

# 8 Basic Concepts of Chemical Bonding

## Visualizing Concepts

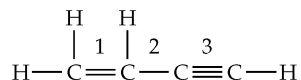
8.2 *Analyze.* Given the size and charge of four different ions, determine their ionic bonding characteristics.

*Plan.* The magnitude of lattice energy is directly proportional to the charges of the two ions and inversely proportional to their separation.  $E_{el} = \frac{1}{d} Q_1 Q_2$ . 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.

8.5 *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:

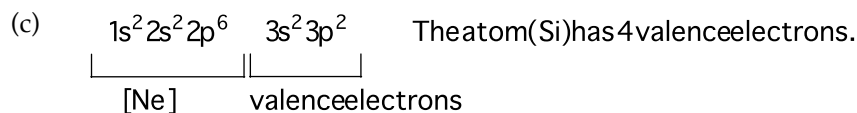


- (b) In order of increasing bond length:  $3 < 1 < 2$
- (c) In order of increasing bond enthalpy (strength):  $2 < 1 < 3$

## Lewis Symbols

8.7 (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)  $\text{N} : [\text{He}] 2s^2 2p^3$   
 $\quad \quad \quad \underline{\quad \quad}$  A nitrogen atom has 5 valence electrons  
Valence electrons



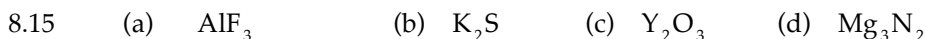
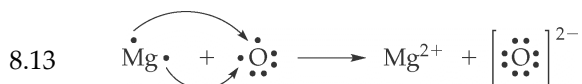
8.9 P:  $1s^2 2s^2 2p^6 3s^2 3p^3$ . The 3s and 3p electrons are valence electrons; the 1s, 2s and 2p electrons are nonvalence or core electrons. Valence electrons are involved in chemical bonding, while nonvalence or core electrons are not.

(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.

8.11



### Ionic Bonding



8.17 (a)  $\text{Sr}^{2+}$ : [Kr], noble-gas configuration

(b)  $\text{Ti}^{2+}$ : [Ar]3d<sup>2</sup>

(c)  $\text{Se}^{2-}$ : [Ar]4s<sup>2</sup>3d<sup>10</sup>4p<sup>6</sup> = [Kr], noble-gas configuration

(d)  $\text{Ni}^{2+}$ : [Ar]3d<sup>8</sup>

(e)  $\text{Br}^-$ : [Ar]4s<sup>2</sup>3d<sup>10</sup>4p<sup>6</sup> = [Kr], noble-gas configuration

(f)  $\text{Mn}^{3+}$ : [Ar]3d<sup>4</sup>

8.19 (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.

8.21 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.

8.23 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  $\text{Cs}^+$  and  $\text{K}^+$  must be approximately equal to the difference between  $\text{Br}^-$  and  $\text{Cl}^-$ . This is somewhat surprising, since  $\text{K}^+$  and  $\text{Cs}^+$  are two rows apart and  $\text{Cl}^-$  and  $\text{Br}^-$  are only one row apart.

8.25 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  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$  from the neutral atoms (see Figure 8.4 for the formation of NaCl).

8.27  $\text{RbCl(s)} \rightarrow \text{Rb}^+(\text{g}) + \text{Cl}^-(\text{g}) \quad \Delta H (\text{lattice energy}) = ?$

By analogy to NaCl, Figure 8.4, the lattice energy is

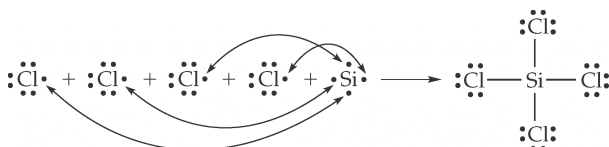
$$\begin{aligned} \Delta H_{\text{latt}} &= -\Delta H_f^\circ \text{RbCl(s)} + \Delta H_f^\circ \text{Rb(g)} + \Delta H_f^\circ \text{Cl(g)} + I_1(\text{Rb}) + E(\text{Cl}) \\ &= -(-430.5 \text{ kJ}) + 85.8 \text{ kJ} + 121.7 \text{ kJ} + 403 \text{ kJ} + (-349 \text{ kJ}) = +692 \text{ kJ} \end{aligned}$$

This value is smaller than that for NaCl (+788 kJ) because  $\text{Rb}^+$  has a larger ionic radius than  $\text{Na}^+$ . 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.

### Covalent Bonding, Electronegativity, and Bond Polarity

- 8.29 (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  $\text{H}_2$ ,  $\text{SO}_2$ , and  $\text{CCl}_4$ , are molecular and have covalent bonds between atoms.
- (c) Covalent because it is a gas even below room temperature.

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



*Check.* Each pair of shared electrons in  $\text{SiCl}_4$  is shown as a line; each atom is surrounded by an octet of electrons.

- 8.33 (a)  $:\ddot{\text{O}}=\ddot{\text{O}}:$
- (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  $\text{O}_2$  has a double bond, the O–O distance will be shorter than the O–O single bond distance.
- 8.35 (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.

8.37 *Plan.* Electronegativity increases going up and to the right in the periodic table.  
*Solve.*

- (a) O            (b) C            (c) P            (d) Be

*Check.* The electronegativity values in Figure 8.6 confirm these selections.

8.39 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

8.41 (a) *Analyze/Plan.* Q is the charge at either end of the dipole.  $Q = \mu/r$ . The values for OH are  $\mu = 1.78 \text{ D}$  and  $r = 0.98 \text{ \AA}$ . Change  $\text{\AA}$  to m and use the definition of debyes and the charge of an electron to calculate effective charge in units of  $e$ .  
*Solve.*

$$Q = \frac{\mu}{r} = \frac{1.78 \text{ D}}{0.98 \text{ \AA}} \times \frac{1 \text{ \AA}}{1 \times 10^{10} \text{ m}} \times \frac{3.34 \times 10^{-30} \text{ C} \cdot \text{m}}{1 \text{ D}} \times \frac{1 e}{1.60 \times 10^{-19} \text{ C}} = 0.38 e$$

- (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. These effective charges can be thought of as the amount of charge “transferred” from H to Cl. From part (a),  $0.38 e$  is transferred from H to O in OH. There is larger charge separation in OH than in HCl, so OH is more polar. The dipole moments,  $1.78 \text{ D}$  for OH and  $1.08$  for HCl, reinforce this conclusion.
- (c) The greater polarity of OH is also predicted by electronegativities. According to electronegativity trends (and values in Figure 8.6), O is more electronegative than Cl. The electronegativity difference between O and H is greater than that between Cl and H, so OH is more polar.

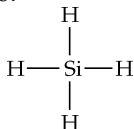
8.43 *Analyze/Plan.* Generally, compounds formed by a metal and a nonmetal are described as ionic, while compounds formed from two or more nonmetals are covalent. However, substances with metals in a high oxidation state often have properties of molecular compounds. In this exercise we know that one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

- (a)  $\text{SiF}_4$ , metalloid and nonmetal, molecular, silicon tetrafluoride.  
 $\text{LaF}_3$ , metal and nonmetal, ionic, lanthanum(III) fluoride
- (b)  $\text{FeCl}_2$ , metal and nonmetal, ionic, iron(II) chloride  
 $\text{ReCl}_6$ , metal in high oxidation state, Re(VI), molecular, rhenium hexachloride
- (c)  $\text{PbCl}_4$ , metal and nonmetal, Pb(IV) is relatively high oxidation state, molecular (by contrast with  $\text{RbCl}$ , which is definitely ionic), lead tetrachloride  
 $\text{RbCl}$ , metal and nonmetal, ionic, rubidium chloride

## Lewis Structures; Resonance Structures

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

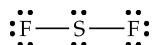
- (a) Count valence electrons:  $4 + (4 \times 1) = 8 e^-$ ,  $4 e^-$  pairs. Follow the procedure in Sample Exercise 8.6.



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

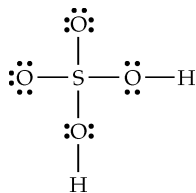


- (c) Valence electrons:  $[6 + (2 \times 7)] = 20 e^-$ ,  $10 e^-$  pairs



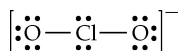
- i. Place the S atom in the middle and connect each F atom with a single bond; this requires  $2 e^-$  pairs.
- ii. Complete the octets of the F atoms with nonbonded pairs of electrons; this requires an additional  $6 e^-$  pairs.
- iii. The remaining  $2 e^-$  pairs complete the octet of the central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

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

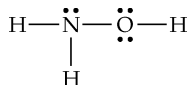


(Choose the Lewis structure that obeys the octet rule, Section 8.7.)

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



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



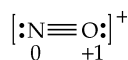
*Check.* In each molecule, bonding  $e^-$  pairs are shown as lines, and each atom is surrounded by an octet of electrons (duet for H).

- 8.47 (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 assume perfect covalency, one extreme for the possible electron distribution in a molecule.
- (c) The other extreme is represented by oxidation numbers, which assume that the more electronegative element holds all electrons in a bond. The true electron distribution is some composite of the two extremes.

8.49 *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.

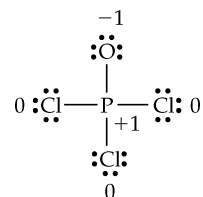
*Solve.* Formal charges are shown near the atoms, oxidation numbers (ox. #) are listed below the structures.

(a) 10  $e^-$ , 5  $e^-$  pairs



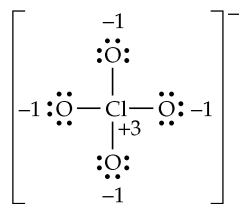
ox. #: N, +3; O, -2

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



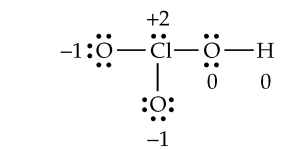
ox #: P, +5; Cl, -1; O, -2

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



ox. #: Cl, +7; O, -2

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

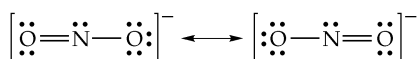


ox. #: Cl, +5; H, +1; O, -2

*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.

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

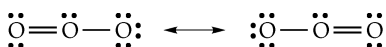
18  $e^-$ , 9  $e^-$  pairs



*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  $\text{O}_3$  is isoelectronic with  $\text{NO}_2^-$ .

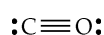


*Check.* The octet rule is satisfied.

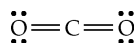
- (c) Since each N–O bond has partial double bond character, the N–O bond length in  $\text{NO}_2^-$  should be shorter than in species with formal N–O single bonds.

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

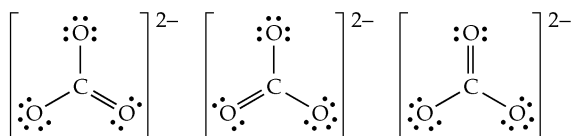
5  $e^-$  pairs



8  $e^-$  pairs

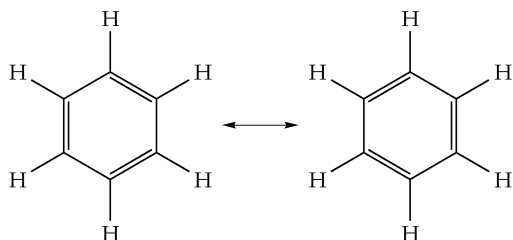


12  $e^-$  pairs



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  $\text{CO}_2$ , and 1.33 for  $\text{CO}_3^{2-}$ . This is also the order of increasing bond length:  $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$ .

- 8.55 (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.

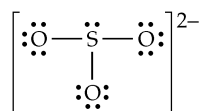
- (b) The resonance model described in (a) has six equivalent C–C bonds, each with some double bond character. That is, more than one pair but less than two pairs of electrons is involved in each C–C bond. This model predicts a uniform C–C bond length that is shorter than a single bond but longer than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

### Exceptions to the Octet Rule

- 8.57 (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 the individual ions in an ionic compound. That is, the cation has lost electrons to achieve an octet and the anion has gained electrons to achieve an octet. For example, in  $\text{MgCl}_2$ , Mg loses 2  $e^-$  to become  $\text{Mg}^{2+}$  with the electron configuration of Ne. Each Cl atom gains one electron to form  $\text{Cl}^-$  with the electron configuration of Ar.

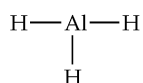
8.59 The most common exceptions to the octet rule are molecules with more than eight electrons around one or more atoms, usually the central atom. Examples:  $\text{SF}_6$ ,  $\text{PF}_5$

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



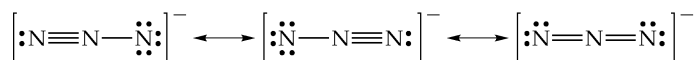
Other resonance structures with one, two, or three double bonds can be drawn. While a structure with three double bonds minimizes formal charges, all structures with double bonds violate the octet rule. Theoretical calculations show that the single best Lewis structure is the one that doesn't violate the octet rule. Such a structure is shown above.

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



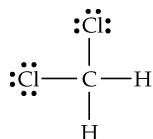
6 electrons around Al; impossible to satisfy octet rule with only 6 valence electrons.

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



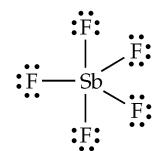
3 resonance structures; all obey octet rule.

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



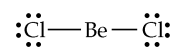
Obeys octet rule.

(e)  $40 e^-$ ,  $20 e^-$  pairs



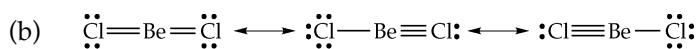
Does not obey octet rule;  $10 e^-$  around central Sb

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

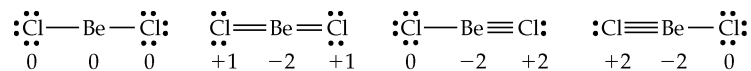


This structure violates the octet rule; Be has only  $4 e^-$  around it.





(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 most important. Note that this is a different conclusion than for molecules that have resonance structures with expanded octets that minimize formal charge.

## Bond Enthalpies

8.65 *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,  $\Delta H$ . *Solve.*

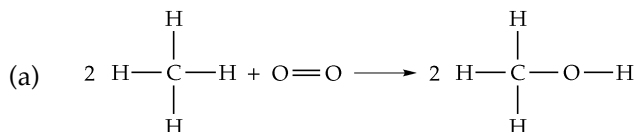
$$(a) \quad \Delta H = 2D(\text{O}-\text{H}) + D(\text{O}-\text{O}) + 4D(\text{C}-\text{H}) + D(\text{C}=\text{C}) \\ - 2D(\text{O}-\text{H}) - 2D(\text{O}-\text{C}) - 4D(\text{C}-\text{H}) - D(\text{C}-\text{C})$$

$$\Delta H = D(\text{O}-\text{O}) + D(\text{C}=\text{C}) - 2D(\text{O}-\text{C}) - D(\text{C}-\text{C}) \\ = 146 + 614 - 2(358) - 348 = -304 \text{ kJ}$$

$$(b) \quad \Delta H = 5D(\text{C}-\text{H}) + D(\text{C}\equiv\text{N}) + D(\text{C}=\text{C}) - 5D(\text{C}-\text{H}) - D(\text{C}\equiv\text{N}) - 2D(\text{C}-\text{C}) \\ = D(\text{C}=\text{C}) - 2D(\text{C}-\text{C}) = 614 - 2(348) = -82 \text{ kJ}$$

$$(c) \quad \Delta H = 6D(\text{N}-\text{Cl}) - 3D(\text{Cl}-\text{Cl}) - D(\text{N}\equiv\text{N}) \\ = 6(200) - 3(242) - 941 = -467 \text{ kJ}$$

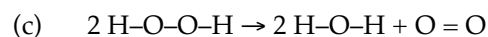
8.67 *Plan.* Draw structural formulas so bonds can be visualized. Then use Table 8.4 and Equation 8.12. *Solve.*



$$\Delta H = 8D(\text{C}-\text{H}) + D(\text{O}=\text{O}) - 6D(\text{C}-\text{H}) - 2D(\text{C}-\text{O}) - 2D(\text{O}-\text{H}) \\ = 2D(\text{C}-\text{H}) + D(\text{O}=\text{O}) - 2D(\text{C}-\text{O}) - 2D(\text{O}-\text{H}) \\ = 2(413) + (495) - 2(358) - 2(463) = -321 \text{ kJ}$$



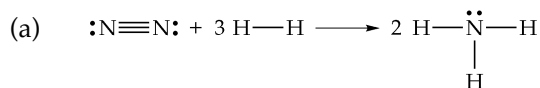
$$\Delta H = D(\text{H}-\text{H}) + D(\text{Br}-\text{Br}) - 2D(\text{H}-\text{Br}) \\ = (436) + (193) - 2(366) = -103 \text{ kJ}$$



$$\Delta H = 4D(\text{O}-\text{H}) + 2D(\text{O}-\text{O}) - 4D(\text{O}-\text{H}) - D(\text{O}=\text{O})$$

$$\Delta H = 2D(\text{O}-\text{O}) - D(\text{O}=\text{O}) = 2(146) - (495) = -203 \text{ kJ}$$

8.69 *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  $\Delta H_{\text{rxn}}$  from  $\Delta H_f^\circ$  values.

$$\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_f^\circ (\text{products}) - \sum n \Delta H_f^\circ (\text{reactants}) \quad \Delta H_f^\circ \text{NH}_3(\text{g}) = -461.9 \text{ kJ}$$

*Solve.*

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= 2\Delta H_f^\circ \text{NH}_3(\text{g}) - 3\Delta H_f^\circ \text{H}_2(\text{g}) - \Delta H_f^\circ \text{N}_2(\text{g}) \\ \Delta H_{\text{rxn}}^\circ &= 2(-461.9) - 3(0) - 0 = -923.8 \text{ kJ}/2 \text{ mol NH}_3 \end{aligned}$$

The  $\Delta H$  calculated from bond enthalpies is slightly more exothermic (more negative) than that obtained using  $\Delta H_f^\circ$  values.

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

### Additional Exercises

8.73 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.

8.75 (a)

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

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 LiBr. The approximate lattice energy of LiBr is  $(834 - 55) \text{ kJ} = 779 \text{ kJ}$ .

(b)

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

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.

		<b>Lattice</b>		<b>Lattice</b>														
		<b>Compound Energy (kJ)</b>		<b>Compound Energy (kJ)</b>														
(c)	578 kJ	<table style="border-collapse: collapse; margin: 0 auto;"> <tr><td style="padding: 2px 5px;">MgO</td><td style="padding: 2px 5px;">3795</td></tr> <tr><td style="padding: 2px 5px;">CaO</td><td style="padding: 2px 5px;">3414</td></tr> <tr><td style="padding: 2px 5px;">SrO</td><td style="padding: 2px 5px;">3217</td></tr> </table>	MgO	3795	CaO	3414	SrO	3217	381 kJ	<table style="border-collapse: collapse; margin: 0 auto;"> <tr><td style="padding: 2px 5px;">MgCl<sub>2</sub></td><td style="padding: 2px 5px;">2326</td></tr> <tr><td style="padding: 2px 5px;"><b>CaCl<sub>2</sub></b></td><td style="padding: 2px 5px;">2195</td></tr> <tr><td style="padding: 2px 5px;">SrCl<sub>2</sub></td><td style="padding: 2px 5px;">2127</td></tr> </table>	MgCl <sub>2</sub>	2326	<b>CaCl<sub>2</sub></b>	2195	SrCl <sub>2</sub>	2127	199 kJ	131 kJ
MgO	3795																	
CaO	3414																	
SrO	3217																	
MgCl <sub>2</sub>	2326																	
<b>CaCl<sub>2</sub></b>	2195																	
SrCl <sub>2</sub>	2127																	

By analogy to the oxides, the difference between the lattice energies of MgCl<sub>2</sub> and CaCl<sub>2</sub> should be approximately 66% of the difference between MgCl<sub>2</sub> and SrCl<sub>2</sub>. That is, 0.66(199 kJ) = 131 kJ. The lattice energy of CaCl<sub>2</sub> is approximately (2326 – 131) kJ = 2195 kJ.

- 8.79 (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,  $\mu$ , is the product of the magnitude of the separated charges, Q, and the distance between them, r.

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

(a)  $\frac{76.0\text{g Ru}}{10107\text{g/mol}} = 0.752 \text{ mol Ru}; 0.752/0.752 = 1 \text{ Ru}$

$\frac{24.0\text{g O}}{15999\text{g/mol}} = 1.50 \text{ mol O}; 1.50/0.762 = 2 \text{ O}$

The empirical formula of compound 1 is RuO<sub>2</sub>.

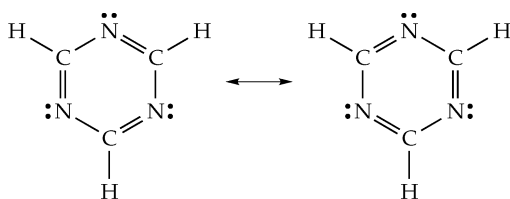
(b)  $\frac{61.2\text{g Ru}}{10107\text{g/mol}} = 0.6055 \text{ mol Ru}; 0.6055/0.6055 = 1 \text{ Ru}$

$\frac{38.8\text{g O}}{15999\text{g/mol}} = 2.425 \text{ mol O}; 2.425/0.6055 = 4 \text{ O}$

The empirical formula of compound 2 is RuO<sub>4</sub>.

- (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°C, is ionic and the yellow substance, m.p. = 25°C, is molecular. Substances with metals in high oxidation states are often molecular. RuO<sub>4</sub> contains Ru(VIII), while RuO<sub>2</sub> contains Ru(IV), so RuO<sub>4</sub> is more likely to be molecular. The yellow compound is RuO<sub>4</sub>, ruthenium tetroxide. The black compound is RuO<sub>2</sub>, ruthenium(IV) oxide.

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

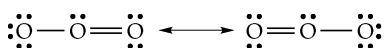


Structures with H bound to N and nonbonded electron pairs on C can be drawn, but the structures above minimize formal charges on the atoms.

- (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 8.55 and 8.56.) From Table 8.5, an average C–N length is  $1.43 \text{ \AA}$ , a C=N length is  $1.38 \text{ \AA}$ . The average of these two lengths is  $1.405 \text{ \AA}$ . The C–N bond length in triazine should be in the range  $1.40\text{--}1.41 \text{ \AA}$ .

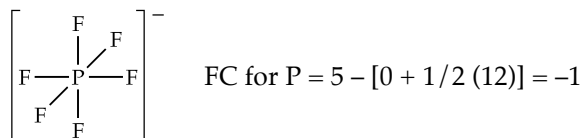
- 8.88 Formal charge (FC) = # valence
- $e^-$
- (# nonbonding
- $e^-$
- +
- $1/2$
- # bonding
- $e^-$
- )

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



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

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



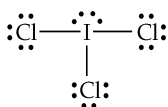
The three nonbonded pairs on each F have been omitted.

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



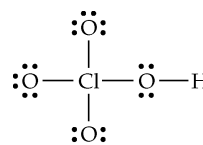
The odd electron is probably on N because it is less electronegative than O. Assuming the odd electron is on N, FC for N =  $5 - [1 + 1/2 (6)] = +1$ . If the odd electron is on O, FC for N =  $5 - [2 + 1/2 (6)] = 0$ .

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



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

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



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

- 8.91
- $\Delta H = 8D(\text{C-H}) - D(\text{C-C}) - 6D(\text{C-H}) - D(\text{H-H})$

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

$$= 2(413) - 348 - 436 = +42 \text{ kJ}$$

$$\Delta H = 8D(\text{C-H}) + 1/2 D(\text{O=O}) - D(\text{C-C}) - 6D(\text{C-H}) - 2D(\text{O-H})$$

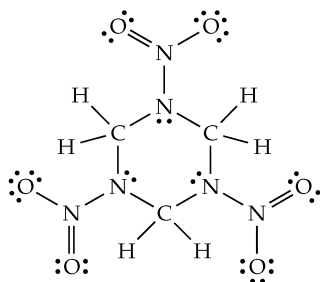
$$= 2D(\text{C-H}) + 1/2 D(\text{O=O}) - D(\text{C-C}) - 2D(\text{O-H})$$

$$= 2(413) + 1/2 (495) - 348 - 2(463) = -200 \text{ kJ}$$

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.

8.94

(a)



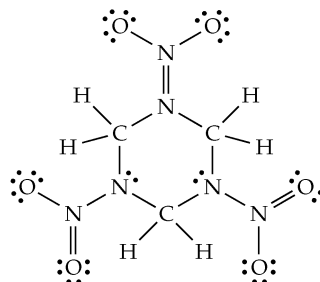
$$\text{C}_3\text{H}_6\text{N}_6\text{O}_6 \quad 12 + 6 + 30 + 36 = 84 e^-, 42 e^- \text{ pairs}$$

$$42 e^- \text{ pairs} - 24 \text{ shared } e^- \text{ pairs} = 18 \text{ unshared (lone) } e^- \text{ pairs}$$

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).

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

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

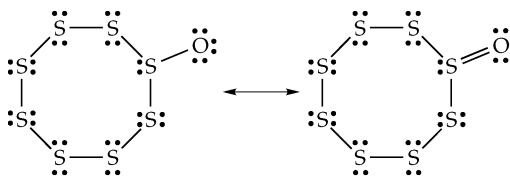
$$= 3(607) + 3(201) + 3(163) + 6(293) + 6(413) - 3(1072) - 3(941) - 6(463)$$

$$= -1668 \text{ kJ/mol C}_3\text{H}_6\text{N}_6\text{O}_6$$

$$5.0 \text{ g C}_3\text{H}_6\text{N}_6\text{O}_6 \times \frac{1 \text{ mol C}_3\text{H}_6\text{N}_6\text{O}_6}{222 \text{ g C}_3\text{H}_6\text{N}_6\text{O}_6} \times \frac{-1668 \text{ kJ}}{\text{mol C}_3\text{H}_6\text{N}_6\text{O}_6} = 37.55 = 38 \text{ kJ}$$

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,  $\Delta H = -2121 \text{ kJ/mol}$ . The actual enthalpy of decomposition is probably somewhere between  $-1668$  and  $-2121 \text{ kJ/mol}$ . The enthalpy change for the decomposition of 5.0 g RDX is then in the range 38–48 kJ.

- 8.96 (a) S–N  $\approx 1.77 \text{ \AA}$  (sum of the bonding atomic radii from Figure 7.7).
- (b) S–O  $\approx 1.75 \text{ \AA}$  (the sum of the bonding atomic radii from Figure 7.7.) Alternatively, half of the S–S distance in  $\text{S}_8$  (1.02) plus half of the O–O distance from Table 8.5 (0.74) is  $1.76 \text{ \AA}$ .
- (c) Owing to the resonance structures for  $\text{SO}_2$ , we assume that the S–O bond in  $\text{SO}_2$  is intermediate between a double and single bond, so the distance of  $1.43 \text{ \AA}$  should be significantly shorter than an S–O single bond distance,  $1.75 \text{ \AA}$ .
- (d)  $54 e^-$ ,  $27 e^-$  pair



The observed S–O bond distance,  $1.48 \text{ \AA}$ , is similar to that in  $\text{SO}_2$ ,  $1.43 \text{ \AA}$ , which can be described by resonance structures showing both single and double S–O bonds. Thus,  $\text{S}_8\text{O}$  must have resonance structures with both single and double S–O bonds. The structure with the S=O bond has  $5 e^-$  pairs about this S atom. To the extent that this resonance form contributes to the true structure, the S atom bound to O has more than an octet of electrons around it.

### Integrative Exercises

- 8.97 (a)  $\text{Ti}^{2+} : [\text{Ar}]3d^2$ ;  $\text{Ca} : [\text{Ar}]4s^2$ . Yes. The two valence electrons in  $\text{Ti}^{2+}$  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) 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.

- 8.100 (a) Assume 100 g.

$$A: \quad 87.7 \text{ g In} / 114.82 = 0.764 \text{ mol In}; 0.764 / 0.384 \approx 2$$

$$12.3 \text{ g S} / 32.07 = 0.384 \text{ mol S}; 0.384 / 0.384 = 1$$

$$B: \quad 78.2 \text{ g In} / 114.82 = 0.681 \text{ mol In}; 0.681 / 0.680 \approx 1$$

$$21.8 \text{ g S} / 32.07 = 0.680 \text{ mol S}; 0.680 / 0.680 = 1$$

$$C: \quad 70.5 \text{ g In} / 114.82 = 0.614 \text{ mol In}; 0.614 / 0.614 = 1$$

$$29.5 \text{ g S} / 32.07 = 0.920 \text{ mol S}; 0.920 / 0.614 = 1.5$$

$$A: \quad In_2S; B: InS; C: In_2S_3$$

- (b) A: In(I); B: In(II); C: In(III)

$$(c) \quad In(I) : [Kr]5s^2 4d^{10}; In(II) : [Kr]5s^1 4d^{10}; In(III) : [Kr]4d^{10}$$

None of these is a noble-gas configuration.

- (d) The ionic radius of  $In^{3+}$  in compound C will be smallest. Removing successive electrons from an atom reduces electron repulsion, increases the effective nuclear charge experienced by the valence electrons and decreases the ionic radius. The higher the charge on a cation, the smaller the radius.
- (e) Lattice energy is directly related to the charge on the ions and inversely related to the interionic distance. Only the charge and size of the In varies in the three compounds. In(I) in compound A has the smallest charge and the largest ionic radius, so compound A has the smallest lattice energy and the lowest melting point. In(III) in compound C has the greatest charge and the smallest ionic radius, so compound C has the largest lattice energy and highest melting point.

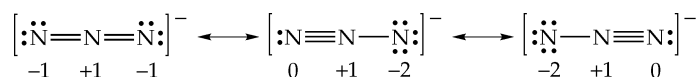
- 8.103 (a) Assume 100 g.

$$6204 \text{ g Ba} \times \frac{1 \text{ mol}}{137.33 \text{ g Ba}} = 0.4518 \text{ mol Ba}; 0.4518 / 0.4518 = 1.0$$

$$3796 \text{ g N} \times \frac{1 \text{ mol}}{140.07 \text{ g N}} = 2.710 \text{ mol N}; 2.710 / 0.4518 = 6.0$$

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 left structure 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.