CHAPTER 9
CHEMICAL BONDING I:
BASIC CONCEPTS

9.15 We use Coulomb's law to answer this question: $E = k\frac{Q_{\text{cation}}Q_{\text{anion}}}{r}$

(a) Doubling the radius of the cation would increase the distance, *r*, between the centers of the ions. A larger value of r results in a smaller energy, *E*, of the ionic bond. Is it possible to say how much smaller *E* will be?

(b) Tripling the charge on the cation will result in tripling of the energy, *E*, of the ionic bond, since the energy of the bond is directly proportional to the charge on the cation, Q_{cation}.

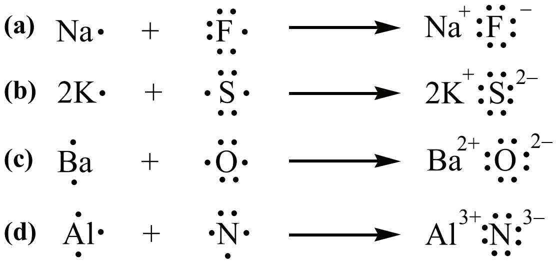
(c) Doubling the charge on both the cation and anion will result in quadrupling the energy, *E*, of the ionic bond.

(d) Decreasing the radius of both the cation and the anion to half of their original values is the same as halving the distance, *r*, between the centers of the ions. Halving the distance results in doubling the energy.

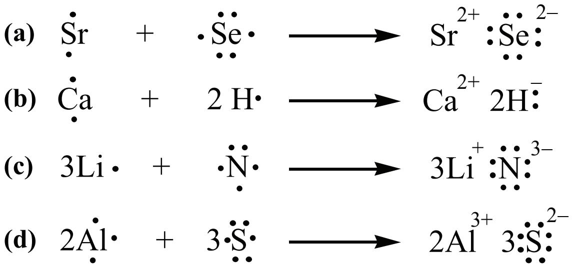
9.16 **(a)** RbI, rubidium iodide **(b)** Cs_2SO_4, cesium sulfate

(c) Sr_3N_2, strontium nitride **(d)** Al_2S_3, aluminum sulfide

9.17 Lewis representations for the ionic reactions are as follows.



9.18 The Lewis representations for the reactions are:



9.19 **(a)** I and Cl should form a molecular compound; both elements are nonmetals. One possibility would be ICl, iodine chloride.

(b) Mg and F will form an ionic compound; Mg is a metal while F is a nonmetal. The substance will be MgF_2, magnesium fluoride.

9.20 **(a)** Covalent (BF_3, boron trifluoride) **(b)** ionic (KBr, potassium bromide)

9.25

$$
\begin{array}{lll}
(1) & Na(s) \rightarrow Na(g) & \Delta H_1^\circ = 108 \text{ kJ/mol} \\
(2) & \frac{1}{2}Cl_2(g) \rightarrow Cl(g) & \Delta H_2^\circ = 121.4 \text{ kJ/mol} \\
(3) & Na(g) \rightarrow Na^+(g) + e^- & \Delta H_3^\circ = 495.9 \text{ kJ/mol} \\
(4) & Cl(g) + e^- \rightarrow Cl^-(g) & \Delta H_4^\circ = -349 \text{ kJ/mol} \\
(5) & Na^+(g) + Cl^-(g) \rightarrow NaCl(s) & \Delta H_5^\circ = ? \\
\hline
 & Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s) & \Delta H_{\text{overall}}^\circ = -411 \text{ kJ/mol}
\end{array}
$$

$$\Delta H_5^\circ = \Delta H_{\text{overall}}^\circ - \Delta H_1^\circ - \Delta H_2^\circ - \Delta H_3^\circ - \Delta H_4^\circ = (-411) - (108) - (121.4) - (495.9) - (-349) = -787 \text{ kJ/mol}$$

The lattice energy of NaCl is **787 kJ/mol**.

9.26

$$
\begin{array}{lll}
(1) & Ca(s) \rightarrow Ca(g) & \Delta H_1^\circ = 121 \text{ kJ/mol} \\
(2) & Cl_2(g) \rightarrow 2Cl(g) & \Delta H_2^\circ = 242.8 \text{ kJ/mol} \\
(3) & Ca(g) \rightarrow Ca^+(g) + e^- & \Delta H_3^{\circ'} = 589.5 \text{ kJ/mol} \\
 & Ca^+(g) \rightarrow Ca^{2+}(g) + e^- & \Delta H_3^{\circ''} = 1145 \text{ kJ/mol} \\
(4) & 2[Cl(g) + e^- \rightarrow Cl^-(g)] & \Delta H_4^\circ = 2(-349 \text{ kJ/mol}) = -698 \text{ kJ/mol} \\
(5) & Ca^{2+}(g) + 2Cl^-(g) \rightarrow CaCl_2(s) & \Delta H_5^\circ = ? \\
\hline
 & Ca(s) + Cl_2(g) \rightarrow CaCl_2(s) & \Delta H_{\text{overall}}^\circ = -795 \text{ kJ/mol}
\end{array}
$$

Thus we write:

$$\Delta H_{\text{overall}}^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^{\circ'} + \Delta H_3^{\circ''} + \Delta H_4^\circ + \Delta H_5^\circ$$

$$\Delta H_5^\circ = (-795 - 121 - 242.8 - 589.5 - 1145 + 698)\text{kJ/mol} = -2195 \text{ kJ/mol}$$

The lattice energy is represented by the reverse of equation (5); therefore, the lattice energy is **+2195 kJ/mol**.

9.35 The degree of ionic character in a bond is a function of the difference in electronegativity between the two bonded atoms. Figure 9.5 lists electronegativity values of the elements. The bonds in order of increasing ionic character are: N–N (zero difference in electronegativity) < S–O (difference 1.0) = Cl–F (difference 1.0) < K–O (difference 2.7) < Li–F (difference 3.0).

9.36 **Strategy:** We can look up electronegativity values in Figure 9.5 of the text. The amount of ionic character is based on the electronegativity difference between the two atoms. The larger the electronegativity difference, the greater the ionic character.

Solution: Let ΔEN = electronegativity difference. The bonds arranged in order of increasing ionic character are:

C–H (ΔEN = 0.4) < Br–H (ΔEN = 0.7) < F–H (ΔEN = 1.9) < Li–Cl (ΔEN = 2.0)

< Na–Cl (ΔEN = 2.1) < K–F (ΔEN = 3.2)

9.37 We calculate the electronegativity differences for each pair of atoms:

DE: 3.8 – 3.3 = 0.5 DG: 3.8 – 1.3 = 2.5 EG: 3.3 – 1.3 = 2.0 DF: 3.8 – 2.8 = 1.0

The order of increasing covalent bond character is: **DG < EG < DF < DE**

9.38 The order of increasing ionic character is:

Cl–Cl (zero difference in electronegativity) < Br–Cl (difference 0.2) < Si–C (difference 0.7)

< Cs–F (difference 3.3).

9.39 **(a)** The two carbon atoms are the same. The bond is covalent.

(b) The elelctronegativity difference between K and I is 2.5 – 0.8 = 1.7. The bond is polar covalent.

(c) The electronegativity difference between N and B is 3.0 – 2.0 = 1.0. The bond is polar covalent.

(d) The electronegativity difference between C and F is 4.0 – 2.5 = 1.5. The bond is polar covalent.

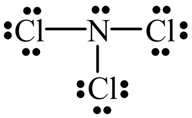
9.40 **(a)** The two silicon atoms are the same. The bond is covalent.

(b) The electronegativity difference between Cl and Si is 3.0 – 1.8 = 1.2. The bond is polar covalent.

(c) The electronegativity difference between F and Ca is 4.0 – 1.0 = 3.0. The bond is ionic.

(d) The electronegativity difference between N and H is 3.0 – 2.1 = 0.9. The bond is polar covalent.

9.43 **(a)**



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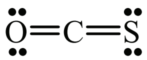

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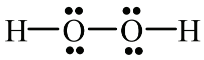

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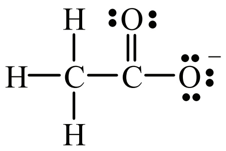

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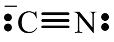

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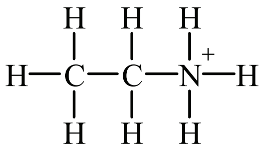
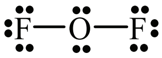


9.44 **(a)**



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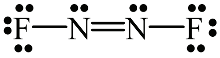

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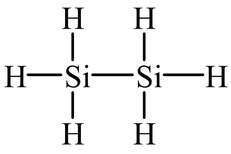

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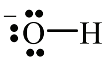

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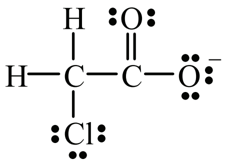

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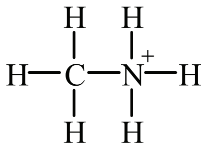
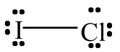


9.45 The lewis dot structures are:

(a)



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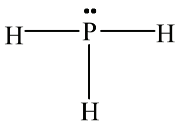

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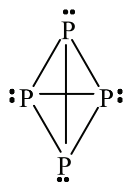

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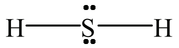

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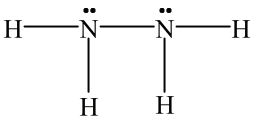

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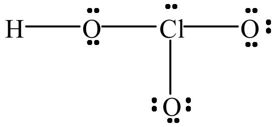
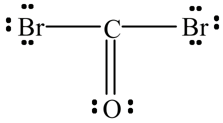


(g)



9.46 **Strategy:** We follow the procedure for drawing Lewis structures outlined in Section 9.6 of the text.

Solution:

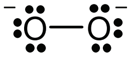
(a)

Step 1: It is obvious that the skeletal structure is: O O

Step 2: The outer-shell electron configuration of O is $2s^2 2p^4$. Also, we must add the negative charges to the number of valence electrons, Thus, there are

$$(2 \times 6) + 2 = 14 \text{ valence electrons}$$

Step 3: We draw a single covalent bond between each O, and then attempt to complete the octets for the O atoms.

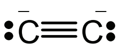


Because this structure satisfies the octet rule for both oxygen atoms, step 4 outlined in the text is not required.

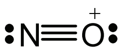
Check: As a final check, we verify that there are 14 valence electrons in the Lewis structure of O_2^-.

Follow the same procedure as part (a) for parts (b), (c), and (d). The appropriate Lewis structures are:

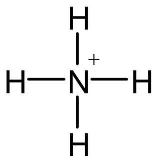
(b)



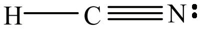
(c)



(d)



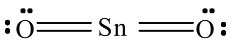
9.47 **(a)** Too many electrons. The correct structure is



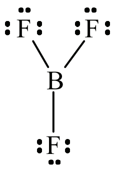
(b) Hydrogen atoms do not form double bonds. The correct structure is

$$H-C\equiv C-H$$

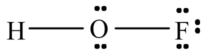
(c) Too few electrons.



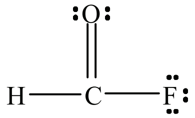
(d) Too many electrons. The correct structure is



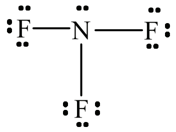
(e) Fluorine has more than an octet. The correct structure is



(f) Oxygen does not have an octet. The correct structure is

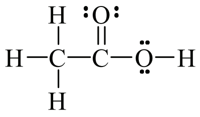


(g) Too few electrons. The correct structure is



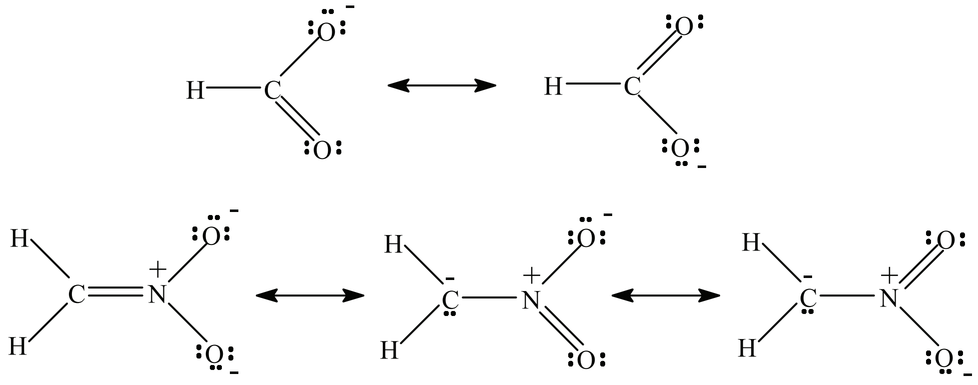
9.48 **(a)** Neither oxygen atom has a complete octet. The left-most hydrogen atom is forming two bonds (4 e^-). Hydrogen can only be surrounded by at most two electrons.

(b) The correct structure is:



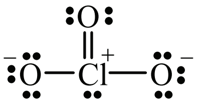
Do the two structures have the same number of electrons? Is the octet rule satisfied for all atoms other than hydrogen, which should have a duet of electrons?

9.51 The resonance structures are:



9.52 **Strategy:** We follow the procedure for drawing Lewis structures outlined in Section 9.6 of the text. After we complete the Lewis structure, we draw the resonance structures.

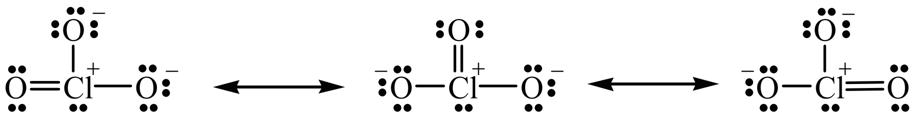
Solution: Following the procedure in Section 9.6 of the text, we come up with the following Lewis structure for ClO_3^-.



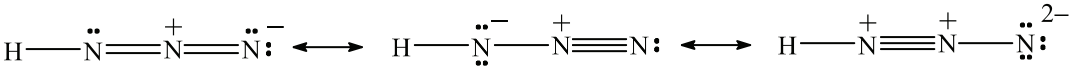
$$O=\overset{+}{Cl}(-O^{-})_2$$

We can draw two more equivalent Lewis structures with the double bond between Cl and a different oxygen atom.

The resonance structures with formal charges are as follows:

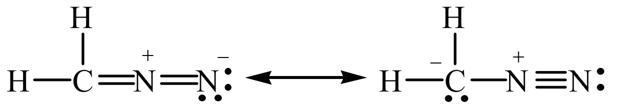


9.53 The structures of the most important resonance forms are:



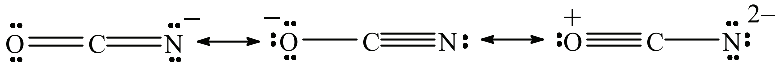
$$H-N=\overset{+}{N}=N^{-} \longleftrightarrow H-N^{-}-\overset{+}{N}\equiv N \longleftrightarrow H-\overset{+}{N}\equiv\overset{+}{N}-N^{2-}$$

9.54 The structures of the most important resonance forms are:



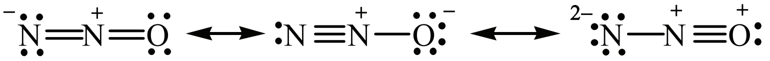
$$H_2C=\overset{+}{N}=N^{-} \longleftrightarrow H_2\overset{-}{C}-\overset{+}{N}\equiv N$$

9.55 Three reasonable resonance structures for OCN^- are:

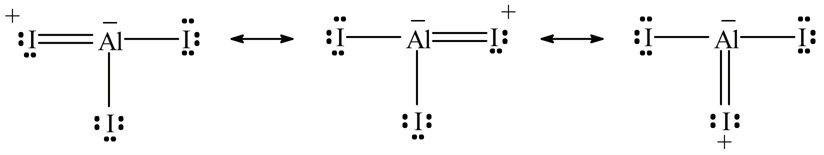


$$O=C=N^{-} \longleftrightarrow {}^{-}O-C\equiv N \longleftrightarrow \overset{+}{O}\equiv C-N^{2-}$$

9.56 Three reasonable resonance structures with the formal charges indicated are

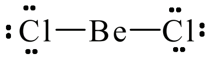


9.61 The resonance structures are

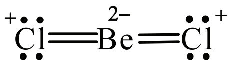


9.62 **Strategy:** We follow the procedure outlined in Section 9.6 of the text for drawing Lewis structures. We assign formal charges as discussed in Section 9.7 of the text.

Solution: Drawing the structure with single bonds between Be and each of the Cl atoms, the octet rule for Be is *not* satisfied. The Lewis structure is:



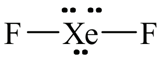
An octet of electrons on Be can only be formed by making two double bonds as shown below:



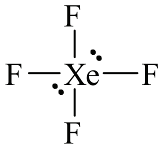
This places a high negative formal charge on Be and positive formal charges on the Cl atoms. This structure distributes the formal charges counter to the electronegativities of the elements. It is not a plausible Lewis structure.

9.63 For simplicity, the three, nonbonding pairs of electrons around the fluorine atoms are omitted.

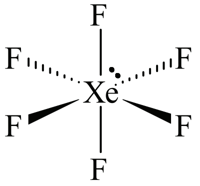
(a)



(b)



(c)



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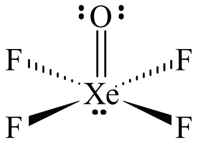
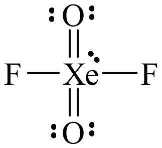
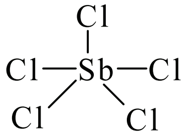


(e)



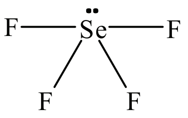
The octet rule is exceeded in each case.

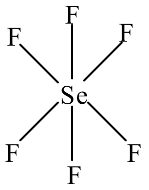
9.64 The outer electron configuration of antimony is $5s^25p^3$. The Lewis structure is shown below. All five valence electrons are shared in the five covalent bonds. The octet rule is not obeyed. (The electrons on the chlorine atoms have been omitted for clarity.)



Can Sb have an expanded octet?

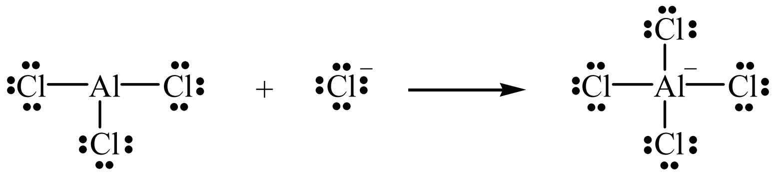
9.65 For simplicity, the three, nonbonding pairs of electrons around the fluorine are omitted.





The octet rule is not satisfied for Se in both compounds (why not?).

9.66 The reaction can be represented as:



The new bond formed is called a **coordinate covalent bond**.

9.69 The enthalpy change for the equation showing ammonia dissociating into a nitrogen atom and three hydrogen atoms is equal to three times the average bond enthalpy of the N–H bond (Why three?).

$$NH_3(g) \rightarrow N(g) + 3H(g) \qquad \Delta H° = 3\Delta H°(N\text{–}H)$$

The equation is the sum of the three equations given in the problem, and by Hess's law (Section 6.6 of the text) the enthalpy change is just the sum of the enthalpies of the individual steps.

$$\begin{array}{ll} NH_3(g) \rightarrow NH_2(g) + H(g) & \Delta H° = 435 \text{ kJ/mol} \\ NH_2(g) \rightarrow NH(g) + H(g) & \Delta H° = 381 \text{ kJ/mol} \\ NH(g) \rightarrow N(g) + H(g) & \Delta H° = 360 \text{ kJ/mol} \\ \hline NH_3(g) \rightarrow N(g) + 3H(g) & \Delta H° = 1176 \text{ kJ/mol} \end{array}$$

$$\boldsymbol{\Delta H°(N - H)} = \frac{1176 \text{ kJ/mol}}{3} = \mathbf{392\ kJ/mol}$$

9.70 **Strategy:** Keep in mind that bond breaking is an energy absorbing (endothermic) process and bond making is an energy releasing (exothermic) process. Therefore, the overall energy change is the difference between these two opposing processes, as described in Equation (9.3) of the text.

Solution: There are two oxygen-to-oxygen bonds in ozone. We will represent these bonds as O–O. However, these bonds might not be true oxygen-to-oxygen single bonds. Using Equation (9.3) of the text, we write:

$$\Delta H^\circ = \sum BE(\text{reactants}) - \sum BE(\text{products})$$

$$\Delta H^\circ = BE(\text{O=O}) - 2BE(\text{O–O})$$

In the problem, we are given ΔH° for the reaction, and we can look up the O=O bond enthalpy in Table 9.4 of the text. Solving for the average bond enthalpy in ozone,

$$-2BE(\text{O–O}) = \Delta H^\circ - BE(\text{O=O})$$

$$BE(\text{O}-\text{O}) = \frac{BE(\text{O=O}) - \Delta H^\circ}{2} = \frac{498.7\text{ kJ/mol} + 107.2\text{ kJ/mol}}{2} = \mathbf{303.0\text{ kJ/mol}}$$

Considering the resonance structures for ozone, is it expected that the O–O bond enthalpy in ozone is between the single O–O bond enthalpy (142 kJ) and the double O=O bond enthalpy (498.7 kJ)?

9.71 When molecular fluorine dissociates, two fluorine atoms are produced. Since the enthalpy of formation of atomic fluorine is in units of kJ/mol, this number is half the bond enthalpy of the fluorine molecule.

$$F_2(g) \rightarrow 2F(g) \qquad \Delta H^\circ = 156.9\text{ kJ/mol}$$

$$\Delta H^\circ = 2\Delta H_f^\circ(\text{F}) - \Delta H_f^\circ(\text{F}_2)$$

$$156.9\text{ kJ/mol} = 2\Delta H_f^\circ(\text{F}) - (1)(0)$$

$$\boldsymbol{\Delta H_f^\circ(\text{F})} = \frac{156.9\text{ kJ/mol}}{2} = \mathbf{78.5\text{ kJ/mol}}$$

9.72 **(a)**

Bonds Broken	*Number Broken*	*Bond Enthalpy* (kJ/mol)	*Enthalpy Change* (kJ)
C – H	12	414	4968
C – C	2	347	694
O = O	7	498.7	3491

Bonds Formed	*Number Formed*	*Bond Enthalpy* (kJ/mol)	*Enthalpy Change* (kJ)
C = O	8	799	6392
O – H	12	460	5520

$$\boldsymbol{\Delta H^\circ} = \text{total energy input} - \text{total energy released}$$

$$= (4968 + 694 + 3491) - (6392 + 5520) = \mathbf{-2759\text{ kJ/mol}}$$

(b) $\Delta H^\circ = 4\Delta H_f^\circ(\text{CO}_2) + 6\Delta H_f^\circ(\text{H}_2\text{O}) - [2\Delta H_f^\circ(\text{C}_2\text{H}_6) + 7\Delta H_f^\circ(\text{O}_2)]$

$$\boldsymbol{\Delta H^\circ} = (4)(-393.5\text{ kJ/mol}) + (6)(-241.8\text{ kJ/mol}) - [(2)(-84.7\text{ kJ/mol}) + (7)(0)] = \mathbf{-2855\text{ kJ/mol}}$$

The answers for part (a) and (b) are different, because *average* bond enthalpies are used for part (a).

9.73 CH_4, CO, and $SiCl_4$ are covalent compounds. KF and $BaCl_2$ are ionic compounds.

9.74 Typically, ionic compounds are composed of a metal cation and a nonmetal anion. RbCl and KO_2 are ionic compounds.

Typically, covalent compounds are composed of two nonmetals. PF_5, BrF_3, and CI_4 are covalent compounds.

9.75 **(a)** electron affinity of fluorine **(b)** bond enthalpy of molecular fluorine

(c) ionization energy of sodium **(d)** standard enthalpy of formation of sodium fluoride

9.76 Recall that you can classify bonds as ionic or covalent based on electronegativity difference.

The melting points (°C) are shown in parentheses following the formulas.

Ionic:	NaF (993)	MgF_2 (1261)	AlF_3 (1291)	
Covalent:	SiF_4 (−90.2)	PF_5 (−83)	SF_6 (−121)	ClF_3 (−83)

Is there any correlation between ionic character and melting point?

9.77 By Hess's law, the overall enthalpy (energy) change in a reaction is equal to the sum of the enthalpy (energy) changes for the individual steps. The reactions shown in the problem are just the sums of the ionization energy of the alkali metal and the electron affinity of the halogen.

(a) Taking data from the referenced figures we have:

$$\begin{array}{ll} \text{Li}(g) \rightarrow \text{Li}^+(g) + e^- & \Delta H^\circ = 520\text{ kJ/mol} \\ \text{I}(g) + e^- \rightarrow \text{I}^-(g) & \Delta H^\circ = -295\text{ kJ/mol} \\ \hline \text{Li}(g) + \text{I}(g) \rightarrow \text{Li}^+(g) + \text{I}^-(g) & \Delta H^\circ = \mathbf{225\text{ kJ/mol}} \end{array}$$

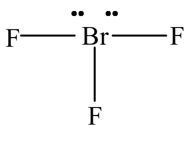
Parts (b) and (c) are solved in an analogous manner.

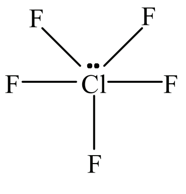
(b) $\text{Na}(g) + \text{F}(g) \rightarrow \text{Na}^+(g) + \text{F}^-(g)$ $\Delta H^\circ = \mathbf{163\text{ kJ/mol}}$

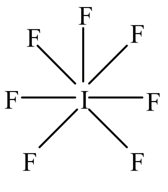
(c) $\text{K}(g) + \text{Cl}(g) \rightarrow \text{K}^+(g) + \text{Cl}^-(g)$ $\Delta H^\circ = \mathbf{71\text{ kJ/mol}}$

9.78 KF is an ionic compound. It is a solid at room temperature made up of K^+ and F^- ions. It has a high melting point, and it is a strong electrolyte. Benzene, C_6H_6, is a covalent compound that exists as discrete molecules. It is a liquid at room temperature. It has a low melting point, is insoluble in water, and is a nonelectrolyte.

9.79 The three pairs of nonbonding electrons around each fluorine have been omitted for simplicity.

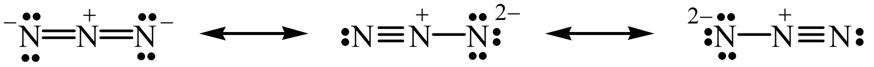






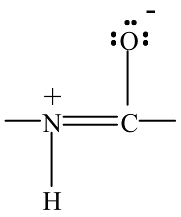
The octet rule is not obeyed in any of the compounds. In order for the octet rule to be obeyed, what would the value of n in the compound ICl_n have to be? [Hint: see Problem 9.45 (a)]

9.80 The resonance structures are:



Which is the most plausible structure based on a formal charge argument?

9.81 A resonance structure is:

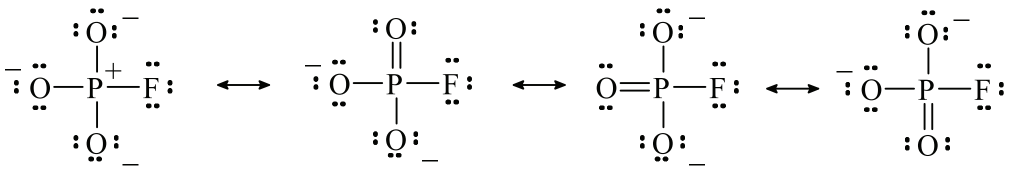


9.82 **(a)** An example of an aluminum species that satisfies the octet rule is the anion $AlCl_4^-$. The Lewis dot structure is drawn in Problem 9.66.

(b) An example of an aluminum species containing an expanded octet is anion AlF_6^{3-}. (How many pairs of electrons surround the central atom?)

(c) An aluminum species that has an incomplete octet is the compound $AlCl_3$. The dot structure is given in Problem 9.66.

9.83 Four resonance structures together with the formal charges are



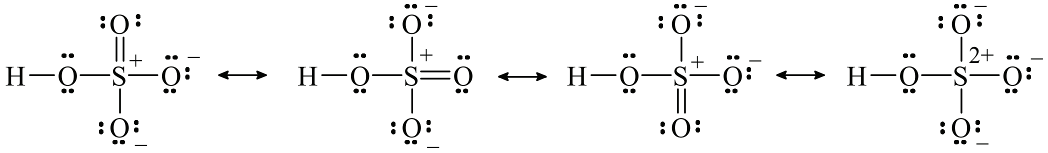
9.84 CF_2 would be very unstable because carbon does not have an octet. (How many electrons does it have?)

LiO_2 would not be stable because the lattice energy between Li^+ and superoxide O_2^- would be too low to stabilize the solid.

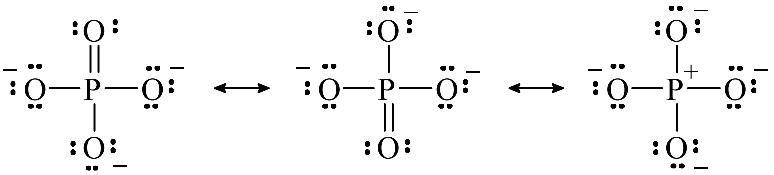
$CsCl_2$ requires a Cs^{2+} cation. The second ionization energy is too large to be compensated by the increase in lattice energy.

PI_5 appears to be a reasonable species (compared to PF_5 in Example 9.10 of the text). However, the iodine atoms are too large to have five of them "fit" around a single P atom.

9.85 Reasonable resonance structures are:

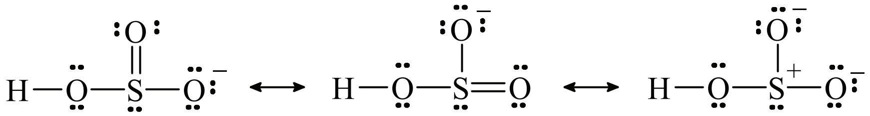
(a) 

(b)

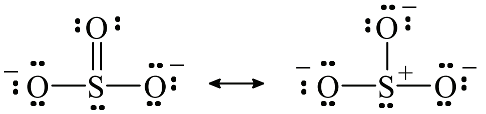


There are two more equivalent resonance structures to the first structure above.

(c)



(d)



There are two more equivalent resonance structures to the first structure.

9.86 **(a)** false **(b)** true **(c)** false **(d)** false

For question (c), what is an example of a second-period species that violates the octet rule?

9.87 If the central atom were more electronegative, there would be a concentration of negative charges at the central atom. This would lead to instability.

9.88 The formation of CH_4 from its elements is:

$$C(s) + 2H_2(g) \longrightarrow CH_4(g)$$

The reaction could take place in two steps:

Step 1: $C(s) + 2H_2(g) \longrightarrow C(g) + 4H(g)$ $\Delta H^\circ_{rxn} = (716 + 872.8)\text{kJ/mol} = 1589\text{ kJ/mol}$

Step 2: $C(g) + 4H(g) \longrightarrow CH_4(g)$ $\Delta H^\circ_{rxn} \approx -4 \times (\text{bond energy of C}-\text{H bond})$

$$= -4 \times 414\text{ kJ/mol} = -1656\text{ kJ/mol}$$

Therefore, $\Delta H^\circ_f(CH_4)$ would be approximately the sum of the enthalpy changes for the two steps. See Section 6.6 of the text (Hess's law).

$$\Delta H^\circ_f(CH_4) = \Delta H^\circ_{rxn}(1) + \Delta H^\circ_{rxn}(2)$$

$$\Delta H^\circ_f(CH_4) = (1589 - 1656)\text{kJ/mol} = \mathbf{-67\ kJ/mol}$$

The actual value of $\Delta H^\circ_f(CH_4) = -74.85$ kJ/mol.

9.89 **(a)** Bond broken: C–H $\Delta H^\circ = 414$ kJ/mol
Bond made: C–Cl $\Delta H^\circ = -338$ kJ/mol

$$\Delta H^\circ_{rxn} = 414 - 338 = 76\text{ kJ/mol}$$

(b) Bond broken: C–H $\Delta H° = 414$ kJ/mol
Bond made: H–Cl $\Delta H° = -431.9$ kJ/mol

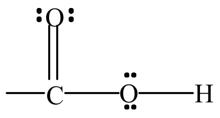
$$\Delta H^\circ_{\text{rxn}} = 414 - 431.9 = -18 \text{ kJ/mol}$$

Based on energy considerations, reaction **(b)** will occur readily since it is exothermic. Reaction (a) is endothermic.

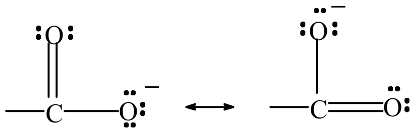
9.90 Only $\mathbf{N_2}$ has a triple bond. Therefore, it has the shortest bond length.

9.91 The rest of the molecule (in this problem, unidentified) would be attached at the end of the free bond.

(a)

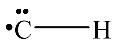


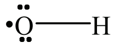
(b)

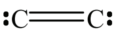


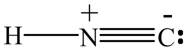
9.92 To be isoelectronic, molecules must have the same number and arrangement of valence electrons. NH_4^+ and CH_4 are isoelectronic (8 valence electrons), as are CO and N_2 (10 valence electrons), as are $B_3N_3H_6$ and C_6H_6 (30 valence electrons). Draw Lewis structures to convince yourself that the electron arrangements are the same in each isoelectronic pair.

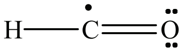
9.93 The Lewis structures are:

(a)  paramagnetic

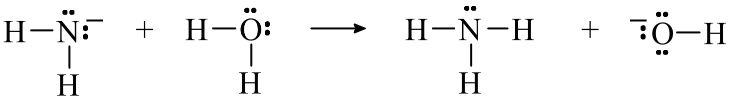
(b)  paramagnetic

(c)  diamagnetic

(d)  diamagnetic

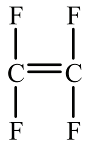
(e)  paramagnetic

9.94 The reaction can be represented as:

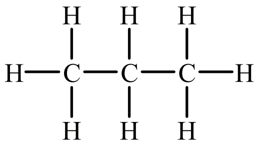


9.95 The Lewis structures are:

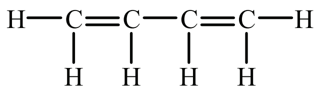
(a)



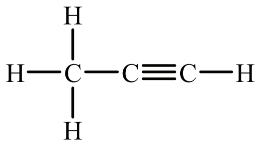
(b)



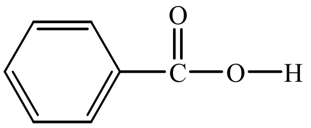
(c)



(d)



(e)



9.96 The central iodine atom in I_3^- has *ten* electrons surrounding it: two bonding pairs and three lone pairs. The central iodine has an expanded octet. Elements in the second period such as fluorine cannot have an expanded octet as would be required for F_3^-.

9.97 See Problem 9.71. The bond enthalpy for F_2 is:

$$F_2(g) \rightarrow F(g) + F(g) \qquad \Delta H^\circ = 156.9\ \text{kJ/mol}$$

The energy for the process $F_2(g) \rightarrow F^+(g) + F^-(g)$ can be found by Hess's law. Thus,

$$\begin{array}{ll}
F_2(g) \rightarrow F(g) + F(g) & \Delta H^\circ = 156.9\ \text{kJ/mol} \\
F(g) \rightarrow F^+(g) + e^- & \Delta H^\circ = 1680\ \text{kJ/mol}\ \ [I_1(\text{F}), \text{see Table 8.2 of the text}] \\
F(g) + e^- \rightarrow F^-(g) & \Delta H^\circ = -328\ \text{kJ/mol}\ \ [EA_1(\text{F}), \text{see Table 8.3 of the text}] \\
\hline
F_2(g) \rightarrow F^+(g) + F^-(g) & \Delta H^\circ = 1509\ \text{kJ/mol}
\end{array}$$

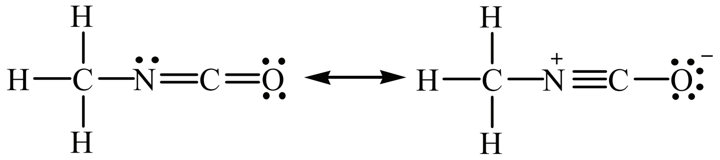
It is much easier to dissociate F_2 into two neutral F atoms than it is to dissociate it into a fluorine cation and anion.

9.98 The skeletal structure is:

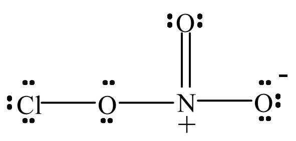
H
H C N C O
H

The number of valence electron is: (1 × 3) + (2 × 4) + 5 + 6 = 22 valence electrons

We can draw two resonance structures for methyl isocyanate.



9.99 A reasonable Lewis structure is:



9.100 **(a)** This is a very good resonance form; there are no formal charges and each atom satisfies the octet rule.

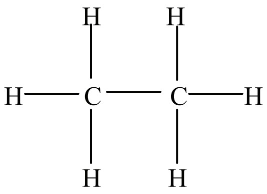
(b) This is a second choice after (a) because of the positive formal charge on the oxygen (high electronegativity).

(c) This is a poor choice for several reasons. The formal charges are placed counter to the electronegativities of C and O, the oxygen atom does not have an octet, and there is no bond between that oxygen and carbon!

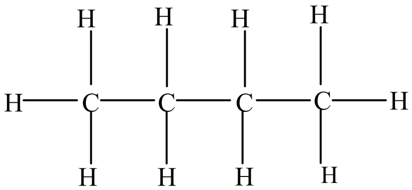
(d) This is a mediocre choice because of the large formal charge and lack of an octet on carbon.

9.101 For C_4H_{10} and C_5H_{12} there are a number of structural isomers.

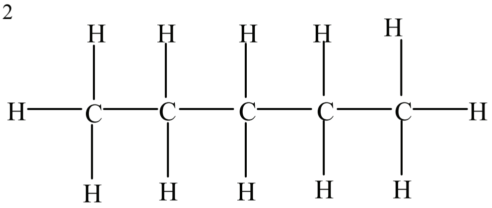
C_2H_6



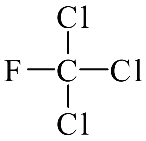
C_4H_{10}

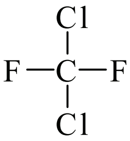


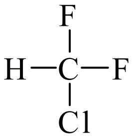
C_5H_{12}

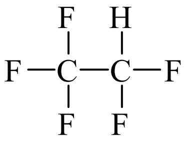


9.102 The nonbonding electron pairs around Cl and F are omitted for simplicity.

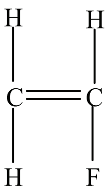


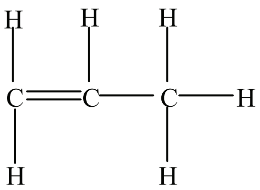


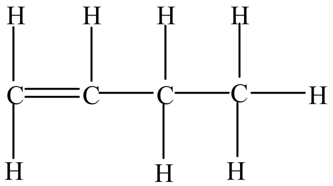




9.103 The structures are (the nonbonding electron pairs on fluorine have been omitted for simplicity):







9.104 **(a)** Using Equation (9.3) of the text,

$\Delta H = \sum BE(\text{reactants}) - \sum BE(\text{products})$

$\boldsymbol{\Delta H} = [(436.4 + 151.0) - 2(298.3)] = \mathbf{-9.2\ kJ/mol}$

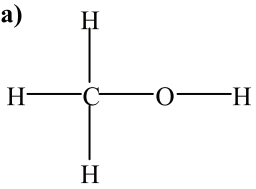
(b) Using Equation (6.18) of the text,

$\Delta H° = 2\Delta H^\circ_f[HI(g)] - \{\Delta H^\circ_f[H_2(g)] + \Delta H^\circ_f[I_2(g)]\}$

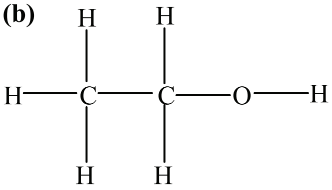
$\boldsymbol{\Delta H°} = (2)(25.9\text{ kJ/mol}) - [(0) + (1)(61.0\text{ kJ/mol})] = \mathbf{-9.2\ kJ/mol}$

9.105 Note that the nonbonding electron pairs have been deleted from oxygen, nitrogen, sulfur, and chlorine for simplicity.

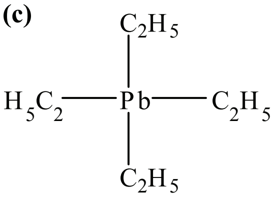
(a)



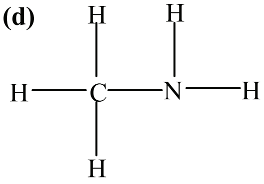
(b)



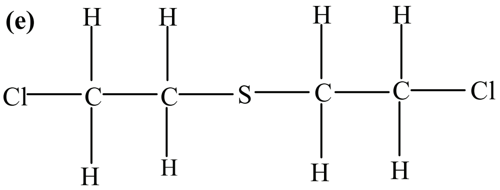
(c)



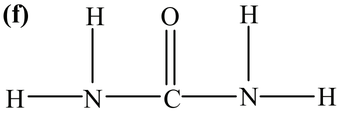
(d)



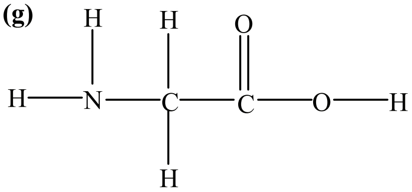
(e)



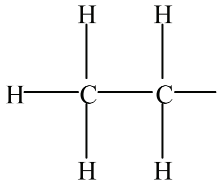
(f)



(g)



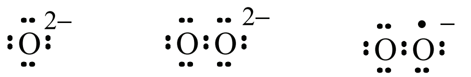
Note: in part (c) above, ethyl = C_2H_5 =



9.106 The Lewis structures are:

(a) $:\overset{-}{C}\equiv\overset{+}{O}:$ **(b)** $:N\equiv\overset{+}{O}:$ **(c)** $:\overset{-}{C}\equiv N:$ **(d)** $:N\equiv N:$

9.107

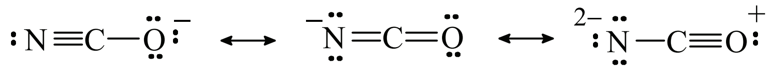


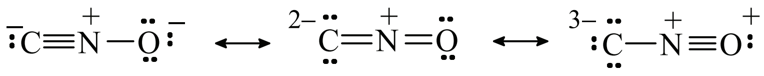
oxide peroxide superoxide

9.108 True. Each noble gas atom already has completely filled *ns* and *np* subshells.

9.109 The resonance structures are:

(a)



(b) 
$\overset{-}{\text{C}}{\equiv}\overset{+}{\text{N}}{-}\overset{-}{\text{O}} \longleftrightarrow \overset{2-}{\text{C}}{=}\overset{+}{\text{N}}{=}\text{O} \longleftrightarrow \overset{3-}{\text{C}}{-}\overset{+}{\text{N}}{\equiv}\overset{+}{\text{O}}$

In both cases, the most likely structure is on the left and the least likely structure is on the right.

9.110 **(a)** The bond enthalpy of F_2^- is the energy required to break up F_2^- into an F atom and an F^- ion.

$$F_2^-(g) \longrightarrow F(g) + F^-(g)$$

We can arrange the equations given in the problem so that they add up to the above equation. See Section 6.6 of the text (Hess's law).

$$\begin{array}{lll} F_2^-(g) \longrightarrow F_2(g) + e^- & \Delta H^\circ = 290\text{ kJ/mol} \\ F_2(g) \longrightarrow 2F(g) & \Delta H^\circ = 156.9\text{ kJ/mol} \\ F(g) + e^- \longrightarrow F^-(g) & \Delta H^\circ = -333\text{ kJ/mol} \\ \hline F_2^-(g) \longrightarrow F(g) + F^-(g) & \end{array}$$

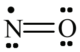
The bond enthalpy of F_2^- is the sum of the enthalpies of reaction.

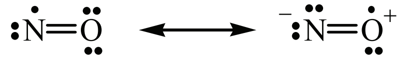
$$\boldsymbol{BE}(\mathbf{F_2^-}) = [290 + 156.9 + (-333\text{ kJ})]\text{kJ/mol} = \mathbf{114\ kJ/mol}$$

(b) The bond in F_2^- is weaker (114 kJ/mol) than the bond in F_2 (156.9 kJ/mol), because the extra electron increases repulsion between the F atoms.

9.111 The description involving a griffin and a unicorn is more appropriate. Both mule and donkey are real animals whereas resonance structures are nonexistent.

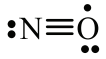
9.112 In **(a)** there is a lone pair on the C atom and the negative formal charge is on the less electronegative C atom.

9.113 Except for nitric oxide, lone pairs of electrons have been left off for simplicity. H–H (hydrogen), O=O (oxygen), N≡N (nitrogen), F–F (fluorine), Cl–Cl (chlorine), Br–Br (bromine), I–I (iodine), C≡O (carbon monoxide), H–F (hydrogen fluoride), H–Cl (hydrogen chloride), H–Br (hydrogen bromide), H–I (hydrogen iodide), and  $\text{N}{=}\text{O}$ (nitric oxide).

9.114 **(a)** 
$\text{N}{=}\text{O} \longleftrightarrow \overset{-}{\text{N}}{=}\overset{+}{\text{O}}$

The first structure is the most important. Both N and O have formal charges of zero. In the second structure, the more electronegative oxygen atom has a formal charge of +1. Having a positive formal charge on an highly electronegative atom is not favorable. In addition, both structures leave one atom with an incomplete octet. This cannot be avoided due to the odd number of electrons.

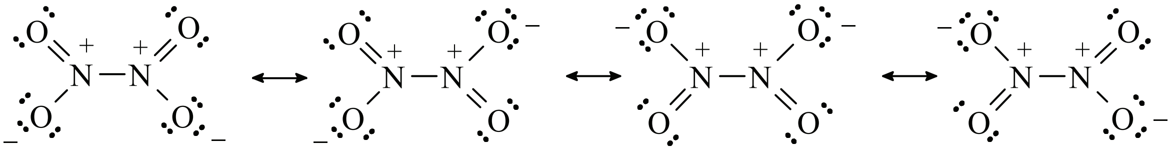
(b) It is not possible to draw a structure with a triple bond between N and O.


$\text{N}{\equiv}\text{O}$

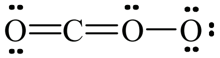
Any structure drawn with a triple bond will lead to an expanded octet. Elements in the second row of the period table cannot exceed the octet rule.

9.115 The unpaired electron on each N atom will be shared to form a covalent bond:

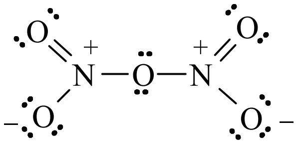
$$O_2N^\bullet + {}^\bullet NO_2 \longrightarrow N_2O_4$$



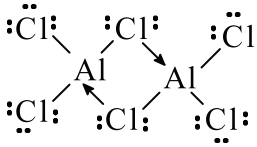
9.116 The OCOO structure violates the octet rule (expanded octet). The structure shown below satisfies the octet rule with 22 valence electrons. However, CO_3^{2-} has 24 valence electrons. Adding two more electrons to the structure would cause at least one atom to exceed the octet rule.



9.117 One resonance form showing formal charges is:

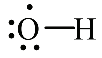


9.118



The arrows indicate coordinate covalent bonds.

9.119 **(a)**



(b) The O–H bond is quite strong (460 kJ/mol). To complete its octet, the OH radical has a strong tendency to form a bond with a H atom.

(c) One C–H bond is being broken, and an O–H bond is being formed.

$$\Delta H = \Sigma\text{BE(reactants)} - \Sigma\text{BE(products)}$$

$$\boldsymbol{\Delta H} = 414 - 460 = \mathbf{-46\ kJ/mol}$$

(d) $$\text{Energy of one O}-\text{H bond} = \frac{460 \times 10^3\ \text{J}}{1\ \text{mol}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{bonds}} = 7.64 \times 10^{-19}\ \text{J/bond}$$

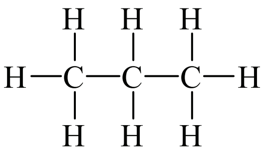
$$\lambda = \frac{hc}{\Delta H} = \frac{(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})(3.00 \times 10^8\ \text{m/s})}{7.64 \times 10^{-19}\ \text{J}}$$

$$\lambda = 2.60 \times 10^{-7}\ \text{m} = \mathbf{260\ nm}$$

9.120 There are four C–H bonds in CH_4, so the average bond enthalpy of a C–H bond is:

$$\frac{1656\text{ kJ/mol}}{4} = 414\text{ kJ/mol}$$

The Lewis structure of propane is:



There are eight C–H bonds and two C–C bonds. We write:

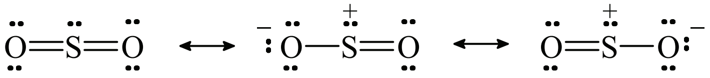
$$8(\text{C–H}) + 2(\text{C–C}) = 4006\text{ kJ/mol}$$

$$8(414\text{ kJ/mol}) + 2(\text{C–C}) = 4006\text{ kJ/mol}$$

$$2(\text{C–C}) = 694\text{ kJ/mol}$$

So, the average bond enthalpy of a C–C bond is: $\frac{694}{2}\text{kJ/mol} = \mathbf{347\ kJ/mol}$

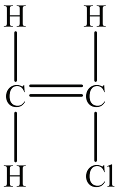
9.121 Three resonance structures with formal charges are:



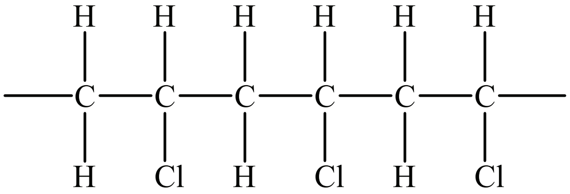
According to the comments in Example 9.11 of the text, the *second* and *third* structures above are more important.

9.122

(a)



(b)



(c) In the formation of poly(vinyl chloride) form vinyl chloride, for every C=C double bond broken, 2 C–C single bonds are formed. No other bonds are broken or formed. The energy changes for 1 mole of vinyl chloride reacted are:

total energy input (breaking C=C bonds) = 620 kJ

total energy released (forming C–C bonds) = 2 × 347 kJ = 694 kJ

$\Delta H° = 620\text{ kJ} - 694\text{ kJ} = -74\text{ kJ}$

The negative sign shows that this is an exothermic reaction. To find the total heat released when 1.0×10^3 kg of vinyl chloride react, we proceed as follows:

$$\text{heat released} = (1.0 \times 10^6\text{ g }C_2H_3Cl) \times \frac{1\text{ mol }C_2H_3Cl}{62.49\text{ g }C_2H_3Cl} \times \frac{-74\text{ kJ}}{1\text{ mol }C_2H_3Cl} = \mathbf{-1.2 \times 10^6\ kJ}$$

9.123 Work done = force × distance

$$= (2.0\times10^{-9}\ \text{N})\times(2\times10^{-10}\ \text{m})$$

$$= 4\times10^{-19}\ \text{N·m}$$

$$= 4\times10^{-19}\ \text{J to break one bond}$$

Expressing the bond enthalpy in kJ/mol:

$$\frac{4\times10^{-19}\ \text{J}}{1\ \text{bond}}\times\frac{1\ \text{kJ}}{1000\ \text{J}}\times\frac{6.022\times10^{23}\ \text{bonds}}{1\ \text{mol}} = \mathbf{2\times10^{2}\ kJ/mol}$$

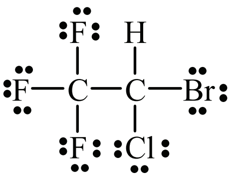
9.124 $\text{EN(O)} = \dfrac{1314+141}{2} = 727.5$ $\text{EN(F)} = \dfrac{1680+328}{2} = 1004$ $\text{EN(Cl)} = \dfrac{1251+349}{2} = 800$

Using Mulliken's definition, the electronegativity of chlorine is greater than that of oxygen, and fluorine is still the most electronegative element. We can convert to the Pauling scale by dividing each of the above by 230 kJ/mol.

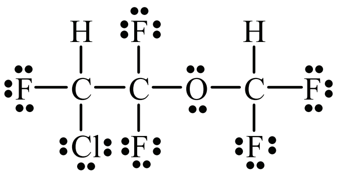
$\text{EN(O)} = \dfrac{727.5}{230} = \mathbf{3.16}$ $\text{EN(F)} = \dfrac{1004}{230} = \mathbf{4.37}$ $\text{EN(Cl)} = \dfrac{800}{230} = \mathbf{3.48}$

These values compare to the Pauling values for oxygen of 3.5, fluorine of 4.0, and chlorine of 3.0.

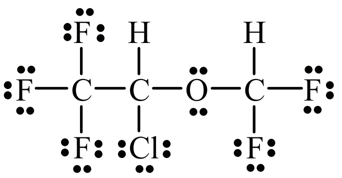
9.125



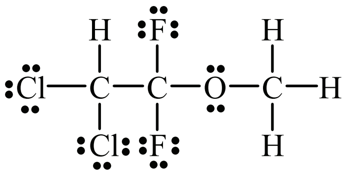
halothane



enflurane



isoflurane



methoxyflurane

9.126 (1) You could determine the magnetic properties of the solid. An $Mg^{+}O^{-}$ solid would be paramagnetic while $Mg^{2+}O^{2-}$ solid is diamagnetic.

(2) You could determine the lattice energy of the solid. $Mg^{+}O^{-}$ would have a lattice energy similar to $Na^{+}Cl^{-}$. This lattice energy is much lower than the lattice energy of $Mg^{2+}O^{2-}$.

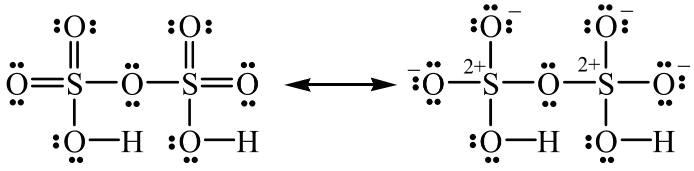
9.127 The equations for the preparation of sulfuric acid starting with sulfur are:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$
$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$
$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

The equations for the preparation of sulfuric acid starting with sulfur trioxide are:

$SO_3(g) + H_2SO_4(aq) \rightarrow H_2S_2O_7(aq)$	Formation of oleum
$H_2S_2O_7(aq) + H_2O(l) \rightarrow 2H_2SO_4(aq)$	Generation of sulfuric acid

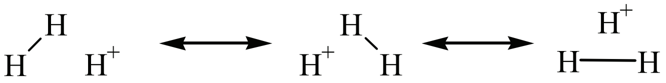
Based on the discussion in Example 9.11 of the text, there are two resonance structures for oleum. Formal charges other than zero are shown in the structures.



9.128 We can arrange the equations for the lattice energy of KCl, ionization energy of K, and electron affinity of Cl, to end up with the desired equation.

$K^+(g) + Cl^-(g) \rightarrow KCl(s)$	$\Delta H° = -699$ kJ/mol (equation for lattice energy of KCl, reversed)
$K(g) \rightarrow K^+(g) + e^-$	$\Delta H° = 418.7$ kJ/mol (ionization energy of K)
$Cl(g) + e^- \rightarrow Cl^-(g)$	$\Delta H° = -349$ kJ/mol (electron affinity of Cl)
$K(g) + Cl(g) \rightarrow KCl(s)$	$\boldsymbol{\Delta H°} = (-699 + 418.7 + -349)\text{ kJ/mol} = \mathbf{-629\ kJ/mol}$

9.129 **(a)**



(b) This is an application of Hess's Law.

$2H + H^+ \rightarrow H_3^+$	$\Delta H = -849$ kJ/mol
$H_2 \rightarrow 2H$	$\Delta H = 436.4$ kJ/mol
$H^+ + H_2 \rightarrow H_3^+$	$\mathbf{\Delta H = -413\ kJ/mol}$

The energy released in forming H_3^+ from H^+ and H_2 is almost as large as the formation of H_2 from 2 H atoms.

9.130 From Table 9.4 of the text, we can find the bond enthalpies of C–N and C=N. The average can be calculated, and then the maximum wavelength associated with this enthalpy can be calculated.

The average bond enthalpy for C–N and C=N is:

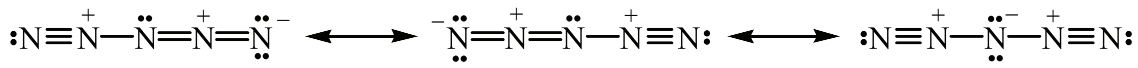
$$\frac{(276 + 615)\text{ kJ/mol}}{2} = 446\text{ kJ/mol}$$

We need to convert this to units of J/bond before the maximum wavelength to break the bond can be calculated. Because there is only 1 CN bond per molecule, there is Avogadro's number of bonds in 1 mole of the amide group.

$$\frac{446\text{ kJ}}{1\text{ mol}} \times \frac{1\text{ mol}}{6.022 \times 10^{23}\text{ bonds}} \times \frac{1000\text{ J}}{1\text{ kJ}} = 7.41 \times 10^{-19}\text{ J/bond}$$

The maximum wavelength of light needed to break the bond is:

$$\lambda_{\mathbf{max}} = \frac{hc}{E} = \frac{(6.63 \times 10^{-34}\text{ J}\cdot\text{s})(3.00 \times 10^{8}\text{ m/s})}{7.41 \times 10^{-19}\text{ J}} = \mathbf{2.68 \times 10^{-7}\ m} = \mathbf{268\ nm}$$

9.131 

9.132 **(a)** We divide the equation given in the problem by 4 to come up with the equation for the decomposition of *1 mole* of nitroglycerin.

$$C_3H_5N_3O_9(l) \rightarrow 3CO_2(g) + \tfrac{5}{2}H_2O(g) + \tfrac{3}{2}N_2(g) + \tfrac{1}{4}O_2(g)$$

We calculate $\Delta H°$ using Equation (6.18) and the enthalpy of formation values from Appendix 3 of the text.

$$\Delta H°_{\text{rxn}} = \sum n\Delta H°_{\text{f}}(\text{products}) - \sum m\Delta H°_{\text{f}}(\text{reactants})$$

$$\boldsymbol{\Delta H°_{\textbf{rxn}}} = (3)(-395.5\text{ kJ/mol}) + \left(\tfrac{5}{2}\right)(-241.8\text{ kJ/mol}) - (1)(-371.1\text{ kJ/mol}) = \mathbf{-1413.9\ kJ/mol}$$

Next, we calculate $\Delta H°$ using bond enthalpy values from Table 9.4 of the text.

Bonds Broken	*Number Broken*	*Bond Enthalpy* (kJ/mol)	*Enthalpy Change* (kJ/mol)
C–H	5	414	2070
C–C	2	347	694
C–O	3	351	1053
N–O	6	176	1056
N=O	3	607	1821

Bonds Formed	*Number Formed*	*Bond Enthalpy* (kJ/mol)	*Enthalpy Change* (kJ/mol)
C=O	6	799	4794
O–H	(5/2)(2) = 5	460	2300
N≡N	1.5	941.4	1412.1
O=O	0.25	498.7	124.7

From Equation (9.3) of the text:

$$\Delta H° = \sum BE(\text{reactants}) - \sum BE(\text{products})$$

$$\boldsymbol{\Delta H°} = (6694 - 8630.8)\text{ kJ/mol} = \mathbf{-1937\ kJ/mol}$$

The $\Delta H°$ values do not agree exactly because average bond enthalpies are used, and nitroglycerin is a liquid (strictly, the bond enthalpy values are for gases).

(b) One mole of nitroglycerin generates, (3 + 2.5 + 1.5 + 0.25) = 7.25 moles of gas. One mole of an ideal gas occupies a volume of 22.41 L at STP.

$$7.25\text{ mol} \times \frac{22.41\text{ L}}{1\text{ mol}} = \mathbf{162\ L}$$

(c) We calculate the pressure exerted by 7.25 moles of gas occupying a volume of 162 L at a temperature of 3000 K.

$$\boldsymbol{P} = \frac{nRT}{V} = \frac{(7.25\text{ mol})(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})(3000\text{ K})}{162\text{ L}} = \mathbf{11.0\ atm}$$