change upon breaking a particular bond. Average bond enthalpies can be determined for a wide variety of covalent bonds. The strengths of covalent bonds increase with the number of electron pairs shared between two atoms. We can use bond enthalpies to estimate the enthalpy change during chemical reactions in which bonds are broken and new bonds formed. The average bond length between two atoms decreases as the number of bonds between the atoms increases, consistent with the bond being stronger as the number of bonds increases.

### VISUALIZING CONCEPTS

8.1 For each of these Lewis symbols, indicate the group in the periodic table in which the element X belongs:
(a) \( \cdot X^+ \)  (b) \( X^- \)  (c) \( X^0 \)  [Section 8.1]

8.2 Illustrated below are four ions—\( A_1, A_2, Z_1, \) and \( Z_2 —\) showing their relative ionic radii. The ions shown in red carry a 1+ charge, and those shown in blue carry a 1– charge. (a) Would you expect to find an ionic compound of formula \( A_1A_2 \)? Explain. (b) Which combination of ions leads to the ionic compound having the largest lattice energy? (c) Which combination of ions leads to the ionic compound having the smallest lattice energy? [Section 8.2]

8.3 The orbital diagram below shows the valence electrons for a 2+ ion of an element. (a) What is the element? (b) What is the electron configuration of an atom of this element? [Section 8.2]

![ orbital diagram ]

8.4 In the Lewis structure shown below, A, D, E, Q, X, and Z represent elements in the first two rows of the periodic table. Identify all six elements. [Section 8.3]

\[
\begin{array}{ccc}
\text{A} & \text{D} & \text{Q} \\
\text{E} & \text{X} & \text{Z}
\end{array}
\]

8.5 The partial Lewis structure below is for a hydrocarbon molecule. In the full Lewis structure, each carbon atom satisfies the octet rule, and there are no unshared electron pairs in the molecule. The carbon–carbon bonds are labeled 1, 2, and 3. (a) Determine where the hydrogen atoms are in the molecule. (b) Rank the carbon–carbon bonds in order of increasing bond length. (c) Rank the carbon–carbon bonds in order of increasing bond enthalpy. [Sections 8.3 and 8.8]

\[
\begin{array}{ccc}
\text{C} & \text{C} & \text{C} \\
\text{A} & \text{D} & \text{Q}
\end{array}
\]

8.6 One possible Lewis structure for the compound xenon trioxide, \( \text{XeO}_3 \), is shown below. (a) Prior to the 1960s, this compound was thought to be impossible. Why? (b) How many other equivalent resonant structures are there for this Lewis structure? (c) Does this Lewis structure satisfy the octet rule? Explain why or why not. (d) Do you think this is the best choice of Lewis structure for \( \text{XeO}_3 \)? [Sections 8.5, 8.6, and 8.7]

![ Lewis structure ]

### EXERCISES

#### Lewis Symbols

8.7 (a) What are valence electrons? (b) How many valence electrons does a nitrogen atom possess? (c) An atom has the electron configuration \( 1s^22s^22p^63s^23p^3 \). How many valence electrons does the atom have?

8.8 (a) What is the octet rule? (b) How many electrons must a sulfur atom gain to achieve an octet in its valence shell? (c) If an atom has the electron configuration \( 1s^22s^22p^3 \), how many electrons must the atom gain to achieve an octet?

8.9 Write the electron configuration for phosphorus. Identify a valence electron in this configuration and a nonvalence electron. From the standpoint of chemical reactivity, what is the important difference between them?

8.10 Write the electron configuration for the element scandium, Sc. How many valence electrons does this atom possess? What distinguishes these valence electrons from the other electrons in the atom?

8.11 Write the Lewis symbol for atoms of each of the following elements: (a) Al, (b) Br, (c) Ar, (d) Sr.

8.12 What is the Lewis symbol for each of the following atoms or ions: (a) K, (b) Si, (c) \( \text{Mg}^{2+} \), (d) \( \text{P}^3– \) ?
Ionic Bonding

8.13 Using Lewis symbols, diagram the reaction between magnesium and oxygen atoms to give the ionic substance MgO.

8.14 Use Lewis symbols to represent the reaction that occurs between Mg and Br atoms.

8.15 Predict the chemical formula of the ionic compound formed between the following pairs of elements: (a) Al and F, (b) K and S, (c) Y and O, (d) Mg and N.

8.16 Which ionic compound is expected to form from combination of the following pairs of elements: (a) barium and oxygen, (b) rubidium and iodine, (c) lithium and sulfur, (d) bromine and magnesium?

8.17 Write the electron configuration for each of the following ions, and determine which ones possess noble-gas configurations: (a) Sr²⁺, (b) Ti⁴⁺, (c) Se²⁻, (d) Ni²⁺, (e) Br⁻, (f) Mn³⁺.

8.18 Write electron configurations for the following ions, and determine which have noble-gas configurations: (a) Zn²⁺, (b) Te⁵⁺, (c) Se⁵⁺, (d) Ru⁵⁺, (e) Ti⁴⁺, (f) Au⁻.

8.19 (a) Define the term lattice energy. (b) Which factors govern the magnitude of the lattice energy of an ionic compound?

8.20 (a) The lattice energies of NaF and MgO are given in Table 8.2. Account for the difference in these two quantities. (b) Account for the difference in the lattice energies of MgCl₂ and SrCl₂, which are also listed in that table.

8.21 The ionic substances KF, CaO, and ScN are isoelectronic (they have the same number of electrons). Examine the lattice energies for these substances in Table 8.2, and account for the trends you observe.

8.22 (a) Does the lattice energy of an ionic solid increase or decrease (i) as the charges of the ions increase, (ii) as the sizes of the ions increase? (b) Using a periodic table, arrange the following substances according to their expected lattice energies, listing them from lowest lattice energy to the highest: LiCl, NaBr, RbBr, MgO. Compare your list with the data in Table 8.2.

8.23 The lattice energies of KBr and CsCl are nearly equal (Table 8.2). What can you conclude from this observation?

8.24 Explain the following trends in lattice energy: (a) MgO > MgCl₂; (b) NaCl > RbBr > CaBr₂; (c) BaO > KF.

8.25 Energy is required to remove two electrons from Ca to form Ca²⁺ and is also required to add two electrons to O to form O²⁻. Why, then, is CaO stable relative to the free elements?

8.26 List the individual steps used in constructing a Born–Haber cycle for the formation of CaBr₂ from the elements. Which of these steps would you expect to be exothermic?

8.27 Use data from Appendix C, Figure 7.11, and Table 7.4 to calculate the lattice energy of RbCl. Is this value greater than or less than the lattice energy of NaCl? Explain.

8.28 By using data from Appendix C, Figure 7.11, Table 7.5, and the value of the second ionization energy for Ca, 1145 kJ/mol, calculate the lattice energy of CaCl₂. Is this value greater than or less than the lattice energy of NaCl? Explain.

Covalent Bonding, Electronegativity, and Bond Polarity

8.29 (a) What is meant by the term covalent bond? (b) Give three examples of covalent bonding. (c) A substance XY, formed from two different elements, boils at –33°C. Is XY likely to be a covalent or an ionic substance? Explain.

8.30 Which of these elements is unlikely to form covalent bonds: S, H, K, Ar, Si? Explain your choices.

8.31 Using Lewis symbols and Lewis structures, diagram the formation of SiCl₄ from Si and Cl atoms.

8.32 Use Lewis symbols and Lewis structures to diagram the formation of PF₃ from P and F atoms.

8.33 (a) Construct a Lewis structure for O₂ in which each atom achieves an octet of electrons. (b) Explain why it is necessary to form a double bond in the Lewis structure. (c) The bond in O₂ is shorter than the O—O bond in compounds that contain an O—O single bond. Explain this observation.

8.34 The C—S bond lengths in carbon disulfide, CS₂, are shorter than would be expected for C—S single bonds. Use a Lewis structure to rationalize this observation.

8.35 (a) What is meant by the term electronegativity? (b) On the Pauling scale what is the range of electronegativity values for the elements? (c) Which element has the greatest electronegativity? (d) Which element has the smallest electronegativity?

8.36 (a) What is the trend in electronegativity going from left to right in a row of the periodic table? (b) How do electronegativity values generally vary going down a column in the periodic table? (c) How do periodic trends in electronegativity relate to those for ionization energy and electron affinity?

8.37 Using only the periodic table as your guide, select the most electronegative atom in each of the following sets: (a) As, Se, Br, I; (b) Al, B, C, Si; (c) Ge, As, P, Sn; (d) Li, Rb, Be, Sr.

8.38 By referring only to the periodic table, select (a) the most electronegative element in group 6A; (b) the least electronegative element in the group Al, Si, P; (c) the most electronegative element in the group Ga, P, Cl, Na; (d) the element in the group K, C, Zn, F, that is most likely to form an ionic compound with Ba.

8.39 Which of the following bonds are polar: (a) B—F, (b) Cl—Cl, (c) Se—O, (d) H—I? Which is the more electronegative atom in each polar bond?

8.40 Arrange the bonds in each of the following sets in order of increasing polarity: (a) C—F, O—F, Be—F; (b) O—Cl, S—Br, C—P; (c) C—S, B—F, N—O.

8.41 From the data in Table 8.3, calculate the effective charges on the H and F atoms of the HF molecule in units of the electronic charge e.

8.42 The iodine monobromide molecule, IBr, has a bond length of 2.49 Å and a dipole moment of 1.21 D. (a) Which atom of the molecule is expected to have a negative charge? Explain. (b) Calculate the effective charges on the I and Br atoms in IBr, in units of the electronic charge e.
8.43 Give the name or chemical formula, as appropriate, for each of the following substances, and in each case predict whether the bonding is better described by the ionic-bonding or covalent-bonding model:
(a) manganese(IV) oxide, (b) phosphorus(III) sulfide, (c) cobalt(II) oxide, (d) Cu₂S, (e) ClF₃, (f) VF₅.

**Lewis Structures; Resonance Structures**

8.45 Draw Lewis structures for the following: (a) SiH₄, (b) CO, (c) SF₅, (d) H₂SO₄ (H is bonded to O), (e) ClO₂⁻, (f) NH₂OH.

8.46 Write Lewis structures for the following: (a) H₂CO (both H atoms are bonded to C), (b) H₂O₂, (c) C₂F₆ (contains a C—C bond), (d) AsO₃³⁻, (e) H₂SO₃ (H is bonded to O), (f) C₃H₂.

8.47 (a) When talking about atoms in a Lewis structure, what is meant by the term formal charge? (b) Does the formal charge of an atom represent the actual charge on that atom? Explain. (c) How does the formal charge of an atom in a Lewis structure differ from the oxidation number of the atom?

8.48 (a) Write a Lewis structure for the phosphorus trifluoride molecule, PF₃. Is the octet rule satisfied for all the atoms in your structure? (b) Determine the oxidation numbers of the P and F atoms. (c) Determine the formal charges of the P and F atoms. (d) Is the oxidation number for the P atom the same as its formal charge? Explain why or why not.

8.49 Write Lewis structures that obey the octet rule for each of the following, and assign oxidation numbers and formal charges to each atom: (a) NO³⁻, (b) POCl₃ (P is bonded to the three Cl atoms and to the O), (c) ClO₄⁻, (d) HClO₃ (H is bonded to O).

8.50 For each of the following molecules or ions of sulfur and oxygen, write a single Lewis structure that obeys the octet rule, and calculate the oxidation numbers and formal charges on all the atoms: (a) SO₂, (b) SO₃, (c) SO₃²⁻, (d) SO₄²⁻.

8.51 (a) Write one or more appropriate Lewis structures for the nitrite ion, NO₂⁻. (b) With what compound of oxygen is it isoelectronic? (c) What would you predict for the lengths of the bonds in this species relative to N—O single bonds?

8.52 Consider the nitryl cation, NO₂⁺. (a) Write one or more appropriate Lewis structures for this species. (b) Are resonance structures needed to describe the structure? (c) With what familiar species is it isoelectronic?

8.53 Predict the ordering of the C—O bond lengths in CO₂, CO₃²⁻, and CO₃⁻.

8.54 Based on Lewis structures, predict the ordering of N—O bond lengths in NO⁺, NO₂⁻, and NO₃⁻.

8.55 (a) Use the concept of resonance to explain why all C—C bonds in benzene are equal in length. (b) The C—N bond lengths in benzene are shorter than C—C single bonds but longer than C—C double bonds. Use the resonance model to explain this observation.

8.56 Mothballs are composed of naphthalene, C₁₀H₈, a molecule of which consists of two six-membered rings of carbon fused along an edge, as shown in this incomplete Lewis structure:

8.57 (a) State the octet rule. (b) Does the octet rule apply to ionic as well as to covalent compounds? Explain, using examples as appropriate.

8.58 Considering the representative nonmetals, what is the relationship between the group number for an element (carbon, for example, belongs to group 14; see the periodic table on the inside front cover) and the number of single covalent bonds that element needs to form to conform to the octet rule?

8.59 What is the most common exception to the octet rule? (a) Give two examples.

8.60 For elements in the third row of the periodic table and beyond, the octet rule is often not obeyed. What factors are usually cited to explain this fact?

8.61 Draw the Lewis structures for each of the following ions or molecules. Identify those that do not obey the octet rule, and explain why they do not. (a) SO₃²⁻, (b) AlH₃⁻, (c) N₃⁻, (d) CH₃Cl₂, (e) SbF₅.

8.62 Draw the Lewis structures for each of the following molecules or ions. Which do not obey the octet rule? (a) CO₂, (b) IO₃⁻, (c) BF₃, (d) BF₅⁻, (e) XeF₂.

8.63 In the vapor phase, BeCl₂ exists as a discrete molecule. (a) Draw the Lewis structure of this molecule, using only single bonds. Does this Lewis structure satisfy the octet rule? (b) What other resonance forms are possible that satisfy the octet rule? (c) Using formal charges, select the resonance form from among all the Lewis structures that is most important in describing BeCl₂.

8.64 (a) Describe the molecule chlorine dioxide, ClO₂, using three possible resonance structures. (b) Do any of these resonance structures satisfy the octet rule for every atom in the molecule? Why or why not? (c) Using formal charges, select the resonance structure(s) that is (are) most important.
Using the bond enthalpies tabulated in Table 8.4, estimate $\Delta H$ for each of the following gas-phase reactions:

(a) \[ \text{H} = \text{C} = \text{C} + \text{H} - \text{O} - \text{O} - \text{H} \rightarrow \]

(b) \[ \text{H} = \text{C} = \text{C} + \text{H} - \text{C} = \text{N} \rightarrow \]

(c) \[ 2 \text{Cl} - \text{N} - \text{Cl} \rightarrow \text{N} = \text{N} + 3 \text{Cl} - \text{Cl} \]

Using bond enthalpies (Table 8.4), estimate $\Delta H$ for the following gas-phase reactions:

(a) \[ \text{Br} - \text{C} - \text{H} + \text{Cl} - \text{Cl} \rightarrow \text{Br} - \text{C} - \text{Cl} + \text{H} - \text{Cl} \]

(b) \[ \text{H} - \text{S} - \text{C} = \text{S} - \text{H} + 2 \text{H} - \text{Br} \rightarrow \]

(c) \[ \text{H} - \text{N} - \text{N} - \text{H} + \text{Cl} - \text{Cl} \rightarrow 2 \text{H} - \text{N} - \text{Cl} \]

Using bond enthalpies (Table 8.4), estimate $\Delta H$ for each of the following reactions:

(a) \[ 2 \text{CH}_4(g) + \text{O}_2(g) \rightarrow 2 \text{CH}_3\text{OH}(g) \]

(b) \[ \text{H}_2(g) + \text{Br}_2(g) \rightarrow 2 \text{HBr}(g) \]

(c) \[ 2 \text{H}_2\text{O}(g) \rightarrow 2 \text{H}_2(g) + \text{O}_2(g) \]

Use bond enthalpies (Table 8.4) to estimate the enthalpy change for each of the following reactions:

(a) \[ 3 \text{H}_2\text{C} = \text{CH}_2(g) \rightarrow \text{C}_6\text{H}_{12}(g) \] (the six carbon atoms from a six-membered ring with two hydrogen atoms on each carbon atom)

(b) \[ \text{SiCl}_4(g) + 3 \text{Cl}_2(g) \rightarrow \text{SiCl}_4(g) + 3 \text{HCl}(g) \]

(c) \[ 8 \text{H}_2\text{O}(g) \rightarrow 8 \text{H}_2(g) + \text{S}_6(s) \]

Ammonia is produced directly from nitrogen and hydrogen by using the Haber process. The chemical reaction is

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2 \text{NH}_3(g) \]

(a) Use bond enthalpies (Table 8.4) to estimate the enthalpy change for the reaction, and tell whether this reaction is exothermic or endothermic. (b) Compare the enthalpy change you calculate in (a) to the true enthalpy change as obtained using $\Delta H_f^\circ$ values.

Use bond enthalpies to estimate the enthalpy change for the reaction of hydrogen with ethene:

\[ \text{H}_2(g) + \text{C}_2\text{H}_4(g) \rightarrow \text{C}_2\text{H}_6(g) \]

(a) Calculate the standard enthalpy change for this reaction, using heats of formation. Why does this value differ from that calculated in (a)?

Given the following bond-dissociation energies, calculate the average bond enthalpy for the Ti–Cl bond:

\[ \Delta H(kJ/mol) \]

<table>
<thead>
<tr>
<th>Bond</th>
<th>$\Delta H(kJ/mol)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl$\text{}_4(g)$</td>
<td>335</td>
</tr>
<tr>
<td>TiCl$\text{}_3(g)$</td>
<td>423</td>
</tr>
<tr>
<td>TiCl$\text{}_2(g)$</td>
<td>444</td>
</tr>
<tr>
<td>TiCl$\text{}(g)$</td>
<td>519</td>
</tr>
</tbody>
</table>

(a) Using average bond enthalpies, predict which of the following reactions will be most exothermic:

(i) \[ \text{C}(g) + 2 \text{F}_2(g) \rightarrow \text{CF}_4(g) \]

(ii) \[ \text{CO}(g) + 3 \text{F}_2 \rightarrow \text{CF}_4(g) + \text{OF}_3(g) \]

(iii) \[ \text{CO}_2(g) + 4 \text{F}_2 \rightarrow \text{CF}_4(g) + 2 \text{OF}_2(g) \]

(b) Explain the trend, if any, that exists between reaction exothermicity and the extent to which the carbon bond is bonded to oxygen.

Based on data in Table 8.2, estimate (within 30 kJ/mol) the lattice energy for (a) LiBr, (b) CsBr, (c) CaCl$\text{}_2$.

From the ionic radii given in Figure 7.7, calculate the potential energy of a Ca$^{2+}$ and O$^{2-}$ ion pair that are just touching (the magnitude of the electronic charge is given on the back inside cover). Calculate the energy of a mole of such pairs. How does this value compare with the lattice energy of CaO (Table 8.2)? Explain the difference.
From Equation 8.4 and the ionic radii given in Figure 7.7, calculate the potential energy of the following pairs of ions. Assume that the ions are separated by a distance equal to the sum of their ionic radii: (a) Na\(^+\), Br\(^-\); (b) Rb\(^+\), Br\(^-\); (c) Sr\(^{2+}\), S\(^2-\).

(a) How does a polar molecule differ from a nonpolar one? (b) Atoms X and Y have different electronegativities. Will the diatomic molecule X—Y necessarily be polar? Explain. (c) What factors affect the size of the dipole moment of a diatomic molecule?

Which of the following molecules or ions contain polar bonds: (a) P\(_4\), (b) H\(_2\)S, (c) NO\(_2\), (d) S\(_2\)\(^2-\)?

For the following collection of nonmetallic elements, O, P, Te, I, B, (a) which two would form the most polar single bond? (b) Which two would form the longest single bond? (c) Which two would be likely to form a compound of formula XY\(_2\)? (d) Which combinations of elements would likely yield a compound of empirical formula XY? In each case explain your answer.

(a) Triazine, C\(_3\)H\(_3\)N\(_3\), is like benzene except that in triazine every other C—H group is replaced by a nitrogen atom. Draw the Lewis structure(s) for the triazine molecule. (b) Estimate the carbon—nitrogen bond distances in the ring.

Using the electronegativities of Br and Cl, estimate the partial charges on the atoms in the Br—Cl molecule. Using these partial charges and the atomic radii given in Figure 7.7, estimate the dipole moment of the molecule. The measured dipole moment is 0.57 D.

Although I\(_3\) is known, F\(_5\) is not. Using Lewis structures, explain why F\(_5\) does not form.

Calculate the formal charge on the indicated atom in each of the following molecules or ions: (a) the central oxygen atom in O\(_3\), (b) phosphorus in PF\(_6\), (c) nitrogen in NO\(_2\), (d) iodine in ICl\(_3\), (e) chlorine in HClO\(_4\) (hydrogen is bonded to O).

(a) Determine the formal charge on the chlorine atom in the hypochlorite ion, ClO\(^-\), and the perchlorate ion, ClO\(_4^-\), if the Cl atom has an octet. (b) What are the oxidation numbers of chlorine in ClO\(^-\) and in ClO\(_4^-\)? (c) What are the essential differences in the definitions of formal charge and oxidation number that lead to the differences in your answers to parts (a) and (b)?

The following three Lewis structures can be drawn for N\(_2\)O:

: N\(\equiv\)N\(\equiv\)O: \(\leftrightarrow\) :N\(\equiv\)N\(\equiv\)O: \(\leftrightarrow\) :N=O=N:

(a) Using formal charges, which of these three resonance forms is likely to be the most important? (b) The N—N bond length in N\(_2\)O is 1.12 Å, slightly longer than a typical N—N bond, and the N—O bond length is 1.19 Å, slightly shorter than a typical N=O bond. (See Table 8.5.) Rationalize these observations in terms of the resonance structures shown previously and your conclusion for (a).

An important reaction for the conversion of natural gas to other useful hydrocarbons is the conversion of methane to ethane.

\[2\text{CH}_4(g) \rightarrow \text{C}_2\text{H}_6(g) + \text{H}_2(g)\]

In practice, this reaction is carried out in the presence of oxygen, which converts the hydrogen produced to water.

\[2\text{CH}_4(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{C}_2\text{H}_6(g) + \text{H}_2\text{O}(g)\]

Use bond enthalpies (Table 8.4) to estimate \(\Delta H\) for these two reactions. Why is the conversion of methane to ethane more favorable when oxygen is used?

Two compounds are isomers if they have the same chemical formula but a different arrangement of atoms. Use bond enthalpies (Table 8.4) to estimate \(\Delta H\) for each of the following gas-phase isomerization reactions, and indicate which isomer has the lower enthalpy:

(a) \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \\
\text{C} \\
\text{O} \\
\text{H} \\
\text{H}
\end{array}
\rightarrow
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \\
\text{C} \\
\text{O} \\
\text{H} \\
\text{H}
\end{array}
\]

Ethanol

(b) \[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{C} \\
\text{H} \\
\text{H}
\end{array}
\rightarrow
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{C} \\
\text{H} \\
\text{H}
\end{array}
\]

Ethylene oxide

Acetaldehyde

(c) \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \\
\text{C} \\
\text{C}
\end{array}
\rightarrow
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \\
\text{C} \\
\text{C}
\end{array}
\]

Cyclopentene

Pentadiene

(d) \[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{N} \\
\equiv \\
\text{C}
\end{array}
\rightarrow
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\equiv \\
\text{N}
\end{array}
\]

Methyl isocyanide

Acetonitrile

With reference to the "Chemistry at Work" box on explosives, (a) use bond enthalpies to estimate the enthalpy change for the explosion of 1.00 g of nitroglycerin. (b) Write a balanced equation for the decomposition of TNT. Assume that, upon explosion, TNT decomposes into N\(_2\)(g), CO\(_2\)(g), H\(_2\)O(g), and C(s).

The "plastic" explosive C-4, often used in action movies, contains the molecule cyclotrimethylentetranitramine, which is often called RDX (for Royal Demolition eXplosive).

\[
\begin{array}{c}
\text{O} \\
\equiv \\
\text{N} \\
\equiv \\
\text{N}
\end{array}
\]

Cyclotrimethylentetranitramine (RDX)
(a) Complete the Lewis structure for the molecule by adding unshared electron pairs where they are needed. (b) Does the Lewis structure you drew in part (a) have any resonance structures? If so, how many? (c) The molecule causes an explosion by decomposing into CO(g), N₂(g), and H₂O(g). Write a balanced equation for the decomposition reaction. (d) With reference to Table 8.4, which is the weakest type of bond in the molecule? (e) Use average bond enthalpies to estimate the enthalpy change when 5.0 g of RDX decomposes.

Consider this reaction involving the hypothetical molecule A−A, which contains a double bond:

\[
\begin{array}{c}
A & A & \rightarrow & A & A \\
\mid & + & \mid & \mid & \mid \\
A & A & \rightarrow & A & A
\end{array}
\]

(a) In terms of \(D(A \rightleftharpoons A)\) and \(D(A \rightarrow A)\), write a general expression for the enthalpy change for this reaction. (b) What must be the relationship between \(D(A \rightleftharpoons A)\) and \(D(A \rightarrow A)\) for the reaction to be exothermic? (c) If the reaction is exothermic, what can you say about the strength of the second bond between the A atoms in \(A \rightleftharpoons A\) relative to the strength of the first bond?

**Integrative Exercises**

8.94 The Ti²⁺ ion is isoelectronic with the Ca atom. (a) Are there any differences in the electron configurations of Ti²⁺ and Ca? (b) With reference to Figure 6.24, comment on the changes in the ordering of the 4s and 3d subshells in Ca and Ti²⁺. (c) Will Ca and Ti²⁺ have the same number of unpaired electrons? Explain.

8.95 (a) Write the chemical equations that are used in calculating the lattice energy of SrCl₂(s) via a Born–Haber cycle. (b) The second ionization energy of Sr(g) is 1064 kJ/mol. Use this fact along with data in Appendix C, Figure 7.11, Figure 7.12, and Table 8.2 to calculate \(\Delta H^\circ\) for SrCl₂(s).

8.96 The electron affinity of oxygen is −141 kJ/mol, corresponding to the reaction

\[O(g) + e^- \rightarrow O^-(g)\]

The lattice energy of K₂O(s) is 2238 kJ/mol. Use these data along with data in Appendix C and Figure 7.11 to calculate the "second electron affinity" of oxygen, corresponding to the reaction

\[O^-(g) + e^- \rightarrow O^{2-}(g)\]

8.97 The reaction of indium, In, with sulfur leads to three binary compounds, which we will assume to be purely ionic. The three compounds have the following properties:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass % In</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>87.7</td>
<td>653</td>
</tr>
<tr>
<td>B</td>
<td>78.2</td>
<td>692</td>
</tr>
<tr>
<td>C</td>
<td>70.5</td>
<td>1050</td>
</tr>
</tbody>
</table>

(a) Determine the empirical formulas of compounds A, B, and C. (b) Give the oxidation state of In in each of the three compounds. (c) Write the electron configuration for the In ion in each compound. Do any of these configurations correspond to a noble-gas configuration? (d) In which compound is theionic radius of In expected to be smallest? Explain. (e) The boiling point of ionic compounds often correlates with the lattice energy. Explain the trends in the melting points of compounds A, B, and C in these terms.

8.98 One scale for electronegativity is based on the concept that the electronegativity of any atom is proportional to the ionization energy of the atom minus its electron affinity: electronegativity = \(k(IE - EA)\), where \(k\) is a proportionality constant. (a) How does this definition explain why the electronegativity of F is greater than that of Cl even though Cl has the greater electron affinity? (b) Why are both ionization energy and electron affinity relevant to the notion of electronegativity? (c) By using data in Chapter 7, determine the value of \(k\) that would lead to an electronegativity of 4.0 for F under this definition. (d) Use your result from part (c) to determine the electronegativities of Cl and O using this scale. Do these values follow the trend shown in Figure 8.6?

8.99 The compound chloral hydrate, known in detective stories as knockout drops, is composed of 14.52% C, 1.83% H, 64.30% Cl, and 19.35% O by mass and has a molar mass of 165.4 g/mol. (a) What is the empirical formula of this substance? (b) What is the molecular formula of this substance? (c) Draw the Lewis structure of the molecule, assuming that the Cl atoms bond to a single C atom and that there is a C—C bond and two C—O bonds in the compound.

8.100 Barium azide is 62.04% Ba and 37.96% N. Each azide ion has a net charge of 1−. (a) Determine the chemical formula of the azide ion. (b) Write three resonance structures for the azide ion. (c) Which structure is most important? (d) Predict the bond lengths in the ion.
[8.101] Acetylene \((C_2H_2)\) and nitrogen \((N_2)\) both contain a triple bond, but they differ greatly in their chemical properties. (a) Write the Lewis structures for the two substances. (b) By referring to the index, look up the chemical properties of acetylene and nitrogen and compare their reactivities. (c) Write balanced chemical equations for the complete oxidation of \(N_2\) to form \(N_2O_5(g)\) and of acetylene to form \(CO_2(g)\) and \(H_2O(g)\). (d) Calculate the enthalpy of oxidation per mole of \(N_2\) and \(C_2H_2\) (the enthalpy of formation of \(N_2O_5(g)\) is \(11.30\) kJ/mol). How do these comparative values relate to your response to part (b)? Both \(N_2\) and \(C_2H_2\) possess triple bonds with quite high bond enthalpies (Table 8.4). What aspect of chemical bonding in these molecules or in the oxidation products seems to account for the difference in chemical reactivities?

[8.102] Under special conditions, sulfur reacts with anhydrous liquid ammonia to form a binary compound of sulfur and nitrogen. The compound is found to consist of \(69.6\%\) S and \(30.4\%\) N. Measurements of its molecular mass yield a value of \(184.3\) g mol\(^{-1}\). The compound occasionally detonates on being struck or when heated rapidly. The sulfur and nitrogen atoms of the molecule are joined in a ring. All the bonds in the ring are of the same length. (a) Calculate the empirical and molecular formulas for the substance. (b) Write Lewis structures for the molecule, based on the information you are given. \([\text{Hint: You should find a relatively small number of dominant Lewis structures.}]\) (c) Predict the bond distances between the atoms in the ring. \((\text{Note: The S—S distance in the \(S_2\) ring is \(2.05\) Å.})\) (d) The enthalpy of formation of the compound is estimated to be \(480\) kJ mol\(^{-1}\). \(\Delta H\) of \(S(g)\) is \(222.8\) kJ mol\(^{-1}\). Estimate the average bond enthalpy in the compound.

[8.103] A common form of elemental phosphorus is the tetrahedral \(P_4\) molecule:

At room temperature phosphorus is a solid. (a) Do you think there are any unshared pairs of electrons in the \(P_4\) molecule? (b) How many \(P—P\) bonds are there in the molecule? (c) Use data in Appendix C to determine the enthalpy of atomization of \(P_4(g)\). (d) Based on these results, what value would you give for \(D(P—P)\)? (e) Is the \(P—P\) bond stronger or weaker than an \(N—N\) single bond?

8.104 Use bond enthalpies (Table 8.4), electron affinities (Figure 7.12), and the ionization energy of hydrogen (1312 kJ/mol) to estimate \(\Delta H\) for the following gas-phase ionization reactions:

(a) \(HF(g) \rightarrow H^+(g) + F^-(g)\)
(b) \(HCl(g) \rightarrow H^+(g) + Cl^- (g)\)
(c) \(HBr(g) \rightarrow H^+(g) + Br^- (g)\)

8.105 Consider benzene \((C_6H_6)\) in the gas phase. (a) Write the reaction for breaking all the bonds in \(C_6H_6(g)\), and use data in Appendix C to determine the enthalpy change for this reaction. (b) Write a reaction that corresponds to breaking all the carbon–carbon bonds in \(C_6H_6(g)\); (c) by combining your answers to parts (a) and (b) and using the average bond enthalpy for \(C—H\) from Table 8.4, calculate the average bond enthalpy for the carbon–carbon bonds in \(C_6H_6(g)\). (d) Comment on your answer from part (c) as compared to the values for \(C—C\) single bonds and \(C=\text{C}\) double bonds in Table 8.4.

8.106 Average bond enthalpies are generally defined for gas-phase molecules. Many substances are liquids in their standard state. \(\cdots\) (Section 5.7) By using appropriate thermochemical data from Appendix C, calculate average bond enthalpies in the liquid state for the following bonds, and compare these values to the gas-phase values given in Table 8.4: (a) \(Br—Br\), from \(Br_2(l)\); (b) \(C—Cl\), from \(CCl_4(l)\); (c) \(O—O\), from \(H_2O_2(l)\) (assume that the \(O—H\) bond enthalpy is the same as in the gas phase). (d) What can you conclude about the process of breaking bonds in the liquid as compared to the gas phase? Explain the difference in the \(\Delta H\) values between the two phases.