



Course Study Guide/Solutions Manual
to accompany:
Organic Chemistry, 3rd Edition
University of Pretoria
Department of Chemistry



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ISBN-10: 1121180612 ISBN-13: 9781121180611

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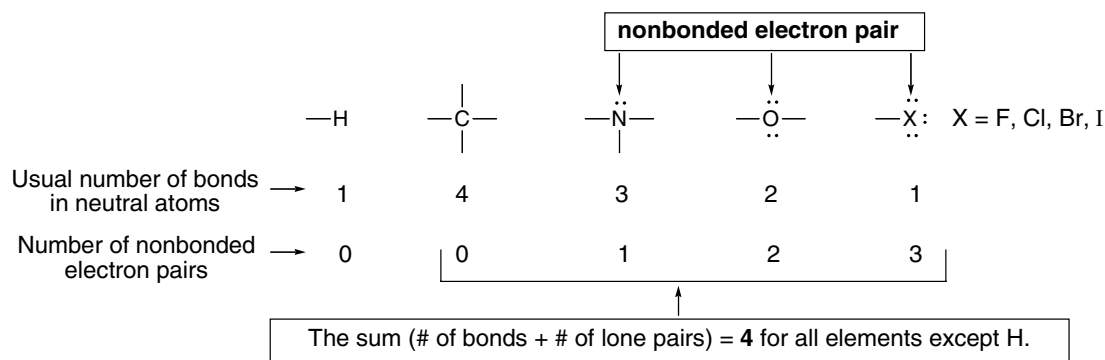
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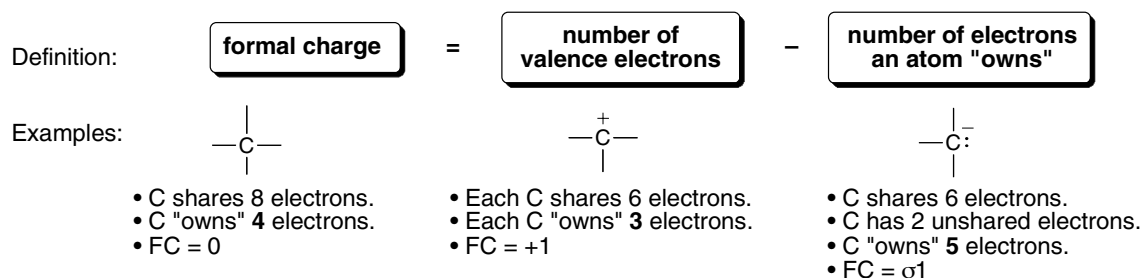
Chapter 1: Structure and Bonding

◆ Important facts

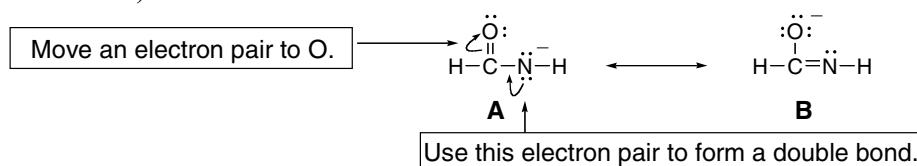
- **The general rule of bonding:** Atoms strive to attain a complete outer shell of valence electrons (Section 1.2). H “wants” 2 electrons. Second-row elements “want” 8 electrons.



- **Formal charge (FC)** is the difference between the number of valence electrons of an atom and the number of electrons it “owns” (Section 1.3C). See Sample Problem 1.4 for a stepwise example.



- **Curved arrow notation** shows the movement of an electron pair. The tail of the arrow always begins at an electron pair, either in a bond or a lone pair. The head points to where the electron pair “moves” (Section 1.5).

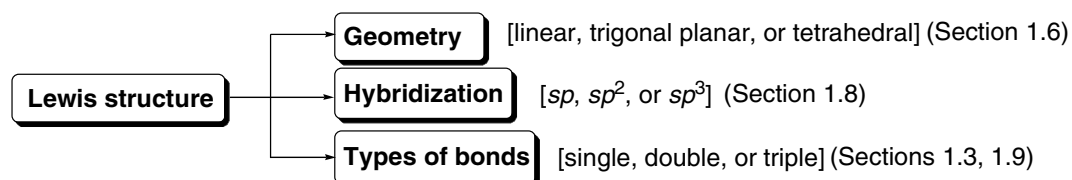


- **Electrostatic potential plots** are color-coded maps of electron density, indicating electron rich and electron deficient regions (Section 1.11).

Chapter 1–2

◆ The importance of Lewis structures (Sections 1.3, 1.4)

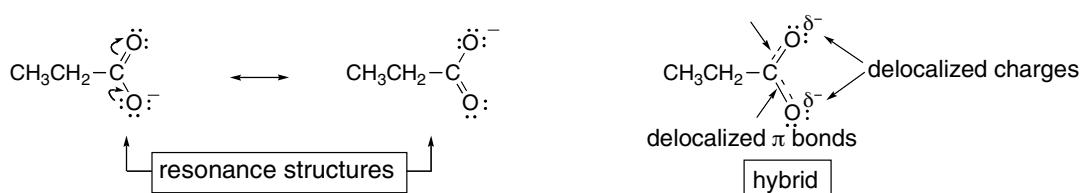
A properly drawn Lewis structure shows the number of bonds and lone pairs present around each atom in a molecule. In a valid Lewis structure, each H has two electrons, and each second-row element has no more than eight. This is the first step needed to determine many properties of a molecule.



◆ Resonance (Section 1.5)

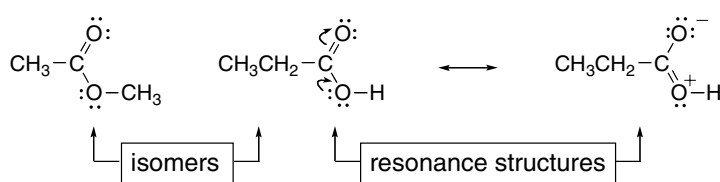
The basic principles:

- Resonance occurs when a compound cannot be represented by a single Lewis structure.
- Two resonance structures differ *only* in the position of nonbonded electrons and π bonds.
- The resonance hybrid is the only accurate representation for a resonance-stabilized compound. A hybrid is more stable than any single resonance structure because electron density is delocalized.



The difference between resonance structures and isomers:

- Two **isomers** differ in the arrangement of *both* atoms and electrons.
- **Resonance structures** differ *only* in the *arrangement of electrons*.



◆ Geometry and hybridization

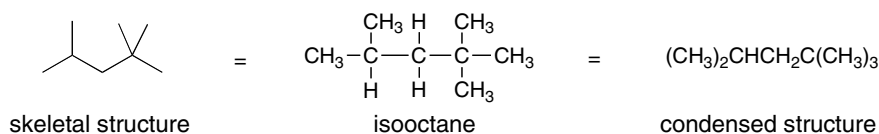
The number of groups around an atom determines both its geometry (Section 1.6) and hybridization (Section 1.8).

Number of groups	Geometry	Bond angle ($^{\circ}$)	Hybridization	Examples
2	linear	180	sp	BeH_2 , $\text{HC}\equiv\text{CH}$
3	trigonal planar	120	sp^2	BF_3 , $\text{CH}_2=\text{CH}_2$
4	tetrahedral	109.5	sp^3	CH_4 , NH_3 , H_2O

Structure and Bonding 1-3

◆ Drawing organic molecules (Section 1.7)

- Shorthand methods are used to abbreviate the structure of organic molecules.



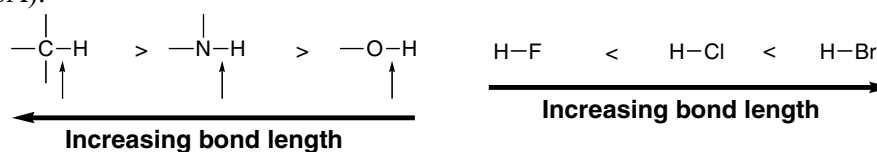
- A carbon bonded to four atoms is tetrahedral in shape. The best way to represent a tetrahedron is to draw two bonds in the plane, one in front, and one behind.

Four equivalent drawings for CH₄

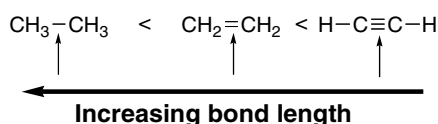
Each drawing has two solid lines, one wedge, and one dashed line.

◆ Bond length

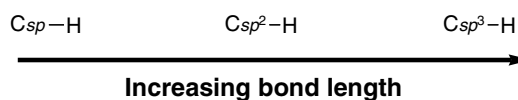
- Bond length decreases across a row and increases down a column of the periodic table (Section 1.6A).



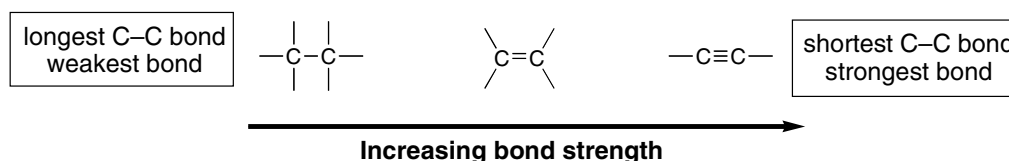
- Bond length decreases as the number of electrons between two nuclei increases (Section 1.10A).



- Bond length increases as the percent *s*-character decreases (Section 1.10B).

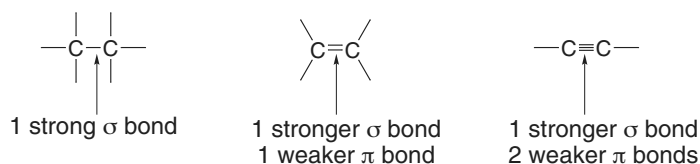


- Bond length and bond strength are inversely related. Shorter bonds are stronger bonds (Section 1.10).



Chapter 1–4

- Sigma (σ) bonds are generally stronger than π bonds (Section 1.9).



◆ Electronegativity and polarity (Sections 1.11, 1.12)

- Electronegativity increases across a row and decreases down a column of the periodic table.
- A polar bond results when two atoms of different electronegativity are bonded together. Whenever C or H is bonded to N, O, or any halogen, the bond is polar.
- A polar molecule has either one polar bond, or two or more bond dipoles that reinforce.

◆ Drawing Lewis structures: A shortcut

Chapter 1 devotes a great deal of time to drawing valid Lewis structures. For molecules with many bonds, it may take quite awhile to find acceptable Lewis structures by using trial-and-error to place electrons. Fortunately, a shortcut can be used to figure out how many bonds are present in a molecule.

Shortcut on drawing Lewis structures—Determining the number of bonds:

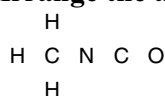
- [1] Count up the number of valence electrons.
- [2] Calculate how many electrons are needed if there were no bonds between atoms and every atom has a filled shell of valence electrons; i.e., hydrogen gets two electrons, and second-row elements get eight.
- [3] Subtract the number obtained in Step [2] from the sum obtained in Step [1]. **This difference tells how many electrons must be shared** to give every H two electrons and every second-row element eight. Since there are two electrons per bond, dividing this difference by two tells how many bonds are needed.

To draw the Lewis structure:

- [1] Arrange the atoms as usual.
- [2] Count up the number of valence electrons.
- [3] Use the shortcut to determine how many bonds are present.
- [4] Draw in the two-electron bonds to all the H's first. Then, draw the remaining bonds between other atoms making sure that no second-row element gets more than eight electrons and that you use the total number of bonds determined previously.
- [5] Finally, place unshared electron pairs on all atoms that do not have an octet of electrons, and calculate formal charge. You should have now used all the valence electrons determined in the first step.

Example: Draw all valid Lewis structures for CH_3NCO using the shortcut procedure.

[1] Arrange the atoms.



- In this case the arrangement of atoms is implied by the way the structure is drawn.

Structure and Bonding 1–5

[2] Count up the number of valence electrons.

$$\begin{array}{rclcl}
 3\text{H's} & \times & 1 \text{ electron per H} & = & 3 \text{ electrons} \\
 2\text{C's} & \times & 4 \text{ electrons per C} & = & 8 \text{ electrons} \\
 1\text{N} & \times & 5 \text{ electrons per N} & = & 5 \text{ electrons} \\
 1\text{O} & \times & 6 \text{ electrons per O} & = & + 6 \text{ electrons} \\
 & & & & \hline
 & & & & \mathbf{22 \text{ electrons total}}
 \end{array}$$

[3] Use the shortcut to figure out how many bonds are needed.

- Number of electrons needed if there were no bonds:

$$\begin{array}{rclcl}
 3 \text{ H's} & \times & 2 \text{ electrons per H} & = & 6 \text{ electrons} \\
 4 \text{ second-row elements} & \times & 8 \text{ electrons per element} & = & + 32 \text{ electrons} \\
 & & & & \hline
 & & & & \mathbf{38 \text{ electrons needed if} \\
 & & & & \mathbf{there were no bonds}}
 \end{array}$$

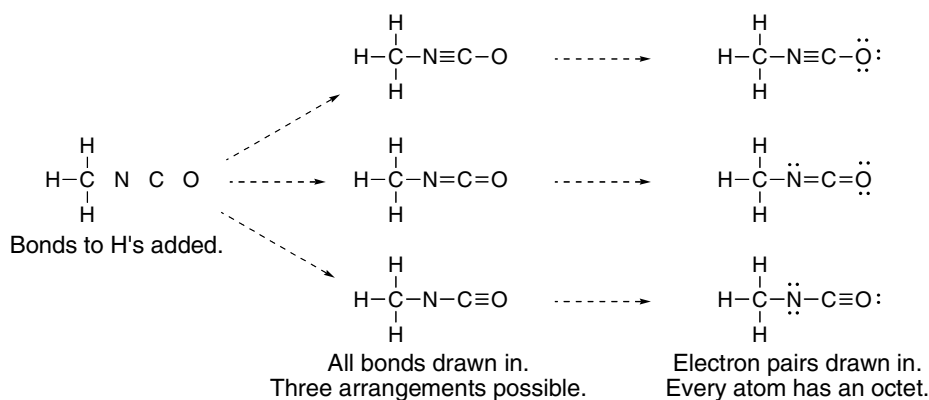
- Number of electrons that must be shared:

$$\begin{array}{r}
 38 \text{ electrons} \\
 - 22 \text{ electrons} \\
 \hline
 \mathbf{16 \text{ electrons must be shared}}
 \end{array}$$

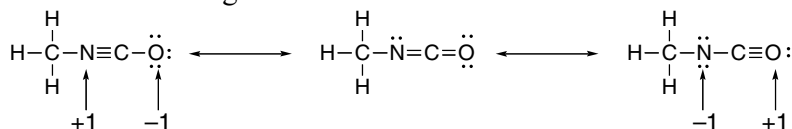
- Since every bond takes two electrons, $16/2 = 8$ bonds are needed.

[4] Draw all possible Lewis structures.

- Draw the bonds to the H's first (three bonds). Then add five more bonds. Arrange them between the C's, N, and O, making sure that no atom gets more than eight electrons. There are three possible arrangements of bonds; i.e., there are three resonance structures.
- Add additional electron pairs to give each atom an octet and check that all 22 electrons are used.



- Calculate the formal charge on each atom.



- You can evaluate the Lewis structures you have drawn. The middle structure is the best resonance structure, since it has no charged atoms.

Note: This method works for compounds that contain second-row elements in which every element gets an octet of electrons. It does NOT necessarily work for compounds with an atom that does not have an octet (such as BF_3), or compounds that have elements located in the third row and later in the periodic table.

Chapter 1–6

Chapter 1: Answers to Problems

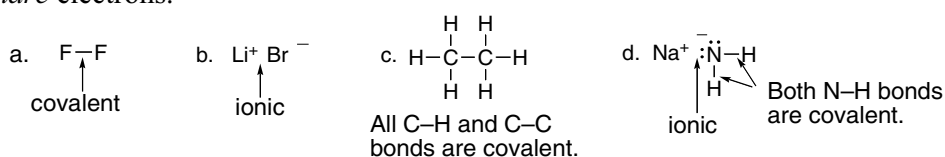
- 1.1 The **mass number** is the number of protons and neutrons. The **atomic number** is the number of protons and is the same for all isotopes.

	Nitrogen-14	Nitrogen-13
a. number of protons = atomic number for N = 7	7	7
b. number of neutrons = mass number – atomic number	7	6
c. number of electrons = number of protons	7	7
d. The group number is the same for all isotopes.	5A	5A

- 1.2 The **atomic number** is the number of protons. The **total number of electrons** in the neutral atom is equal to the number of protons. The number of **valence electrons** is equal to the group number for second-row elements. The **group number** is located above each column in the periodic table.

	a. atomic number	b. total number of e ⁻	c. valence e ⁻	d. group number
[1] ³¹ ₁₅ P	15	15	5	5A
[2] ¹⁹ ₉ F	9	9	7	7A
[3] ² ₁ H	1	1	1	1A

- 1.3 **Ionic bonds** form when an element on the far left side of the periodic table transfers an electron to an element on the far right side of the periodic table. **Covalent bonds** result when two atoms *share* electrons.



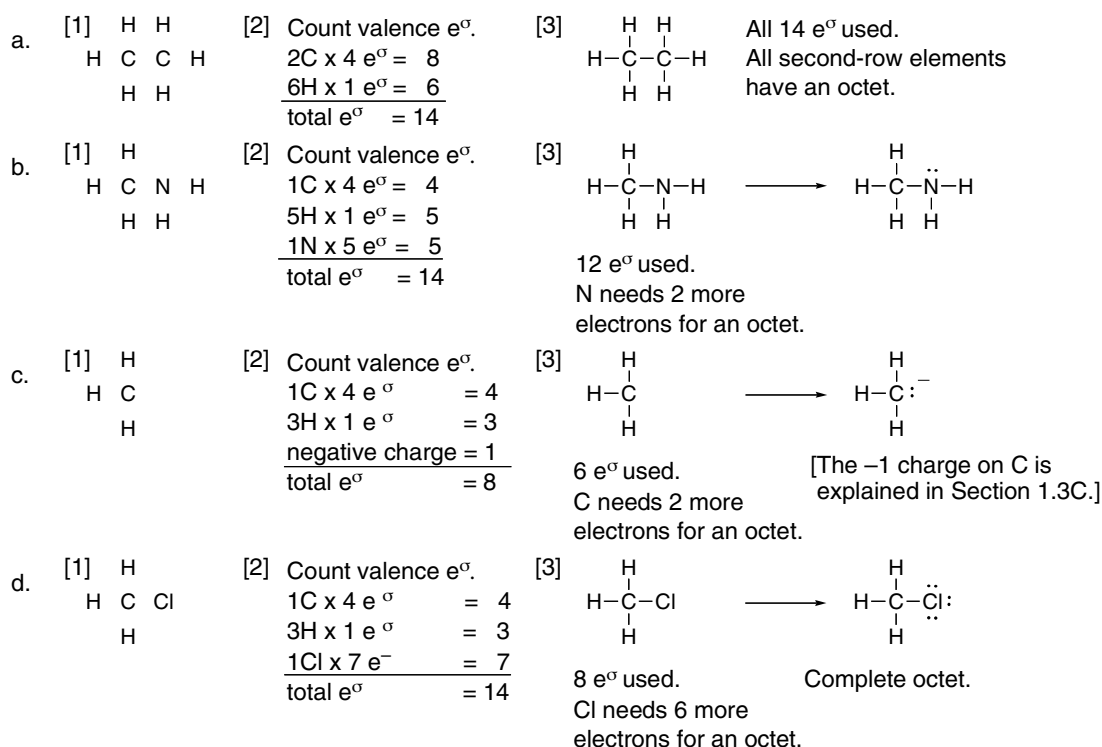
- 1.4 a. Ionic bonding is observed in NaF since Na is in group 1A and has only one valence electron, and F is in group 7A and has seven valence electrons. When F gains one electron from Na, they form an ionic bond.
b. Covalent bonding is observed in CFC₃ since carbon is a nonmetal in the middle of the periodic table and does not readily transfer electrons.

- 1.5 Atoms with one, two, three, or four valence electrons form one, two, three, or four bonds, respectively. Atoms with five or more valence electrons form $[8 - (\text{number of valence electrons})]$ bonds.

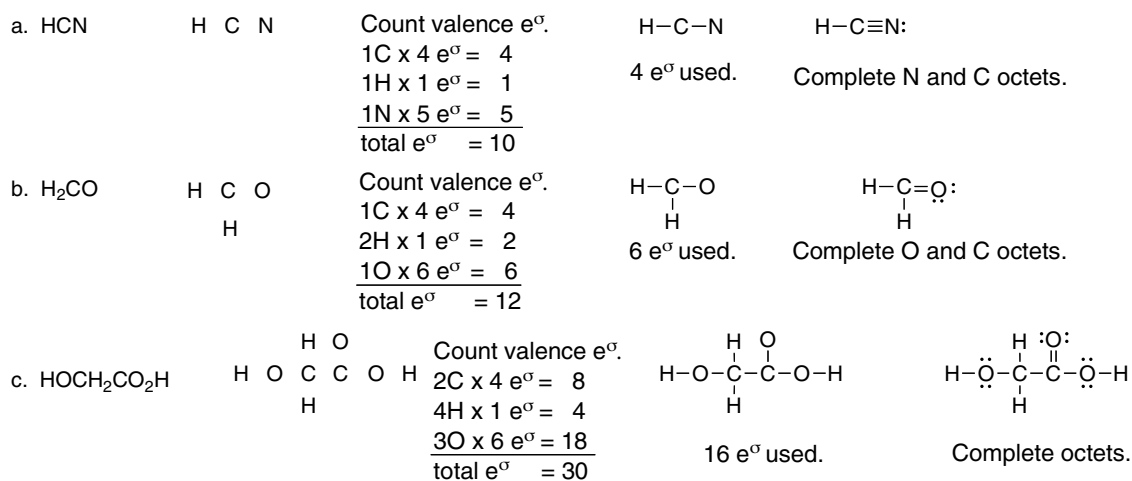
- a. O 8 σ 6 valence e^σ = 2 bonds c. Br 8 σ 7 valence e^σ = 1 bond
b. Al 3 valence e^σ = 3 bonds d. Si 4 valence e^σ = 4 bonds

Structure and Bonding 1-7

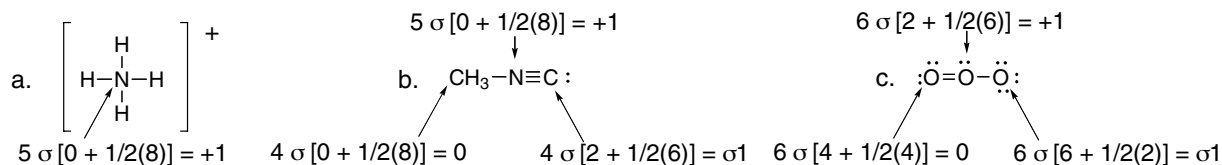
- 1.6 [1] Arrange the atoms with the H's on the periphery.
 [2] Count the valence electrons.
 [3] Arrange the electrons around the atoms. Give the H's 2 electrons first, and then fill the octets of the other atoms.
 [4] Assign formal charges (Section 1.3C).



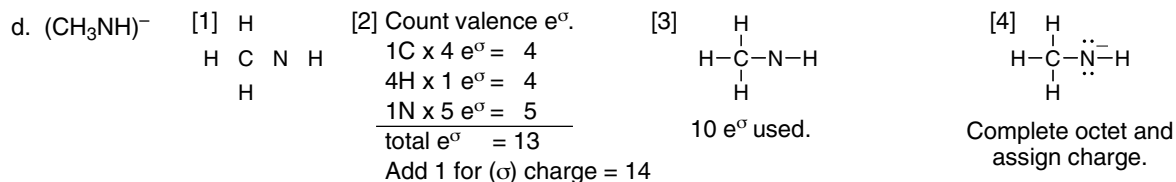
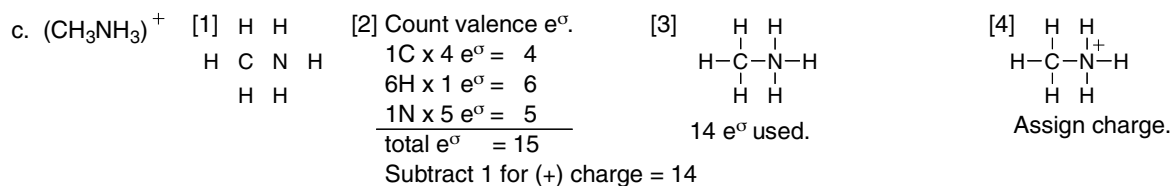
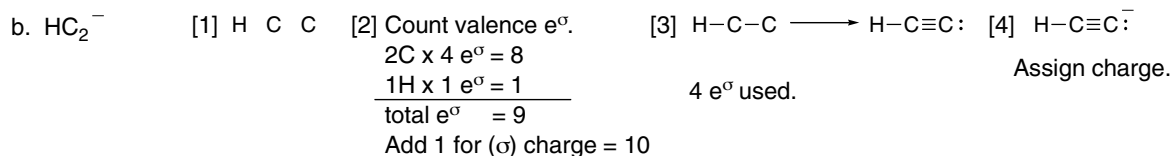
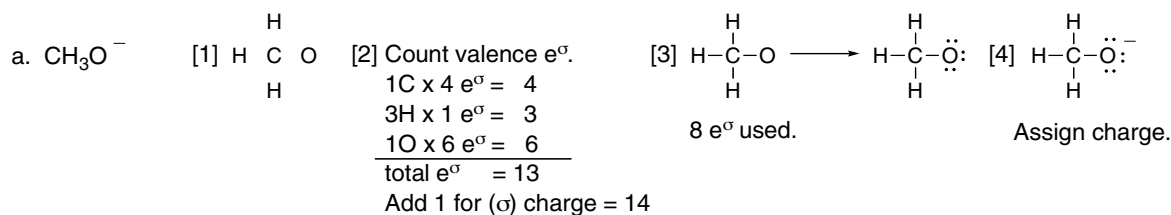
- 1.7 Follow the directions from Answer 1.6.



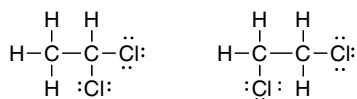
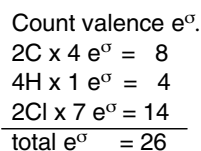
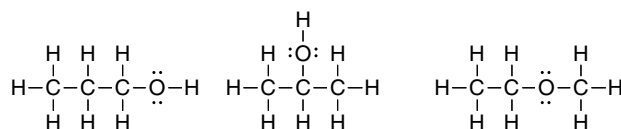
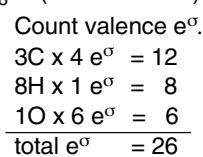
Chapter 1-8

1.8 Formal charge (FC) = number of valence electrons – [number of unshared electrons + 1/2 (number of shared electrons)]


1.9



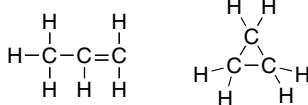
1.10

a. $\text{C}_2\text{H}_4\text{Cl}_2$ (two isomers)b. $\text{C}_3\text{H}_8\text{O}$ (three isomers)

Structure and Bonding 1-9

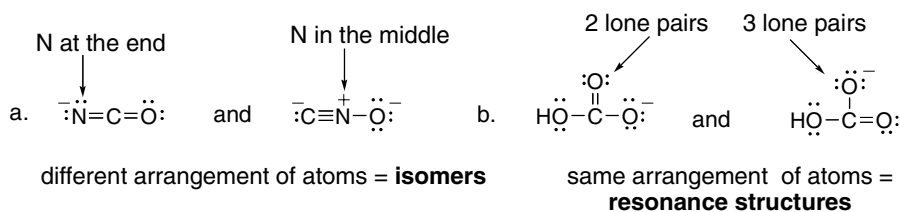
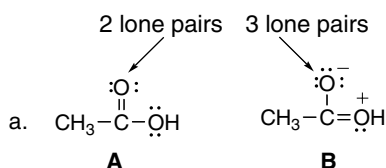
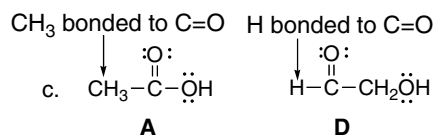
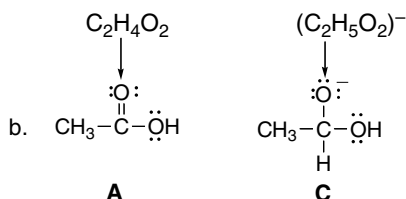
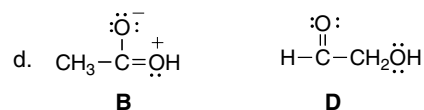
c. C_3H_6 (two isomers)

$$\begin{array}{l} \text{Count valence } e^\sigma \\ 3C \times 4 e^\sigma = 12 \\ 6H \times 1 e^\sigma = 6 \\ \hline \text{total } e^\sigma = 18 \end{array}$$

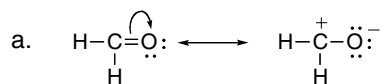


1.11 Two different definitions:

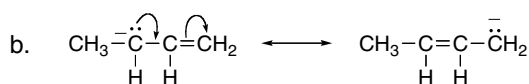
- **Isomers** have the same molecular formula and a *different* arrangement of atoms.
- **Resonance structures** have the same molecular formula and the *same* arrangement of atoms.

1.12 **Isomers** have the same molecular formula and a *different* arrangement of atoms.**Resonance structures** have the same molecular formula and the *same* arrangement of atoms.same arrangement of atoms = **resonance structures**different arrangement of atoms = **isomers**different molecular formulas = **neither**different arrangement of atoms = **isomers**

1.13 Curved arrow notation shows the movement of an electron pair. The tail begins at an electron pair (a bond or a lone pair) and the head points to where the electron pair moves.



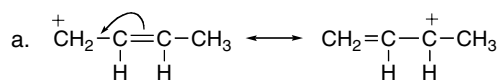
The net charge is the same in both resonance structures.



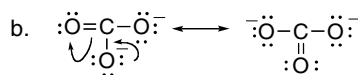
The net charge is the same in both resonance structures.

Chapter 1–10

1.14 Compare the resonance structures to see what electrons have “moved.” Use **one curved arrow to show the movement of each electron pair**.

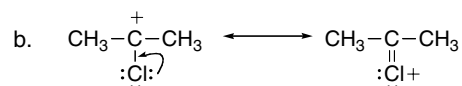
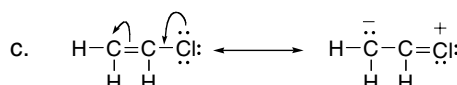
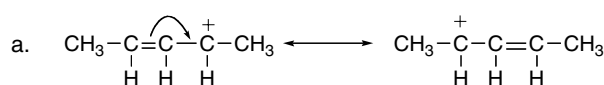


One electron pair moves:
one curved arrow.

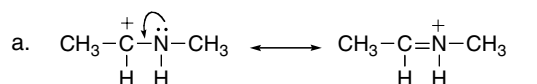


Two electron pairs move:
two curved arrows.

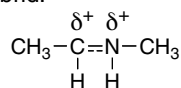
1.15 To draw another resonance structure, **move electrons only in multiple bonds and lone pairs** and keep the number of unpaired electrons constant.



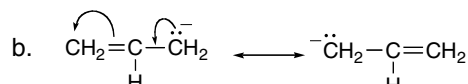
1.16 A “better” resonance structure is one that has more bonds and fewer charges. The better structure is the major contributor and all others are minor contributors. To draw the resonance hybrid, use dashed lines for bonds that are in only one resonance structure, and use partial charges when the charge is on different atoms in the resonance structures.



hybrid:

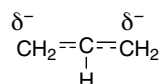


All atoms have octets.
one more bond
major contributor

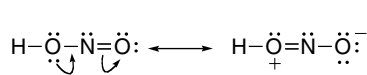


These two resonance structures are equivalent.
They both have one charge and the same number of bonds. They are **equal contributors** to the hybrid.

hybrid:

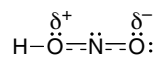


1.17 Draw a second resonance structure for nitrous acid.



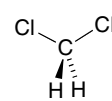
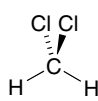
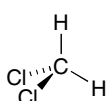
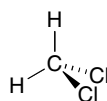
major contributor
fewer charges

minor contributor



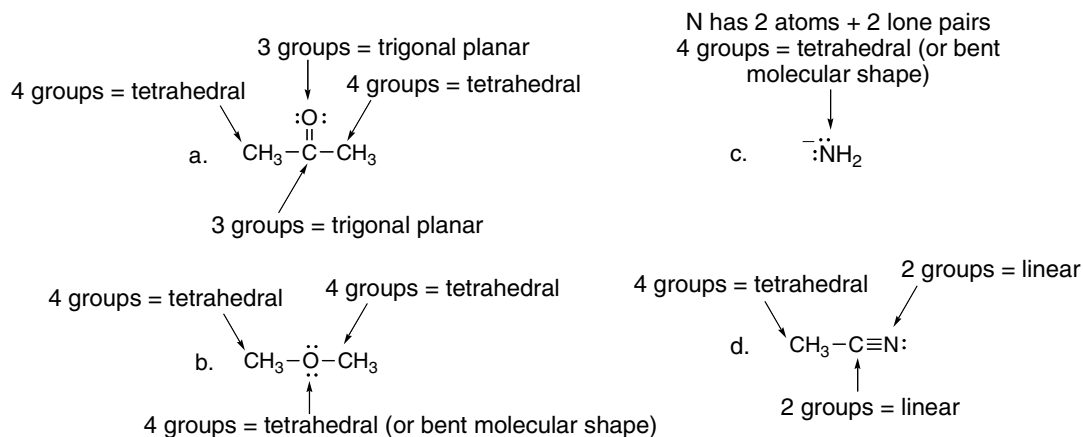
hybrid

1.18 All representations have a carbon with two bonds in the plane of the page, one in front of the page (solid wedge) and one behind the page (dashed line). Four possibilities:

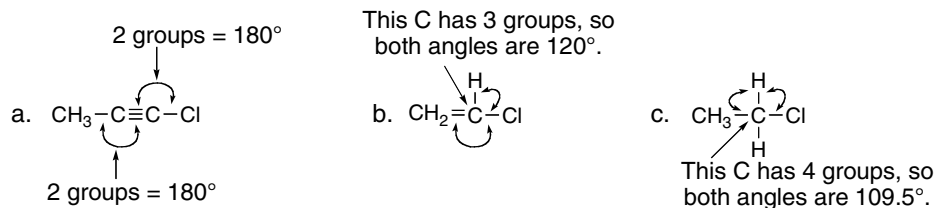


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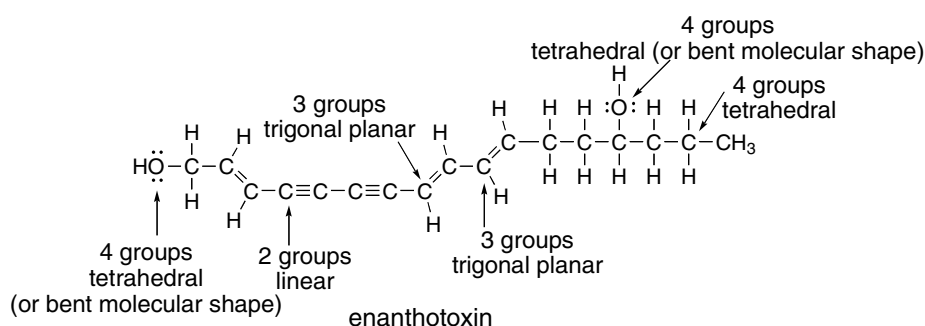
1.19 To predict the geometry around an atom, **count the number of groups (atoms + lone pairs)**, making sure to draw in any needed lone pairs or hydrogens: 2 groups = linear, 3 groups = trigonal planar, 4 groups = tetrahedral.



1.20 To predict the bond angle around an atom, **count the number of groups (atoms + lone pairs)**, making sure to draw in any needed lone pairs or hydrogens: 2 groups = 180° , 3 groups = 120° , 4 groups = 109.5° .

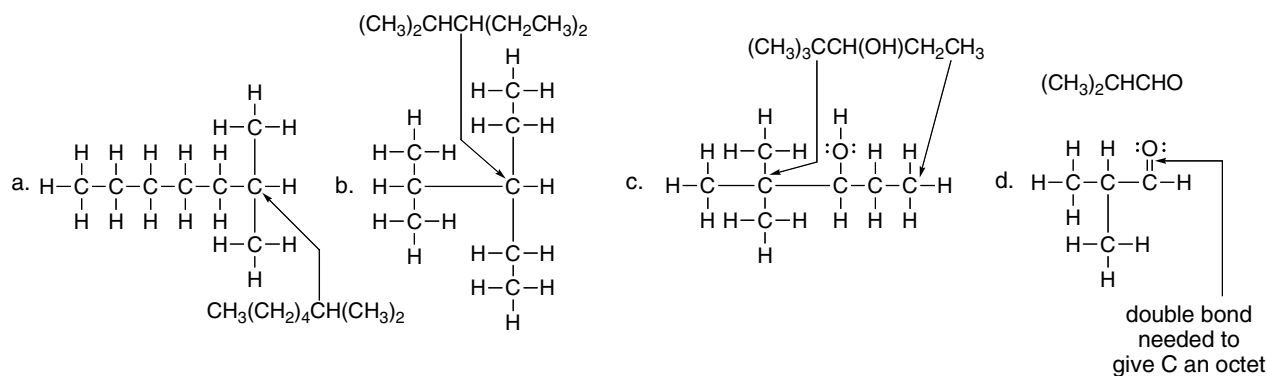


1.21 To predict the geometry around an atom, use the rules in Answer 1.19.

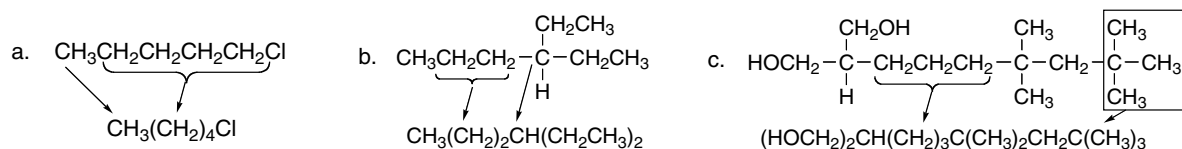


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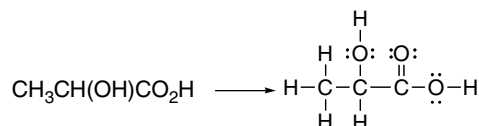
1.22 Reading from left to right, draw the molecule as a Lewis structure. Always check that carbon has four bonds and all heteroatoms have an octet by adding any needed lone pairs.



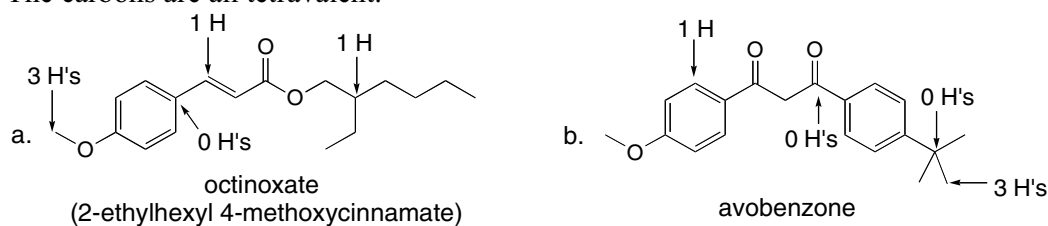
1.23 Simplify each condensed structure using parentheses.



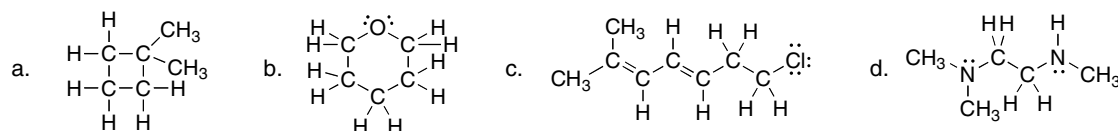
1.24 Draw the Lewis structure of lactic acid.



1.25 In shorthand or skeletal drawings, **all line junctions or ends of lines represent carbon atoms.** The carbons are all tetravalent.

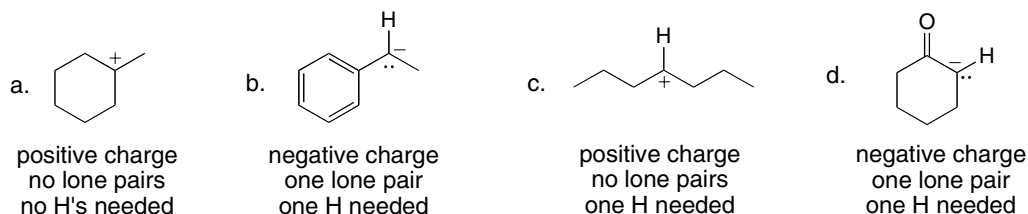


1.26 In shorthand or skeletal drawings, **all line junctions or ends of lines represent carbon atoms.** Convert by writing in all carbons, and then adding hydrogen atoms to make the carbons tetravalent.

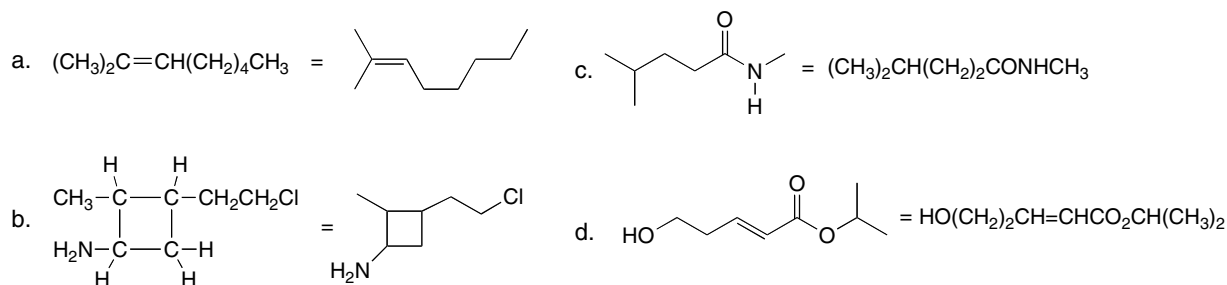


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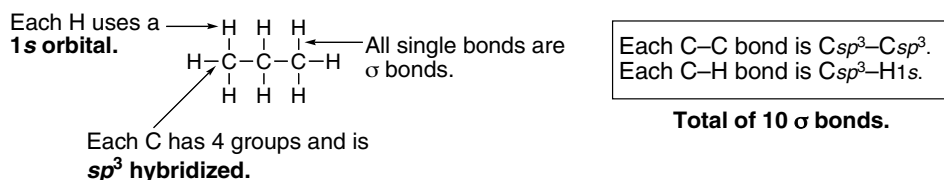
1.27 A charge on a carbon atom takes the place of one hydrogen atom. **A negatively charged C has one lone pair, and a positively charged C has none.**



1.28 Draw each indicated structure. Recall that in the skeletal drawings, a carbon atom is located at the intersection of any two lines and at the end of any line.

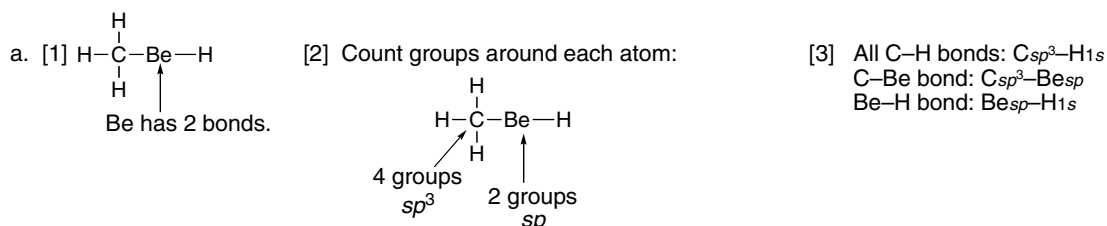


1.29 To determine the orbitals used in bonding, **count the number of groups** (atoms + lone pairs):
4 groups = sp^3 , 3 groups = sp^2 , 2 groups = sp , H atom = $1s$ (no hybridization).
All covalent single bonds are σ , and all double bonds contain one σ and one π bond.

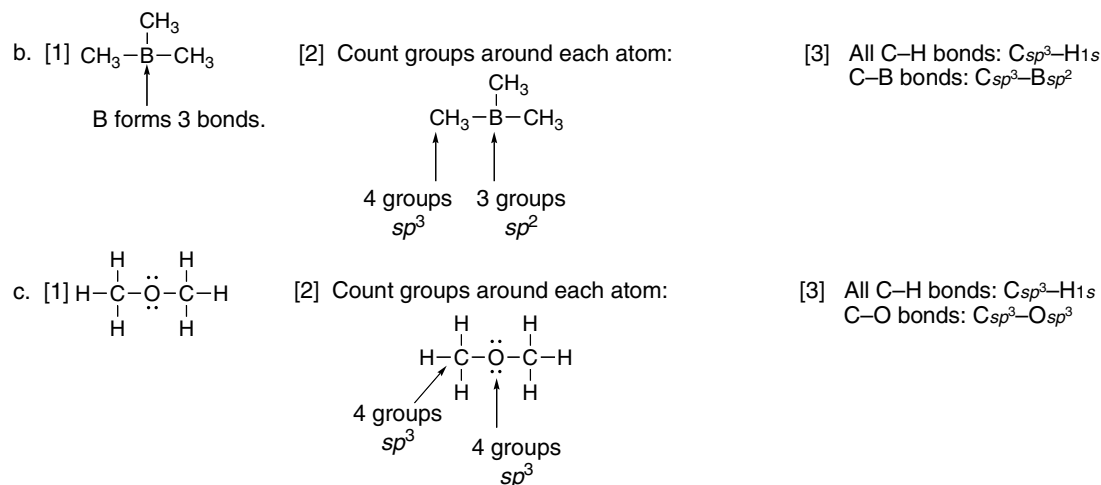


1.30 [1] Draw a valid Lewis structure for each molecule.
[2] **Count the number of groups** around each atom: 4 groups = sp^3 , 3 groups = sp^2 , 2 groups = sp ,
H atom = $1s$ (no hybridization).

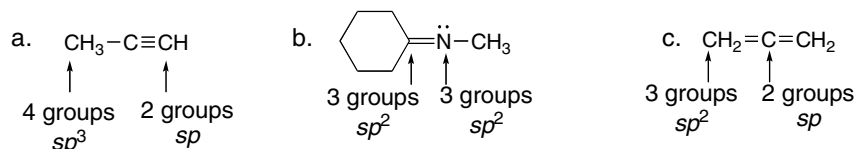
Note: **Be and B** (Groups 2A and 3A) do not have enough valence e^- to form an octet, **and do not form an octet in neutral molecules.**



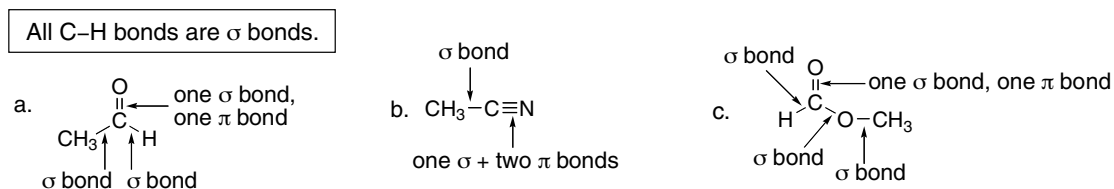
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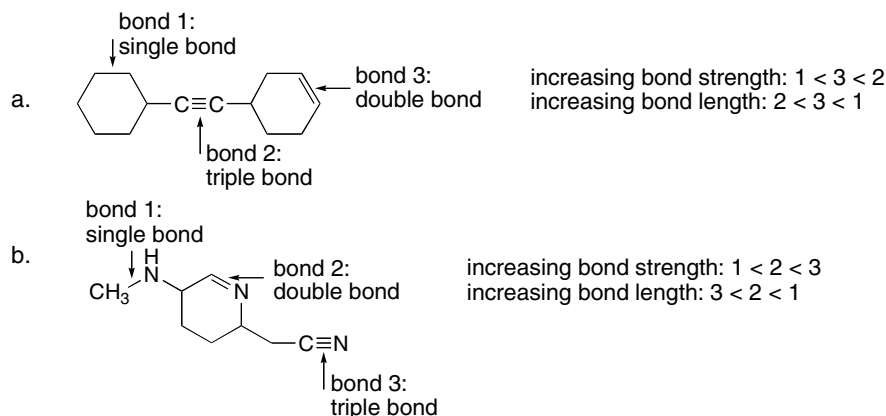
1.31 To determine the hybridization, **count the number of groups** around each atom: 4 groups = sp^3 , 3 groups = sp^2 , 2 groups = sp , H atom = $1s$ (no hybridization).



1.32 All single bonds are σ . Multiple bonds contain one σ bond, and all others are π bonds.

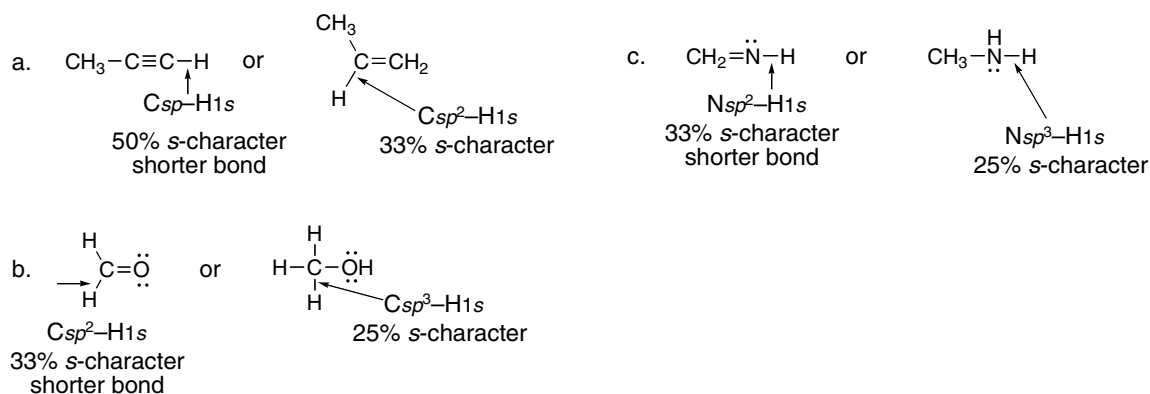


1.33 Bond length and bond strength are inversely related: **longer bonds are weaker bonds**. Single bonds are weaker and longer than double bonds, which are weaker and longer than triple bonds.

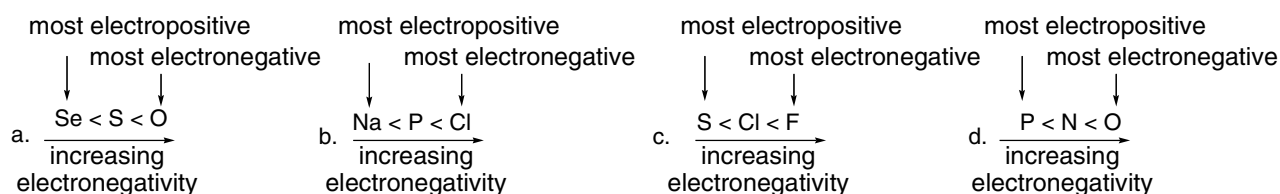


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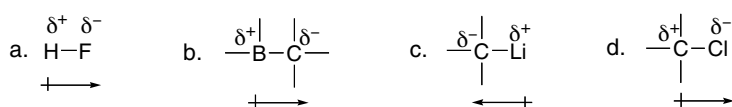
1.34 Bond length and bond strength are inversely related: **longer bonds are weaker bonds**. Single bonds are weaker and longer than double bonds, which are weaker and longer than triple bonds. Increasing percent *s*-character increases bond strength and decreases bond length.



1.35 Electronegativity increases across a row of the periodic table and decreases down a column. Look at the relative position of the atoms to determine their relative electronegativity.

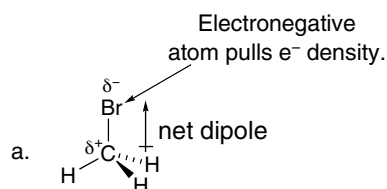


1.36 Dipoles result from unequal sharing of electrons in covalent bonds. More electronegative atoms “pull” electron density towards them, making a dipole. **Dipole arrows point towards the atom of higher electron density.**

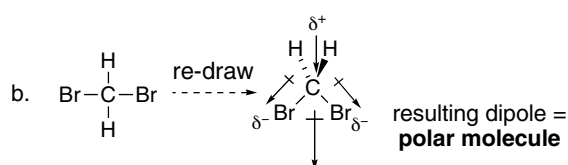


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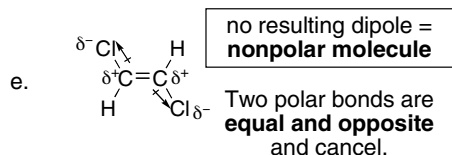
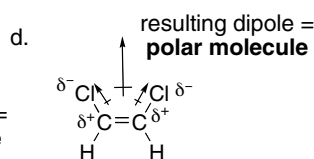
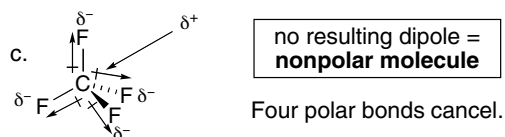
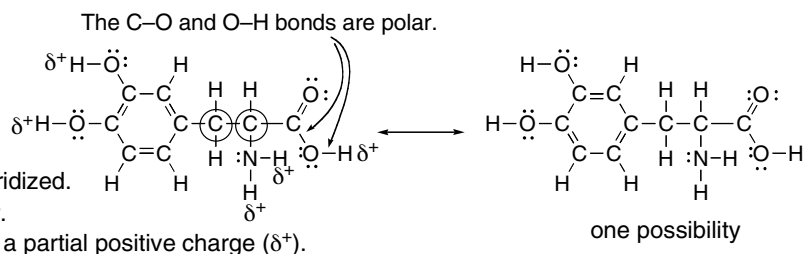
1.37 Polar molecules result from a net dipole. To determine polarity, draw the molecule in three dimensions around any polar bonds, draw in the dipoles, and look to see whether the dipoles cancel or reinforce.



All C–H bonds have no dipole.
one polar bond
net dipole = **polar molecule**



Note: You must draw the molecule in three dimensions to observe the net dipole. In the Lewis structure, it appears the dipoles would cancel out, when in fact they add to make a polar molecule.

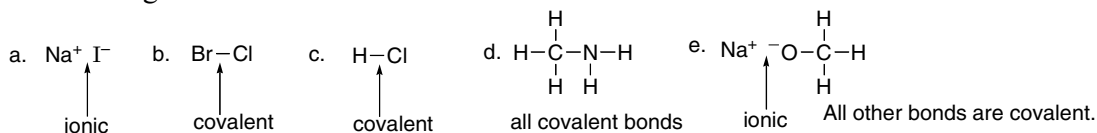
**1.38**

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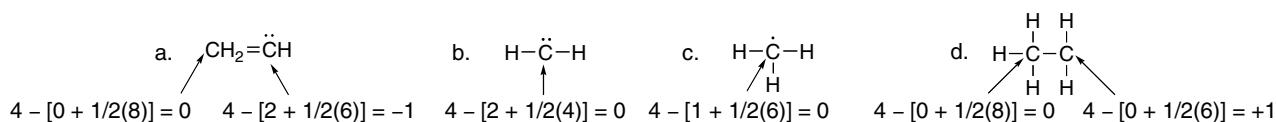
1.39 Use the definitions in Answer 1.1.

	Iodine-123	Iodine-131
a. number of protons = atomic number for I = 53	53	53
b. number of neutrons = mass number – atomic number	70	78
c. number of electrons = number of protons	53	53
d. The group number is the same for all isotopes.	7A	7A

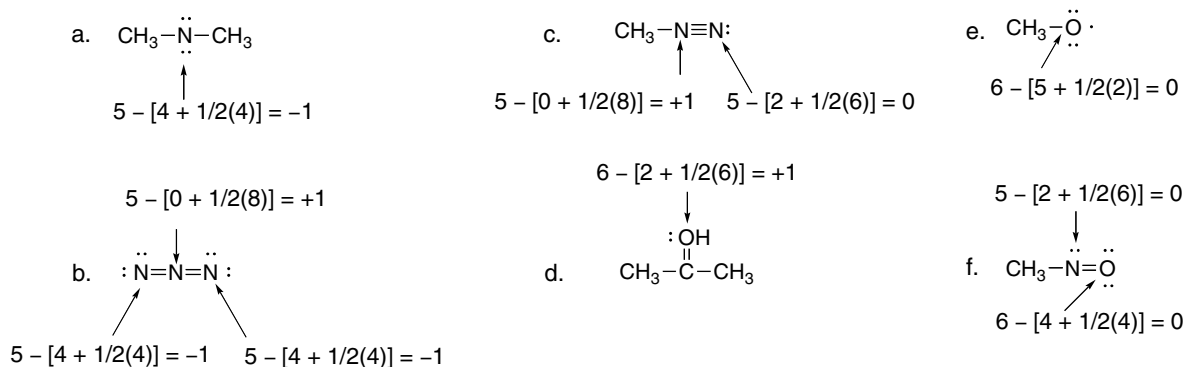
1.40 Use bonding rules in Answer 1.3.



1.41 **Formal charge (FC)** = number of valence electrons – [number of unshared electrons + 1/2 (number of shared electrons)]. C is in group 4A.

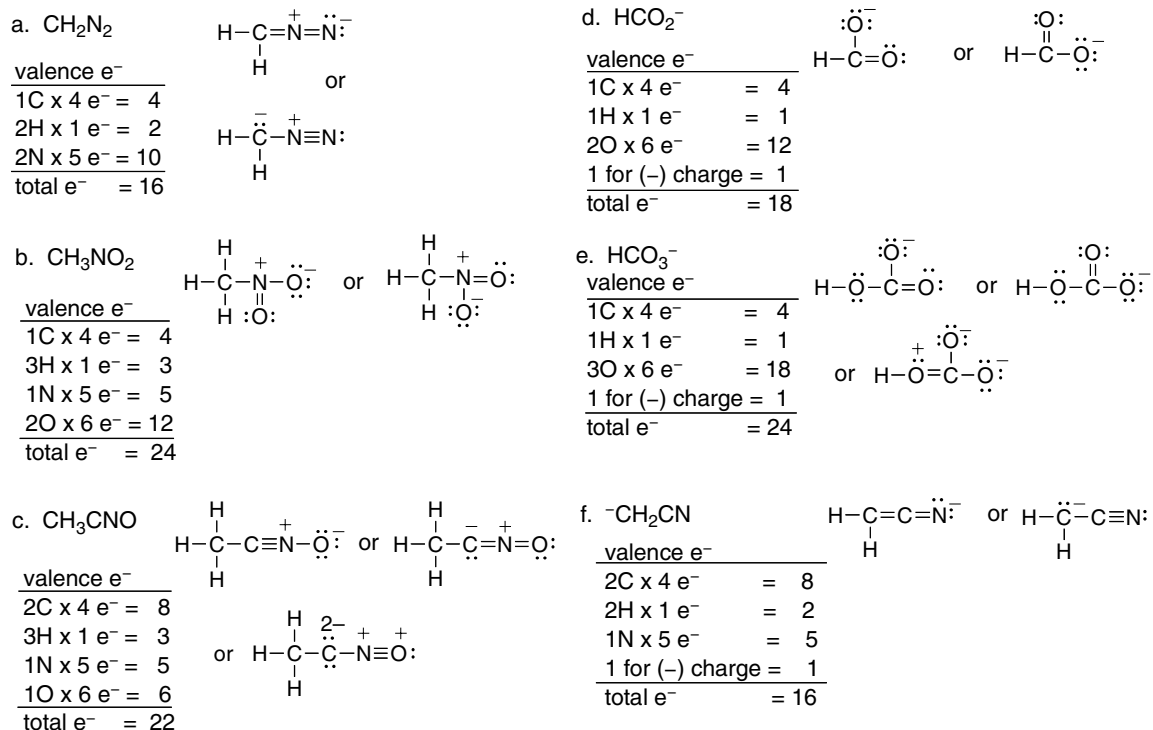


1.42 **Formal charge (FC)** = number of valence electrons – [number of unshared electrons + 1/2 (number of shared electrons)]. N is in group 5A and O is in group 6A.

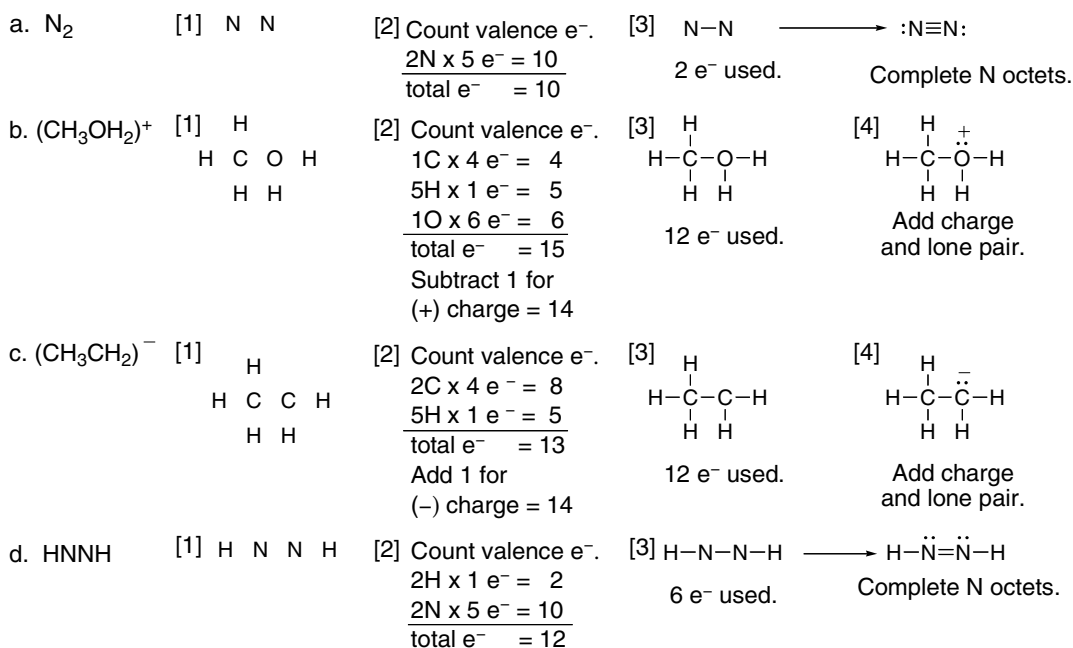


Chapter 1-18

1.43 Follow the steps in Answer 1.6 to draw Lewis structures.



1.44 Follow the steps in Answer 1.6 to draw Lewis structures.



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