density around the nitrogen nucleus, which is in accord with the fact that the nitrogen is the least electronegative of the three elements.

PRACTICE EXAMPLE A: Phosphorus pentachloride, $PCl_5(g)$, can be made from the reaction of $PCl_3(g)$ and $Cl_2(g)$. By using only data from Appendix D, estimate the average bond energy for the P—Cl bond. Assume that the P—Cl bond energies are the same in PCl_3 and PCl_5. With reference to the geometries of PCl_3 and PCl_5, explain why the P—Cl bond energies are probably not the same in these two molecules.

PRACTICE EXAMPLE B: The condensed structural formulas of formamide and formaldoxime are H_2NCHO and H_2CNOH, respectively. One of these molecules is much more stable than the other. **(a)** Sketch the structures of these molecules, using dash and wedge symbols, indicate the various bond angles, and use bond energies to determine which molecule is more stable. **(b)** Experiment shows that the H—N—H angle in formamide is 119° and the N—C—O angle is 124°. Draw a Lewis structure for formamide that is consistent with this structural information.

Exercises

Lewis Theory

1. Write Lewis symbols for the following atoms. **(a)** Kr; **(b)** Ge; **(c)** N; **(d)** Ga; **(e)** As; **(f)** Rb.
2. Write Lewis symbols for the following ions. **(a)** H^-; **(b)** Sn^{2+}; **(c)** K^+; **(d)** Br^-; **(e)** Se^{2-}; **(f)** Sc^{3+}.
3. Write plausible Lewis structures for the following molecules that contain only single covalent bonds. **(a)** FCl; **(b)** I_2; **(c)** SF_2; **(d)** NF_3; **(e)** H_2Te.
4. Each of the following molecules contains at least one multiple (double or triple) covalent bond. Give a plausible Lewis structure for **(a)** HCN; **(b)** $SC(NH_2)_2$; **(c)** F_2CO; **(d)** Cl_2SO; **(e)** C_2H_2; **(f)** SO_2.
5. By means of Lewis structures, represent bonding between the following pairs of elements: **(a)** Cs and Br; **(b)** H and Sb; **(c)** B and Cl; **(d)** Cs and Cl; **(e)** Li and O; **(f)** Cl and I. Your structures should show whether the bonding is essentially ionic or covalent.
6. Which of the following have Lewis structures that *do not* obey the octet rule: NF_3, $B(OH)_3$, $SiF_6{}^{2-}$, SO_3, $PH_4{}^+$, $PO_4{}^{3-}$, ClO_2, C_2H_4, $SO(CH_3)$.
7. Give several examples for which the following statement proves to be incorrect. "All atoms in a Lewis structure have an octet of electrons in their valence shells."
8. Suggest reasons why the following do not exist as stable molecules: **(a)** H_3; **(b)** HHe; **(c)** He_2; **(d)** H_3O.
9. Describe what is wrong with each of the following Lewis structures.

   (a) $H-H-\ddot{N}-\underset{..}{\ddot{O}}-H$

   (b) $Ca-\underset{..}{\ddot{O}}:$

10. Describe what is wrong with each of the following Lewis structures.

    (a) $:\underset{..}{\ddot{O}}-\underset{..}{\ddot{Cl}}-\underset{..}{\ddot{O}}:$

    (b) $[\cdot\dot{C}=\ddot{N}:]^-$

11. Only one of the following Lewis structures is correct. Select that one and indicate the errors in the others.

    (a) cyanate ion $[:\underset{..}{\ddot{O}}-C=\ddot{N}:]^-$

    (b) carbide ion $[C\equiv C:]^{2-}$

    (c) hypochlorite ion $[:\underset{..}{\ddot{Cl}}-\underset{..}{\ddot{O}}:]^-$

    (d) nitrogen(II) oxide $:\ddot{N}=\ddot{O}:$

12. Indicate what is wrong with each of the following Lewis structures. Replace each one with a more acceptable structure.

    (a) Mg $:\underset{..}{\ddot{O}}:$

    (b) $[:\underset{..}{\ddot{O}}-\dot{N}=\ddot{O}:]^+$

    (c) $[:\underset{..}{\ddot{Cl}}]^+[:\underset{..}{\ddot{O}}:]^{2-}[\underset{..}{\ddot{Cl}}:]^+$

    (d) $[:\ddot{S}-C=\ddot{N}:]^-$

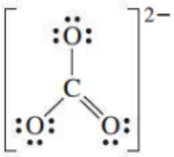
Ionic Bonding

13. Write Lewis structures for the following ionic compounds: **(a)** calcium chloride; **(b)** barium sulfide; **(c)** lithium oxide; **(d)** sodium fluoride.
14. Under appropriate conditions, both hydrogen and nitrogen can form monatomic anions. What are the Lewis symbols for these ions? What are the Lewis structures of the compounds **(a)** lithium hydride; **(b)** calcium hydride; **(c)** magnesium nitride?
15. Derive the correct formulas for the following ionic compounds by writing Lewis structures. **(a)** lithium sulfide; **(b)** sodium fluoride; **(c)** calcium iodide; **(d)** scandium chloride.
16. Each of the following ionic compounds consists of a combination of monatomic and polyatomic ions. Represent these compounds with Lewis structures. **(a)** $Al(OH)_3$; **(b)** $Ca(CN)_2$; **(c)** NH_4F; **(d)** $KClO_3$; **(e)** $Ba_3(PO_4)_2$.

Formal Charge

17. Assign formal charges to each of the atoms in the following structures.

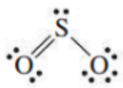
(a) $[H—C≡C:]^-$

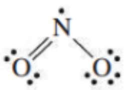
(b) 

(c) $[CH_3—CH—CH_3]^+$

18. Assign formal charges to each of the atoms in the following structures.

(a) :I—I:

(b) 

(c) 

19. Both oxidation state and formal charge involve conventions for assigning valence electrons to bonded atoms in compounds, but clearly they are not the same. Describe several ways in which these concepts differ.

20. Although the notion that a Lewis structure in which formal charges are zero or held to a minimum seems to apply in most instances, describe several significant situations in which this appears not to be the case.

21. What is the formal charge of the indicated atom in each of the following structures?
(a) the central O atom in O_3
(b) Al in AlH_4^-
(c) Cl in ClO_3^-
(d) Si in SiF_6^{2-}
(e) Cl in ClF_3

22. Assign formal charges to the atoms in the following species, and then select the more likely skeletal structure.
(a) H_2NOH or H_2ONH
(b) SCS or CSS
(c) NFO or FNO
(d) $SOCl_2$ or $OSCl_2$ or OCl_2S
(e) F_3SN and F_3NS

23. The concept of formal charge helped us to choose the more plausible of the Lewis structures for NO_2^+ given in expressions (10.14) and (10.15). Can it similarly help us to choose a single Lewis structure as most plausible for CO_2H^+? Explain.

24. Show that the idea of minimizing the formal charges in a structure is at times in conflict with the observation that compact, symmetrical structures are more commonly observed than elongated ones with many central atoms. Use ClO_4^- as an illustrative example.

Lewis Structures

25. Write acceptable Lewis structures for the following molecules: **(a)** H_2NNH_2; **(b)** HOClO; **(c)** $(HO)_2SO$; **(d)** HOOH; **(e)** SO_4^{2-}.

26. Two molecules that have the same formulas but different structures are said to be isomers. (In isomers, the same atoms are present but linked together in different ways.) Draw acceptable Lewis structures for *two* isomers of C_2O_4. [*Hint:* The C atoms and two O atoms form a square.]

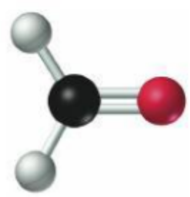
27. The following polyatomic anions involve covalent bonds between O atoms and the central nonmetal atom. Propose an acceptable Lewis structure for each. **(a)** SO_3^{2-}; **(b)** NO_2^-; **(c)** CO_3^{2-}; **(d)** HO_2^-.

28. Represent the following ionic compounds by Lewis structures: **(a)** barium hydroxide; **(b)** sodium nitrite; **(c)** magnesium iodate; **(d)** aluminum sulfate.

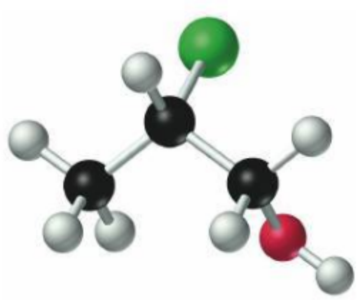
29. Write a plausible Lewis structure for crotonaldehyde, $CH_3CHCHCHO$, a substance used in tear gas and insecticides.

30. Write a plausible Lewis structure for C_3O_2, a substance known as carbon suboxide.

31. Write Lewis structures for the molecules represented by the following molecular models.

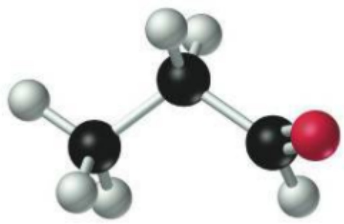


(a)

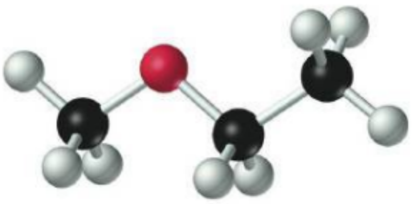


(b)

32. Write Lewis structures for the molecules represented by the following molecular models.



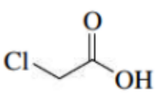
(a)



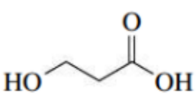
(b)

33. Write Lewis structures for the molecules represented by the following line-angle formulas. [*Hint:* Recall page 70 and Figure 3-2.]

(a)

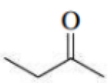


(b)



34. Write Lewis structures for the molecules represented by the following line-angle formulas. [*Hint:* Recall page 70 and Figure 3-2.]

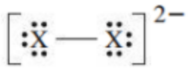
(a)



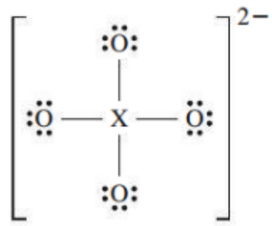
(b)

35. Identify the main group that the element X belongs to in each of the following Lewis structures. For the types of molecule shown, give an example that exists.

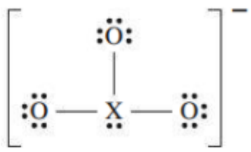
(a)



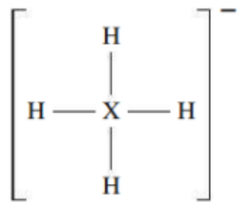
(b)



(c)

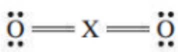


(d)

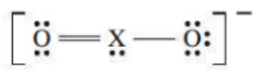


36. Identify the main group that the element X belongs to in each of the following Lewis structures. For the types of molecule shown, give an example that exists.

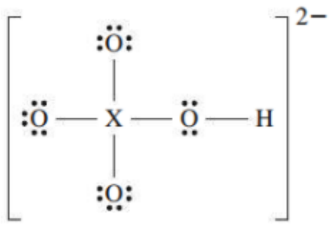
(a)



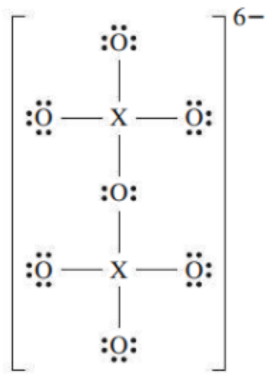
(b)



(c)



(d)



Polar Covalent Bonds and Electrostatic Potential Maps

37. Use your knowledge of electronegativities, but *do not* refer to tables or figures in the text, to arrange the following bonds in terms of *increasing* ionic character: C—H, F—H, Na—Cl, Br—H, K—F.

38. Which of the following molecules would you expect to have a resultant dipole moment (μ)? Explain. **(a)** F_2; **(b)** NO_2; **(c)** BF_3; **(d)** HBr; **(e)** H_2CCl_2; **(f)** SiF_4; **(g)** OCS.

39. What is the percent ionic character of each of the following bonds? **(a)** S—H; **(b)** O—Cl; **(c)** Al—O; **(d)** As—O.

40. Plot the data of Figure 10-6 as a function of atomic number. Does the property of electronegativity conform to the periodic law? Do you think it should?

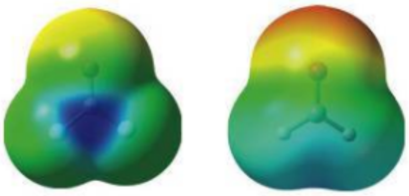
41. Use a cross-base arrow ($\leftarrow\!\!\!+$) to represent the polarity of the bond in each of the following diatomic molecules. Then use the data below to calculate, in the manner described on page 447, the partial charges (δ) on the atoms in each molecule. Express the partial charges as a decimal fraction of the elementary charge, $e = 1.602 \times 10^{-19}$ C, for example $\delta = +0.17e$ or $\delta = -0.17e$.

	Bond Length, pm	Dipole Moment, D
ClF	162.8	0.8881
RbF	227.0	8.547
SnO	183.3	4.3210
BaO	194.0	7.954

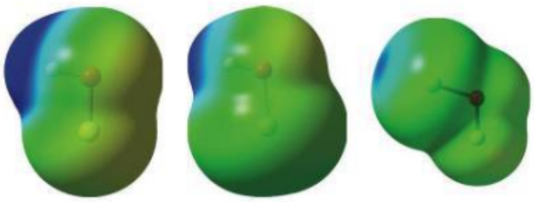
42. Use a cross-base arrow ($\leftarrow\!\!\!+$) to represent the polarity of the bond in each of the following diatomic molecules. Then use the data below to calculate the partial charges (δ) on the atoms in each molecule. Express the partial charges in the manner described in Exercise 41.

	Bond Length, pm	Dipole Moment, D
OH	98.0	1.66
CH	131.1	1.46
CN	117.5	1.45
CS	194.4	1.96

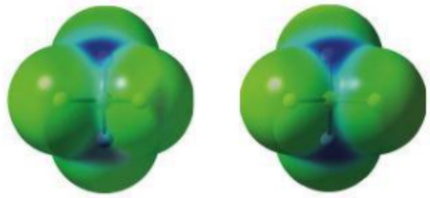
43. Which electrostatic potential map corresponds to $F_2C{=}O$, and which to $H_2C{=}O$?



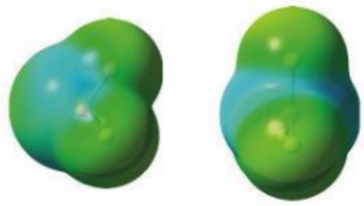
44. Match the correct electrostatic potential map corresponding to HOCl, FOCl, and HOF.



45. Two electrostatic potential maps are shown, one corresponding to a molecule containing only S and F, the other Si and F. Match them. What are the molecular formulas of the compounds?



46. Two electrostatic potential maps are shown, one corresponding to a molecule containing only Cl and F, the other P and F. Match them. What are the molecular formulas of the compounds?

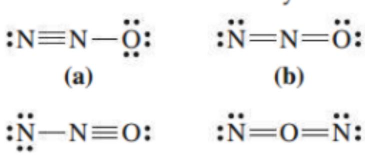


Resonance

47. Through appropriate Lewis structures, show that the phenomenon of resonance is involved in the nitrite ion.

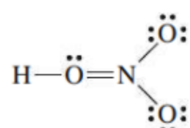
48. Which of the following species requires a resonance hybrid for its Lewis structure? Explain. **(a)** CO_2; **(b)** OCl^-; **(c)** CO_3^{2-}; **(d)** OH^-.

49. Dinitrogen oxide (nitrous oxide, or "laughing gas") is sometimes used as an anesthetic. Here are some data about the N_2O molecule: N—N bond length = 113 pm; N—O bond length = 119 pm. Use these data and other information from the chapter to comment on the plausibility of each of the following Lewis structures shown. Are they all valid? Which ones do you think contribute most to the resonance hybrid?



(a) (b) (c) (d)

50. The Lewis structure of nitric acid, $HONO_2$, is a resonance hybrid. How important do you think the contribution of the following structure is to the resonance hybrid? Explain.



51. Draw Lewis structures for the following species, indicating formal charges and resonance where applicable:
(a) HCO_2^-
(b) HCO_3^-
(c) FSO_3^-
(d) $N_2O_3^{2-}$ (the nitrogen atoms are joined centrally with one oxygen atom on one N and two on the other)

52. Draw Lewis structures for the following species, indicating formal charges and resonance where applicable:
(a) $HOSO_3^-$
(b) H_2NCN
(c) FCO_2^-
(d) S_2N_2 (a cyclic structure with S and N alternating)

Odd-Electron Species

53. Write plausible Lewis structures for the following odd-electron species: **(a)** CH_3; **(b)** ClO_2; **(c)** NO_3.

54. Write plausible Lewis structures for the following free radicals: **(a)** $\cdot C_2H_5$; **(b)** $HO_2\cdot$; **(c)** $ClO\cdot$.

55. Which of the following species would you expect to be diamagnetic and which paramagnetic? **(a)** OH^-; **(b)** OH; **(c)** NO_3; **(d)** SO_3; **(e)** SO_3^{2-}; **(f)** HO_2.

56. Write a plausible Lewis structure for NO_2, and indicate whether the molecule is diamagnetic or paramagnetic. Two NO_2 molecules can join together (*dimerize*) to form N_2O_4. Write a plausible Lewis structure for N_2O_4, and comment on the magnetic properties of the molecule.

Expanded Valence Shells

57. In which of the following species is it *necessary* to employ an expanded valence shell to represent the Lewis structure: PO_4^{3-}, PI_3, ICl_3, $OSCl_2$, SF_4, ClO_4^-? Explain your choices.

58. Describe the carbon-to-sulfur bond in H_2CSF_4. That is, is it most likely a single, double, or triple bond?

Molecular Shapes

59. Use VSEPR theory to predict the geometric shapes of the following molecules and ions: **(a)** N_2; **(b)** HCN; **(c)** NH_4^+; **(d)** NO_3^-; **(e)** NSF.
60. Use VSEPR theory to predict the geometric shapes of the following molecules and ions: **(a)** PCl_3; **(b)** SO_4^{2-}; **(c)** $SOCl_2$; **(d)** SO_3; **(e)** BrF_4^+.
61. Each of the following is either linear, angular (bent), planar, tetrahedral, or octahedral. Indicate the correct shape of **(a)** H_2S; **(b)** N_2O_4; **(c)** HCN; **(d)** $SbCl_6^-$; **(e)** BF_4^-.
62. Predict the geometric shapes of **(a)** CO; **(b)** $SiCl_4$; **(c)** PH_3; **(d)** ICl_3; **(e)** $SbCl_5$; **(f)** SO_2; **(g)** AlF_6^{3-}.
63. One of the following ions has a *trigonal-planar* shape: SO_3^{2-}; PO_4^{3-}; PF_6^-; CO_3^{2-}. Which ion is it? Explain.
64. Two of the following have the same shape. Which two, and what is their shape? What are the shapes of the other two? NI_3, HCN, SO_3^{2-}, NO_3^-.
65. Each of the following molecules contains one or more multiple covalent bonds. Draw plausible Lewis structures to represent this fact, and predict the shape of each molecule. **(a)** CO_2; **(b)** Cl_2CO; **(c)** $ClNO_2$.
66. Sketch the probable geometric shape of a molecule of **(a)** N_2O_4 (O_2NNO_2); **(b)** C_2N_2 (NCCN); **(c)** C_2H_6 (H_3CCH_3); **(d)** C_2H_6O (H_3COCH_3).
67. Use the VSEPR theory to predict the shapes of the anions **(a)** ClO_4^-; **(b)** $S_2O_3^{2-}$ (that is, SSO_3^{2-}); **(c)** PF_6^-; **(d)** I_3^-.
68. Use the VSEPR theory to predict the shape of **(a)** the molecule OSF_2; **(b)** the molecule O_2SF_2; **(c)** the ion SF_5^-; **(d)** the ion ClO_4^-; **(e)** the ion ClO_3^-.
69. The molecular shape of BF_3 is planar (see Table 10.1). If a fluoride ion is attached to the B atom of BF_3 through a coordinate covalent bond, the ion BF_4^- results. What is the shape of this ion?
70. Explain why it is not necessary to find the Lewis structure with the smallest formal charges to make a successful prediction of molecular geometry in the VSEPR theory. For example, write Lewis structures for SO_2 having different formal charges, and predict the molecular geometry based on these structures.
71. Comment on the similarities and differences in the molecular structure of the following triatomic species: CO_2, NO_2^-, O_3, and ClO_2^-.
72. Comment on the similarities and differences in the molecular structure of the following four-atom species: NO_3^-, CO_3^{2-}, SO_3^{2-}, and ClO_3^-.
73. Draw a plausible Lewis structure for the following series of molecules and ions: **(a)** ClF_2^-; **(b)** ClF_3; **(c)** ClF_4^-; **(d)** ClF_5. Describe the electron group geometry and molecular structure of these species.
74. Draw a plausible Lewis structure for the following series of molecules and ions: **(a)** SiF_6^{2-}; **(b)** PCl_3; **(c)** $AsCl_5$; **(d)** ClF_3; **(e)** XeF_4. Describe the electron group geometry and molecular structure of these species.

Shapes of Molecules with More Than One Central Atom

75. Sketch the propyne molecule, $CH_3C{\equiv}CH$. Indicate the bond angles in this molecule. What is the maximum number of atoms that can be in the same plane?
76. Sketch the propene molecule, $CH_3CH{=}CH_2$. Indicate the bond angles in this molecule. What is the maximum number of atoms that can be in the same plane?
77. Lactic acid has the formula $CH_3CH(OH)COOH$. Sketch the lactic acid molecule, and indicate the various bond angles.
78. Levulinic acid has the formula $CH_3(CO)CH_2CH_2COOH$. Sketch the levulinic acid molecule, and indicate the various bond angles.
79. Sketch, by using the dash and wedge symbolism, the H_2NCH_2CHO molecule, and indicate the various bond angles.
80. One of the isomers of chloromethanol has the formula $ClCH_2OH$. Sketch, by using the dash and wedge symbolism, this isomer of chloromethanol, and indicate the various bond angles.

Polar Molecules

81. Predict the shapes of the following molecules, and then predict which would have resultant dipole moments: **(a)** SO_2; **(b)** NH_3; **(c)** H_2S; **(d)** C_2H_4; **(e)** SF_6; **(f)** CH_2Cl_2.
82. Which of the following molecules would you expect to be polar? **(a)** HCN; **(b)** SO_3; **(c)** CS_2; **(d)** OCS; **(e)** $SOCl_2$; **(f)** SiF_4; **(g)** POF_3. Give reasons for your conclusions.
83. The molecule H_2O_2 has a resultant dipole moment of 2.2 D. Can this molecule be linear? If not, describe a shape that might account for this dipole moment.
84. Refer to the Integrative Example. A compound related to nitryl fluoride is nitrosyl fluoride, FNO. For this molecule, indicate **(a)** a plausible Lewis structure and **(b)** the geometric shape. **(c)** Explain why the measured resultant dipole moment for FNO is larger than the value for FNO_2.

Bond Lengths

85. *Without* referring to tables in the text, indicate which of the following bonds you would expect to have the greatest bond length, and give your reasons. **(a)** O_2; **(b)** N_2; **(c)** Br_2; **(d)** BrCl.

86. Estimate the lengths of the following bonds and indicate whether your estimate is likely to be too high or too low: **(a)** I—Cl; **(b)** C—F.

87. A relationship between bond lengths and single-bond covalent radii of atoms is given on page 449. Use this relationship together with appropriate data from Table 10.2 to estimate these single-bond lengths. **(a)** I—Cl; **(b)** O—Cl; **(c)** C—F; **(d)** C—Br.

88. In which of the following molecules would you expect the oxygen-to-oxygen bond to be the *shortest*? Explain. **(a)** H_2O_2, **(b)** O_2, **(c)** O_3.

89. Refer to the Integrative Example. Use data from the chapter to estimate the length of the N—F bond in FNO_2.

90. Write a Lewis structure of the hydroxylamine molecule, H_2NOH. Then, with data from Table 10.2, determine all the bond lengths.

Bond Energies

91. A reaction involved in the formation of ozone in the upper atmosphere is $O_2 \longrightarrow 2\,O$. *Without* referring to Table 10.3, indicate whether this reaction is endothermic or exothermic. Explain.

92. Use data from Table 10.3, but *without performing detailed calculations*, determine whether each of the following reactions is exothermic or endothermic.
(a) $CH_4(g) + I(g) \longrightarrow \cdot CH_3(g) + HI(g)$
(b) $H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$

93. Use data from Table 10.3 to estimate the enthalpy change ($\Delta_r H$) for the following reaction.

$$C_2H_6(g) + Cl_2(g) \longrightarrow C_2H_5Cl(g) + HCl(g) \qquad \Delta_r H = ?$$

94. One of the chemical reactions that occurs in the formation of photochemical smog is $O_3 + NO \longrightarrow NO_2 + O_2$. Estimate $\Delta_r H$ for this reaction by using appropriate Lewis structures and data from Table 10.3.

95. Estimate the standard enthalpies of formation at 25 °C and 1 bar of **(a)** OH(g); **(b)** $N_2H_4(g)$. Write Lewis structures and use data from Table 10.3, as necessary.

96. Use $\Delta_r H$ for the reaction in Example 10-15 and other data from Appendix D to estimate $\Delta_f H°[CH_3Cl(g)]$.

97. Use bond energies from Table 10.3 to estimate $\Delta_r H$ for the following reaction.

$$C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g) \qquad \Delta_r H = ?$$

98. Equations (1) and (2) can be combined to yield the equation for the formation of $CH_4(g)$ from its elements.

(1)	$C(s) \longrightarrow C(g)$		$\Delta_r H = 717\ \text{kJ mol}^{-1}$
(2)	$C(g) + 2\,H_2(g) \longrightarrow CH_4(g)$		$\Delta_r H = ?$
Overall:	$C(s) + 2\,H_2(g) \longrightarrow CH_4(g)$		$\Delta_f H° = -75\ \text{kJ mol}^{-1}$

Use the preceding data and a bond energy of 436 kJ mol^{-1} for H_2 to estimate the C—H bond energy. Compare your result with the value listed in Table 10.3.

99. One reaction involved in the sequence of reactions leading to the destruction of ozone is

$$NO_2(g) + O(g) \longrightarrow NO(g) + O_2(g)$$

Calculate $\Delta_r H°$ for this reaction by using the thermodynamic data in Appendix D. Use your $\Delta_r H°$ value, plus data from Table 10.3, to estimate the nitrogen–oxygen bond energy in NO_2. [*Hint:* The structure of nitrogen dioxide, NO_2, is best represented as a resonance hybrid of two equivalent Lewis structures.]

100. A reaction involved in the sequence of reactions leading to the destruction of ozone is

$$O_3(g) + O(g) \longrightarrow 2\,O_2(g) \qquad \Delta_r H° = -394\ \text{kJ mol}^{-1}$$

Estimate the oxygen-oxygen bond energy in ozone by using the oxygen–oxygen bond energy in dioxygen from Table 10.3. Compare this value with the O—O and O=O bond energies in Table 10.3. How could you explain any differences?

Integrative and Advanced Exercises

101. Given the bond-dissociation energies: nitrogen-to-oxygen bond in NO, 631 kJ mol^{-1}; H—H in H_2, 436 kJ mol^{-1}; N—H in NH_3, 389 kJ mol^{-1}; O—H in H_2O, 463 kJ mol^{-1}; calculate $\Delta_r H$ for the reaction below.

$$2\,NO(g) + 5\,H_2(g) \longrightarrow 2\,NH_3(g) + 2\,H_2O(g)$$

102. The following statements are not made as carefully as they might be. Criticize each one.
(a) Lewis structures with formal charges are incorrect.
(b) Triatomic molecules have a planar shape.
(c) Molecules in which there is an electronegativity difference between the bonded atoms are polar.

103. A compound consists of 42.44% N and 57.56% F, by mass. Write a plausible Lewis structure based on the empirical formula of this compound.

104. A 0.325 g sample of a gaseous hydrocarbon occupies a volume of 193 mL at 749 mmHg and 26.1 °C. Determine the molecular mass, and write a plausible condensed structural formula for this hydrocarbon.

105. A 1.24 g sample of a hydrocarbon, when completely burned in an excess of $O_2(g)$, yields 4.04 g CO_2 and 1.24 g H_2O. Draw a plausible structural formula for the hydrocarbon molecule. [*Hint:* There is more than one possible arrangement of the C and H atoms.]

106. Draw Lewis structures for two different molecules with the formula C_3H_4. Is either of these molecules linear? Explain.

107. Sodium azide, NaN_3, is the nitrogen gas-forming substance used in automobile air-bag systems. It is an ionic compound containing the azide ion, N_3^-. In this ion, the two nitrogen-to-nitrogen bond lengths are 116 pm. Describe the resonance hybrid Lewis structure of this ion.

108. Use the bond-dissociation energies of $N_2(g)$ and $O_2(g)$ in Table 10.3, together with data from Appendix D, to estimate the bond-dissociation energy of NO(g).

109. Hydrogen azide, HN_3, is a liquid that explodes violently when subjected to physical shock. In the HN_3 molecule, one nitrogen-to-nitrogen bond length is 113 pm, and the other is 124 pm. The H—N—N bond angle is 112°. Draw Lewis structures and a sketch of the molecule consistent with these facts.

110. A few years ago the synthesis of a salt containing the N_5^+ ion was reported. What is the likely shape of this ion—linear, bent, zigzag, tetrahedral, seesaw, or square-planar? Explain your choice.

111. Carbon suboxide has the formula C_3O_2. The carbon-to-carbon bond lengths are 130 pm and carbon-to-oxygen, 120 pm. Propose a plausible Lewis structure to account for these bond lengths, and predict the shape of the molecule.

112. In certain polar solvents, PCl_5 undergoes an ionization reaction in which a Cl^- ion leaves one PCl_5 molecule and attaches itself to another. The products of the ionization are PCl_4^+ and PCl_6^-. Draw a sketch showing the changes in geometric shapes that occur in this ionization (that is, give the shapes of PCl_5, PCl_4^+, and PCl_6^-).

$$2\,PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$$

113. Estimate the enthalpy of formation of HCN using bond energies from Table 10.3, data from elsewhere in the text, and the reaction scheme outlined as follows.

$$\begin{array}{lll}
(1)\ C(s) & \rightarrow C(g) & \Delta_r H^\circ = ? \\
(2)\ C(g) + \tfrac{1}{2}N_2(g) + \tfrac{1}{2}H_2(g) & \rightarrow HCN(g) & \Delta_r H^\circ = ? \\
\hline
\textit{Overall:}\ C(g) + \tfrac{1}{2}N_2(g) + \tfrac{1}{2}H_2(g) & \rightarrow HCN(g) & \Delta_f H^\circ = ?
\end{array}$$

114. The standard enthalpy of formation of $H_2O_2(g)$ is -136 kJ mol^{-1}. Use this value, with other appropriate data from the text, to estimate the oxygen-to-oxygen single-bond energy. Compare your result with the value listed in Table 10.3.

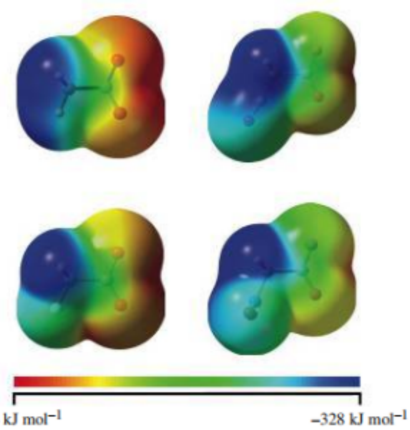
115. Use the VSEPR theory to predict a probable shape of the molecule F_4SCH_2, and explain the source of any ambiguities in your prediction.

116. The standard enthalpy of formation of methanethiol, $CH_3SH(g)$, is -22.9 kJ mol^{-1}. Methanethiol can be synthesized by the reaction of gaseous methanol and $H_2S(g)$. Water vapor is another product. Use this information and data from elsewhere in the text to estimate the carbon-to-sulfur bond energy in methanethiol.

117. For LiBr, the dipole moment (measured in the gas phase) and the bond length (measured in the solid state) are 7.268 D and 217 pm, respectively. For NaCl, the corresponding values are 9.001 D and 236.1 pm. **(a)** Calculate the percent ionic character for each bond. **(b)** Compare these values with the expected ionic character based on differences in electronegativity (see Figure 10-7). **(c)** Account for any differences in the values obtained in these two different ways.

118. One possibility for the electron-group geometry for *seven* electron groups is pentagonal-bipyramidal, as found in the IF_7 molecule. Write the VSEPR notation for this molecule. Sketch the structure of the molecule, labeling all the bond angles.

119. The extent to which an acid (HA) ionizes in water depends upon the stability of the anion (A^-); the more stable the anion, the more extensive is the dissociation of the acid. The anion is most stable when the negative charge is distributed over the whole anion rather than localized at one particular atom. Consider the following acids: acetic acid, fluoroacetic acid, cyanoacetic acid, and nitroacetic acid. Draw Lewis structures for their anions, including contributing resonance structures. Rank the acids in order of increasing extent of ionization. Electrostatic potential maps for the four anions are provided on the next page. Identify which map corresponds to which anion, and discuss whether the maps confirm conclusions based on Lewis structures.

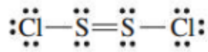


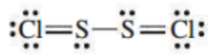
120. R. S. Mulliken proposed that the electronegativity (EN) of an atom is given by

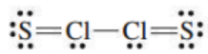
$$EN = k \times (E_i - E_{ea})$$

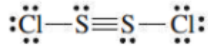
where E_i and E_{ea} are the ionization energy and electron affinity of the atom, respectively. Using the electron affinities and ionization energy values for the halogen atoms up to iodine, estimate the value of k by employing the electronegativity values in Figure 10-6. Estimate the electron affinity of At.

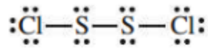
121. When molten sulfur reacts with chlorine gas, a vile-smelling orange liquid forms. When analyzed, the liquid compound has the empirical formula SCl. Several possible Lewis structures are shown below. Criticize these structures and choose the best one.

(a) 

(b) 

(c) 

(d) 

(e) 

122. Hydrogen azide, HN_3, can exist in two forms. One form has the three nitrogen atoms connected in a line; and the nitrogen atoms form a triangle in the other. Construct Lewis structures for these isomers and describe their shapes. Other interesting derivatives are nitrosyl azide (N_4O) and trifluoromethyl azide (CF_3N_3). Describe the shapes of these molecules based on a line of nitrogen atoms.

123. A pair of isoelectronic species for C and N exist with the formula X_2O_4 in which there is an X—X bond. A corresponding fluoride of boron also exists. Draw Lewis structures for these species and describe their shapes.

124. Acetone $(CH_3)_2C{=}O$, a ketone, will react with a strong base (A^-) to produce the enolate anion, $CH_3(C{=}O)CH_2^-$. Draw the Lewis structure of the enolate anion, and describe the relative contributions of any resonance structures.

125. The species PBr_4^- has been synthesized and has been described as a tetrahedral anion. Comment on this description.

126. One of the allotropes of sulfur is a ring of eight sulfur atoms. Draw the Lewis structure for the S_8 ring. Is the ring likely to be planar? The S_8 ring can be oxidized to produce S_8O. In S_8O, the oxygen atom is bonded to one of the S atoms and the S_8 ring is still intact. Draw the Lewis structure for S_8O.

127. One of the allotropes of phosphorus consists of four phosphorus atoms at the corners of a tetrahedron. Draw a Lewis structure for this allotrope that satisfies the octet rule. The P_4 molecule can be oxidized to P_4O_6, where the oxygen atoms insert between the phosphorus atoms. Draw the Lewis structure of this oxide. Are the P—O—P bonds linear?

Feature Problems

128. In this problem, we examine the basis of three different electronegativity scales and work through the same types of calculations as those performed by the people who initially suggested these scales. The scale developed by Robert Mulliken employs ionization energies (E_i) and electron affinities (E_{ea}) whereas the scale developed by Linus Pauling is based on bond dissociation energies (D). The scale developed by A. Louis Allred and Eugene G. Rochow employs effective nuclear charges (Z_{eff}) and covalent radii (r_{cov}). The key equations for each scale are given below.

Electronegativity Scale	Defining Equation
Pauling[a]	$EN_A - EN_B = \sqrt{\dfrac{D_{A-B} - \frac{1}{2}(D_{A-A} + D_{B-B})}{1\ \text{eV}}}$
Mulliken[b, c]	$EN = 0.336 \times \left(\dfrac{E_i + E_{ea}}{2\ \text{eV}}\right) - 0.165$
Allred-Rochow[c]	$EN = \dfrac{3590\ Z_{eff}}{(r_{cov}/1\ \text{pm})^2} + 0.744$

[a]Originally, Pauling defined EN_H to be 2.1, the value chosen to give the elements C to F electronegativity values from 2.5 to 4.0.

[b] Strictly speaking, the E_i and E_{ea} values used in this expression are not the experimentally observed values for an isolated atom but those calculated for an atom as it exists in a molecule. Also, E_{ea} in this formula is the energy change for $X^-(g) \rightarrow X(g) + e^-$.

[c]The constants in these equations (0.336 and –0.165 or 3590 and 0.744) are chosen to ensure the EN values span essentially the same range as Pauling's values.

In devising his scale, Pauling observed that the bond energy, D_{A-B}, for the A–B bond is greater than the average of the A–A and B–B bond energies, $\frac{1}{2}(D_{A-A} + D_{B-B})$, and he attributed the increase in bond strength to the partial ionic character of the A–B bond.

Mulliken argued that the ionization energy (E_i) and electron affinity (E_{ea}) are of equal importance for the electronegativity of an atom. Therefore, he suggested that the average of these two quantities, $(E_i + E_{ea})/2$, be used to define the electronegativity of an atom.

Allred and Rochow focused on the attractive Coulombic force between an electron near the "surface" of an atom and the nucleus of that atom. They argued that the magnitude of this force is proportional to $(e)(Z_{eff}e)/r_{cov}^2 = e^2Z_{eff}/r_{cov}^2$, where $e = 1.602 \times 10^{-19}$ C is the magnitude of the charge of an electron, $Z_{eff}e$ is the nuclear charge experienced by an electron near the atom's surface, and r_{cov} is the covalent radius and a realistic measure of the size of an atom.

The values of D, Z_{eff}, and r_{cov} given below are the actual values used by Pauling and by Allred and Rochow in their original papers. Use the data below and the equations above to calculate the electronegativities of F, Cl, Br, and I. Summarize your results in a table having four columns: Atom, EN(Pauling), EN(Mulliken), EN(Allred-Rochow). [*Hint:* The Pauling values you calculate will not be exactly equal to those in Figure 10-6. The values in Figure 10-6 are based on bond dissociation energies from a wider range of molecules than we are considering in this problem.]

	Atom, X				
	H	F	Cl	Br	I
E_i, eV	13.5985	17.423	12.9677	11.8139	10.4513
E_{ea}, eV	0.7542	3.399	3.617	3.365	3.059
D(H—X), eV	4.44	6.39	4.38	3.74	3.07
D(X—X), eV	4.44	2.80	2.468	1.962	1.535
Z_{eff}	1	4.86	5.75	7.25	7.25
r_{cov}, pm	–	71.5	99.4	114.2	133.4

129. On page 447, the bond angle in the H_2O molecule is given as 104° and the resultant dipole moment as $\mu = 1.84$ D.
(a) By an appropriate geometric calculation, determine the value of the H—O bond dipole in H_2O.
(b) Use the same method as in part (a) to estimate the bond angle in H_2S, given that the H—S bond dipole is 0.67 D and that the resultant dipole moment is $\mu = 0.93$ D.
(c) Refer to Figure 10-16. Given the bond dipoles 1.87 D for the C—Cl bond and 0.30 D for the C—H bond, together with $\mu = 1.04$ D, estimate the H—C—Cl bond angle in $CHCl_3$.

130. Alternative strategies to the one used in this chapter have been proposed for applying the VSEPR theory to molecules or ions with a single central atom. In general, these strategies do not require writing Lewis structures. In one strategy, we write
(1) the total number of electron pairs = [(number of valence electrons) ± (electrons required for ionic charge)]/2
(2) the number of bonding electron pairs = (number of atoms) − 1
(3) the number of electron pairs around central atom = total number of electron pairs − 3 × [number of terminal atoms (excluding H)]
(4) the number of lone-pair electrons = number of central atom pairs − number of bonding pairs
After evaluating items 2, 3, and 4, establish the VSEPR notation and determine the molecular shape. Use this method to predict the geometrical shapes of the following: **(a)** PCl_5; **(b)** NH_3; **(c)** ClF_3; **(d)** SO_2; **(e)** ClF_4^-; **(f)** PCl_4^+. Justify each of the steps in the strategy, and explain why it yields the same results as the VSEPR method based on Lewis structures. How does the strategy deal with multiple bonds?

Self-Assessment Exercises

131. In your own words, define the following terms: **(a)** valence electrons; **(b)** electronegativity; **(c)** bond-dissociation energy; **(d)** double covalent bond; **(e)** coordinate covalent bond.

132. Briefly describe each of the following ideas: **(a)** formal charge; **(b)** resonance; **(c)** expanded valence shell; **(d)** bond energy.

133. Explain the important distinctions between **(a)** ionic and covalent bonds; **(b)** lone-pair and bond-pair electrons; **(c)** molecular geometry and electron-group geometry; **(d)** bond dipole and resultant dipole moment; **(e)** polar molecule and nonpolar molecule.

134. Of the following species, the one with a triple covalent bond is **(a)** NO_3^-; **(b)** CN^-; **(c)** CO_2; **(d)** $AlCl_3$.

135. The formal charges on the O atoms in the ion $[ONO]^+$ is **(a)** −2; **(b)** −1; **(c)** 0; **(d)** +1.

136. Which molecule is nonlinear? **(a)** SO_2; **(b)** CO_2; **(c)** HCN; **(d)** NO.

137. Which molecule is nonpolar? **(a)** SO_3; **(b)** CH_2Cl_2; **(c)** NH_3; **(d)** FNO.

138. The highest bond-dissociation energy is found in **(a)** O_2; **(b)** N_2; **(c)** Cl_2; **(d)** I_2.

139. The greatest bond length is found in **(a)** O_2; **(b)** N_2; **(c)** Br_2; **(d)** BrCl.

140. Draw plausible Lewis structures for the following species; use expanded valence shells where necessary. **(a)** Cl_2O; **(b)** PF_3; **(c)** CO_3^{2-}; **(d)** BrF_5.

141. Predict the shapes of the following sulfur-containing species. **(a)** SO_2; **(b)** SO_3^{2-}; **(c)** SO_4^{2-}.

142. Which of the following ionic compounds is composed of only nonmetal atoms? **(a)** NH_4NO_3; **(b)** $Al_2(SO_4)_3$; **(c)** Na_2SO_3; **(d)** $AlCl_3$; **(e)** none of these.

143. Which of the following molecules does not obey the octet rule? **(a)** HCN; **(b)** PF_3; **(c)** CS_2; **(d)** NO; **(e)** none of these.

144. Which of the following molecules has no polar bonds? **(a)** H_2CO; **(b)** CCl_4; **(c)** OF_2; **(d)** N_2O; **(e)** none of these.

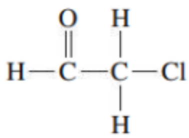
145. The electron-group geometry of H_2O is **(a)** tetrahedral; **(b)** trigonal planar; **(c)** bent; **(d)** linear; **(e)** none of these.

146. For each of the following compounds, give the names of the electron-group geometry and the molecular shape. Sketch the molecule and indicate on the sketch the direction of the dipole moment, if any. For the sketches, use the wedge-and-dash notation. **(a)** SiF_4; **(b)** NF_3 **(c)** SF_4; **(d)** IF_5.

147. Use bond enthalpies from Table 10.3 to determine whether $CH_4(g)$, $CH_3OH(g)$, $H_2CO(g)$, or $HCOOH(g)$ produces the most energy *per gram* when burned completely in $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$. Is there any relationship between the oxidation state of carbon and the heat of combustion (in kJ kg^{-1} or kJ mol^{-1})?

148. Without referring to tables or figures in the text other than the periodic table, indicate which of the following atoms, Bi, S, Ba, As, or Mg, has the intermediate value when they are arranged in order of increasing electronegativity.

149. Use data from Tables 10.2 and 10.3 to determine for each bond in this following structure **(a)** the bond length and **(b)** the bond energy.



150. What is the VSEPR theory? On what physical basis is the VSEPR theory founded?

151. Use the NH_3 molecule as an example to explain the difference between molecular geometry and electron-group geometry.

152. If you have four electron pairs around a central atom, under what circumstances can you have a pyramidal molecule? Similarly, how can you have a bent molecule? What are the expected bond angles in each case?

153. Draw three resonance structures for the sulfine molecule, H_2CSO. Do not consider ring structures.

154. Construct a concept map illustrating the connections between Lewis dot structures, the shapes of molecules, and polarity.