

# Chapter 5

## The Covalent Bond

1. What two opposing forces dictate the bond length? (Why do bonds form and what keeps the bonds from getting any shorter?)

The bond length is the distance at which the repulsion of the two nuclei equals the attraction of the valence electrons on one atom and the nucleus of the other.

3. List the following bonds in order of increasing bond length: H-Cl, H-Br, H-O.

H-O < H-Cl < H-Br. The order of increasing atom size.

5. Use electronegativities to describe the nature (purely covalent, mostly covalent, polar covalent, or ionic) of the following bonds.

a) P-Cl	$\Delta\chi = 3.0 - 2.1 = 0.9$	polar covalent	b) K-O	$\Delta\chi = 3.5 - 0.8 = 2.7$	ionic
c) N-H	$\Delta\chi = 3.0 - 2.1 = 0.9$	polar covalent	d) Tl-Br	$\Delta\chi = 2.8 - 1.7 = 1.1$	polar covalent

7. Name the following compounds:

a) S <sub>2</sub> Cl <sub>2</sub>	disulfur dichloride	b) CCl <sub>4</sub>	carbon tetrachloride
c) PCl <sub>5</sub>	phosphorus pentachloride	d) HCl	hydrogen chloride

9. Write formulas for each of the following compounds:

a) dinitrogen tetroxide	N <sub>2</sub> O <sub>4</sub>	b) nitrogen monoxide	NO	c) dinitrogen pentoxide	N <sub>2</sub> O <sub>5</sub>
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11. Consider the U-V, W-X, and Y-Z bonds. The valence orbital diagrams for the orbitals involved in the bonds are shown in the margin. Use an arrow to show the direction of the bond dipole in the polar bonds or indicate "not polar" for the nonpolar bond(s). Rank the bonds in order of increasing polarity.

The bond dipole points toward the more electronegative atom in the bond, which is the atom with the lower energy orbital. The magnitude of the dipole increases as the electronegativity difference (orbital energy difference) increases. The W-X bond is not polar because the orbital energies of W and X are identical, and the Y-Z bond is more polar than the U-V bond because the energy separation of the bonding orbitals is greater. W-X < U-V < Y-Z

13. Use an arrow to indicate the bond dipole direction in each of the following bonds:

a) S-O	b) C-H	c) O-H	d) C-O	
→	←*	←	→	Note the C-H bond is essentially nonpolar.

15. Use only the position of the atoms on the periodic table to list the following bonds in order of decreasing polarity:

a) S-O, Se-O, As-O	As-O > Se-O > S-O	Increasing electronegativity of non-oxygen atom
b) F-F, H-F, N-F	H-F > N-F > F-F	Increasing electronegativity of non-fluorine atom
c) P-Cl, Sb-Cl, Sn-Cl	Sn-Cl > Sb-Cl > P-Cl	Increasing electronegativity of non-chlorine atom

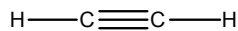
17. For each of the species listed below, indicate the number of electrons required to give each atom an octet or duet (ER), the number of valence electrons (VE), and the number of shared pairs (SP) in the Lewis structure.

a) N <sub>2</sub> O <sub>4</sub>	b) CH <sub>4</sub> O	c) HBrO <sub>2</sub>	d) S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>
ER 6(8) = 48	2(8) + 4(2) = 24	3(8) + 2 = 26	10(8) = 80
VE 2(5) + 4(6) = 34	4 + 4(1) + 6 = 14	1 + 7 + 2(6) = 20	10(6) + 2 = 62
SP $\frac{1}{2}(48 - 34) = 7$	$\frac{1}{2}(24 - 14) = 5$	$\frac{1}{2}(26 - 20) = 3$	$\frac{1}{2}(80 - 62) = 9$

# The Covalent Bond

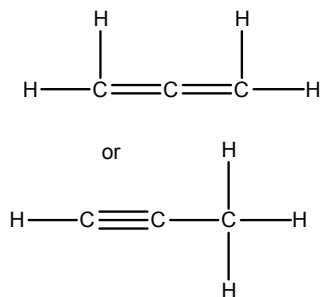
19. Draw Lewis structures for each of the following organic compounds and indicate all nonzero formal charges.

a)  $C_2H_2$



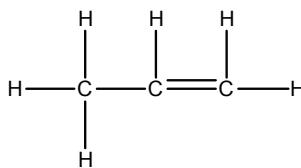
ER=20 VE=10 SP=5

b)  $C_3H_4$



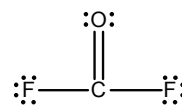
ER=32 VE=16 SP=8

c)  $C_3H_6$



ER=36 VE=18 SP=9

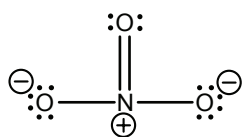
d)  $COF_2$



ER=32 VE=24 SP=4

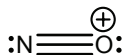
21. Draw Lewis structures for each of the following ions and indicate all nonzero formal charges.

a)  $NO_3^{1-}$



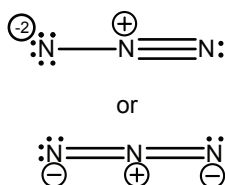
ER=32 VE=24 SP=4

b)  $NO^{1+}$



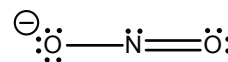
ER=16 VE=10 SP=3

c)  $N_3^{1-}$



ER=24 VE=16 SP=4

d)  $NO_2^{1-}$

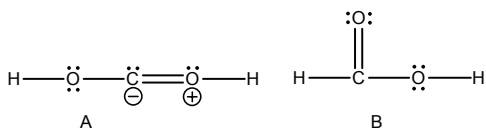


ER=24 VE=18 SP=3

23. For which ions in Exercises 20 and 21 are more than one resonance form important?

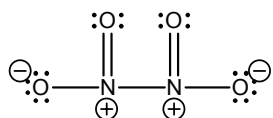
$CO_3^{2-}$ ,  $CHO_2^{1-}$ ,  $NO_3^{1-}$ , and  $NO_2^{1-}$  all have more than one important resonance form. Although two resonance structures can be drawn for  $N_3^{1-}$ , the one that places a -2 formal charge on a nitrogen is not expected to be important.

25. Which of the Lewis structures of formic acid is preferred? Justify your answer.



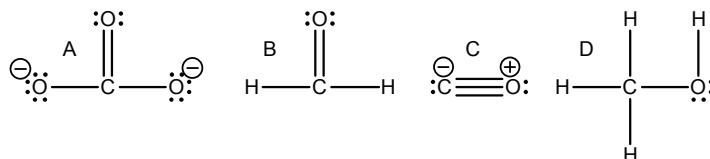
Structure A involves charge separation, but structure B does not. Structure B is preferred.

27. In the Lewis structure of  $N_2O_4$ , each nitrogen is bound to one nitrogen and two oxygens. What are the formal charges and oxidation states of the nitrogen atoms?



The formal charges are shown in the Lewis structure. Oxygen is more electronegative than nitrogen so all bonding N-O electrons are assigned to oxygen when determining oxidation states. The electron pair in the N-N bond is split between the two nitrogen atoms. Nitrogen is in group 5A, but only the one electron in the N-N bond is assigned to in determining the oxidation state:  $OX_N = 5 - 1 = +4$ . The nitrogen atoms are each in the +4 oxidation state. Each oxygen is assigned eight electrons for an oxidation state of -2. Note that the same results could have been obtained by applying the rules given in Section 4.3.

29. List the following in order of increasing carbon-oxygen bond lengths and bond energies:



CO bond order

$4/3$

2

3

1

Bond length increases as the bond order decreases:  $C < B < A < D$

Bond energy increases as the bond order increases:  $D < A < B < C$

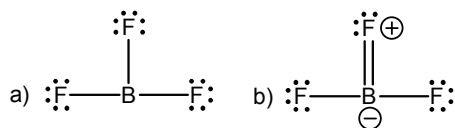
31. List the following in order of increasing N-N bond lengths and bond energies:  $\text{N}_2\text{H}_2$ ,  $\text{N}_2$ ,  $\text{N}_2\text{H}_4$ .

N-N bond orders:  $\text{N}_2\text{H}_2 = 1$ ;  $\text{N}_2 = 3$ ; and  $\text{N}_2\text{H}_4 = 2$

Bond lengths in order of decreasing bond orders.  $\text{N}_2 < \text{N}_2\text{H}_2 < \text{N}_2\text{H}_4$

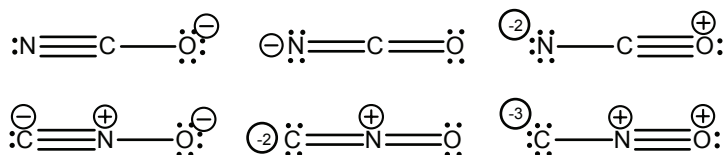
Bond energies in order of increasing bond orders.  $\text{N}_2\text{H}_4 < \text{N}_2\text{H}_2 < \text{N}_2$

33. Draw two structures for  $\text{BF}_3$ , one that obeys the octet rule and one in which boron is electron deficient. Based on formal charge considerations, which structure is preferred?



The structure in which boron is electron deficient (a) is preferred because (b) places positive formal charge on the fluorine atom and negative formal charge on the much less electronegative boron atom.

35. Draw Lewis structures that show all nonzero formal charge for the three resonance forms of the cyanate ion ( $\text{NCO}^{1-}$ ) and the fulminate ion ( $\text{CNO}^{1-}$ ). In each case, determine resonance structure that is most important in describing the bonding in the ion. The cyanate ion is a stable ion, but the fulminate ion is used in explosives. Suggest a reason for this dramatic difference in stability.



The first Lewis structure in each row is the preferred structure, because each minimizes formal charge and places negative formal charge on the oxygen. However, even the preferred structure of  $\text{CNO}^{1-}$  has formal charge on each atom. In addition, it places positive formal charge on nitrogen and negative formal charge on carbon, which are the opposite positions that electronegativities would predict. All of which contribute to the instability of the fulminate ion.

37. Apply the discussion given in Exercise 36 to acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ .

- a) Use the method of Section 4.4 to determine the oxidation state of the carbon.

$2x + 4(1) + 2(-2) = 0$ , so  $x = 0$ , the average of the two oxidation states.

- b) Use the Lewis structure of acetic acid shown in the margin of the textbook and the method presented in Section 5.8 to determine the oxidation state of each carbon atom in  $\text{HC}_2\text{H}_3\text{O}_2$ . Does either carbon have the oxidation state derived in part a)?

Carbon bound only to H atoms. The C-H bonding electrons are assigned to the carbon. One of the C-C bonding electrons is assigned to this carbon.  $\text{OX} = 4 - 3(2) - 1(1) = -3$

Carbon bound to oxygen atoms. None of the C-O bonding electrons and one of the C-C bonding electrons are assigned to this carbon.  $\text{OX} = 4 - 1(1) = +3$

The average of these two oxidation states is  $\frac{1}{2}(-3 + 3) = -0$ , the same result obtained in part a. However, neither carbon atom has that oxidation state.

39. Lone pairs are often left out of molecular drawings, but, as we shall see in Chapter 6, they are important in determining the shape of the molecule. Indicate any missing lone pairs in the following. (Assume that all atoms except H obey the octet rule.)

