   c. IF₂⁻  
   d. IF₄⁻  
   e. IF₆⁻  
   f. IOF₃⁻

53. TeF₅⁻ has \(6 + 5(7) + 1 = 42\) valence electrons.

\[
\begin{bmatrix}
: \text{F}^- & \text{F}^- \\
: \text{F}^- & \text{Te} & : \\
: \text{F}^- & : \\
\end{bmatrix}^-
\]

The lone pair of electrons around Te exerts a stronger repulsion than the bonding pairs, pushing the four square planar F's away from the lone pair and thus reducing the bond angles between the axial F atom and the square planar F atoms.