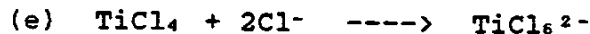
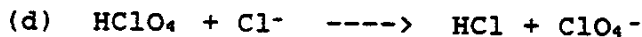
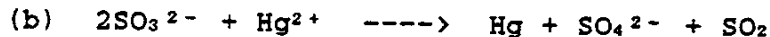
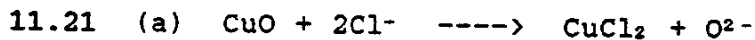


11.20 The soft Cu^+ ion is better solvated (and thereby stabilized) by the softer base DMSO, while the harder Cu^{2+} is better solvated by H_2O .



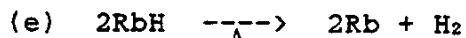
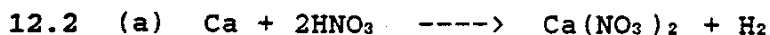
11.22 Using data from Table 11.8, $\xi^\circ = -1.02$ V; then $\log K = n\xi^\circ/0.05916 = -17.24$, and $K = 6 \times 10^{-18}$.

11.23 The potentials are -0.28 V for (a), $+1.24$ V for (b), and $+1.11$ V for (c). Hence in tendency to go to completion, (b) > (c) > (a).

CHAPTER 12

12.1 (a) The low electronegativity of K makes hydrogen electron-rich (hydride-like) in KH. Conversely, the higher electronegativity of Br makes hydrogen electron poor (H^+ -like) in HBr. (b) The highly electronegative chlorine of HOCl draws electron density toward it and contributes to the electropositive nature (acidity) of the hydrogen. NaOH is dissociated to OH^- in water, and OH^- is a potent base. (c) Brønsted acidity is enhanced when hydrogen is bonded to a highly electronegative element, and also when the H-X bond is weak. In the $\text{H}_2\text{S}/\text{H}_2\text{Se}$ comparison it is the bond energy

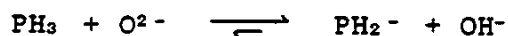
factor that dominates.



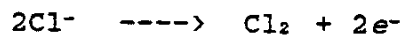
12.3 One mole of metallic palladium can absorb about 0.8 moles of hydrogen atoms. Therefore, about 2.5 moles (266 g) of Pd are needed per mole H_2 . The required volume is about $266/12.0$ or 22 cm^3 - roughly $1/1000$ the volume of $\text{H}_2(g)$ at STP.

12.4 (a) "Ionic" hydrides retain varying amounts of covalent character. This affects the internuclear distance. (b) The radius of Li^+ varies with its coordination number, complicating the problem. If 76 pm is chosen (Table 6.7), then the radius ratio is $76/150 = 0.51$ and the rock salt lattice is (correctly) predicted. (c) If $r(\text{Mg}^{2+})$ is taken to be 72 pm then the radius ratio is 0.48 . The rutile lattice is predicted. (d) Yes, since LiH has greater covalent character than CsH . Increased orbital overlap decreases the bond distance.

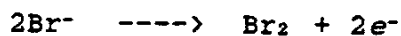
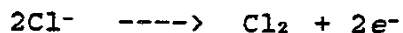
12.5 PH_3 behaves as a Brønsted base in the presence of strong acid, and as an acid in the presence of base. For example,



12.6 The slow evolution of $\text{H}_2(g)$ is observed. The relevant equation is $\text{Sr} + 2\text{H}_2\text{O} \rightarrow \text{Sr}(\text{OH})_2 + \text{H}_2$.



(Na^+ is the more easily reduced cation).



12.8 Unlike the other Group 2 hydrides, BeH_2 is primarily covalent because of the small difference in electronegativity between Be and H. The structure is thought to be a linear polymer, similar to BeCl_2 (Figure 12.6).

12.9 (a) The products are LiF and BaI_2 (hard/hard and soft/soft). (b) The products are Na_2SO_3 and $\text{CO}_2(g)$. The reaction is thermodynamically favored because of the great stability of CO_2 (see Chapter 13). (c) The products are Na_2O and O_2 . (Peroxides produce O_2 upon heating.) (d) The products are BeF_4^{2-} and S^{2-} ; the hard acid Be^{2+} prefers the harder base. (e) The products are Li_2O , N_2O_4 , and O_2 . (See Equation 12.61 and the accompanying discussion.)

12.10 The oxidation half reaction $\text{Cs} \rightarrow \text{Cs}^+ + 1e^-$ is strongly favored ($\xi^0 = +2.923 \text{ V}$). The reduction of ozone

follows the half-reaction $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$, for which $\xi^0 = +2.07$ V. There is therefore a tremendous driving force for the formation of O_2 rather than O_3^- . Hence CsO_3 must be made by a less direct route (Equation 12.36).

12.11 Metals having strongly positive electron affinities are good candidates. Ag ($EA_1 = +1.30$ eV), Li (+0.62 eV), and Al (+0.46 eV, very close to that of Cs) can be suggested.

12.12 The crown ether coordinates to K^+ , promoting the reaction $KOH + \text{crown} \rightarrow K(\text{crown})^+ + OH^-$. This destroys ion pairing, and frees the basic hydroxide ion.

12.13 Li^+ is the hardest acid among the Group 1 cations, so it has the greatest affinity for water.

12.14 (a) One might expect the rate of migration to decrease with increasing size of the cation, but the opposite trend is observed. (b) The cations are solvated, and so must "drag along" water molecules. Li^+ , with the highest charge density, has the greatest attraction for H_2O ; these polarized H_2O 's attract others. Therefore what might be called the "effective size" of $[M(H_2O)]_x^+$ in aqueous solution decreases going down Group 1.

12.15 This is a hard-soft effect. Li^+ is a harder acid than K^+ , while NH_3 is a harder base than $S_2O_3^{2-}$.

12.16 Factors that influence standard reduction potentials include enthalpies of atomization, ionization, and hydration (see Figure 9.3). Because these show varying trends for the

Group 1 metals, the standard reduction potential does not vary smoothly.

12.17 (a) Ca (Ca^{2+} has the greatest charge-to-size ratio.)
(b) Ca (Ca^{2+} is the hardest of the three acids.) (c) Ca
(Among KF, CaF_2 , and SrF_2 , CaF_2 has the greatest lattice energy.)
(d) K (K^+ has the smallest charge-to-size ratio.)

12.18 Using data from Tables 1.7, 1.10, and 9.1, the overall comparison to sodium is probably the closest.

12.19 (a) The single valence electron of each element of Group 1 is particularly well-shielded from the nucleus, making it relatively easy to remove. (b) Li^+ interacts more strongly with hard than with soft acids (ie, favors F^- and H_2O relative to Cl^-). (c) The lattice energy of BaS (a 2+/2- salt) is much greater than that of BaCl_2 . Also, the soft acid Ba^{2+} favors the soft base S^{2-} . (d) Ca delocalizes two electrons per atom, while K delocalizes only one. (e) Ca is smaller, giving it a greater metallic lattice energy.

12.20 (a) $\text{C}_2\text{H}_5\text{Br} + \text{Mg} \rightarrow \text{C}_2\text{H}_5\text{MgBr}$
(b) $\text{CH}_3\text{Br} + 2\text{Li} \rightarrow \text{LiBr} + \text{LiCH}_3$
(c) $\text{C}_6\text{H}_5\text{OH} + n\text{-BuLi} \rightarrow \text{Li}^+\text{OC}_6\text{H}_5^- + \text{C}_4\text{H}_{10}$
(d) $\text{SnCl}_4 + 4\text{NaC}_2\text{H}_5 \rightarrow \text{Sn}(\text{C}_2\text{H}_5)_4 + 4\text{NaCl}$
(e) $\text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{CH}_3\text{MgI} \rightarrow (\text{CH}_3)_3\text{COMgI}$

CHAPTER 13

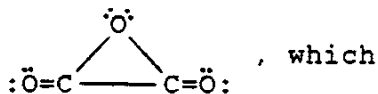
13.1 (a) Methane is the only air-stable MH_4 hydride of Group 14 because of its stronger, shorter, and less polar bonds.

(b) BMe_3 is the most thermally stable of the Group 13 trimethyls. This correlates with the fact that in bond energy, $B-C > Al-C > Ga-C > \text{etc.}$ Also, unlike the others, BMe_3 does not dimerize. (c) The B-B bond is the strongest homonuclear bond of Group 13. Hence B-B compounds are generally more stable than their heavier analogues. (d) Homonuclear multiple bonding decreases with increasing size. As a result, the chemistry of C=C and C≡C bonds is much more extensive than for the other members of Group 14.

13.3 The bond angles are 109° , consistent with sp^3 hybridization (and hence covalency). Like most other covalent polymers, Be_2C is insoluble in water and has a very high melting point.

13.4 (a) C_2O_2 ($:\ddot{O}=C=C=\ddot{O}:$), a compound of low thermal stability because of the reaction $C_2O_2 \rightarrow 2CO$; (b) C_2O_3 ;

(c) One possibility is the epoxide $:\ddot{O}=C \begin{array}{c} \diagup \ddot{O} \diagdown \\ \text{---} \end{array} C=\ddot{O}:$, which readily decomposes to $CO + CO_2$.



13.5 (a) $HCO_2H \xrightarrow{\Delta} CO + H_2O$

(b) $C_3O_2 + 2H_2O \rightarrow HOC(O)-CH_2-C(O)OH$

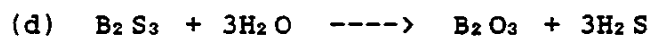
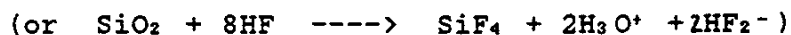
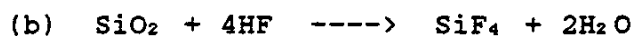
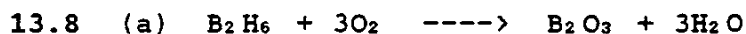
(c) $C_3O_2 + 2R_2NH \rightarrow R_2NC(O)-CH_2-C(O)NR_2$

13.6 (a) $Se=C=O \rightarrow Se + CO$

(b) $Cl-C(O)-C(O)-OH \rightarrow HCl + CO + CO_2$

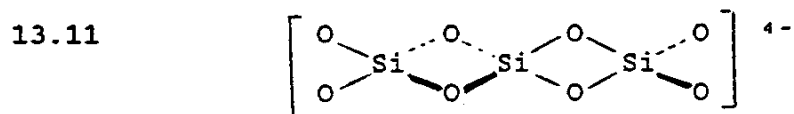
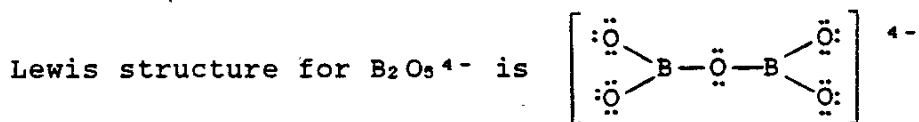
(c) $(NH_4)HCO_3 \rightarrow NH_3 + H_2O + CO_2$

13.7 (a) $\text{SiH}_4 + 2\text{O}_2 \rightarrow \frac{1}{n}(\text{SiO}_2)_n + 2\text{H}_2\text{O}$; (b) The combustion of silane is favored relative to methane both thermodynamically (very strong Si-O bonds are formed) and kinetically (the Si-H bonds are weaker than C-H, and the central atom is less hindered). (c) No - Sn-H bonds are weak relative to Sn-O.



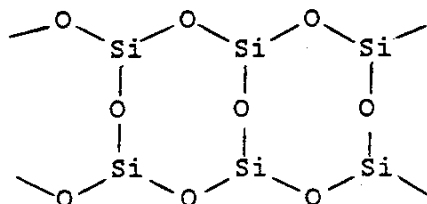
13.9 (a), (c), and (d) are thermodynamically favored.

13.10 The octet rule and normal valences are consistent with the indicated charges. See Figures 13.6(a) and 13.7(d). The



Using Equation 4.1, e^- needed = $11(8) = 88$; e^- available = $3(4) + 8(6) + n = 60 + n$ (n = negative charge); bonded electrons = 24 (12 single bonds); $n = 88 - 60 - 24 = 4$.

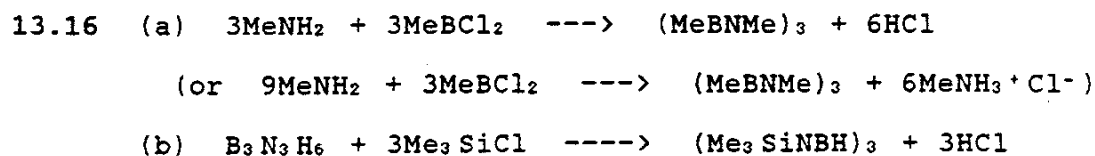
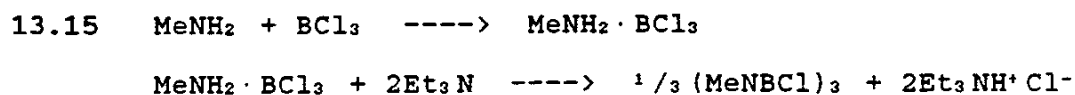
13.12 Figure 13.7(e) equates to



Each Si also has a terminal oxygen, not shown. (a) The structure is a system of fused 8-membered rings with alternating Si and O atoms. (b) Building a second ring onto the first requires two silicons (each with a terminal oxygen) plus three ring oxygens, consistent with the 2:5 molar ratio. (c) The terminal oxygens have negative charges, giving $\text{Si}_2\text{O}_5^{2-}$.

13.13 (a) The divalent compounds of Group 14 have considerable ionic character. Ge^{2+} is formed more readily than Si^{2+} because of the lower first two ionization energies of germanium. (b) The M-H bond is slightly stronger for $\text{M} = \text{Si}$ because of silicon's smaller size. The large difference in the M-F bond energies results from the more extensive dative π interaction in the Si-F bond.

13.14 Intermolecular reactions of this type are hindered by sterically large groups such as *t*-butyl. Large substituents often favor intramolecular decompositions because they destabilize the ground state relative to the transition state. The fact that *t*- $\text{BuMe}_2\text{SiNH}_2$ is the more stable of the two compounds is consistent with an intermolecular process (assuming a common mechanism).





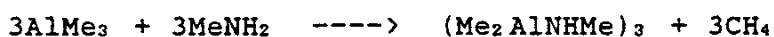
13.17 (a) Other metal cations which are present in the ore (different metal hydroxides precipitate and/or redissolve at different pH's). (b) Cryolite lowers the melting point of the mixture, permitting the process to be carried out at a reduced temperature.

13.18 One-eighth of the tetrahedral and one-half of the octahedral sites are occupied; this satisfies the stoichiometry $MgAl_2O_4$.

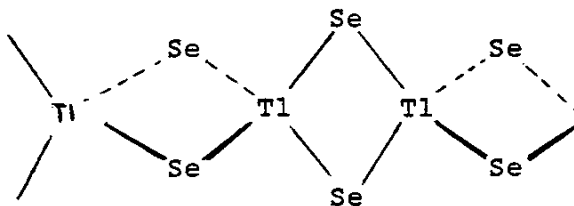
13.19 $BeCl_2$ is the polymer (see Figure 12.6) and $AlCl_3$ the dimer. This is a consequence of the fact that each Be requires two dative bonds, while Al requires only one; the octet rule is obeyed in each case.

13.20 The equation $[Ga(H_2O)]_6^{3+} \text{ ---->} GaOOH + 3H^+ + 4H_2O$ can be written. Since H^+ is a product, this reaction is inhibited by low pH.

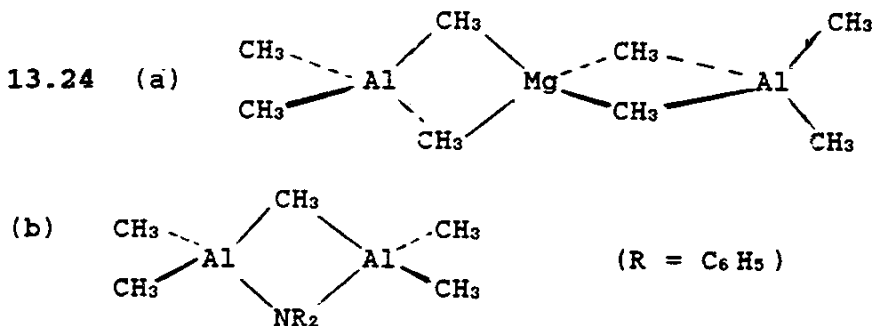
13.21 The product is a cyclic trimer with alternating aluminum and nitrogen atoms. The equation is



13.22 $Tl^+TlSe_2^-$, with Tl^I and Tl^{III} . The anion is a linear aggregate:



13.23 This is probably due to a combination of hybridization differences and steric effects.



13.25 The GaS structure is somewhat similar to the zinc blende lattice, with each gallium surrounded by four sulfurs in a tetrahedral array; the bonding is covalent. TlS (with the apparent Tl^I oxidation state) is better formulated as Tl⁺TlS₂⁻, with thallium in two different oxidation states.

13.26 (a) Both cations are diamagnetic, with completely-filled valence subshells ($6s^2$ for Tl⁺ and $4d^{10}$ for Ag⁺). Tl⁺ is the larger of the two (150 vs. 115 pm for CN = 6), but both are large, soft, monovalent cations. They have similar hydrolysis constants ($pK_h = 13.3$ for Tl⁺ and 11.8 for Ag⁺). Both elements have small IE_1 's and large IE_2 's, causing the M^I state to be stable. (b) Ag⁺ is much easier to reduce (+0.799 vs. -0.336 V). The Ag^{II} state, though reactive, can be observed in aqueous solution (Table 9.1), but Tl^{II} cannot.

13.27 (a) Tl³⁺ is a hard acid, so it prefers oxygen to sulfur donors. (b) The oxygens occupy apical positions for both steric and electronic reasons. (c) D_{3h} .

CHAPTER 14

14.1 (a) Interpolation between the values for Po and Rn suggest an ionization energy of about 9.6 eV and an electronegativity of about 2.2. (b) Probably - the ionization energies, electronegativities, and covalent radii are all expected to be similar. (c) Extrapolation from the X-F (X = halogen) series suggests a value of 250-280 kJ/mol. By analogy to Te-F (diagonal relationship), 330 kJ/mol is predicted. A reasonable estimate is 280-300 kJ/mol.

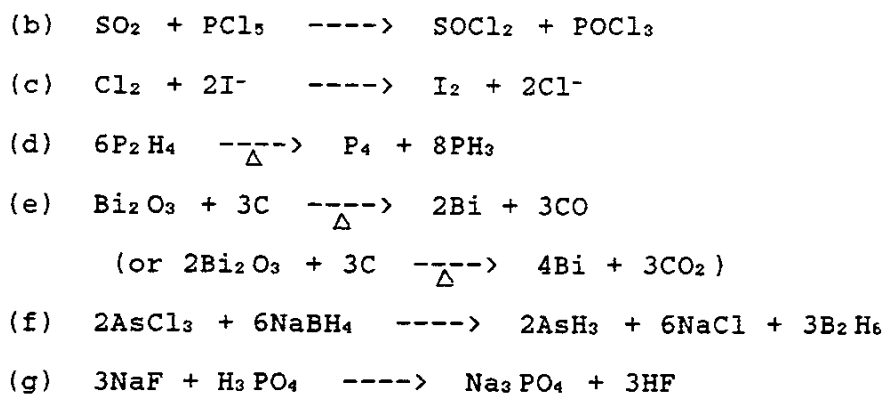
14.2 Recall that the synthesis of the first noble gas compound was based on the relatively low ionization energy of Xe. Since IE_1 for Ar is greater than that for Xe, argon should be more reluctant to engage in bonding.

14.3 (a) A general equation is $H_2S_n \rightarrow (n-1)/8 S_8 + H_2S$. Since both the reactants and products contain 2 S-H and (n-1) S-S bonds, ΔH must be about zero. (b) Reactions which increase the number of moles of gas (in this case H_2S) are usually favored by entropy. (c) The balanced equation is $6P_2H_4 \rightarrow P_4 + 8PH_3$. Both the reactants and products have 6 P-P and 24 P-H bonds, so ΔH must again be close to zero. ΔS is positive, and drives the reaction.

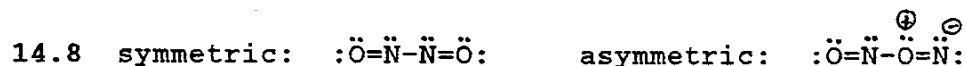
14.4 (a) H_2Se ; (b) NH_3 ; (c) AsH_3 ; (d) AsH_3 .

14.5 Neither is strongly exothermic. The reactions are driven by gas evolution (HF and HCl).

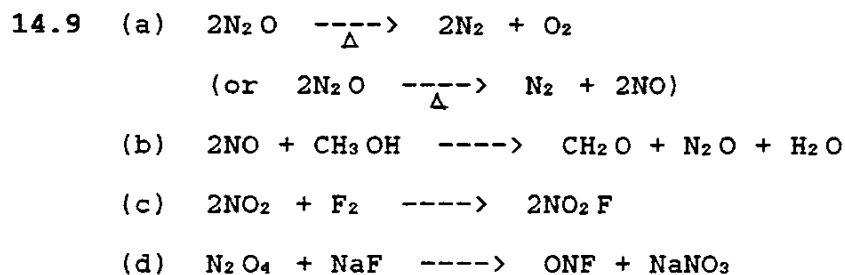
14.6 (a) $OF_2 + PF_3 \rightarrow POF_3 + F_2$



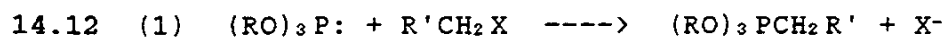
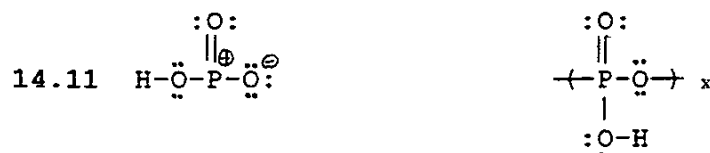
14.7 NO has one fewer proton, so its MO's (including the HOMO) are less stable than those of O₂.

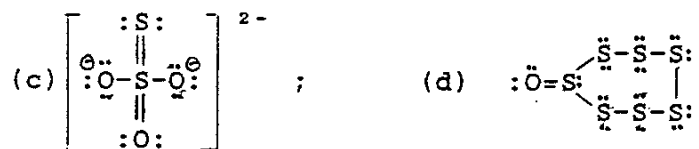
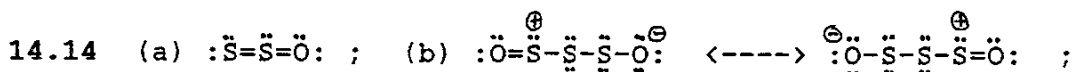
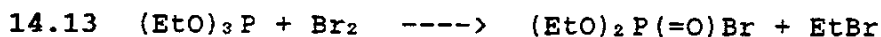
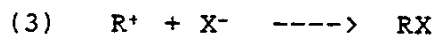
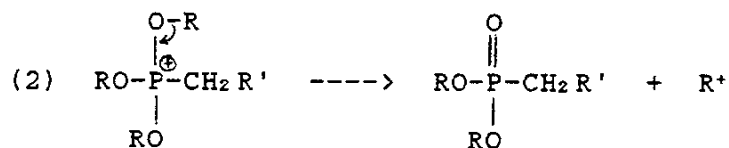


(a) symmetric; (b) there are five bonds in each case; ΔH is probably close to zero; (c) because the nitrogen bearing the negative formal charge is a basic site.

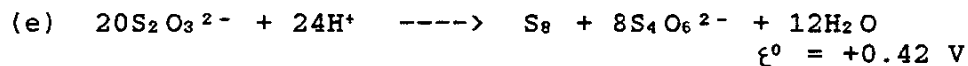
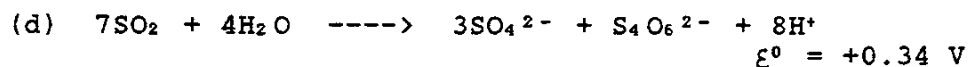
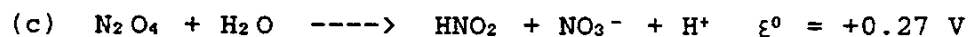
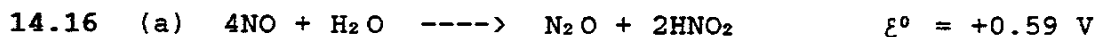


14.10 It is a nitryl salt: 2NO_2^+ , $\text{S}_2\text{O}_7^{2-}$.





14.15 The tin center is a soft Lewis acid site, and so prefers the softer base (S); the harder acid BF_3 prefers donation by oxygen.



14.17 The general decomposition reaction is $\text{O}_2\text{X}_2 \quad \text{-----} \quad \text{O}_2 + \text{X}_2$. ΔH for these reactions can therefore be estimated as $2E(\text{O-X}) + E(\text{O-O}) - E(\text{O=O}) - E(\text{X-X})$. Then using data from Tables 4.3 and 4.6,

$$\text{for } \text{X} = \text{F}: \quad \Delta H = 2(214) + 143 - 494 - 154 = -77 \text{ kJ/mol}$$

$$\text{for } \text{X} = \text{Cl}: \quad \Delta H = 2(207) + 143 - 494 - 240 = -177 \text{ kJ/mol}$$

The strong Cl-Cl bond relative to F-F accounts for most of the difference.

14.18 (a) PCl_3F_2 ; (b) $\text{P}(\text{OMe})_3 + 3\text{HCl}$; (c) $\text{Cl}_3\text{P}=\text{S}$; (d) $t\text{-BuPCl}_2 + \text{LiCl}$; (e) $\text{Et}_2\text{NPCl}_2 + \text{Me}_3\text{SiCl}$; (f) $\text{P}(\text{NEt}_2)_3 + 3\text{Me}_3\text{SiCl}$.

14.19 (a)
$$\begin{array}{c} \text{:O:} \quad \text{:O:} \\ \parallel \quad \parallel \\ \text{:}\ddot{\text{F}}\text{-S-}\ddot{\text{O}}\text{-}\ddot{\text{O}}\text{-S-}\ddot{\text{F}}\text{:} \\ \parallel \quad \parallel \\ \text{:O:} \quad \text{:O:} \end{array}$$
; (b) the O-O bond; (c) The

addition of two electrons cleaves the O-O bond, producing two moles of SO_3F^- .

14.20 $\text{Sb}_2\text{F}_{11}^-$ is $[\text{F}_5\text{Sb-F-SbF}_5]^-$, octahedral about each antimony with one shared fluorine. $\text{Sb}_3\text{F}_{16}^-$ is $[\text{F}_5\text{Sb-F-SbF}_4\text{-F-SbF}_5]^-$ - again octahedral about each antimony, with two shared fluorines.

14.21 The correct structures are $\text{H}\ddot{\text{O}}\text{-}\ddot{\text{N}}=\ddot{\text{O}}\text{:}$ and $\text{:}\ddot{\text{F}}\text{-}\overset{\oplus}{\text{N}}\begin{array}{l} \text{=}\ddot{\text{O}}\text{:} \\ \text{=}\ddot{\text{O}}\text{:} \end{array}\ominus$. In

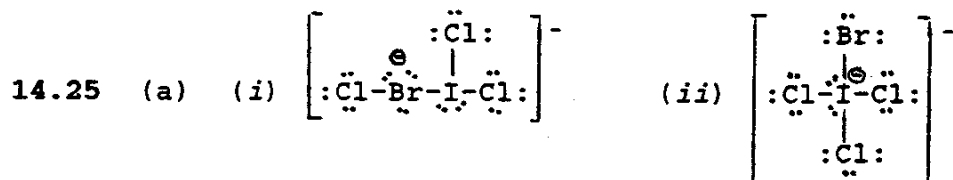
the first case all formal charges are zero, and the strong O-H bond contributes to the stability of the molecule. The analogous structure for NO_2F is disfavored because of the weakness of the O-F bond. Also, FONO would have severe adjacent atom lone pair repulsions, while FNO_2 avoids such repulsions.

14.22 The P-F bond is stronger than P-Cl, but Cl-Cl is stronger than F-F.

14.23 (a) tetrahedral electron geometry, $\angle\text{F-I-F}$ slightly less than 109° ; (b) linear (trigonal bipyramidal electron geometry with the lone pairs in equatorial positions), $\angle\text{F-I-F}$

= 180°; (c) square planar, with bond angles of 90°; (d) square pyramidal, with bond angles slightly less than 90°.

14.24 Probably IF_2^+ , since it is the only one in which the central atom's d orbitals are not involved in the σ bonding. Recall that bond energies vary with hybridization: $sp^3 > sp^3 d > sp^3 d^2$.



(b) Both central atoms of i have $sp^3 d$ hybridization. $\angle \text{Cl-Br-I}$ should be 180° (the three lone pairs occupy equatorial positions about Br). The electron geometry about I should be T-shaped, with bond angles of about 90°. ii is valence isoelectronic with ICl_4^- ; a square planar geometry is predicted.

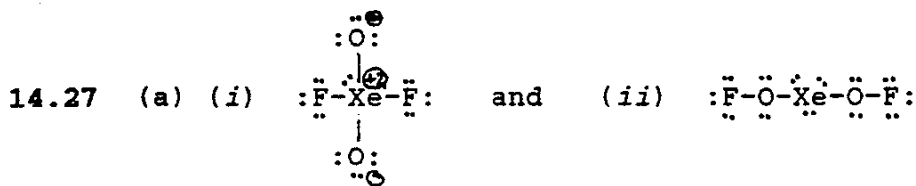
14.26 The relevant equation is $8\text{SX}_2 \rightarrow \text{S}_8 + 8\text{X}_2$, for which $\Delta H = 16E(\text{S-X}) - 8E(\text{S-S}) - 8E(\text{X-X})$. Using data from Table 4.6,

$$\text{for } X = \text{H: } \Delta H = 16(367) - 8(266) - 8(432) = + 288 \text{ kJ/mol}$$

$$\text{for } X = \text{F: } \Delta H = 16(342) - 8(266) - 8(154) = +2112 \text{ kJ/mol}$$

$$\text{for } X = \text{Cl: } \Delta H = 16(271) - 8(266) - 8(240) = + 288 \text{ kJ/mol}$$

The results are similar those for PX_3 , but SCl_2 and H_2S are predicted to be equally stable. (ΔH_f° of H_2S is actually a bit more negative than that of SCl_2 .)



(b) Formal charge considerations favor the "wrong" structure. However, that Lewis structure ignores partial π bonding, which is important for the Xe-O bonds of (i).

14.28 (a) $D_{\infty h}$; (b) C_{2v} ; (c) D_{4h} ; (d) D_{5h} ; (e) $D_{\infty h}$; (f) D_{4h} ; (g) C_{4v} ; (h) C_{3v} .

14.29 (a) $\Delta H = 3E(X-X) - 6E(Z-X)$. For $X = F$, $+100 = 3(154) - 6x$; $x = 60$ kJ/mol. Any X-Z bond energy greater than 60 kJ/mol might permit synthesis. The same treatment for $X = Cl$ shows that a Z-X bond energy greater than 103 kJ/mol is necessary. (b) $\Delta H = 3E(O=O) - 6E(Z-O)$; $+100 = 3(494) - 6x$; $x = 230$ kJ/mol.

14.30 There are six MO's - 2 bonding, 2 non-bonding, and 2 antibonding. Populating these orbitals with 10 valence electrons produces a bond order of 1.0. (This ignores the possibility of d -orbital participation.) The HOMO is antibonding. Note that the decomposition $\text{XeH}_2 \rightarrow \text{Xe} + \text{H}_2$ would produce a stronger bond, so XeH_2 is thermally unstable.

14.31 (a) The molecule is square planar (point group D_{4h}). The reducible representation for the six vectors (four bonds and two lone pairs) is

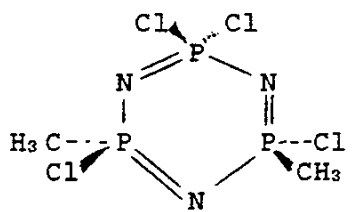
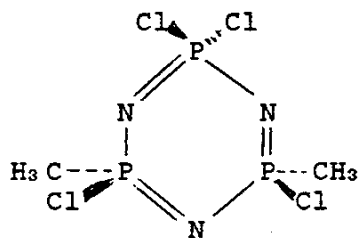
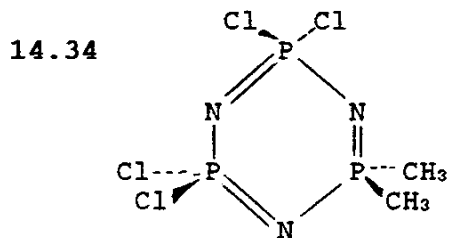
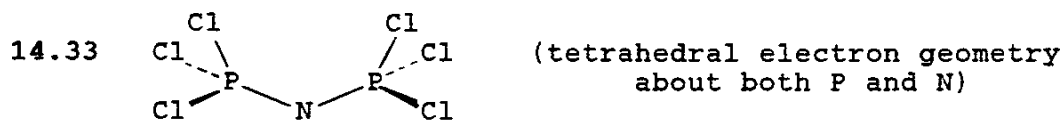
E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
6	2	2	2	0	0	0	4	4	2

which reduces to $2A_{1g} + B_{1g} + A_{2u} + E_u$. This is consistent with sp^3d^2 hybridization, with the involved d orbitals being $d_{x^2-y^2}$ and d_{z^2} . (b) Using the C_{3v} character table, the reducible representation is

E	$2C_3$	$3\sigma_v$
4	1	2

which reduces to $2A_1 + E$ and is consistent with sp^3 hybridization.

14.32 I_2 is a Lewis acid, I^- a Lewis base, and I_3^- the adduct: $I_2 + I^- \rightarrow I_3^-$. I_2 is a stronger acid than either Cl_2 or Br_2 (its vacant π^* orbital is the most stable of the three), so the reaction is most favored when $X = I$.



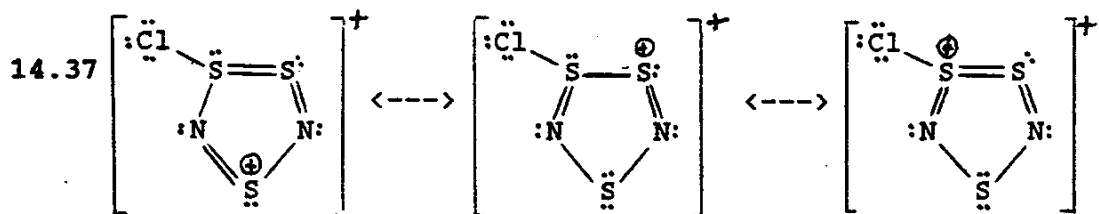
14.35 (a) The 1,2 isomer (with adjacent nitrogens) is

unknown. It is destabilized by repulsions across the short N-N bond. (b) same as (a).

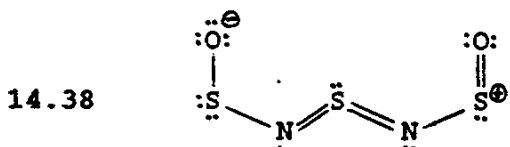
14.36 Four equivalent resonance structures can be drawn:



This planar system has $14 \pi e^-$, and meets the Hückel $4n + 2$ criterion for aromaticity.



(Others are possible as well.)



14.39 A is Me_2NPCl_2 , produced via a redistribution reaction. Oxidation with sulfur yields $\text{S}=\text{P}(\text{NMe}_2)\text{Cl}_2$.

14.40 The other product is AsF_3 . Se_4^{2+} is formed by oxidation. Arsenic(V) is concurrently reduced to As^{III} , leading to its isolation as AsF_3 .

CHAPTER 15

15.2 (a) Transition metals can undergo loss of one or more electrons (complete loss, as in ionic bonding, or partial, as in polar covalent bonding) without a great expenditure of energy. For example, iron has two common positive oxidation