

8 Basic Concepts of Chemical Bonding

Visualizing Concepts

8.1 *Analyze/Plan.* Count the number of electrons in the Lewis symbol. This corresponds to the 'A'-group number of the family. *Solve.*

- (a) Group 4A or 14
- (b) Group 2A or 2
- (c) Group 5A or 15

(These are the appropriate groups in the s and p blocks, where Lewis symbols are most useful.)

8.2 *Analyze.* Given the size and charge of four different ions, determine their ionic bonding characteristics.

Plan. The magnitude of lattice energy is directly proportional to the charges of the two ions and inversely proportional to their separation. $E_{el} = \kappa Q_1 Q_2 / d$. Apply these concepts to A, B, X and Y.

- (a) AY and BX have a 1:1 ratio of cations and anions. In an ionic compound, the total positive and negative charges must be equal. In order to form a 1:1 compound, the magnitude of positive charge on the cation must equal the magnitude of negative charge on the anion. A^{2+} combines with Y^{2-} and B^+ combines with X^- to form 1:1 compounds.
- (b) AY has the larger lattice energy. The A–Y and B–X separations are nearly equal. (A is smaller than B, but X is smaller than Y, so the differences in cation and anion radii approximately cancel.) In AY, $Q_1 Q_2 = (2)(2) = 4$, while in BX, $Q_1 Q_2 = (1)(1) = 1$.
- (c) BX has the smaller lattice energy. To recap the arguments in part (b), the d values in the two compounds are similar and BX has the smaller $Q_1 Q_2$, so it has the smaller lattice energy.

8.3 *Analyze.* Given a schematic "slab" of NaCl(s), where Cl^- anions are green and Na^+ cations are purple, answer questions regarding the electrostatic interactions between various ions. *Plan.* $E_{el} = \kappa Q_1 Q_2 / d$. Use geometry to estimate or calculate distances when needed. *Solve.*

- (a) Purple-green interactions are attractive; these are electrostatic attractions between two oppositely charged ions. The sign of E_{el} for these interactions is negative (–). Purple-purple and green-green interactions are repulsive; these are electrostatic attractions between two ions with the same charge. The sign of E_{el} for these interactions is positive (+).

- (b) The magnitudes of the 1–5 and 3–5 interactions are equal and are larger than the magnitude of the 1–3 interaction. Since 1, 3 and 5 all have the same charge, the magnitude of their interactions depends on the distance between the ions; the shorter the distance the larger the magnitude of the interaction. The distances between any green and any purple ion are the same, d . The distance between 1 and 3 is then $2d$. The 1–5 and 3–5 distances are the hypotenuse of a right isosceles triangle and are equal. This distance is $\sqrt{2}d$, which is shorter than the 1–3 distance of $2d$.
- (c) The magnitude of the attractive 1–2 interaction is greater than the magnitude of the repulsive 1–5 interaction. Again, the magnitudes of the charges of the ions are equal, so the ion-ion distances determine the magnitude of the interactions. The 1–2 distance, d , is shorter than the 1–5 distance, $\sqrt{2}d$. The magnitude of the attractive 1–2 interaction is greater than the magnitude of the repulsive 1–5 interaction.
- (d) Since the magnitude of the attractive 1–2 interaction is greater than the magnitude of the repulsive 1–3 interaction, the overall sum of interactions in the solid is attractive. For attractive interactions, the sign of E_{ei} is negative. This means that the grid (lattice) of ions in the solid has lower energy than a random collection of the same number and kinds of isolated ions; NaCl is a “stable” solid.

8.4 *Analyze/Plan.* Count the valence electrons in the orbital diagram, take ion charge into account, and find the element with this orbital electron count on the periodic table. Write the complete electron configuration for the ion. *Solve.*

- (a) This ion has six 4d electrons. Transition metals, or d-block elements, have valence electrons in d-orbitals. Transition metal ions first lose electrons from the 5s orbital, then from 4d if required by the charge. This 2+ ion has lost two electrons from 5s, none from 4d. The transition metal with six 4d-electrons is ruthenium, Ru.
- (b) The electron configuration of Ru is $[\text{Kr}]5s^24d^6$. (The configuration of Ru^{2+} is $[\text{Kr}]4d^6$).

8.5 *Analyze/Plan.* This question is a “reverse” Lewis structure. Count the valence electrons shown in the Lewis structure. For each atom, assume zero formal charge and determine the number of valence electrons an unbound atom has. Name the element. *Solve.*

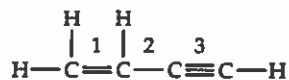
- A: 1 shared e^- pair = 1 valence electron + 3 unshared pairs = 7 valence electrons, F
 E: 2 shared pairs = 2 valence electrons + 2 unshared pairs = 6 valence electrons, O
 D: 4 shared pairs = 4 valence electrons, C
 Q: 3 shared pairs = 3 valence electrons + 1 unshared pair = 5 valence electrons, N
 X: 1 shared pair = 1 valence electron, no unshared pairs, H
 Z: same as X, H

Check. Count the valence electrons in the Lewis structure. Does the number correspond to the molecular formula CH_2ONF ? $12 e^-$ pair in the Lewis structure. $\text{CH}_2\text{ONF} = 4 + 2 + 6 + 5 + 7 = 24 e^-$, $12 e^-$ pair. The molecular formula we derived matches the Lewis structure.

- 8.6 (a) HNO_2 , 18 valence e^- , 9 e^- pairs NO_2^- , 18 valence e^- , 9 e^- pairs
 $\text{H}-\ddot{\text{O}}-\ddot{\text{N}}=\ddot{\text{O}}$ $[\ddot{\text{O}}-\ddot{\text{N}}=\ddot{\text{O}}]^-$
- (b) The formal charge on N is zero, in both species.
- (c) NO_2^- is expected to exhibit resonance; the double bond can be drawn to either oxygen atom. An alternate resonance structure for HNO_2 can be drawn, but it has nonzero formal charges on the oxygen atoms. This structure is less likely than the one shown above.
- (d) Assuming that the structure shown above is the main contributor to the structure of HNO_2 , the $\text{N}=\text{O}$ bond length in HNO_2 will be shorter than the $\text{N}-\text{O}$ lengths in NO_2^- . Because there are two equivalent resonance structures for NO_2^- , the $\text{N}-\text{O}$ lengths are approximately an average of $\text{N}-\text{O}$ single and double bond lengths. These are longer than the full $\text{N}=\text{O}$ double bond in HNO_2 .

8.7 *Analyze/Plan.* Since there are no unshared pairs in the molecule, we use single bonds to H to complete the octet of each C atom. For the same pair of bonded atoms, the greater the bond order, the shorter and stronger the bond. *Solve.*

- (a) Moving from left to right along the molecule, the first C needs two H atoms, the second needs one, the third needs none, and the fourth needs one. The complete molecule is:



- (b) In order of increasing bond length: $3 < 1 < 2$
- (c) In order of increasing bond enthalpy (strength): $2 < 1 < 3$

8.8 *Analyze/Plan.* Given an oxyanion of the type XO_4^{n-} , find the identity of X from elements in the third period. Use the generic Lewis structure to determine the identity of X, and to draw the ion-specific Lewis structures. Use the definition of formal charge, [$\#$ of valence electrons - $\#$ of nonbonding electrons - ($\#$ bonding electrons/2)], to draw Lewis structures where X has a formal charge of zero. *Solve.*

- (a) According to the generic Lewis structure, each anion has 12 nonbonding and 4 bonding electron pairs, for a total of 32 electrons. Of these 32 electrons, the 4 O atoms contribute $(4 \times 6) = 24$, and the overall negative charges contribute 1, 2 or 3.
 $\# \text{ X electrons} = 32 - 24 - n$.

For $n = 1^-$, X has $(32 - 24 - 1) = 7$ valence electrons. X is Cl, and the ion is ClO_4^- .

For $n = 2^-$, X has $(32 - 24 - 2) = 6$ valence electrons. X is S, and the ion is SO_4^{2-} .

For $n = 3^-$, X has $(32 - 24 - 3) = 5$ valence electrons. X is P, and the ion is PO_4^{3-} .

Check. The identity of the ions is confirmed in Table 2.5.

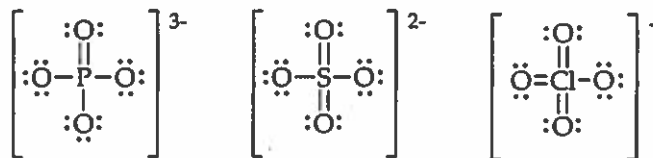
- (b) In the generic Lewis structure, X has 0 nonbonding electrons and $(8/2) = 4$ bonding electrons. Differences in formal charge are due to difference in the number of valence electrons on X.

For PO_4^{3-} , formal charge of P is $(5 - 4) = +1$.

For SO_4^{2-} , formal charge of S is $(6 - 4) = +2$.

For ClO_4^- , formal charge of Cl is $(7 - 4) = +3$.

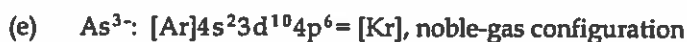
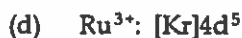
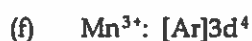
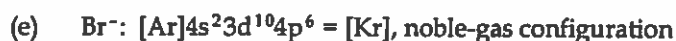
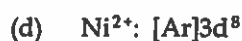
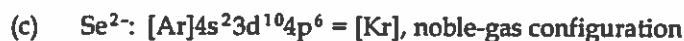
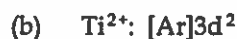
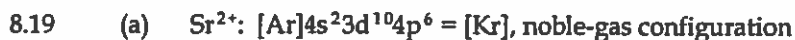
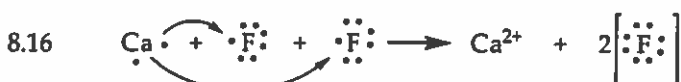
- (c) In order to reduce the formal charge of X to zero, X must have more bonding electrons. This is accomplished by changing the appropriate number of lone pairs on O to multiple bonds between X and O.



Lewis Symbols (section 8.1)

- 8.9 (a) Valence electrons are those that take part in chemical bonding, those in the outermost electron shell of the atom. This usually means the electrons beyond the core noble-gas configuration of the atom, although it is sometimes only the outer shell electrons.
- (b) N: $[\text{He}] 2s^2 2p^3$
└──────────┘ A nitrogen atom has 5 valence electrons.
 Valence electrons
- (c) $1s^2 2s^2 2p^6 \quad 3s^2 3p^2$ The atom (Si) has 4 valence electrons.
└──────────┘ └──────────┘
 [Ne] valence electrons
- 8.10 (a) Atoms will gain, lose, or share electrons to achieve the nearest noble-gas electron configuration. Except for H and He, this corresponds to eight electrons in the valence shell, thus the term octet rule.
- (b) S: $[\text{Ne}] 3s^2 3p^4$ A sulfur atom has six valence electrons, so it must gain two electrons to achieve an octet.
- (c) $1s^2 2s^2 2p^3 = [\text{He}] 2s^2 2p^3$ The atom (N) has five valence electrons and must gain three electrons to achieve an octet.
- 8.11 Si: $1s^2 2s^2 2p^6 3s^2 3p^2$. The 3s and 3p electrons are valence electrons; the 1s, 2s and 2p electrons are nonvalence or core electrons. Valence electrons are involved in chemical bonding, while nonvalence or core electrons are not.
- 8.12 (a) Ti: $[\text{Ar}] 4s^2 3d^2$. Ti has four (4) valence electrons. These valence electrons are available for chemical bonding, while core electrons do not participate in chemical bonding.
- (b) Hf: $[\text{Xe}] 6s^2 4f^{14} 5d^2$
- (c) If Hf and Ti both behave as if they have four (4) valence electrons, the 6s and 5d orbitals in Hf behave as valence orbitals and the 4f behaves as a core orbital. This is reasonable because 4f is complete and 4f electrons are, on average, closer to the nucleus than 5d or 6s electrons.
- 8.13 (a) $\cdot\text{Al}\cdot$ (b) $:\ddot{\text{Br}}:$ (c) $:\ddot{\text{Ar}}:$ (d) $\dot{\text{Sr}}$
- 8.14 (a) K \cdot (b) $\cdot\ddot{\text{As}}\cdot$ (c) $[\text{Sn}]^{2+}$ (d) $[\text{:}\ddot{\text{N}}:]^{3-}$

Ionic Bonding



8.21 (a) *Lattice energy* is the energy required to totally separate one mole of solid ionic compound into its gaseous ions.

(b) The magnitude of the lattice energy depends on the magnitudes of the charges of the two ions, their radii, and the arrangement of ions in the lattice. The main factor is the charges, because the radii of ions do not vary over a wide range.

8.22 (a) NaCl , 788 kJ/mol; KF , 808 kJ/mol

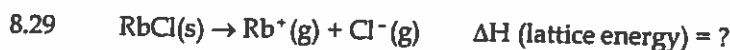
The two factors that affect lattice energies are ionic charge and radius. The ionic charges, $1+$ and $1-$, are the same in the two compounds. Since lattice energy is inversely proportional to the ion separation (d), we expect the compound with the smaller lattice energy, NaCl , to have the larger ion separation. That is, the K-F distance should be shorter than the Na-Cl distance.

(b) Na-Cl , $1.16 \text{ \AA} + 1.67 \text{ \AA} = 2.83 \text{ \AA}$

K-F , $1.52 \text{ \AA} + 1.19 \text{ \AA} = 2.71 \text{ \AA}$

This estimate of the relative ion separations agrees with the estimate from lattice energies. Ionic radii indicate that the K-F distance is shorter than the Na-Cl distance.

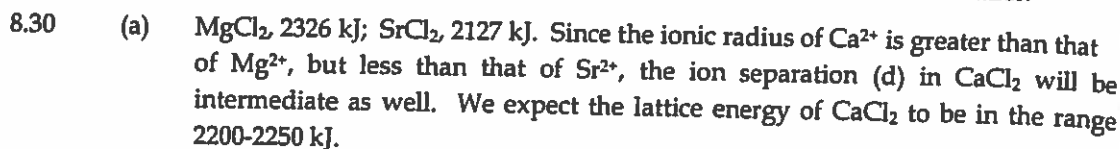
- 8.23 KF, 808 kJ/mol; CaO, 3414 kJ/mol; ScN, 7547 kJ/mol
- The sizes of the ions vary as follows: $\text{Sc}^{3+} < \text{Ca}^{2+} < \text{K}^+$ and $\text{F}^- < \text{O}^{2-} < \text{N}^{3-}$. Therefore, the inter-ionic distances are similar. According to Coulomb's law for compounds with similar ionic separations, the lattice energies should be related as the product of the charges of the ions. The lattice energies above are approximately related as (1)(1): (2)(2): (3)(3) or 1:4:9. Slight variations are due to the small differences in ionic separations.
- 8.24 (a) According to Equation 8.4, electrostatic attraction increases with increasing charges of the ions and decreases with increasing radius of the ions. Thus, lattice energy (i) increases as the charges of the ions increase and (ii) decreases as the sizes of the ions increase.
- (b) $\text{KI} < \text{LiBr} < \text{MgS} < \text{GaN}$. Lattice energy increases as the charges on the ions increase. The ions in KI and LiBr all have 1+ and 1- charges. K^+ is larger than Li^+ , and I^- is larger than Br^- . The ion separation is larger in KI, so it has the smaller lattice energy.
- 8.25 Since the ionic charges are the same in the two compounds, the K-Br and Cs-Cl separations must be approximately equal. Since the radii are related as $\text{Cs}^+ > \text{K}^+$ and $\text{Br}^- > \text{Cl}^-$, the difference between Cs^+ and K^+ must be approximately equal to the difference between Br^- and Cl^- . This is somewhat surprising, since K^+ and Cs^+ are two rows apart and Cl^- and Br^- are only one row apart.
- 8.26 (a) The ions have 1+ and 1- charges in all three compounds. In NaCl the cationic and anionic radii are smaller than in the other two compounds, so it has the largest lattice energy. In RbBr and CsBr, the anion is the same, but the Cs cation is larger, so CsBr has the smaller lattice energy.
- (b) In BaO, the magnitude of the charges of both ions is 2; in KF, the magnitudes are 1. Charge considerations alone predict that BaO will have the higher lattice energy. The distance effect is less clear; O^{2-} and F^- are isoelectronic, so F^- , with the larger Z, has a slightly smaller radius. Ba^{2+} is two rows lower on the periodic table than K^+ , but it has a greater positive charge, so the radii are probably similar. In any case, the ionic separations in the two compounds are not very different, and the charge effect dominates.
- (c) In SrO, the ions have 2+ and 2- charges. In SrCl_2 the Cl^- anions have 1- charges, so SrO has the larger lattice energy. Also, O^{2-} has a substantially smaller ionic radius than Cl^- , so distance effects also predict that SrO will have the larger lattice energy.
- 8.27 Equation 8.4 predicts that as the oppositely charged ions approach each other, the energy of interaction will be large and negative. This more than compensates for the energy required to form Ca^{2+} and O^{2-} from the neutral atoms (see Figure 8.5 for the formation of NaCl).
- 8.28 $\text{Ba(s)} \rightarrow \text{Ba(g)}; \text{Ba(g)} \rightarrow \text{Ba}^+(\text{g}) + 1\text{e}^-; \text{Ba}^+(\text{g}) \rightarrow \text{Ba}^{2+}(\text{g}) + 1\text{e}^-;$
 $\text{I}_2(\text{s}) \rightarrow 2\text{I(g)}; 2\text{I(g)} + 2\text{e}^- \rightarrow 2\text{I}^-(\text{g}), \text{ exothermic};$
 $\text{Ba}^{2+}(\text{g}) + 2\text{I}^-(\text{g}) \rightarrow \text{BaI}_2(\text{s}), \text{ exothermic}$



By analogy to NaCl, Figure 8.5, the lattice energy is

$$\begin{aligned} \Delta H_{\text{latt}} &= -\Delta H_f^\circ \text{RbCl(s)} + \Delta H_f^\circ \text{Rb(g)} + \Delta H_f^\circ \text{Cl(g)} + I_1(\text{Rb}) + E(\text{Cl}) \\ &= -(-430.5 \text{ kJ}) + 85.8 \text{ kJ} + 121.7 \text{ kJ} + 403 \text{ kJ} + (-349 \text{ kJ}) = +692 \text{ kJ/mol} \end{aligned}$$

This value is smaller than that for NaCl (+788 kJ/mol) because Rb^+ has a larger ionic radius than Na^+ . This means that the value of d in the denominator of Equation 8.4 is larger for RbCl, and the potential energy of the electrostatic attraction is smaller.



(b) By analogy to Figure 8.5:

$$\begin{aligned} \Delta H_{\text{latt}} &= -\Delta H_f^\circ \text{CaCl}_2 + \Delta H_f^\circ \text{Ca(g)} + 2\Delta H_f^\circ \text{Cl(g)} + I_1(\text{Ca}) + I_2(\text{Ca}) + 2E(\text{Cl}) \\ &= -(-795.8 \text{ kJ}) + 179.3 \text{ kJ} + 2(121.7 \text{ kJ}) + 590 \text{ kJ} + 1145 \text{ kJ} + 2(-349 \text{ kJ}) = +2256 \text{ kJ} \end{aligned}$$

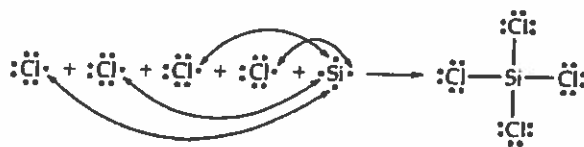
This value is near the range predicted in part (a).

Covalent Bonding, Electronegativity, and Bond Polarity (sections 8.3 and 8.4)

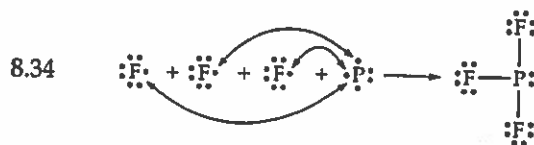
- 8.31 (a) A *covalent bond* is the bond formed when two atoms share one or more pairs of electrons.
 (b) Any simple compound whose component atoms are nonmetals, such as H_2 , SO_2 , and CCl_4 , are molecular and have covalent bonds between atoms.
 (c) Covalent because it is a gas even below room temperature.

- 8.32 K and Ar. K is an active metal with one valence electron. It is most likely to achieve an octet by losing this single electron and to participate in ionic bonding. Ar has a stable octet of valence electrons; it is not likely to form chemical bonds of any type.

- 8.33 *Analyze/Plan.* Follow the logic in Sample Exercise 8.3. *Solve.*



Check. Each pair of shared electrons in SiCl_4 is shown as a line; each atom is surrounded by an octet of electrons.



- 8.35 (a) $\text{:}\ddot{\text{O}}=\ddot{\text{O}}\text{:}$
 (b) A double bond is required because there are not enough electrons to satisfy the octet rule with single bonds and unshared pairs.

- (c) The greater the number of shared electron pairs between two atoms, the shorter the distance between the atoms. If O_2 has a double bond, the O–O distance will be shorter than the O–O single bond distance.
- 8.36 (a) The H atoms must be terminal because H can form only one bond.
 14 e^- , 7 e^- pairs

$$H-\ddot{O}-\ddot{O}-H$$
- (b) From Solution 8.35, O_2 has a double bond. The O–O bond in H_2O_2 is a single bond, and thus longer than the O–O double bond in O_2 .
- 8.37 (a) *Electronegativity* is the ability of an atom in a molecule (a bonded atom) to attract electrons to itself.
- (b) The range of electronegativities on the Pauling scale is 0.7–4.0.
- (c) Fluorine, F, is the most electronegative element.
- (d) Cesium, Cs, is the least electronegative element that is not radioactive.
- 8.38 (a) The electronegativity of the elements increases going from left to right across a row of the periodic table.
- (b) Electronegativity decreases going down a family of the periodic table.
- (c) Generally, the trends in electronegativity are the same as those in ionization energy and opposite those in electron affinity. That is, the more positive the ionization energy and the more negative the electron affinity (ignoring a few exceptions), the greater the electronegativity of an element.
- 8.39 *Plan.* Electronegativity increases going up and to the right in the periodic table.
Solve.
- (a) Mg (b) S (c) C (d) As
- Check.* The electronegativity values in Figure 8.7 confirm these selections.
- 8.40 Electronegativity increases going up and to the right in the periodic table.
- (a) O (b) Al (c) Cl (d) F
- 8.41 The bonds in (a), (c) and (d) are polar because the atoms involved differ in electronegativity. The more electronegative element in each polar bond is:
- (a) F (c) O (d) I
- 8.42 The more different the electronegativity values of the two elements, the more polar the bond.
- (a) $O-F < C-F < Be-F$. This order is clear from the periodic trend.
- (b) $S-Br < C-P < O-Cl$. Refer to the electronegativity values in Figure 8.7 to confirm the order of bond polarity. The 3 pairs of elements all have the same positional relationship on the periodic table. The more electronegative element is one row above and one column to the left of the less electronegative element. This leads us to conclude that ΔEN is similar for the 3 bonds, which is confirmed by values in Figure 8.7. The most polar bond, O–Cl, involves the most electronegative

element, O. Generally, the largest electronegativity differences tend to be between row 2 and row 3 elements. The 2 bonds in this exercise involving elements in row 2 and row 3 do have slightly greater ΔEN than the S-Br bond, between elements in rows 3 and 4.

- (c) C-S < N-O < B-F. You might predict that N-O is least polar since the elements are adjacent on the table. However, the big decrease going from the second row to the third means that the electronegativity of S is not only less than that of O, but essentially the same as that of C. C-S is the least polar.

- 8.43 (a) *Analyze/Plan.* Q is the charge at either end of the dipole. $Q = \mu/r$. The values for HBr are $\mu = 0.82$ D and $r = 1.41$ Å. Change Å to m and use the definition of debyes and the charge of an electron to calculate effective charge in units of e . *Solve.*

$$Q = \frac{\mu}{r} = \frac{0.82 \text{ D}}{1.41 \text{ Å}} \times \frac{1 \text{ Å}}{1 \times 10^{-10} \text{ m}} \times \frac{3.34 \times 10^{-30} \text{ C} \cdot \text{m}}{1 \text{ D}} \times \frac{1 e}{1.60 \times 10^{-19} \text{ C}} = 0.12 e$$

- (b) From Sample Exercise 8.5, the effective charges on H and Cl in the HCl molecule are $+0.178 e$ and $-0.178 e$, respectively. From part (a), the effective charges on H and Br are $+0.12 e$ and $-0.12 e$. HBr has a smaller dipole moment and longer bond length than HCl; these properties both contribute to the smaller charge separation in HBr.

- 8.44 (a) The more electronegative element, Br, will have a stronger attraction for the shared electrons and adopt a partial negative charge.

- (b) Q is the charge at either end of the dipole.

$$Q = \frac{\mu}{r} = \frac{1.21 \text{ D}}{2.49 \text{ Å}} \times \frac{1 \text{ Å}}{1 \times 10^{-10} \text{ m}} \times \frac{3.34 \times 10^{-30} \text{ C} \cdot \text{m}}{1 \text{ D}} \times \frac{1 e}{1.60 \times 10^{-19} \text{ C}} = 0.1014 = 0.101 e$$

The charges on I and Br are $0.101 e$.

- 8.45 *Analyze/Plan.* Generally, compounds formed by a metal and a nonmetal are described as ionic, while compounds formed from two or more nonmetals are covalent. However, substances with metals in a high oxidation state often have properties of molecular compounds. In this exercise we know that one substance in each pair is molecular and one is ionic; we may need to distinguish by comparison. *Solve.*

- (a) SiF_4 , metalloid and nonmetal, molecular, silicon tetrafluoride
 LaF_3 , metal and nonmetal, ionic, lanthanum(III) fluoride
- (b) FeCl_2 , metal and nonmetal, ionic, iron(II) chloride
 ReCl_6 , metal in high oxidation state, Re(VI), molecular, rhenium hexachloride
- (c) PbCl_4 , metal and nonmetal, Pb(IV) is relatively high oxidation state, molecular (by contrast with RbCl , which is definitely ionic), lead tetrachloride
 RbCl , metal and nonmetal, ionic, rubidium chloride

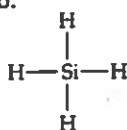
- 8.46 Generally, compounds formed by a metal and a nonmetal are described as ionic, while compounds formed from two or more nonmetals are covalent. However, substances with metals in a high oxidation states often have properties of molecular compounds.

- (a) TiCl_4 , metal and nonmetal, Ti(IV) is a relatively high oxidation state, molecular (by contrast with CaF_2 , which is definitely ionic), titanium tetrachloride
 CaF_2 , metal and nonmetal, ionic, calcium fluoride
- (b) ClF_3 , two nonmetals, molecular, chlorine trifluoride
 VF_3 , metal and nonmetal, ionic, vanadium(III) fluoride
- (c) SbCl_5 , metalloid and nonmetal, molecular, antimony pentachloride
 AlF_3 , metal and nonmetal, ionic, aluminum fluoride

Lewis Structures; Resonance Structures (sections 8.5 and 8.6)

8.47 *Analyze.* Counting the correct number of valence electrons is the foundation of every Lewis structure. *Plan/Solve.*

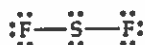
- (a) Count valence electrons: $4 + (4 \times 1) = 8 e^-$, 4 e^- pairs. Follow the procedure in Sample Exercise 8.6.



- (b) Valence electrons: $4 + 6 = 10 e^-$, 5 e^- pairs

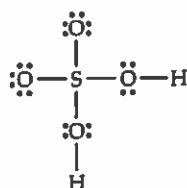


- (c) Valence electrons: $[6 + (2 \times 7)] = 20 e^-$, 10 e^- pairs

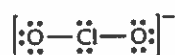


- Place the S atom in the middle and connect each F atom with a single bond; this requires 2 e^- pairs.
- Complete the octets of the F atoms with nonbonded pairs of electrons; this requires an additional 6 e^- pairs.
- The remaining 2 e^- pairs complete the octet of the central S atom.

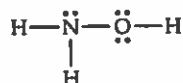
- (d) (Draw the structure that obeys the octet rule, for now.) 32 valence e^- , 16 e^- pairs



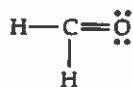
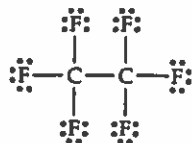
- (e) Follow Sample Exercise 8.8. 20 valence e^- , 10 e^- pairs



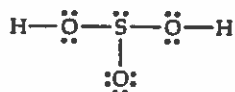
- (f) 14 valence e^- , 7 e^- pairs



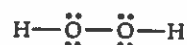
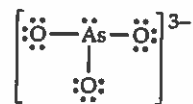
Check. In each molecule, bonding e^- pairs are shown as lines, and each atom is surrounded by an octet of electrons (duet for H).

8.48 (a) 12 valence e^- , 6 e^- pairs(c) 50 valence e^- , 25 e^- pairs

(The Lewis structure that obeys the octet rule)

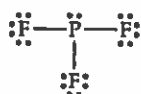
(e) 26 valence e^- , 13 e^- pairs

(The Lewis structure that obeys the octet rule)

(b) 14 valence e^- , 7 e^- pairs(d) 26 valence e^- , 13 e^- pairs(f) 10 e^- , 5 e^- pairs8.49 (a) *Formal charge* is the charge on each atom in a molecule, assuming all atoms have the same electronegativity.

(b) Formal charges are not actual charges. They are a bookkeeping system that assumes perfect covalency, one extreme for the possible electron distribution in a molecule.

(c) The other extreme is represented by oxidation numbers, a bookkeeping system which assumes that the more electronegative element holds all electrons in a bond. The true electron distribution is some composite of the two extremes.

8.50 (a) 26 e^- , 13 e^- pairs

The octet rule is satisfied for all atoms in the structure.

(b) F is more electronegative than P. Assuming F atoms hold all shared electrons, the oxidation number of each F is -1. The oxidation number of P is +3.

(c) Assuming perfect sharing, the formal charges on all F and P atoms are 0.

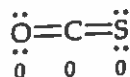
(d) The oxidation number on P is +3; the formal charge is 0. These represent extremes in the possible electron distribution, not the best picture. By virtue of their greater electronegativity, the F atoms carry a partial negative charge, and the P atom a partial positive charge.

8.51 *Analyze/Plan.* Draw the correct Lewis structure: count valence electrons in each atom, total valence electrons and electron pairs in the molecule or ion; connect bonded atoms with a line, place the remaining e^- pairs as needed, in nonbonded pairs or multiple bonds, so that each atom is surrounded by an octet (or duet for H). Calculate formal

charges: assign electrons to individual atoms [nonbonding e^- + $1/2$ (bonding e^-)]; formal charge = valence electrons - assigned electrons. Assign oxidation numbers, assuming that the more electronegative element holds all electrons in a bond.

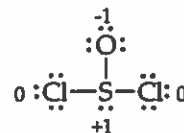
Solve. Formal charges are shown near the atoms, oxidation numbers (ox. #) are listed below the structures.

(a) 16 e^- , 8 e^- pairs



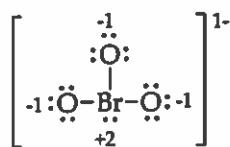
ox. #: O, -2; C, +4; S, -2

(b) 26 valence e^- , 13 e^- pairs



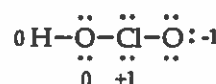
ox #: S, +4; Cl, -1; O, -2

(c) 26 valence e^- , 13 e^- pairs



ox. #: Br, +5; O, -2

(d) 20 valence e^- , 10 e^- pairs

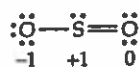


ox. #: Cl, +3; H, +1; O, -2

Check. Each atom is surrounded by an octet (or duet) and the sum of the formal charges and oxidation numbers is the charge on the particle.

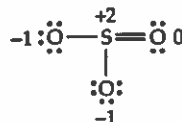
8.52 Formal charges are given near the atoms, oxidation numbers are listed below the structures.

(a) 18 e^- , 9 e^- pairs



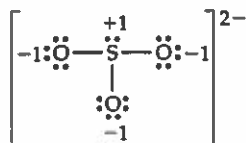
ox. #: S, +4; O, -2

(b) 24 e^- , 12 e^- pairs



ox. #: S, +6; O, -2

(c) 26 e^- , 13 e^- pairs



ox. #: S, +4; O, -2

(d) $\text{SO}_2 < \text{SO}_3 < \text{SO}_3^{2-}$

Double bonds are shorter than single bonds. SO_2 has two resonance structures with alternating single and double bonds, for an approximate average "one-and-a-half" bond. SO_3 has three resonance structures with one double and two single bonds, for an approximately, "one-and-a-third" bond. SO_3^{2-} has all single bonds. The order of increasing bond length is the order of decreasing bond type.

SO_2 (1.5) < SO_3 (1.3) < SO_3^{2-} (1.0).

- 8.53 (a) *Plan.* Count valence electrons, draw all possible correct Lewis structures, taking note of alternate placements for multiple bonds. *Solve.*

18 e⁻, 9 e⁻ pairs



Check. The octet rule is satisfied.

- (b) *Plan.* Isoelectronic species have the same number of valence electrons and the same electron configuration. *Solve.*

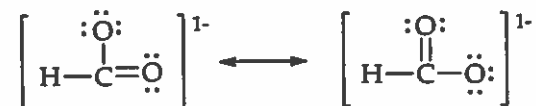
A single O atom has 6 valence electrons, so the neutral ozone molecule O₃ is isoelectronic with NO₂⁻.



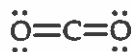
Check. The octet rule is satisfied.

- (c) Since each N-O bond has partial double bond character, the N-O bond length in NO₂⁻ should be shorter than N-O single bonds but longer than N=O double bonds.

- 8.54 (a) 18 e⁻, 9 e⁻ pairs



- (b) Yes, resonance structures are required to describe the structure.
 (c) The Lewis structure of CO₂ (16 e⁻, 8 e⁻ pairs) is



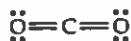
In CO₂ the C-O bonds are full double bonds with two shared pairs of electrons. In HCO₂⁻ the two resonance structures indicate that the C-O bonds have partial, but not full double bond character. The C-O bond lengths in formate will be longer than those in CO₂.

- 8.55 *Plan/Solve.* The Lewis structures are as follows:

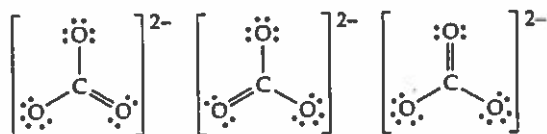
5 e⁻ pairs



8 e⁻ pairs



12 e⁻ pairs



The more pairs of electrons shared by two atoms, the shorter the bond between the atoms. The average number of electron pairs shared by C and O in the three species is 3 for CO, 2 for CO₂, and 1.33 for CO₃²⁻. This is also the order of increasing bond length: CO < CO₂ < CO₃²⁻.

8.56 The Lewis structures are as follows:

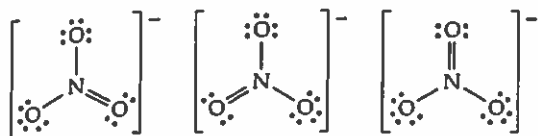
5 e⁻ pairs



9 e⁻ pairs



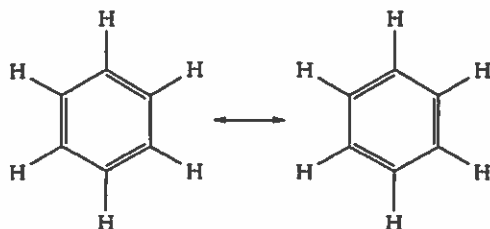
12 e⁻ pairs



The average number of electron pairs in the N-O bond is 3.0 for NO⁺, 1.5 for NO₂⁻, and 1.33 for NO₃⁻. The more electron pairs shared between two atoms, the shorter the bond. Thus the N-O bond lengths vary in the order NO⁺ < NO₂⁻ < NO₃⁻.

8.57

(a) Two equally valid Lewis structures can be drawn for benzene.

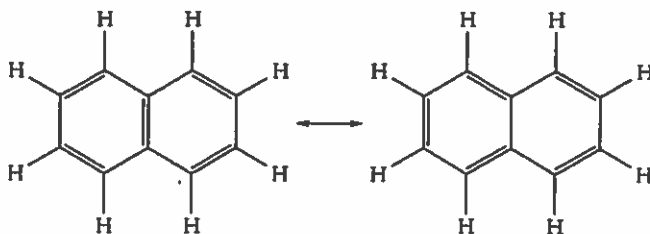


Each structure consists of alternating single and double C-C bonds; a particular bond is single in one structure and double in the other. The concept of resonance dictates that the true description of bonding is some hybrid or blend of the two Lewis structures. The most obvious blend of these two resonance structures is a molecule with six equivalent C-C bonds, each with some but not total double-bond character. If the molecule has six equivalent C-C bonds, the lengths of these bonds should be equal.

(b) The resonance model described in (a) has six equivalent C-C bonds, each with some double bond character. That is, more than one pair but less than two pairs of electrons is involved in each C-C bond. This model predicts a uniform C-C bond length that is shorter than a single bond but longer than a double bond.

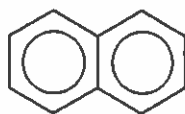
8.58

(a)



(b) The resonance model of this molecule has bonds that are neither single nor double, but somewhere in between. This results in bond lengths that are intermediate between C-C single and C=C double bond lengths.

(c)



Exceptions to the Octet Rule (section 8.7)

- 8.59 (a) The *octet rule* states that atoms will gain, lose, or share electrons until they are surrounded by eight valence electrons.
- (b) The octet rule applies to both ionic and covalent compounds, with some exceptions. In ionic compounds, the cation has lost electrons to achieve an octet and the anion has gained electrons to achieve an octet. For example, in MgCl_2 , Mg loses $2 e^-$ to become Mg^{2+} with the electron configuration of Ne. Each Cl atom gains one electron to form Cl^- with the electron configuration of Ar. In covalent compounds, such as CCl_4 , atoms share electrons in order to surround themselves with an octet.

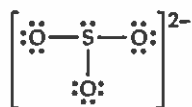
8.60 Carbon, in group 4A, needs to form four single bonds to achieve an octet, as in CH_4 . Nitrogen, in group 5A, needs to form three, as in NH_3 . If G = group number and n = the number of single bonds, $G + n = 8$ is a general relationship for the representative non-metals.

Check: O as in H_2O ($G = 6A$) + ($n = 2$ bonds) = 8

8.61 No chlorine oxide will obey the octet rule. Oxygen has six valence electrons, an even number. Any number of oxygen atoms in the molecule will result in an even number of valence electrons from oxygen. Chlorine has seven valence electrons, an odd number. For neutral chlorine oxide molecules, the total number of valence electrons will be an (odd + even) sum, which is always an odd number. A molecule with an odd number of valence electrons cannot obey the octet rule.

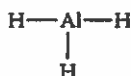
8.62 In the third period, atoms have the space and available orbitals to accommodate extra electrons. Since atomic radius increases going down a family, elements in the third period and beyond are less subject to destabilization from additional electron-electron repulsions. Also, the third shell contains d orbitals that are relatively close in energy to 3s and 3p orbitals (the ones that accommodate the octet) and provide an allowed energy state for the extra electrons.

- 8.63 (a) $26 e^-$, $13 e^-$ pairs



Other resonance structures with one, two, or three double bonds can be drawn. While a structure with three double bonds minimizes formal charges, all structures with double bonds violate the octet rule. The octet rule vs formal charge debate is ongoing.

- (b) $6 e^-$, $3 e^-$ pairs



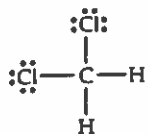
6 electrons around Al; impossible to satisfy octet rule with only 6 valence electrons.

- (c) 16 e
- ⁻
- , 8 e
- ⁻
- pairs



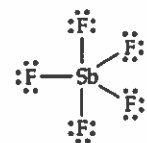
3 resonance structures; all obey octet rule.

- (d) 20 e
- ⁻
- , 10 e
- ⁻
- pairs



Obey octet rule.

- (e) 40 e
- ⁻
- , 20 e
- ⁻
- pairs

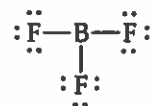
Does not obey octet rule; 10 e⁻ around central Sb

- 8.64 (a) 11 e
- ⁻
- , 5.5 e
- ⁻
- pairs



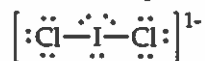
Does not obey the octet rule.

- (b) 24 e
- ⁻
- , 12 e
- ⁻
- pairs



Does not obey the octet rule.

- (c) 22 e
- ⁻
- , 11 e
- ⁻
- pairs



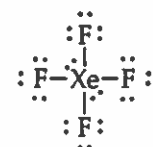
Does not obey the octet rule.

- (d) 32 e
- ⁻
- , 16 e
- ⁻
- pairs

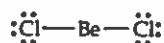


The structure on the left obeys the octet rule, while the one on the right minimizes formal charges but does not obey the octet rule.

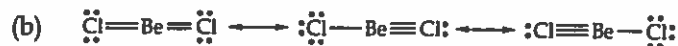
- (e) 36 e
- ⁻
- , 18 e
- ⁻
- pairs



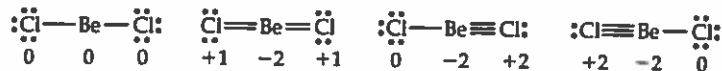
Does not obey the octet rule.

8.65 (a) $16 e^-$, $8 e^-$ pairs

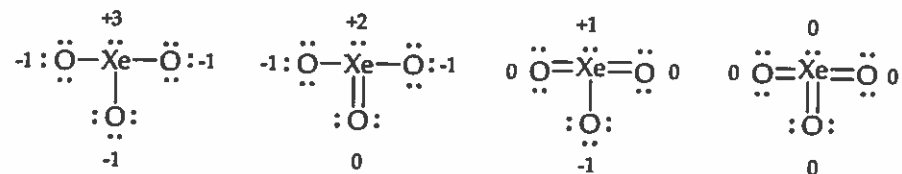
This structure violates the octet rule; Be has only $4 e^-$ around it.



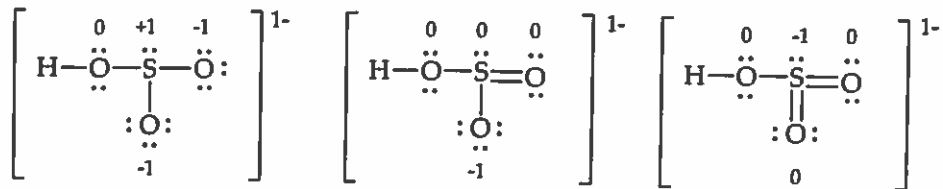
(c) The formal charges on each of the atoms in the four resonance structures are:



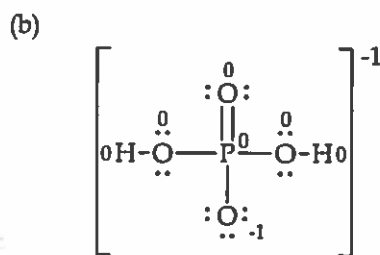
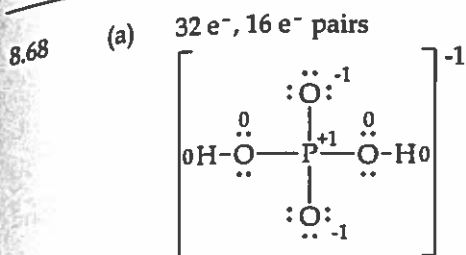
Formal charges are minimized on the structure that violates the octet rule; this form is probably dominant.

8.66 (a) $26 e^-$, $13 e^-$ pairs

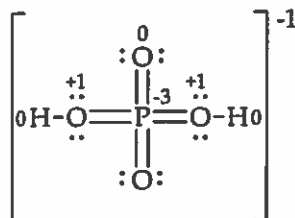
- (b) Yes, the structure with no double bonds obeys the octet rule for all atoms.
- (c) The structure with one double bond has 3 resonance structures (3 possible positions for the double bond), as does the structure with two double and one single bond (3 possible positions for the single bond). The total number of resonance structures is then 8.
- (d) The structure with 3 double bonds minimizes formal charges on all atoms.

8.67 $26 e^-$, $13 e^-$ pairs

Three resonance structures for HSO_3^- are shown above. Because we are dealing with an ion with a $1-$ charge, the sum of the formal charges of the atoms will be -1 . That is, no correct Lewis structure will have all atoms with zero formal charge. The structure with no double bonds obeys the octet rule for all atoms, but does not lead to minimum formal charge. The structures with one and two double bonds both minimize formal charge but do not obey the octet rule. Of these two, the structure with one double bond is preferred because the formal charge is localized on the more electronegative oxygen atom.



- (c) With no restrictions on the size of the 'expanded' octet around P, there are many structures that neither obey the octet rule nor minimize formal charge. A fairly extreme example is shown below.



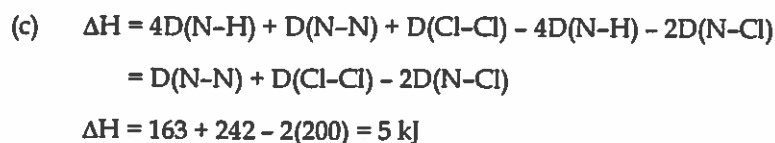
Bond Enthalpies (section 8.8)

- 8.69 *Analyze.* Given: structural formulas. Find: enthalpy of reaction.

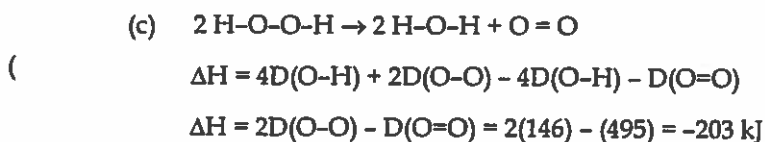
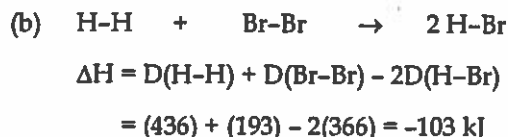
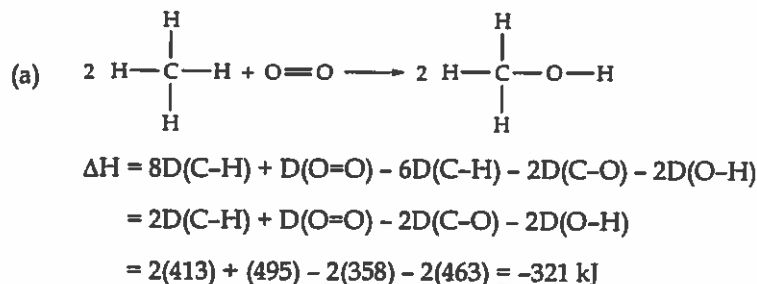
Plan. Count the number and kinds of bonds that are broken and formed by the reaction. Use bond enthalpies from Table 8.4 and Equation 8.12 to calculate the overall enthalpy of reaction, ΔH . *Solve.*

- (a) $\Delta H = 2D(\text{O-H}) + D(\text{O-O}) + 4D(\text{C-H}) + D(\text{C=C})$
 $\quad - 2D(\text{O-H}) - 2D(\text{O-C}) - 4D(\text{C-H}) - D(\text{C-C})$
 $\Delta H = D(\text{O-O}) + D(\text{C=C}) - 2D(\text{O-C}) - D(\text{C-C})$
 $\quad = 146 + 614 - 2(358) - 348 = -304 \text{ kJ}$
- (b) $\Delta H = 5D(\text{C-H}) + D(\text{C}\equiv\text{N}) + D(\text{C=C}) - 5D(\text{C-H}) - D(\text{C}\equiv\text{N}) - 2D(\text{C-C})$
 $\quad = D(\text{C=C}) - 2D(\text{C-C}) = 614 - 2(348) = -82 \text{ kJ}$
- (c) $\Delta H = 6D(\text{N-Cl}) - 3D(\text{Cl-Cl}) - D(\text{N}\equiv\text{N})$
 $\quad = 6(200) - 3(242) - 941 = -467 \text{ kJ}$

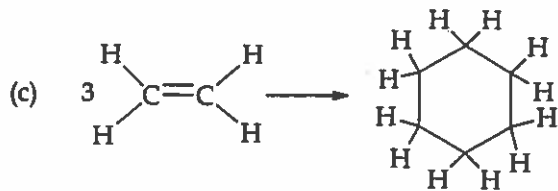
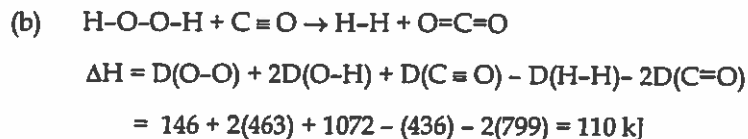
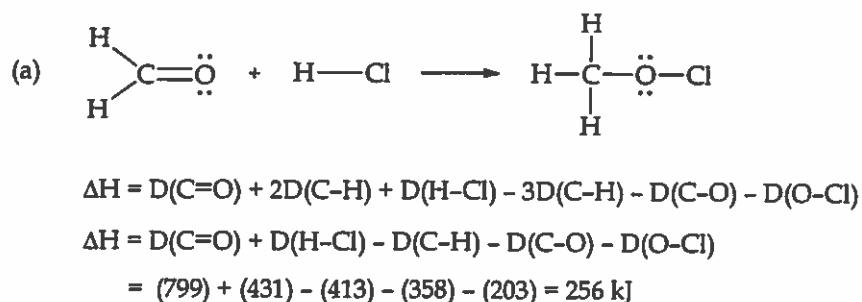
- 8.70 (a) $\Delta H = 3D(\text{C-Br}) + D(\text{C-H}) + D(\text{Cl-Cl}) - 3D(\text{C-Br}) - D(\text{C-Cl}) - D(\text{H-Cl})$
 $\quad = D(\text{C-H}) + D(\text{Cl-Cl}) - D(\text{C-Cl}) - D(\text{H-Cl})$
 $\Delta H = 413 + 242 - 328 - 431 = -104 \text{ kJ}$
- (b) $\Delta H = 4D(\text{C-H}) + 2D(\text{C-S}) + 2D(\text{S-H}) + D(\text{C-C}) + 2D(\text{H-Br})$
 $\quad - 4D(\text{S-H}) - D(\text{C-C}) - 2D(\text{C-Br}) - 4D(\text{C-H})$
 $\quad = 2D(\text{C-S}) + 2D(\text{H-Br}) - 2D(\text{S-H}) - 2D(\text{C-Br})$
 $\Delta H = 2(259) + 2(366) - 2(339) - 2(276) = 20 \text{ kJ}$



8.71 *Plan.* Draw structural formulas so bonds can be visualized. Then use Table 8.4 and Equation 8.12. *Solve.*



8.72 *Plan.* Draw structural formulas when needed. *Solve.*



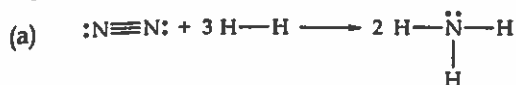
$$\Delta H = 3D(\text{C}=\text{C}) + 12D(\text{C}-\text{H}) - 12D(\text{C}-\text{H}) - 6D(\text{C}-\text{C})$$

$$\Delta H = 3D(\text{C}=\text{C}) - 6D(\text{C}-\text{C})$$

$$\Delta H = 3(614) - 6(348) = -246 \text{ kJ}$$

8.73

Plan. Draw structural formulas so bonds can be visualized. Then use Table 8.4 and Equation 8.12. *Solve.*



$$\begin{aligned} \Delta H &= D(\text{N}\equiv\text{N}) + 3D(\text{H}-\text{H}) - 6D(\text{N}-\text{H}) = 941 \text{ kJ} + 3(436 \text{ kJ}) - 6(391 \text{ kJ}) \\ &= -97 \text{ kJ}/2 \text{ mol NH}_3; \text{ exothermic} \end{aligned}$$

(b) *Plan.* Use Equation 5.31 to calculate $\Delta H_{\text{rxn}}^\circ$ from ΔH_f° values.

$$\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_f^\circ (\text{products}) - \sum n \Delta H_f^\circ (\text{reactants}). \quad \Delta H_f^\circ \text{NH}_3(\text{g}) = -46.19 \text{ kJ.}$$

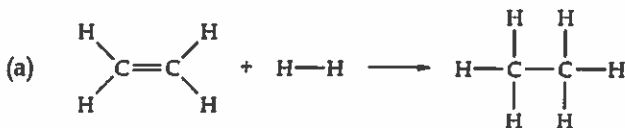
Solve.

$$\Delta H_{\text{rxn}}^\circ = 2 \Delta H_f^\circ \text{NH}_3(\text{g}) - 3 \Delta H_f^\circ \text{H}_2(\text{g}) - \Delta H_f^\circ \text{N}_2(\text{g})$$

$$\Delta H_{\text{rxn}}^\circ = 2(-46.19) - 3(0) - 0 = -92.38 \text{ kJ}/2 \text{ mol NH}_3$$

The ΔH calculated from bond enthalpies is slightly more exothermic (more negative) than that obtained using ΔH_f° values.

8.74



$$\Delta H = 4D(\text{C}-\text{H}) + D(\text{C}=\text{C}) + D(\text{H}-\text{H}) - 6D(\text{C}-\text{H}) - D(\text{C}-\text{C})$$

$$= D(\text{C}=\text{C}) + D(\text{H}-\text{H}) - 2D(\text{C}-\text{H}) - D(\text{C}-\text{C})$$

$$\Delta H = 614 + 436 - 2(413) - 348 = -124 \text{ kJ}$$

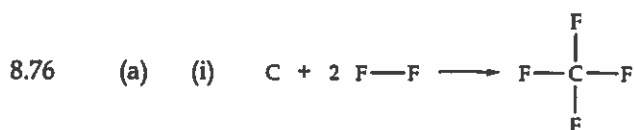
$$(b) \quad \Delta H^\circ = \Delta H_f^\circ \text{C}_2\text{H}_6(\text{g}) - \Delta H_f^\circ \text{C}_2\text{H}_4(\text{g}) - \Delta H_f^\circ \text{H}_2(\text{g})$$

$$= -84.68 - 52.30 - 0 = -136.98 \text{ kJ}$$

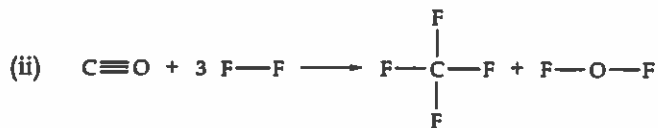
The values of ΔH for the reaction differ because the bond enthalpies used in part (a) are average values that can differ from one compound to another. For example, the exact enthalpy of a C-H bond in C_2H_4 is probably not equal to the enthalpy of a C-H bond in C_2H_6 . Thus, reaction enthalpies calculated from average bond enthalpies are estimates. On the other hand, standard enthalpies of formation are measured quantities and should lead to accurate reaction enthalpies. The advantage of average bond enthalpies is that they can be used for reactions where no measured enthalpies of formation are available.

8.75

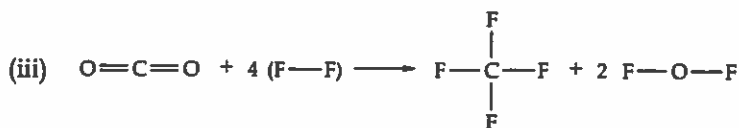
The average Ti-Cl bond enthalpy is just the average of the four values listed. 430 kJ/mol.



$$\Delta H = 2D(F-F) - 4D(C-F) = 2(155) - 4(485) = -1630 \text{ kJ}$$



$$\begin{aligned} \Delta H &= D(C \equiv O) + 3D(F-F) - 4D(C-F) - 2D(O-F) \\ &= 1072 + 3(155) - 4(485) - 2(190) = -783 \text{ kJ} \end{aligned}$$



$$\begin{aligned} \Delta H &= 2D(C=O) + 4D(F-F) - 4D(C-F) - 4D(O-F) \\ &= 2(799) + 4(155) - 4(485) - 4(190) = -482 \text{ kJ} \end{aligned}$$

Reaction (i) is most exothermic.

- (b) The more oxygen atoms bound to carbon, the less exothermic the reaction in this series.

Additional Exercises

8.77 Six nonradioactive elements in the periodic table have Lewis symbols with single dots. Yes, they are in the same family, assuming H is placed with the alkali metals, as it is on the inside cover of the text. This is because the Lewis symbol represents the number of valence electrons of an element, and all elements in the same family have the same number of valence electrons. By definition of a family, all elements with the same Lewis symbol must be in the same family.

$$8.78 \quad E = kQ_1Q_2/d; \quad k = 8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$$

$$(a) \quad Na^+, Br^-: E = \frac{-8.99 \times 10^9 \text{ J}\cdot\text{m}}{\text{C}^2} \times \frac{(1 \times 1.60 \times 10^{-19} \text{ C})^2}{(1.16 + 1.82) \times 10^{-10} \text{ m}} = -7.7230 \times 10^{-19} \text{ J} \\ = -7.72 \times 10^{-19} \text{ J}$$

The sign of E is negative because one of the interacting ions is an anion; this is an attractive interaction.

$$\text{On a molar basis: } -7.723 \times 10^{-19} \times 6.022 \times 10^{23} = -4.65 \times 10^5 \text{ J} = -465 \text{ kJ}$$

$$(b) \quad Rb^+, Br^-: E = \frac{-8.99 \times 10^9 \text{ J}\cdot\text{m}}{\text{C}^2} \times \frac{(1 \times 1.60 \times 10^{-19} \text{ C})^2}{(1.66 + 1.82) \times 10^{-10} \text{ m}} = -6.61 \times 10^{-19} \text{ J}$$

$$\text{On a molar basis: } -3.98 \times 10^5 \text{ J} = -398 \text{ kJ}$$

$$(c) \quad Sr^{2+}, S^{2-}: E = \frac{-8.99 \times 10^9 \text{ J}\cdot\text{m}}{\text{C}^2} \times \frac{(2 \times 1.60 \times 10^{-19} \text{ C})^2}{(1.32 + 1.70) \times 10^{-10} \text{ m}} = -3.05 \times 10^{-18} \text{ J}$$

$$\text{On a molar basis: } -1.84 \times 10^6 \text{ J} = -1.84 \times 10^3 \text{ kJ}$$

8.79 (a) Lattice energy is proportional to Q_1Q_2/d . For each of these compounds, Q_1Q_2 is the same. The anion H^- is present in each compound, but the ionic radius of the cation increases going from Be to Ba. Thus, the value of d (the cation-anion separation) increases and the ratio Q_1Q_2/d decreases. This is reflected in the decrease in lattice energy going from BeH_2 to BaH_2 .

(b) Again, Q_1Q_2 for ZnH_2 is the same as that for the other compounds in the series and the anion is H^- . The lattice energy of ZnH_2 , 2870 kJ, is closest to that of MgH_2 , 2791 kJ. The ionic radius of Zn^{2+} is similar to that of Mg^{2+} .

8.80 (a)

Lattice Compound Energy (kJ)	Lattice Compound Energy (kJ)
106 kJ $\left[\begin{array}{cc} \text{NaCl} & 788 \\ \text{NaBr} & 732 \\ \text{NaI} & 682 \end{array} \right]$ 56 kJ	104 kJ $\left[\begin{array}{cc} \text{LiCl} & 834 \\ \text{LiBr} & 779 \\ \text{LiI} & 730 \end{array} \right]$ 55 kJ

The difference in lattice energy between LiCl and LiI is 104 kJ. The difference between NaCl and NaI is 106 kJ; the difference between NaCl and NaBr is 56 kJ, or 53% of the difference between NaCl and NaI. Applying this relationship to the Li salts, $0.53(104 \text{ kJ}) = 55 \text{ kJ}$ difference between LiCl and LiI. The approximate lattice energy of LiBr is $(834 - 55) \text{ kJ} = 779 \text{ kJ}$.

(b)

Lattice Compound Energy (kJ)	Lattice Compound Energy (kJ)
106 kJ $\left[\begin{array}{cc} \text{NaCl} & 788 \\ \text{NaBr} & 732 \\ \text{NaI} & 682 \end{array} \right]$ 56 kJ	57 kJ $\left[\begin{array}{cc} \text{CsCl} & 657 \\ \text{CsBr} & 627 \\ \text{CsI} & 600 \end{array} \right]$ 30 kJ

By analogy to the Na salts, the difference between lattice energies of CsCl and CsBr should be approximately 53% of the difference between CsCl and CsI. The lattice energy of CsBr is approximately 627 kJ.

(c)

Lattice Compound Energy (kJ)	Lattice Compound Energy (kJ)
578 kJ $\left[\begin{array}{cc} \text{MgO} & 3795 \\ \text{CaO} & 3414 \\ \text{SrO} & 3217 \end{array} \right]$ 381 kJ	199 kJ $\left[\begin{array}{cc} \text{MgCl}_2 & 2326 \\ \text{CaCl}_2 & 2195 \\ \text{SrCl}_2 & 2127 \end{array} \right]$ 131 kJ

By analogy to the oxides, the difference between the lattice energies of $MgCl_2$ and $CaCl_2$ should be approximately 66% of the difference between $MgCl_2$ and $SrCl_2$. That is, $0.66(199 \text{ kJ}) = 131 \text{ kJ}$. The lattice energy of $CaCl_2$ is approximately $(2326 - 131) \text{ kJ} = 2195 \text{ kJ}$.

8.81 The charge on M is likely to be 3+. According to Table 8.2, the lattice energy for an ionic compound with the general formula MX and a charge of 2+ on the metal will be in the range of $3\text{--}4 \times 10^3 \text{ kJ/mol}$. The charge on M must be greater than 2+. ScN, where the charge on Sc is 3+, has a lattice energy of 7547 kJ/mol. It is reasonable to conclude that the charge on M is 3+, and the M-X distance is greater than the Sc-N distance.

8.82
$$E = \frac{-8.99 \times 10^9 \text{ J} \cdot \text{m}}{\text{C}^2} \times \frac{4(1.60 \times 10^{-19} \text{ C})^2}{(1.14 + 1.26) \times 10^{-10} \text{ m}} = -3.836 \times 10^{-18} = -3.84 \times 10^{-18} \text{ J}$$

On a molar basis: $(-3.836 \times 10^{-18} \text{ J})(6.022 \times 10^{23}) = -2.310 \times 10^6 \text{ J} = -2310 \text{ kJ}$

Note that the absolute value of this potential energy is less than the lattice energy of CaO, 3414 kJ/mol. The difference represents the added energy of putting all the $\text{Ca}^{2+}\text{O}^{2-}$ ion pairs together in a three-dimensional array, similar to the one in Figure 8.3.

- 8.83 By analogy to the Born-Haber cycle for NaCl(s), Figure 8.4, the enthalpy of formation for $\text{NaCl}_2(\text{s})$ is

$$\Delta H_f^\circ \text{NaCl}_2(\text{s}) = -\Delta H_{\text{latt}} \text{NaCl}_2 + \Delta H_f^\circ \text{Na}(\text{g}) + 2 \Delta H_f^\circ \text{Cl}(\text{g}) + I_1(\text{Na}) + I_2(\text{Na}) + 2E(\text{Cl})$$

$$\begin{aligned} \text{(a)} \quad \Delta H_f^\circ \text{NaCl}_2(\text{s}) &= -\Delta H_{\text{latt}} \text{NaCl}_2 + 107.7 \text{ kJ} + 2(121.7 \text{ kJ}) + 496 \text{ kJ} + 4562 \text{ kJ} \\ &\quad + 2(-349 \text{ kJ}) \end{aligned}$$

$$\Delta H_f^\circ \text{NaCl}_2(\text{s}) = -\Delta H_{\text{latt}} \text{NaCl}_2 + 4711 \text{ kJ}$$

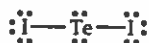
The collective energy of the "other" steps in the cycle (vaporization and ionization of Na^+ , dissociation of Cl_2 and electron affinity of Cl) is +4711 kJ. In order for the sign of $\Delta H_f^\circ \text{NaCl}_2$ to be negative, the lattice energy would have to be greater than 4711 kJ.

$$\text{(b)} \quad \Delta H_f^\circ \text{NaCl}_2(\text{s}) = -(2326 \text{ kJ}) + 4711 \text{ kJ} = 2385 \text{ kJ}$$

This value is large and positive.

- 8.84 (a) A polar molecule has a measurable dipole moment; its centers of positive and negative charge do not coincide. A nonpolar molecule has a zero net dipole moment; its centers of positive and negative charge do coincide.
- (b) Yes. If X and Y have different electronegativities, they have different attractions for the electrons in the molecule. The electron density around the more electronegative atom will be greater, producing a charge separation or dipole in the molecule.
- (c) $\mu = Qr$. The dipole moment, μ , is the product of the magnitude of the separated charges, Q, and the distance between them, r.

- 8.85 (a) B-O. The most polar bond will be formed by the two elements with the greatest difference in electronegativity. Since electronegativity increases moving right and up on the periodic table, the possibilities are B-O and Te-O. These two bonds are likely to have similar electronegativity differences (3 columns apart vs. 3 rows apart). Values from Figure 8.6 confirm the similarity, and show that B-O is slightly more polar.
- (b) Te-I. Both are in the fifth row of the periodic table and have the two largest covalent radii among this group of elements.
- (c) TeI_2 . Te needs to participate in two covalent bonds to satisfy the octet rule, and each I atom needs to participate in one bond, so by forming a TeI_2 molecule, the octet rule can be satisfied for all three atoms.



- (d) B_2O_3 . Although this is probably not a purely ionic compound, it can be understood in terms of gaining and losing electrons to achieve a noble-gas configuration. If each B atom were to lose $3 e^-$ and each O atom were to gain $2 e^-$, charge balance and the octet rule would be satisfied.

P_2O_3 . Each P atom needs to share 3 e^- and each O atom 2 e^- to achieve an octet. Although the correct number of electrons seem to be available, a correct Lewis structure is difficult to imagine. In fact, phosphorus (III) oxide exists as P_4O_6 rather than P_2O_3 (Chapter 22).

$$8.86 \quad (a) \quad Q = \frac{\mu}{r} = \frac{1.24 \text{ D}}{1.60 \text{ \AA}} \times \frac{1 \text{ \AA}}{1 \times 10^{-10} \text{ m}} \times \frac{3.34 \times 10^{-30} \text{ C} \cdot \text{m}}{1 \text{ D}} \times \frac{1 e}{1.60 \times 10^{-19} \text{ C}} = 0.1618 = 0.162 e$$

(b) From Figure 8.7, the electronegativity of Cl is 3.0 and that of O is 3.5. Since O is the more electronegative element, we expect it to have a negative charge in the ClO molecule.

(c) 13 e^- , 6.5 e^- pairs



Formal charges are minimized for the Lewis structure on the right. This is possible because Cl is a third-row element and can accommodate an expanded octet. The small electronegativity difference and calculated charges both point to a slightly polar covalent molecule. The true bonding situation is a blend of the two extreme Lewis structures, with the right-most structure making the larger contribution.

8.87 Estimate relative attraction for the bonding electron pair by calculating the relative electronegativity of the two atoms. From Figure 8.7, the electronegativity of Br is 2.8 and of Cl is 3.0.

Br has $2.8 / (3.0 + 2.8) = 0.48$ of the charge of the bonding e^- pair.

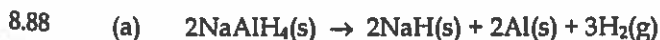
Cl has $3.0 / (3.0 + 2.8) = 0.52$ of the charge of the bonding e^- pair.

This amounts to $0.52 \times 2e = 1.04e$ on Cl or $0.04e$ more than a neutral Cl atom. This implies a -0.04 charge on Cl and $+0.04$ charge on Br.

From Figure 7.7, the covalent radius of Br is 1.14 \AA and of Cl is 0.99 \AA . The Br-Cl separation is 2.13 \AA .

$$\mu = Qr = 0.04e \times \frac{1.60 \times 10^{-19} \text{ C}}{e} \times 2.13 \text{ \AA} \times \frac{1 \times 10^{-10} \text{ m}}{\text{\AA}} \times \frac{1 \text{ D}}{3.34 \times 10^{-30} \text{ C} \cdot \text{m}} = 0.41 \text{ D}$$

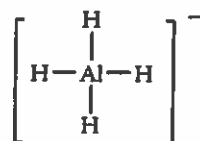
Clearly, this method is approximate. The estimated dipole moment of 0.41 D is within 28% of the measured value of 0.57 D.



(b) Hydrogen is the only nonmetal in NaAlH_4 , so we expect it to be most electronegative. (The position of H on the periodic table is problematic. Its electronegativity does not fit the typical trend for Gp 1A elements.) For the two metals, Na and Al, electronegativity increases moving up and to the right on the periodic table, so Al is more electronegative. The least electronegative element in the compound is Na.

- (c) Covalent bonds hold polyatomic anions together; elements involved in covalent bonding have smaller electronegativity differences than those that are involved in ionic bonds. Possible covalent bonds in NaAlH_4 are Na-H and Al-H . Al and H have a smaller electronegativity difference than Na and H and are more likely to form covalent bonds. The anion has an overall $1-$ charge, so it can be thought of as four hydride ions and one Al^{3+} ion. The formula is AlH_4^- . For the purpose of counting valence electrons, assume neutral atoms.

$8 e^-$, $4 e^-$ pairs



- 8.89 I_3^- has a Lewis structure with an expanded octet of electrons around the central I.



F cannot accommodate an expanded octet because it is too small and has no available d orbitals in its valence shell.

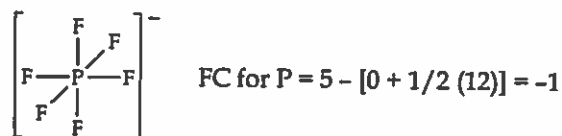
- 8.90 Formal charge (FC) = # valence e^- - (# nonbonding e^- + $1/2$ # bonding e^-)

- (a) $18 e^-$, $9 e^-$ pairs



FC for the central O = $6 - [2 + 1/2 (6)] = +1$

- (b) $48 e^-$, $24 e^-$ pairs



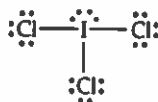
The three nonbonded pairs on each F have been omitted.

- (c) $17 e^-$; $8 e^-$ pairs, 1 odd e^-



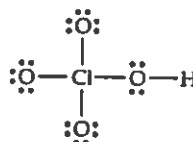
The odd electron is probably on N because it is less electronegative than O. Assuming the odd electron is on N, FC for N = $5 - [1 + 1/2 (6)] = +1$. If the odd electron is on O, FC for N = $5 - [2 + 1/2 (6)] = 0$.

- (d) $28 e^-$, $14 e^-$ pairs



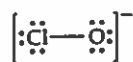
FC for I = $7 - [4 + 1/2 (6)] = 0$

- (e) $32 e^-$, $16 e^-$ pairs

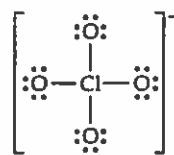


FC for Cl = $7 - [0 + 1/2 (8)] = +3$

8.91

(a) $14e^-$, $7e^-$ pairs

$$\text{FC on Cl} = 7 - [6 + 1/2(2)] = 0$$

 $32e^-$, $16e^-$ pairs

$$\text{FC on Cl} = 7 - [0 + 1/2(8)] = +3$$

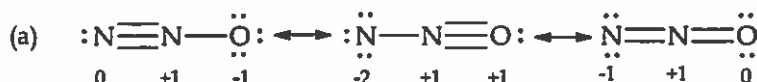
(b) The oxidation number of Cl is +1 in ClO^- and +7 in ClO_4^- .

(c) No, it is not uncommon for formal charge and oxidation state to be different. The definition of formal charge assumes that all bonding pairs of electrons are equally shared by the two bonded atoms, that all bonds are purely covalent. The definition of oxidation number assumes that the more electronegative element in the bond gets all of the bonding electrons, that the bonds are purely ionic. These two definitions represent the two extremes of how electron density is distributed between bonded atoms.

In ClO^- and ClO_4^- , Cl is the less electronegative element, so the oxidation numbers have a higher positive value than the formal charges. The true description of the electron density distribution is somewhere between the extremes indicated by formal charge and oxidation number.

(d) Oxidizing power is the tendency of a substance to be reduced, to gain electrons. Oxidation numbers show the maximum electron deficiency (or excess) of a substance. The higher the oxidation number of the central atom in an oxyanion, the greater its electron deficiency and oxidizing power. Formal charges can also be used to show oxidizing (or reducing) power, but trends are less obvious because the magnitudes are smaller.

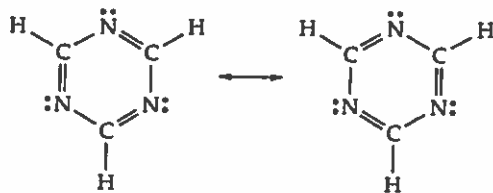
8.92



In the leftmost structure, the more electronegative O atom has the negative formal charge, so this structure is likely to be most important.

(b) In general, the more shared pairs of electrons between two atoms, the shorter the bond, and vice versa. That the N-N bond length in N_2O is slightly longer than the typical $\text{N}=\text{N}$ indicates that the middle and right resonance structures where the N atoms share less than three electron pairs are contributors to the true structure. That the N-O bond length is slightly shorter than a typical $\text{N}=\text{O}$ indicates that the middle structure, where N and O share more than two electron pairs, does contribute to the true structure. This physical data indicates that while formal charge can be used to predict which resonance form will be more important to the observed structure, the influence of minor contributors on the true structure cannot be ignored.

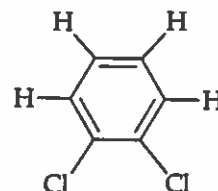
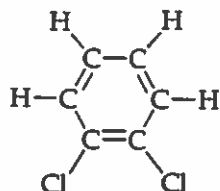
- 8.93 (a)
- $12 + 3 + 15 = 30$
- valence
- e^-
- ,
- $15 e^-$
- pairs.



Structures with H bound to N and nonbonded electron pairs on C can be drawn, but the structures above minimize formal charges on the atoms.

- (b) The resonance structures indicate that triazine will have six equal C-N bond lengths, intermediate between C-N single and C-N double bond lengths. (See Solutions 8.57 and 8.58.) From Table 8.5, an average C-N length is
- 1.43 \AA
- , a C=N length is
- 1.38 \AA
- . The average of these two lengths is
- 1.405 \AA
- . The C-N bond length in triazine should be in the range
- $1.40\text{--}1.41 \text{ \AA}$
- .

- 8.94 (a)
- $24 + 4 + 14 = 42$
- valence
- e^-
- ,
- $21 e^-$
- pairs. (b)



- (c) In benzene, the six C atoms are equivalent. In ortho-dichlorobenzene, the two C atoms bound to Cl are not equivalent to the four C atoms bound to H. In the two resonance structures above, one has a double bond between the C atoms bound to Cl, and the other has a single bond in this position. The two ortho-dichlorobenzene resonance structures are not equivalent like the resonance structures of benzene.

- 8.95 An experimentally determined molecular structure will reveal bond lengths and angles of the B-A=B molecule. If resonance structures are important, the two B-A bond lengths will be identical, or nearly so. If the molecule features one single and one double bond, the lengths will be significantly different. (While bond angles often reveal bonding details, in this case bond lengths are telling.)

$$\begin{aligned} 8.96 \quad \Delta H &= 8D(\text{C-H}) - D(\text{C-C}) - 6D(\text{C-H}) - D(\text{H-H}) \\ &= 2D(\text{C-H}) - D(\text{C-C}) - D(\text{H-H}) \\ &= 2(413) - 348 - 436 = +42 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta H &= 8D(\text{C-H}) + 1/2 D(\text{O=O}) - D(\text{C-C}) - 6D(\text{C-H}) - 2D(\text{O-H}) \\ &= 2D(\text{C-H}) + 1/2 D(\text{O=O}) - D(\text{C-C}) - 2D(\text{O-H}) \\ &= 2(413) + 1/2 (495) - 348 - 2(463) = -200 \text{ kJ} \end{aligned}$$

The fundamental difference in the two reactions is the formation of 1 mol of H-H bonds versus the formation of 2 mol of O-H bonds. The latter is much more exothermic, so the reaction involving oxygen is more exothermic.

8.97 (a) $\Delta H = 5D(\text{C-H}) + D(\text{C-C}) + D(\text{C-O}) + D(\text{O-H}) - 6D(\text{C-H}) - 2D(\text{C-O})$
 $= D(\text{C-C}) + D(\text{O-H}) - D(\text{C-H}) - D(\text{C-O})$
 $= 348 \text{ kJ} + 463 \text{ kJ} - 413 \text{ kJ} - 358 \text{ kJ}$

$\Delta H = +40 \text{ kJ}$; ethanol has the lower enthalpy

(b) $\Delta H = 4D(\text{C-H}) + D(\text{C-C}) + 2D(\text{C-O}) - 4D(\text{C-H}) - D(\text{C-C}) - D(\text{C=O})$
 $= 2D(\text{C-O}) - D(\text{C=O})$
 $= 2(358 \text{ kJ}) - 799 \text{ kJ}$

$\Delta H = -83 \text{ kJ}$; acetaldehyde has the lower enthalpy

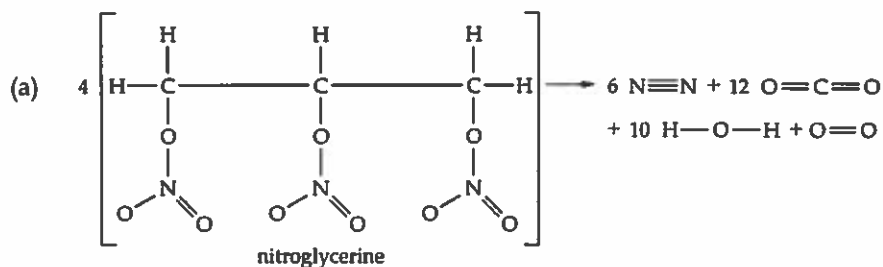
(c) $\Delta H = 8D(\text{C-H}) + 4D(\text{C-C}) + D(\text{C=C}) - 8D(\text{C-H}) - 2D(\text{C-C}) - 2D(\text{C=C})$
 $= 2D(\text{C-C}) - D(\text{C=C})$
 $= 2(348 \text{ kJ}) - 614 \text{ kJ}$

$\Delta H = +82 \text{ kJ}$; cyclopentene has the lower enthalpy

(d) $\Delta H = 3D(\text{C-H}) + D(\text{C-N}) + D(\text{C}\equiv\text{N}) - 3D(\text{C-H}) - D(\text{C-C}) - D(\text{C}\equiv\text{N})$
 $= D(\text{C-N}) - D(\text{C-C})$
 $= 293 \text{ kJ} - 348 \text{ kJ}$

$\Delta H = -55 \text{ kJ}$; acetonitrile has the lower enthalpy

8.98



$$\Delta H = 20D(\text{C-H}) + 8D(\text{C-C}) + 12D(\text{C-O}) + 24D(\text{O-N}) + 12D(\text{N=O})$$

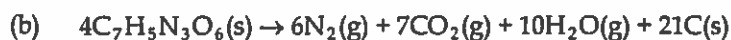
$$- [6D(\text{N}\equiv\text{N}) + 24D(\text{C=O}) + 20D(\text{H-O}) + D(\text{O=O})]$$

$$\Delta H = 20(413) + 8(348) + 12(358) + 24(201) + 12(607)$$

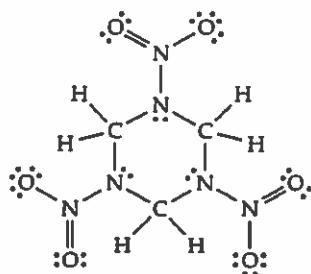
$$- [6(941) + 24(799) + 20(463) + 495]$$

$$= -7129 \text{ kJ}$$

$$1.00 \text{ g C}_3\text{H}_5\text{N}_3\text{O}_9 \times \frac{1 \text{ mol C}_3\text{H}_5\text{N}_3\text{O}_9}{227.1 \text{ g C}_3\text{H}_5\text{N}_3\text{O}_9} \times \frac{-7129 \text{ kJ}}{4 \text{ mol C}_3\text{H}_5\text{N}_3\text{O}_9} = 7.85 \text{ kJ/g C}_3\text{H}_5\text{N}_3\text{O}_9$$



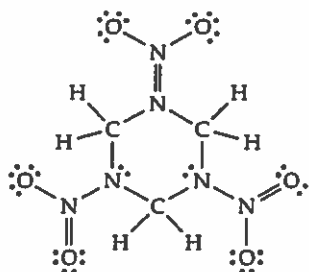
8.99 (a)



Use unshared pairs to complete octets on terminal O atoms (15 unshared pairs) and ring N atoms (3 unshared pairs).

- (b) No C=N bonds in the 6-membered ring are possible, because all C octets are complete with 4 bonds to other atoms. N=N are possible, as shown below. There are 8 possibilities involving some combination of N-N and N=N groups [1 with 0 N=N, 3 with 1 N=N, 3 with 2 N=N, 1 with 3 N=N]. A resonance structure with 1 N=N is shown below.

Each terminal O=N-O group has two possible placements for the N=O. This generates 8 structures with 0 N=N groups (and 3 O=N-O groups), 4 with 1 N=N and 2 O=N-O, 2 with 2 N=N and 1 O=N-O, and 1 with 3 N=N and no O=N-O. This sums to a total of 15 resonance structures (that I can visualize). Can you find others?



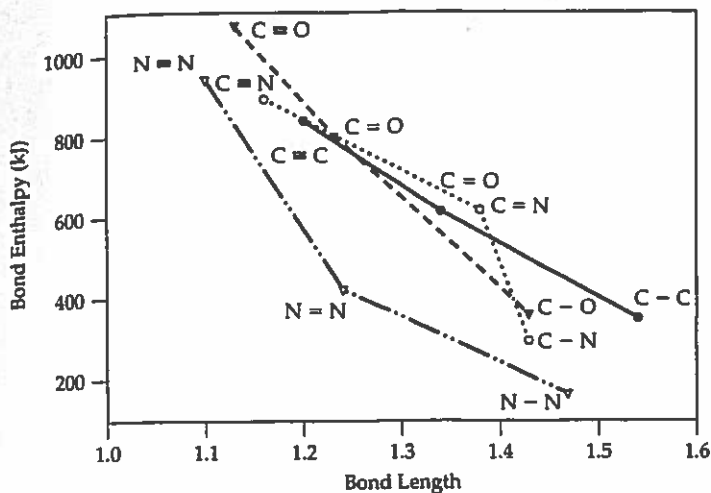
- (c) $\text{C}_3\text{H}_6\text{N}_6\text{O}_6(\text{s}) \rightarrow 3\text{CO}(\text{g}) + 3\text{N}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$
- (d) The molecule contains N=O, N=N, C-H, C-N, N-O, and N-N bonds. According to Table 8.4, N-N bonds have the smallest bond enthalpy and are weakest.
- (e) Calculate the enthalpy of decomposition for the resonance structure drawn in part (a).

$$\begin{aligned} \Delta H &= 3D(\text{N}=\text{O}) + 3D(\text{N}-\text{O}) + 3D(\text{N}-\text{N}) + 6D(\text{N}-\text{C}) + 6D(\text{C}-\text{H}) \\ &\quad - 3D(\text{C}=\text{O}) - 3D(\text{N}=\text{N}) - 6D(\text{O}-\text{H}) \\ &= 3(607) + 3(201) + 3(163) + 6(293) + 6(413) - 3(1072) - 3(941) - 6(463) \\ &= -1668 \text{ kJ/mol } \text{C}_3\text{H}_6\text{N}_6\text{O}_6 \end{aligned}$$

$$5.0 \text{ g } \text{C}_3\text{H}_6\text{N}_6\text{O}_6 \times \frac{1 \text{ mol } \text{C}_3\text{H}_6\text{N}_6\text{O}_6}{222.1 \text{ g } \text{C}_3\text{H}_6\text{N}_6\text{O}_6} \times \frac{-1668 \text{ kJ}}{\text{mol } \text{C}_3\text{H}_6\text{N}_6\text{O}_6} = -37.55 = -38 \text{ kJ}$$

While exchanging N=O and N-O bonds has no effect on the enthalpy calculation, structures with N=N and 2 N-O do have different enthalpy of decomposition. For the resonance structure with 3 N=N and 6 N-O bonds instead of 3 N-N, 3 N-O and 3 N=O, $\Delta H = -2121$ kJ/mol. The actual enthalpy of decomposition is probably somewhere between -1668 and -2121 kJ/mol. The enthalpy change for the decomposition of 5.0 g RDX is then in the range of -38 to -48 kJ.

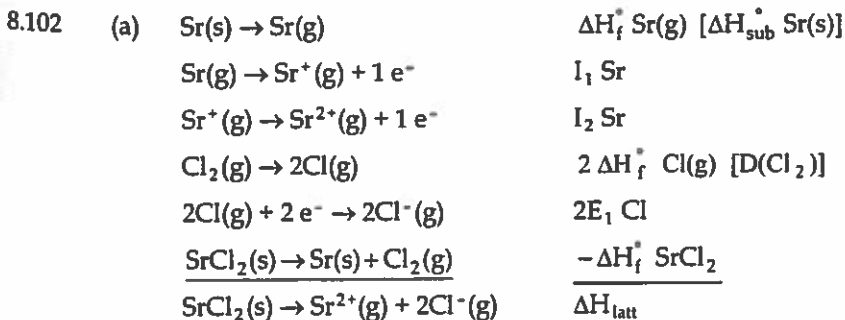
8.100

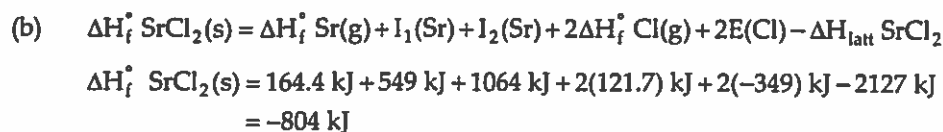


When comparing the same pair of bonded atoms (C-N vs. C=N vs. C≡N), the shorter the bond the greater the bond energy, but the two quantities are not necessarily directly proportional. The plot clearly shows that there are no simple length/strength correlations for single bonds alone, double bonds alone, triple bonds alone, or among different pairs of bonded atoms (all C-C bonds vs. all C-N bonds, etc.).

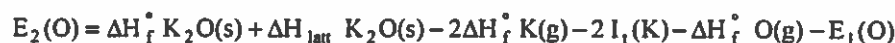
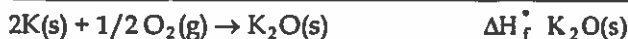
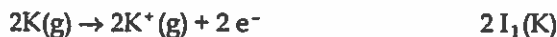
Integrative Exercises

- 8.101 (a) $\text{Ti}^{2+} : [\text{Ar}]3d^2$; $\text{Ca} : [\text{Ar}]4s^2$. Yes. The two valence electrons in Ti^{2+} and Ca are in different principle quantum levels and different subshells.
- (b) According to the Aufbau Principle, valence electrons will occupy the lowest energy empty orbital. Thus, in Ca the 4s is lower in energy than the 3d, while in Ti^{2+} , the 3d is lower in energy than the 4s.
- (c) No. Since there is only one 4s orbital, the two valence electrons in Ca are paired. There are five degenerate 3d orbitals, so the two valence electrons in Ti^{2+} are unpaired. Ca has no unpaired electrons, Ti^{2+} has two.





8.103 The pathway to the formation of K_2O can be written:



$$= +750 \text{ kJ}$$

8.104 To calculate empirical formulas, assume 100 g of sample.

$$\text{(a)} \quad \frac{76.0 \text{ g Ru}}{101.07 \text{ g/mol}} = 0.752 \text{ mol Ru}; 0.752/0.752 = 1 \text{ Ru}$$

$$\frac{24.0 \text{ g O}}{15.9994 \text{ g/mol}} = 1.50 \text{ mol O}; 1.50/0.762 = 2 \text{ O}$$

The empirical formula of compound 1 is RuO_2 .

$$\text{(b)} \quad \frac{61.2 \text{ g Ru}}{101.07 \text{ g/mol}} = 0.6055 \text{ mol Ru}; 0.6055/0.6055 = 1 \text{ Ru}$$

$$\frac{38.8 \text{ g O}}{15.9994 \text{ g/mol}} = 2.425 \text{ mol O}; 2.425/0.6055 = 4 \text{ O}$$

The empirical formula of compound 2 is RuO_4 .

(c) Ionic compounds have very high melting points, while the melting points of molecular compounds are lower and variable. Clearly the black powder, m.p. $> 1200^\circ\text{C}$, is ionic and the yellow substance, m.p. $= 25^\circ\text{C}$, is molecular. Substances with metals in high oxidation states are often molecular. RuO_4 contains Ru(VIII), while RuO_2 contains Ru(IV), so RuO_4 is more likely to be molecular. The yellow compound is RuO_4 , ruthenium tetroxide. The black compound is RuO_2 , ruthenium(IV) oxide.

8.105 (a) Even though Cl has the greater (more negative) electron affinity, F has a much larger ionization energy, so the electronegativity of F is greater.

$$\text{F: } k(\text{IE}-\text{EA}) = k(1681 - (-328)) = k(2009)$$

$$\text{Cl: } k(\text{IE}-\text{EA}) = k(1251 - (-349)) = k(1600)$$

(b) Electronegativity is the ability of an atom in a molecule to attract electrons to itself. It can be thought of as the ability to hold its own electrons (as measured by ionization energy) and the capacity to attract the electrons of other atoms (as measured by electron affinity). Thus, both properties are relevant to the concept of electronegativity.

(c) $EN = k(IE - EA)$. For F: $4.0 = k(2009)$, $k = 4.0/2009 = 2.0 \times 10^{-3}$

(d) Cl: $EN = 2.0 \times 10^{-3} (1600) = 3.2$

O: $EN = 2.0 \times 10^{-3} (1314 - (-141)) = 2.9$

These values do not follow the trend on Figure 8.7. The Pauling scale on the figure shows O to be second only to F in electronegativity, more electronegative than Cl. The simple definition $EN = k(IE - EA)$ that employs thermochemical properties of isolated, gas phase atoms does not take into account the complex bonding environment of molecules.

8.106 (a) Assume 100 g.

$$14.52 \text{ g C} \times \frac{1 \text{ mol}}{12.011 \text{ g C}} = 1.209 \text{ mol C}; 1.209 / 1.209 = 1$$

$$1.83 \text{ g H} \times \frac{1 \text{ mol}}{1.008 \text{ g H}} = 1.816 \text{ mol H}; 1.816 / 1.209 = 1.5$$

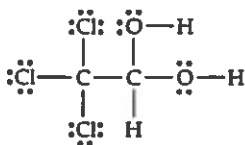
$$64.30 \text{ g Cl} \times \frac{1 \text{ mol}}{35.453 \text{ g Cl}} = 1.814 \text{ mol Cl}; 1.814 / 1.209 = 1.5$$

$$19.35 \text{ g O} \times \frac{1 \text{ mol}}{15.9994 \text{ g O}} = 1.209 \text{ mol O}; 1.209 / 1.209 = 1.0$$

Multiplying by 2 to obtain an integer ratio, the empirical formula is $\text{C}_2\text{H}_3\text{Cl}_3\text{O}_2$.

(b) The empirical formula mass is $2(12.0) + 3(1.0) + 3(35.5) + 2(16) = 165.5$. The empirical formula is the molecular formula.

(c) $44 e^-$, $22 e^-$ pairs



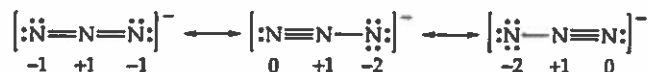
8.107 (a) Assume 100 g.

$$62.04 \text{ g Ba} \times \frac{1 \text{ mol}}{137.33 \text{ g Ba}} = 0.4518 \text{ mol Ba}; 0.4518 / 0.4518 = 1.0$$

$$37.96 \text{ g N} \times \frac{1 \text{ mol}}{14.007 \text{ g N}} = 2.710 \text{ mol N}; 2.710 / 0.4518 = 6.0$$

The empirical formula is BaN_6 . Ba has an ionic charge of $2+$, so there must be two $1-$ azide ions to balance the charge. The formula of each azide ion is N_3^- .

- (b)
- $16 e^-$
- ,
- $8 e^-$
- pairs



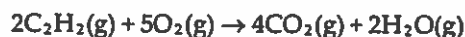
- (c) The structure with two double bonds minimizes formal charges and is probably the main contributor.
- (d) The two N–N bond lengths will be equal. The two minor contributors would individually cause unequal N–N distances, but collectively they contribute equally to the lengthening and shortening of each bond. The N–N distance will be approximately 1.24 Å, the average N=N distance.

- 8.108 (a)
- C_2H_2
- :
- $10 e^-$
- ,
- $5 e^-$
- pair
- N_2
- :
- $10 e^-$
- ,
- $5 e^-$
- pair



- (b) The enthalpy of formation for N_2 is 0 kJ/mol and for C_2H_2 is 226.77 kJ/mol. N_2 is an extremely stable, unreactive compound. Under appropriate conditions, it can be either oxidized or reduced. C_2H_2 is a reactive gas, used in combination with O_2 for welding and as starting material for organic synthesis.

- (c)
- $2\text{N}_2(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}_5(\text{g})$



- (d) $\Delta H_{\text{rxn}}^\circ (\text{N}_2) = 2\Delta H_f^\circ \text{N}_2\text{O}_5(\text{g}) - 2\Delta H_f^\circ \text{N}_2(\text{g}) - 5\Delta H_f^\circ \text{O}_2(\text{g})$
 $= 2(11.30) - 2(0) - 5(0) = 22.60 \text{ kJ}$

$$\Delta H_{\text{ox}}^\circ = 11.30 \text{ kJ/mol N}_2$$

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ (\text{C}_2\text{H}_2) &= 4\Delta H_f^\circ \text{CO}_2(\text{g}) + 2\Delta H_f^\circ \text{H}_2\text{O}(\text{g}) - 2\Delta H_f^\circ \text{C}_2\text{H}_2(\text{g}) - 5\Delta H_f^\circ \text{O}_2(\text{g}) \\ &= 4(-393.5 \text{ kJ}) + 2(-241.82 \text{ kJ}) - 2(226.77 \text{ kJ}) - 5(0) \\ &= -2511.18 \text{ kJ} \end{aligned}$$

$$\Delta H_{\text{ox}}^\circ (\text{C}_2\text{H}_2) = -1255.6 \text{ kJ/mol C}_2\text{H}_2$$

The oxidation of C_2H_2 is highly exothermic, which means that the energy state of the combined products is much lower than that of the reactants. The reaction is "downhill" in an energy sense, and occurs readily. The oxidation of N_2 is mildly endothermic (energy of products higher than reactants) and the reaction does not readily occur. This is in agreement with the general reactivities from part (b).

Referring to bond enthalpies in Table 8.4, when the C–H bonds are taken into account, even more energy is required for bond breaking in the oxidation of C_2H_2 than in the oxidation of N_2 . The difference seems to be in the enthalpies of formation of the products. $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ have extremely exothermic ΔH_f° values, which cause the oxidation of C_2H_2 to be energetically favorable. $\text{N}_2\text{O}_5(\text{g})$ has an endothermic ΔH_f° value, which causes the oxidation of N_2 to be energetically unfavorable.

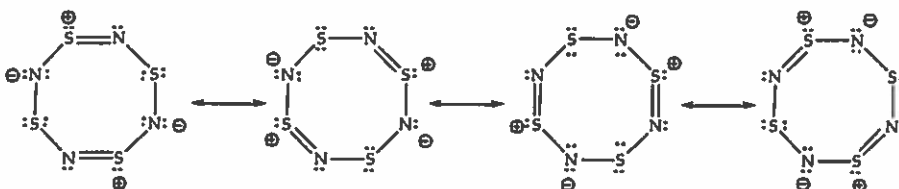
8.109 (a) Assume 100 g of compound

$$69.6 \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g}} = 2.17 \text{ mol S}$$

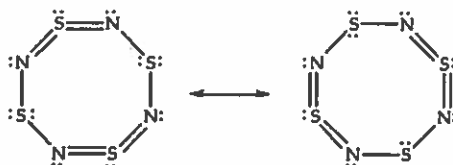
$$30.4 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g}} = 2.17 \text{ mol N}$$

S and N are present in a 1:1 mol ratio, so the empirical formula is SN. The empirical formula mass is 46. $\text{MM}/\text{FW} = 184.3/46 = 4$ The molecular formula is S_4N_4 .

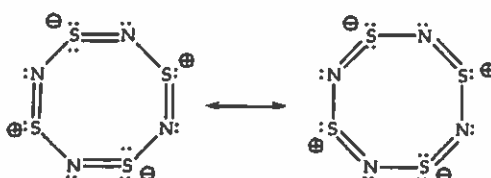
(b) $44 e^-$, $22 e^-$ pairs. Because of its small radius, N is unlikely to have an expanded octet. Begin with alternating S and N atoms in the ring. Try to satisfy the octet rule with single bonds and lone pairs. At least two double bonds somewhere in the ring are required.



These structures carry formal charges on S and N atoms as shown. Other possibilities include:



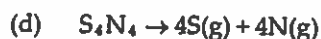
These structures have zero formal charges on all atoms and are likely to contribute to the true structure. Note that the S atoms that are shown with two double bonds are not necessarily linear, because S has an expanded octet. Other resonance structures with four double bonds are:



In either resonance structure, the two 'extra' electron pairs can be placed on any pair of S atoms in ring, leading to a total of 10 resonance structures. The sulfur atoms alternately carry formal charges of +1 and -1. Without further structural information, it is not possible to eliminate any of the above structures. Clearly, the S_4N_4 molecule stretches the limits of the Lewis model of chemical bonding.

(c) Each resonance structure has 8 total bonds and more than 8 but less than 16 bonding e^- pairs, so an "average" bond will be intermediate between a S-N single and double bond. We estimate an average S-N single bond length to be 1.77 Å (sum of bonding atomic radii from Figure 7.7). We do not have a direct value for a S-N double bond length. Comparing double and single bond lengths

for C–C (1.34 Å, 1.54 Å), N–N (1.24 Å, 1.47 Å) and O–O (1.21 Å, 1.48 Å) bonds from Table 8.5, we see that, on average, a double bond is approximately 0.23 Å shorter than a single bond. Applying this difference to the S–N single bond length, we estimate the S–N double bond length as 1.54 Å. Finally, the intermediate S–N bond length in S_4N_4 should be between these two values, approximately 1.60–1.65 Å. (The measured bond length is 1.62 Å.)



$$\Delta H = 4\Delta H_f^\circ S(g) + 4\Delta H_f^\circ N(g) - \Delta H_f^\circ S_4N_4$$

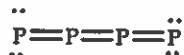
$$\Delta H = 4(222.8 \text{ kJ}) + 4(472.7 \text{ kJ}) - 480 \text{ kJ} = 2302 \text{ kJ}$$

This energy, 2302 kJ, represents the dissociation of 8 S–N bonds in the molecule; the average dissociation energy of one S–N bond in S_4N_4 is then 2302 kJ/8 bonds = 287.8 kJ.

8.110 (a) Yes. In the structure shown in the exercise, each P atom needs 1 unshared pair to complete its octet. This is confirmed by noting that only 6 of the 10 valence e^- pairs are bonding pairs.

(b) There are six P–P bonds in P_4 .

(c) $20 e^-$, $10 e^-$ pr



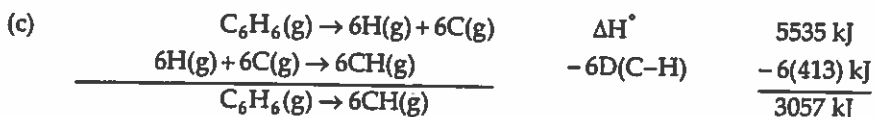
In this Lewis structure, the octet rule is satisfied for all atoms. However, it requires P=P, which is uncommon because P has a covalent radius that is too large to accommodate the side-to-side π overlap of parallel p orbitals required for double bond formation.

(d) From left to right, the formal charges are on the P atoms in the linear structure are $-1, +1, +1, -1$. In the tetrahedral structure, all formal charges are zero. Clearly the linear structure does not minimize formal charge and is probably less stable than the tetrahedral structure, owing to the difficulty of P=P bond formation (see above).



$$\Delta H^\circ = 6\Delta H_f^\circ H(g) + 6\Delta H_f^\circ C(g) - \Delta H_f^\circ C_6H_6(g)$$

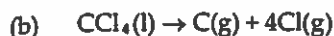
$$\Delta H^\circ = 6(217.94) \text{ kJ} + 6(718.4) \text{ kJ} - 82.9 \text{ kJ} = 5535 \text{ kJ}$$



3057 kJ is the energy required to break the six C–C bonds in $C_6H_6(g)$. The average bond dissociation energy for one carbon-carbon bond in $C_6H_6(g)$ is

$$\frac{3057 \text{ kJ}}{6 \text{ C–C bonds}} = 509.5 \text{ kJ.}$$

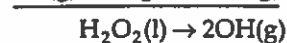
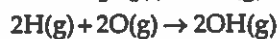
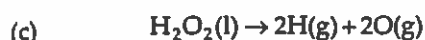
- (d) The value of 509.5 kJ is between the average value for a C–C single bond (348 kJ) and a C=C double bond (614 kJ). It is somewhat greater than the average of these two values, indicating that the carbon-carbon bond in benzene is a bit stronger than we might expect.



$$\Delta H^\circ = \Delta H_f^\circ \text{C}(\text{g}) + 4\Delta H_f^\circ \text{Cl}(\text{g}) - \Delta H_f^\circ \text{CCl}_4(\text{l})$$

$$= 718.4 \text{ kJ} + 4(121.7) \text{ kJ} - (-139.3) \text{ kJ} = 1344.5$$

$$\frac{1344.5 \text{ kJ}}{4 \text{ C-Cl bonds}} = 336.1 \text{ kJ}$$



$$D(\text{O}-\text{O})(\text{l}) = 2\Delta H_f^\circ \text{H}(\text{g}) + 2\Delta H_f^\circ \text{O}(\text{g}) - \Delta H_f^\circ \text{H}_2\text{O}_2(\text{l}) - 2D(\text{O}-\text{H})(\text{g})$$

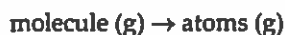
$$= 2(217.94) \text{ kJ} + 2(247.5) \text{ kJ} - (-187.8) \text{ kJ} - 2(463) \text{ kJ}$$

$$= 193 \text{ kJ}$$

- (d) The data are listed below.

bond	D gas kJ/mol	D liquid kJ/mol
Br–Br	193	223.6
C–Cl	328	336.1
O–O	146	192.7

Breaking bonds in the liquid requires more energy than breaking bonds in the gas phase. For simple molecules, bond dissociation from the liquid phase can be thought of in two steps:



The first step is evaporation or vaporization of the liquid and the second is bond dissociation in the gas phase. Average bond enthalpy in the liquid phase is then the sum of the enthalpy of vaporization for the molecule and the gas phase bond dissociation enthalpies, divided by the number of bonds dissociated. This is greater than the gas phase bond dissociation enthalpy owing to the contribution from the enthalpy of vaporization.