Chapter 1: Covalent Bonding and Shapes of Molecules

Problems

1.1 Write and compare the ground-state electron configurations for the elements in each set.

Elements in the same group of the periodic table have the same number of valence electrons, which are indicated in bold.

(a) Carbon = $1s^2\mathbf{2s^2 2p^2}$ Silicon = $1s^2 2s^2 2p^6 \mathbf{3s^2 3p^2}$ 4 valence electrons

(b) Oxygen = $1s^2\mathbf{2s^2 2p^4}$ Sulfur = $1s^2 2s^2 2p^6 \mathbf{3s^2 3p^4}$ 6 valence electrons

(c) Nitrogen = $1s^2\mathbf{2s^2 2p^3}$ Phosphorus = $1s^2 2s^2 2p^6 \mathbf{3s^2 3p^3}$ 5 valence electrons

1.2 Show how the gain of two electrons by a sulfur atom to form a sulfide ion leads to a stable octet:

$$S + 2e^- \longrightarrow S^{2-}$$

The electron configuration of the sulfur atom is $1s^2 2s^2 2p^6 \mathbf{3s^2 3p^4}$. When sulfur gains two electrons to form S^{2-}, the electron configuration becomes $1s^2 2s^2 2p^6 \mathbf{3s^2 3p^6}$. The valence shell has a full octet and corresponds to the configuration of the noble gas Ar.

1.3 Judging from their relative positions in the Periodic Table, which element in each pair has the larger electronegativity?

In general, electronegativity increases from left to right within a period, and from bottom to top within a group.

(a) Li or K: both elements are in the same group, with Li being more electronegative.

(b) N or P: both elements are in the same group, with N being more electronegative.

(c) C or Si: both elements are in the same group, with C being more electronegative.

1.4 Classify each bond as nonpolar covalent, polar covalent, or ionic.

The classification of a bond can be determined by the difference in electronegativity between the bonded atoms. However, these classifications are very broad, and even though two bonds can be in the same category, one may be more polar than the other.

Bond	*Difference in electronegativity*	*Type of bond*
S−H	2.5 – 2.1 = 0.4	nonpolar covalent
P−H	2.1 – 2.1 = 0.0	nonpolar covalent
C−F	4.0 – 2.5 = 1.5	polar covalent
C−Cl	3.0 – 2.5 = 0.5	polar covalent

1.5 Using the symbols δ− and δ+, indicate the direction of polarity in these polar covalent bonds.

In a polar covalent bond, the atom that is more electronegative has a δ− charge, while the less-electronegative atom has a δ+ charge.

(a) $\overset{\delta+}{\text{C}}\text{–}\overset{\delta-}{\text{N}}$ N is more electronegative than C

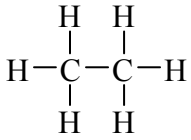
(b) $\overset{\delta+}{\text{N}}\text{–}\overset{\delta-}{\text{O}}$ O is more electronegative than N

(c) $\overset{\delta+}{\text{C}}\text{–}\overset{\delta-}{\text{Cl}}$ Cl is more electronegative than C

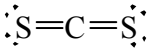
1.6 Draw Lewis structures, showing all valence electrons, for these molecules:

For uncharged molecules, the total number of electrons described by the Lewis structures equals the total of the number of valence electrons contributed by each atom.

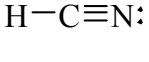
(a) C_2H_6 has a total of 14 valence electrons (4 from each C and 1 from each H). Because H can only have one bond, the only possible connectivity of the atoms is shown on the right.



(b) CS_2 has a total of 16 valence electrons (4 from each C and 6 from each S). In uncharged molecules, C generally forms 4 bonds, and S, which is in the same group as O, generally forms two bonds.



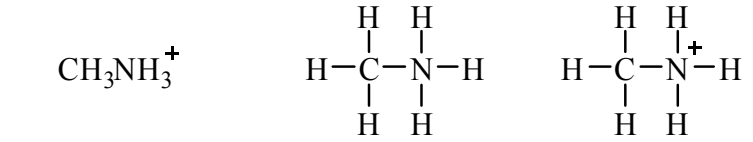
(c) HCN has a total of 10 valence electrons (1 from H, 4 from C, and 5 from N). H can form only one bond, and in uncharged molecules, C generally forms 4 bonds while N forms 3 bonds.



1.7 Draw Lewis structures for these ions, and show which atom in each bears the formal charge(s):

For positively charged species, the total number of valence electrons described by the Lewis structure is equal to the number of valence electrons contributed by each atom, less the number of electrons necessary to obtain the correct positive charge.

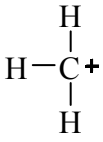
(a) $CH_3NH_3^+$ has a total of 14 valence electrons (1 from each H, 4 from each C, and 5 from N, minus one electron to form a positive charge). The connectivity of the atoms is suggested by the structural formula.



The formal charge of an atom is equal to the number of valence electrons in the neutral, unbounded atom, less the full number of unshared electrons (nonbonding or lone electrons) and half the number of shared electrons.

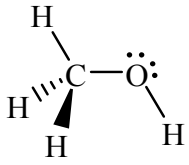
No atoms have unshared electrons. The formal charge of C is: 4 valence electrons – ½(8 shared electrons, two from each bond) = 0. Likewise, the formal charge of N is: 5 valence electrons – ½(8 shared electrons, two from each bond) = +1.

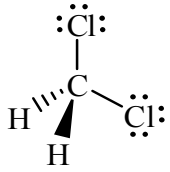
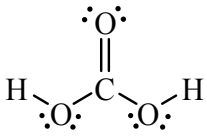
(b) CH_3^+ has a total of 6 valence electrons (1 from each H and 4 from C, minus one electron to form a positive charge). Carbon, with only three bonds and no unshared electrons, has a formal charge of: 4 – ½(6 electrons, two from each bond) = +1. It can be generalized that C with three bonds and no unshared electrons has a +1 formal charge.



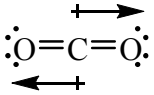
1.8 Predict all bond angles for these molecules:

To predict bond angles, the best strategy is to start with the Lewis structures, because they allow the number of regions of electron density on an atom to be determined. The number of regions of electron density determines the geometric shape of the electron arrangement and hence the bond angles.

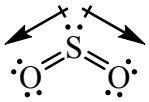
Formula	*Lewis structure*	*Bond angles*
CH_3OH		Both the C and the O atoms each have four regions of electron density, so the bond angles are all 109.5°.

CH_2Cl_2		The C atom has four regions of electron density, hence a bond angle of 109.5°.
H_2CO_3		The C atom has three regions of electron density, hence a bond angle of 120°. The non-terminal O atoms each have four regions of electron density, hence bond angles of 109.5°.

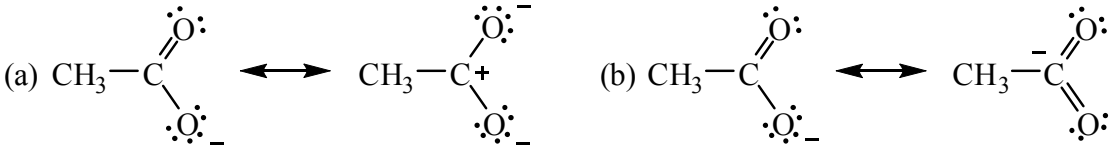
1.9 Both carbon dioxide, CO_2, and sulfur dioxide, SO_2, are triatomic molecules. Account for the fact that carbon dioxide is a nonpolar molecule whereas sulfur dioxide is a polar molecule.



For a molecule to be polar, it requires a geometry in which the bond dipole moments do not cancel out. The linear shape of CO_2 results in a cancellation of the dipoles moments. In SO_2, which has a bent shape, the dipole moments do not cancel out.

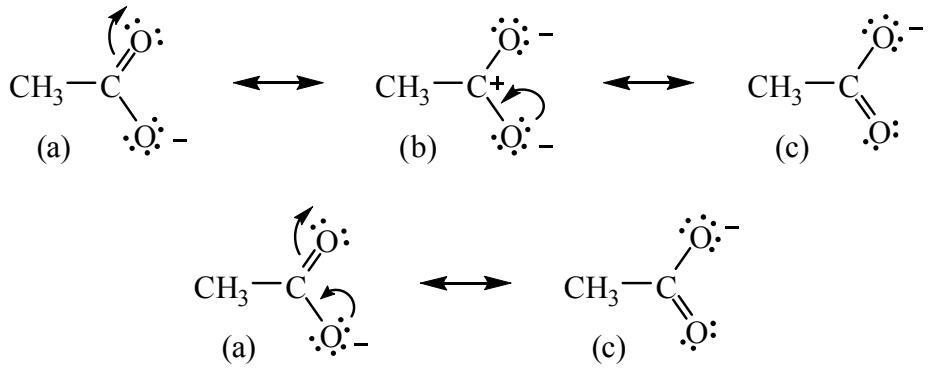


1.10 Which sets are pairs of contributing structures?



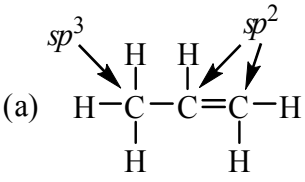
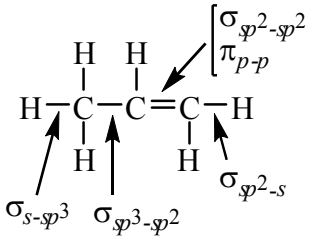
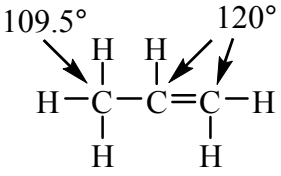
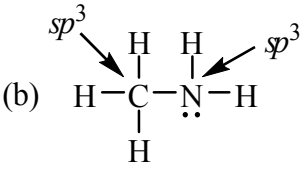
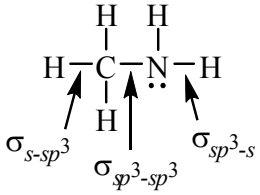
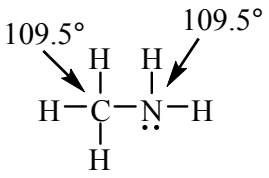
Contributing structures differ only in the distribution of the electrons, and each contributing structure itself must be a correct Lewis structure. Pair (a) is a set of contributing structures. Pair (b) is not a set of contributing structures; although they differ in electronic distributions, the structure on the right violates the octet rule and is an unacceptable Lewis structure.

1.11 Use curved arrows to show the redistribution of valence electrons in converting contributing structure (a) to (b) and then (b) to (c). Also show, using curved arrows, how (a) can be converted to (c) without going through (b).

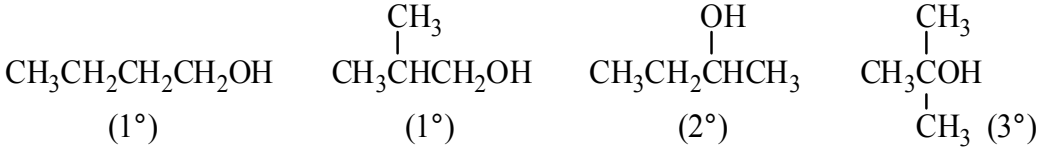


1.12 Describe the bonding in these molecules in terms of the atomic orbitals involved, and predict all bond angles. (a) $CH_3CH{=}CH_2$ (b) CH_3NH_2

With the exception of hydrogen (1*s* configuration), all other atoms are hybridized. The orbitals used to form the respective σ and π bonds are also indicated.

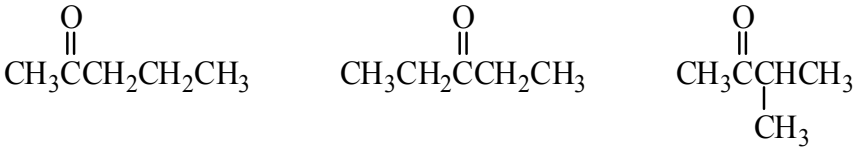
Hybridization	*Bonding*	*Bond angles*
(a) 		
(b) 		

1.13 Write condensed structural formulas for the four alcohols with the molecular formula $C_4H_{10}O$. Classify each as primary, secondary, or tertiary.



1.14 Write condensed structural formulas for the three secondary amines with the molecular formula $C_4H_{11}N$.

1.15 Write condensed structural formulas for the three ketones with the molecular formula $C_5H_{10}O$.



1.16 Write condensed structural formulas for the two carboxylic acids with the molecular formula $C_4H_8O_2$.

Chemical Connections

1A. What geometric feature distinguishes the bond angles about each carbon in C_{60} from the bond angles of a typical compound containing carbon with three regions of electron density?

Normally, a carbon atom with three regions of electron density has a trigonal planar geometry and bond angles of 120°. Although all the carbon atoms in C_{60} each have three regions of electron density, the bond angles C_{60} must be strained and slightly less than 120° to allow the formation of a spherical structure. If all the angles remained at 120°, C_{60} cannot be a bucky*ball*!

Graphite, on the other hand, has bond angles that are perfectly 120°. As expected, graphite is a perfectly flat molecule.

Quick Quiz

1. These bonds are arranged in order of increasing polarity: C−H < N−H < O−H. ***True***. The difference in electronegativity between C and H is the lowest of the three, while the electronegativity difference between O and H is the highest of the three.

2. All atoms in a contributing structure must have complete valence shells. ***False***. Although structures are most stable when they have complete valence shells, it is not a requirement.

3. An electron in a 1*s* orbital is held closer to the nucleus than an electron in a 2*s* orbital. ***True***. The 1*s* orbital is closer to the nucleus than the 2*s*. When comparing orbitals of the same type, their distance from the nucleus increases with the principal quantum number (*n*).

4. A sigma bond and a pi bond have in common that each can result from the overlap of atomic orbitals. ***True***. Atomic orbitals may also hybridize before bonding.

5. The molecular formula of the smallest aldehyde is C_3H_6O, and that of the smallest ketone is also C_3H_6O. ***False***. While the smallest ketone is C_3H_6O (propanone), the formula of the smallest aldehyde is CH_2O (formaldehyde).

6. To predict whether a covalent molecule is polar or nonpolar, you must know both the polarity of each covalent bond and the geometry (shape) of the molecule. ***True***. Whether a molecule is polar or nonpolar depends on the vector sum of the bond dipoles. Just because a molecule has polar bonds does not necessarily mean that the molecule is polar.

7. An orbital is a region of space that can hold two electrons. ***True***. The maximum capacity of each orbital is two electrons.

8. In the ground-state electron configuration of an atom, only the lowest-energy orbitals are occupied. ***True***. By definition, the ground-state configuration is the electron configuration of lowest energy. These electrons must be in the orbitals of lowest energy.

9. Electronegativity generally increases with atomic number. ***False***. Electronegativity generally increases across a period, from left to right, and up a group, from bottom to top.

10. Paired electron spins means that the two electrons are aligned with their spins North Pole to North Pole and South Pole to South Pole. ***False***. Electrons that are spin-paired must have opposite spin.

11. According to the Lewis model of bonding, atoms bond together in such a way that each atom participating in the bond acquires an outer-shell electron configuration matching that of the noble gas nearest it in atomic number. ***True***. Most atoms usually have an electron configuration that consists of a full octet.

12. A primary amine contains one N−H bond, a secondary amine contains two N−H bonds, and a tertiary amine contains three N−H bonds. ***False***. Amines are classified based on the number of alkyl groups and not the number of hydrogens that are bonded to the nitrogen.

13. All bond angles in sets of contributing structures must be the same. ***False***. Contributing structures differ only in the distribution of electrons. Bond angles may be different.

14. Electronegativity is a measure of an atom's attraction for electrons it shares in a chemical bond with another atom. ***True***. An atom that is more electronegative will more strongly attract a bonding pair of electrons towards itself.

15. An orbital can hold a maximum of two electrons with their spins paired. ***True***. Note that electrons that are spin-paired are of opposite spin.

16. Fluorine in the upper right corner of the Periodic Table is the most electronegative element; hydrogen, in the upper left corner, is the least electronegative element. ***False***. While this statement is true for fluorine, it is incorrect for hydrogen. Elements with the lowest electronegativity are in the bottom-left corner of the Periodic Table.

17. A primary alcohol has one −OH group, a secondary alcohol has two −OH groups, and a tertiary alcohol has three −OH groups. ***False***. Alcohols are classified not by the number of −OH groups, but by the number of carbons bonded to the carbon bearing the −OH group.

18. H_2O and NH_3 are polar molecules, but CH_4 is nonpolar. ***True***. Water and ammonia have polar bonds, and their shapes (bent and trigonal pyramidal, respectively) do not allow the bond dipole moments to cancel out. Methane has nonpolar bonds and is also tetrahedral.

19. Electronegativity generally increases from top to bottom in a column of the Periodic Table. ***False***. The opposite is true; electronegativity decreases from top to bottom in a group.

20. All contributing structures must have the same number of valence electrons. ***True***. Contributing structures only involve the movement of electrons and not their addition or removal.

21. A carbon-carbon double bond is formed by the overlap of sp^2 hybrid orbitals, and a triple bond is formed by the overlap of sp^3 hybrid orbitals. ***False***. Triple bonds involve *sp* hybrid orbitals. In both double and triple bonds, *p* atomic orbitals are also involved.

22. A covalent bond formed by sharing two electrons is called a double bond. ***False***. A covalent bond consisting of two electrons is a single bond.

23. The functional groups of an alcohol, an aldehyde, and a ketone have in common the fact that each contains a single oxygen atom. ***True***. However, note that the oxygen atom of an alcohol is also bonded to a hydrogen atom.

24. Electrons in atoms are confined to regions of space called principal energy levels. ***False***. The regions of space are called orbitals.

25. In a single bond, two atoms share one pair of electrons; in a double bond, they share two pairs of electrons; and in a triple bond, they share three pairs of electrons. ***True***. Each bond involves the sharing of one pair of electrons.

26. The Lewis structure for ethene, C_2H_4, must show eight valence electrons. ***False***. Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron, giving a total of twelve valence electrons.

27. The Lewis structure for formaldehyde, CH_2O, must show eight valence electrons. ***False***. It has twelve valence electrons: four from C, one from each H, and six from O.

28. The letters VSEPR stand for valence-shell electron pair repulsion. ***True***. VSEPR considers only the electrons present in the valence shell.

29. In predicting bond angles about a central atom in a covalent bond, VSEPR considers only shared pairs (pairs of electrons involved in forming covalent bonds). ***False***. VSEPR considers both bonding and nonbonding pairs of electrons.

30. An *sp* hybrid orbital may contain a maximum of four electrons, an sp^2 hybrid orbital may contain a maximum of six valence electrons, and an sp^3 hybrid orbital may contain a maximum of eight electrons. ***False***. Each hybrid orbital is still a single orbital, which can hold a no more than of two electrons. However, there are two separate *sp*, three separate sp^2, and four separate sp^3 hybrid orbitals, which when summed, give the totals stated.

31. For a central atom surrounded by three regions of electron density, VSEPR predicts bond angles of 360°/3 = 120°. ***True***. However, this equation does not always apply. For example, if there are four regions of electron density, the angle is 109.5°, not 360°/4 = 90°. Always look for the geometric shape that maximizes the separation of the regions of electron density. Do not simply divide 360° by the number of regions of electron density.

32. The three 2*p* orbitals are aligned parallel to each other. ***False***. They are perpendicular (orthogonal or 90°) to each other.

33. All molecules with polar bonds are polar. ***False***. Molecules with polar bonds are polar only if the dipole moments of the bonds do not cancel out. If the dipole moments of the bonds cancel out, such as in CO_2, the molecule is nonpolar.

34. Electronegativity generally increases from left to right across a period of the Periodic Table. ***True***. Electronegativity also increases going up a group, from bottom to top.

35. A compound with the molecular formula C_3H_6O may be an aldehyde, a ketone, or a carboxylic acid. ***False***. A carboxylic acid contains the carboxyl functional group, which has two oxygen atoms. A compound that contains both an ether and an alkene, or an alcohol and an alkene, could also have the molecular formula C_3H_6O.

36. Dichloromethane, CH_2Cl_2 is polar, but tetrachloromethane, CCl_4, is nonpolar. ***True***. Although both compounds have a tetrahedral shape, the bond dipole moments in dichloromethane do not cancel out.

37. A covalent bond is formed between atoms whose difference in electronegativity is less than 1.9. ***True***. When the difference in electronegativity is greater than 1.9, the bond is ionic.

38. Each principal energy level can hold two electrons. ***False***. Each *orbital* can hold two electrons. Each principal energy level n can hold a maximum of $2n^2$ electrons.

39. Atoms that share electrons to achieve filled valence shells form covalent bonds. ***True***. Covalent bonding involves the sharing of electrons. If the electrons were not shared, the bond would be ionic instead of covalent.

40. Contributing structures differ only in the distribution of valence electrons. ***True***. Contributing structures do not involve different positions of atoms, only electrons.

41. In creating hybrid orbitals (sp, sp^2, and sp^3), the number of hybrid orbitals created is equal to the number of atomic orbitals hybridized. ***True***. For example, the use of three orbitals (one s and two p) in sp^2 hybridization results in the formation of three sp^2 hybrid orbitals.

42. VSEPR treats the two electron pairs of a double bond and the three electron pairs of a triple bond as one region of electron density. ***True***. A single bond, double bond, triple bond, and a nonbonding pair each count as a single region of electron density.

43. If the difference in electronegativity between two atoms is zero (they have identical electronegativities), then the two atoms will not form a covalent bond. ***False***. The bond formed is still a covalent bond, it is a nonpolar covalent bond.

44. A carbon-carbon triple bond is a combination of one sigma bond and two pi bonds. ***True***. The sigma bond is formed by the overlap of hybrid orbitals, while the two pi bonds are formed by the overlap of p orbitals.

45. A carbon-carbon double bond is a combination of two sigma bonds. ***False***. A double bond consists of one sigma bond and one pi bond.

46. An s orbital has the shape of a sphere with the center of the sphere at the nucleus. ***True***. Regardless of the principal energy level, an s orbital is always spherical.