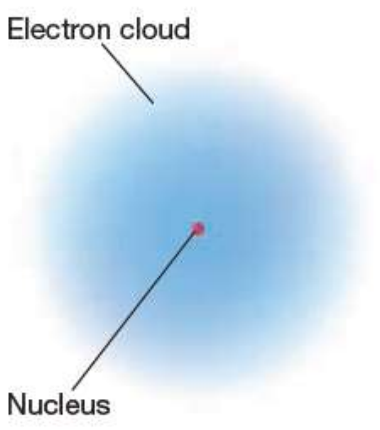
Chapter 1
The Basics
Bonding and Molecular Structure

- **Organic chemistry**: *is the chemistry of compounds that contain the element carbon*.

1.1 Atomic Structure

- **Compounds:** are made up of **elements** combined in different proportions.
- **Elements:** are made up of **atoms** of same type.
- **An atom:** consists of a dense, positively charged *nucleus* containing **protons** and **neutrons** and a surrounding cloud of **electrons**.
- **Atomic number** (*Z*): is a number equal to the number of protons in its nucleus.
- **Valence shell:** is the outermost energy level of an atom.
  - The most important shell **because** the electrons of this shell are the ones that an atom uses in making chemical bonds with other atoms to form compounds.
  - **Valence electrons:** are the number of electrons in the valence shell.
    - Number of valence electrons equal to the group number of the atom.

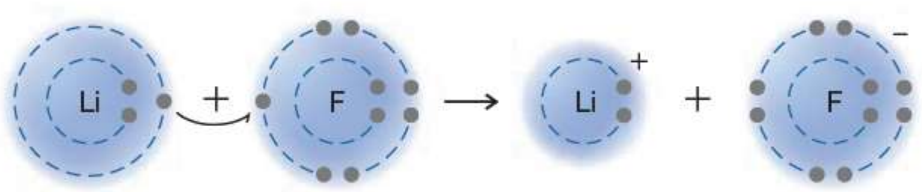


1.2 Chemical Bonds: The Octet Rule

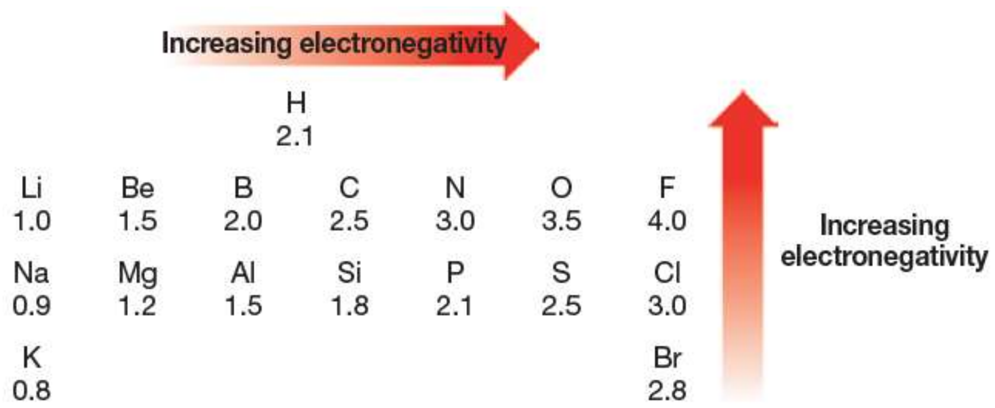
- Atoms work on bonding to achieve noble gas electronic configuration **because** these configurations are known to be highly stable.
- **Octet rule:** is the tendency for an atom to achieve a configuration where its valence shell contains eight electrons.
- Two major types of chemical bonds were proposed:
  1. **Ionic bonds:** are formed by the transfer of one or more electrons from one atom to another to create ions.
  2. **Covalent bonds:** result when atoms share electrons.

1.2A Ionic Bonds

- Atoms may gain or lose electrons and form charged particles called **ions**.
  - Ions form **because** atoms can achieve the electronic configuration of a noble gas by gaining or losing electrons.
- An **ionic bond**: is an attractive force between oppositely charged ions.
- **For example:** the reaction of lithium and fluorine atoms:
  - The lithium atom leaves a lithium cation (Li^{+}); the gain of an electron by the fluorine atom gives a fluoride anion (F^{-}).



- **Electronegativity**: is a measure of the ability of an atom to attract electrons.
  - Electronegativity ***increases*** as we go across a horizontal row of the periodic table from left to right and it ***increases*** as we go up a vertical column



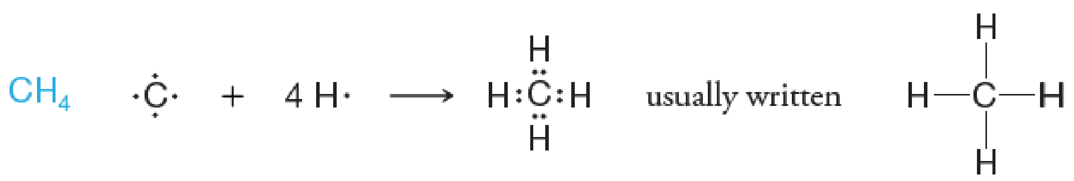
1.2B Covalent Bonds and Lewis Structures

- **Covalent bonds:** form by sharing of electrons between atoms of similar electronegativities to achieve the configuration of a noble gas.
- **Molecules** are composed of atoms joined exclusively or predominantly by covalent bonds.
  - Molecules may be represented by electron-dot formulas or by formulas where each pair of electrons shared by two atoms is represented by a line.
  - A **dash structural formula** has lines that show bonding electron pairs and includes elemental symbols for the atoms in a molecule.
- **Examples:**

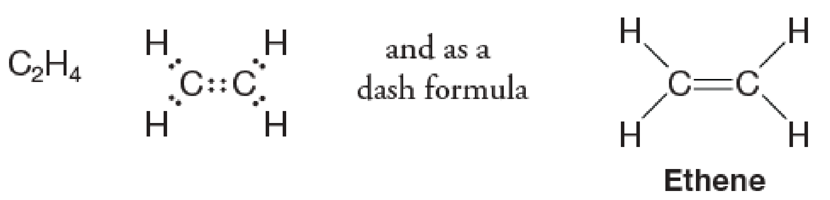
1. Hydrogen molecule (H_2)

2. Chlorine molecule (Cl_2)

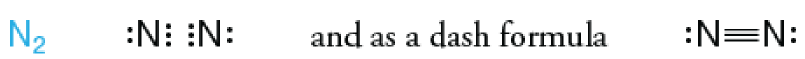
3. Methane molecule (CH_4)



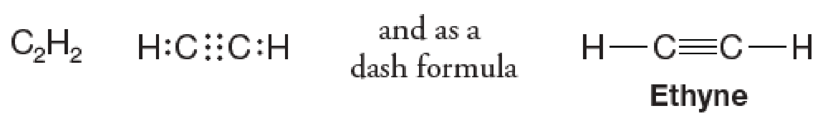
4. Ethene molecule (C_2H_4)



5. Nitrogen molecule (N_2)



6. Ethyne molecule (C_2H_2)

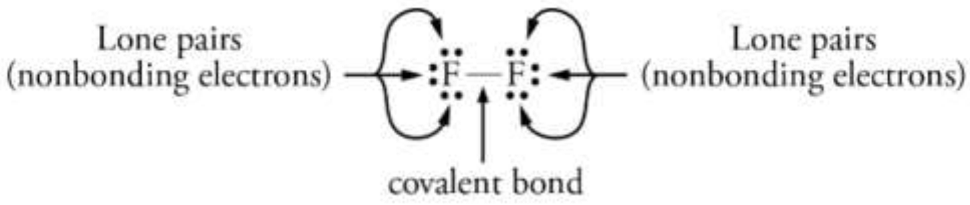


1.3 Lewis Structures

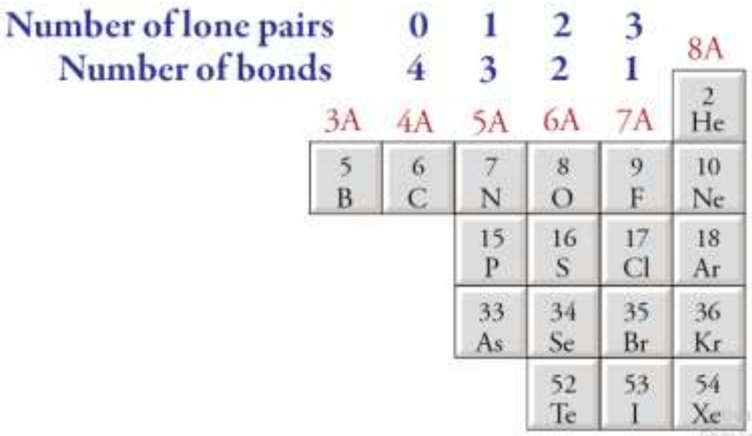
➢ **Lewis structures**: *are electron dot representations for molecules*.

A Procedure for Drawing Lewis Structures

1. Determine the total number of valence electrons in the structure.
   - *For a **negative ion**, add one electron for each negative charge*
   - *For a **positive ion**, subtract one electron for each positive charge.*
2. Identify the ***central*** atom (the atom with the lowest EN) and ***terminal*** atoms.
   - *Hydrogen atoms are always terminal atoms.*
   - *Carbon atoms are always central atoms.*
3. Write the ***skeleton*** structure, and join the atoms in this structure by *single* covalent bonds.
4. For each single bond in the skeletal structure, subtract ***two*** from the total number of valence electrons.
   - With the valence electrons remaining,
     - ***First*** complete the octets of the terminal atoms.
     - ***Then***, to the extent possible, complete the octets of the central atom(s).
     - At this point, if the central atom lacks an octet, form *multiple* covalent bonds by converting unshared (lone pair) electrons from terminal atoms into bond pairs.

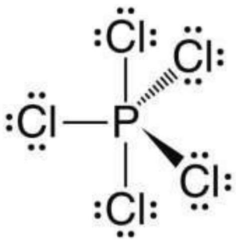
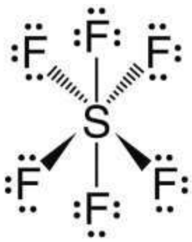


Most Common Bonding Patterns for Nonmetals

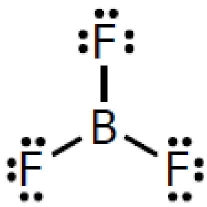


1.3A Exceptions to the Octet Rule

1. Expanded Octet: Elements in the 3rd row in the periodic table have d orbitals that can be used for bonding and may not obey the Octet Rule.

2. Incomplete Octet: Some highly reactive molecules or ions have atoms with fewer than eight electrons in their outer shell



1.4 Formal Charge

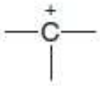
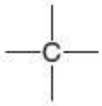
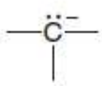
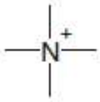
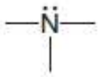
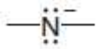
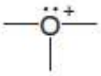
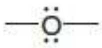
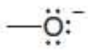
- **Formal charge:** *is the charge assigned to individual atoms in a Lewis structure.*
  - By calculating formal charge, we determine how the number of electrons around a particular atom compares to its number of valence electrons.
  - Formal charge is calculated as follows:

Formal charge = [no. of valence electrons] – [electrons in lone pairs + 1/2 the number of bonding electrons]

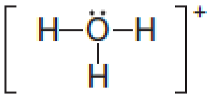
F.C. = (Valence electrons) – (non-bonding electrons) – (1/2 (bonding electrons))

F.C. = (Valence electrons) – (non-bonding electrons) – (no. of bonds)

Formal Charge Observed with Common Bonding Patterns for C, N, and O

Atom	Number of valence electrons	Formal charge +1	Formal charge 0	Formal charge –1
C	4			
N	5			
O	6			

Sample Problem 1.1 Determine the formal charge on each atom in the ion H_3O^+.



Solution

For each atom, two steps are needed:

Step [1] Determine the number of electrons an atom "owns."

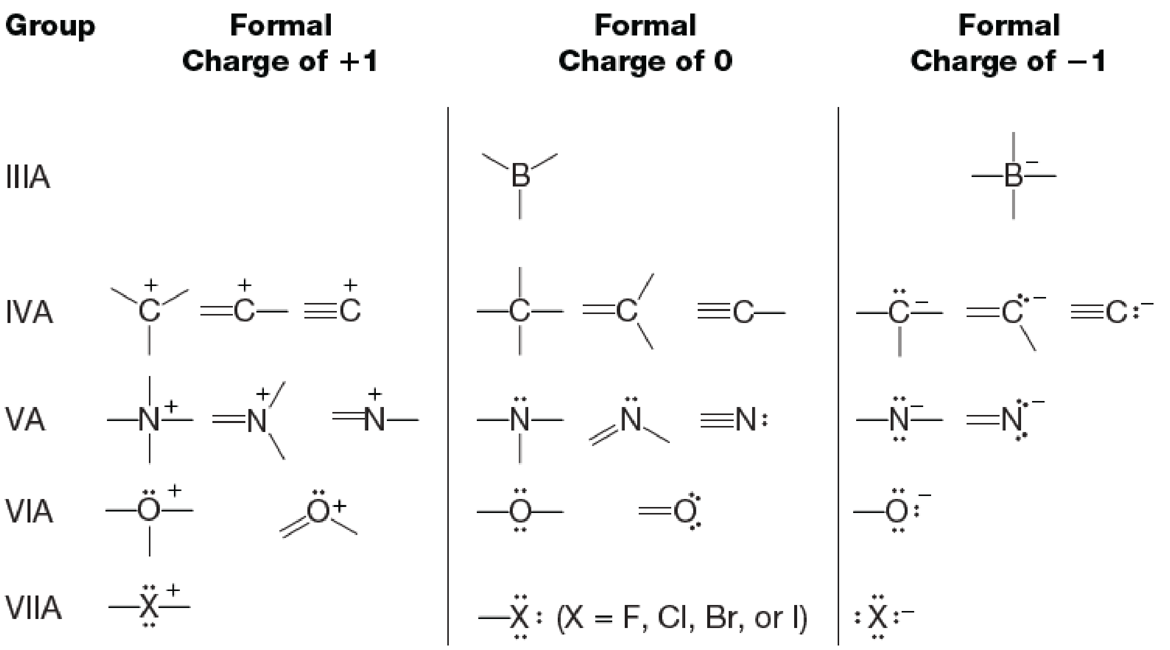
Step [2] Subtract this sum from its number of valence electrons.

O atom	H atoms
[1] number of electron s "owned" by O 2 + 1/2 (6) = 5 **[2]** formal charge on O 6 − 5 = **+1**	**[1]** number of electrons "owned" by each H 0 + 1/2 (2) = 1 **[2]** formal charge on each H 1 − 1 = **0**

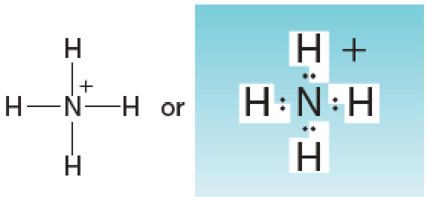
General rules to determine the plausibility of a Lewis structure based on its formal charge.

1. The sum of the formal charges in a Lewis structure must equal zero for a neutral molecule and must equal the magnitude of the charge for an ion.
2. Where formal charges are required, they should be as small as possible.
3. Negative formal charges usually appear on the most EN atoms; positive formal charges, on the least EN atoms.

TABLE 1.2 A SUMMARY OF FORMAL CHARGES



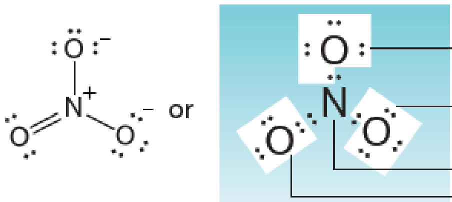
Ammonium Ion



For hydrogen:	valence electrons of free atom	=	1
	subtract assigned electrons	=	−1
	Formal charge on each hydrogen	=	0
For nitrogen:	valence electrons of free atom	=	5
	subtract assigned electrons	=	$-(^1/_2)8$
	Formal charge on nitrogen	=	+1

Overall charge on ion = 4(0) + 1 = +1

Nitrate Ion



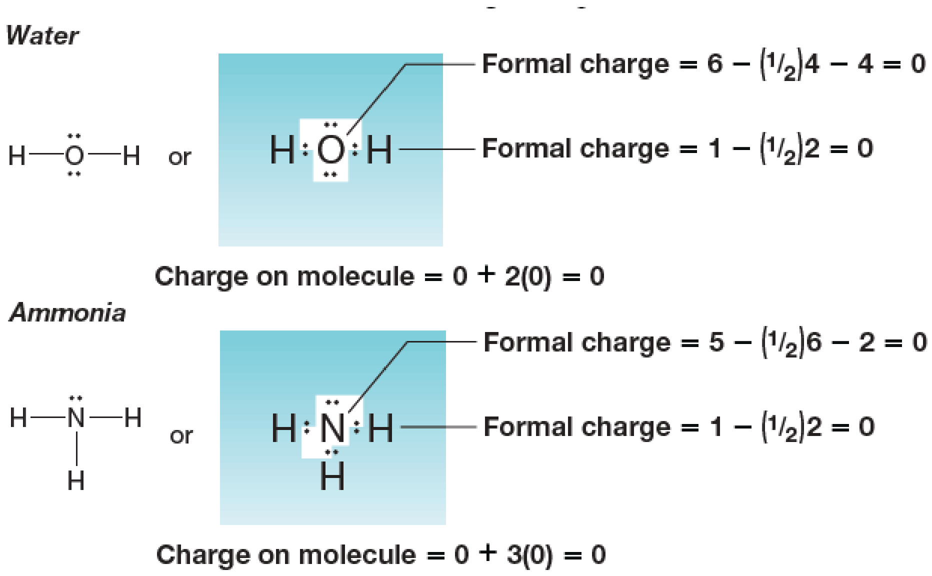
Formal charge = $6 - (^1/_2)2 - 6 = -1$

Formal charge = $6 - (^1/_2)2 - 6 = -1$

Formal charge = $5 - (^1/_2)8 = +1$

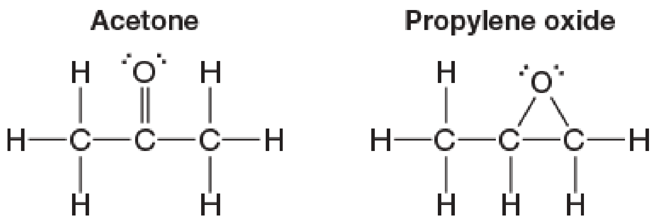
Formal charge = $6 - (^1/_2)4 - 4 = 0$

Charge on ion = 2(−1) + 1 + 0 = −1

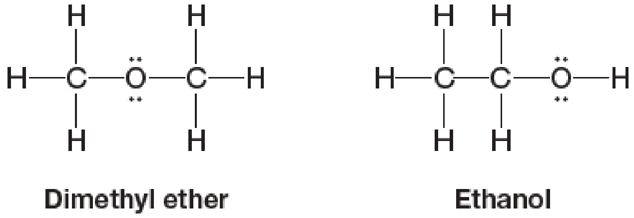


1.5 Isomers

- **Isomers:** are compounds that have the same *molecular formula* but different structures.
- **Constitutional isomers:** are different compounds that have the same molecular formula but differ in the sequence in which their atoms are bonded.
  - Constitutional isomers usually have different *physical properties* (e.g., melting point, boiling point, and density) and different *chemical properties* (reactivity).
  - **Examples:**
    - Acetone and propylene oxide



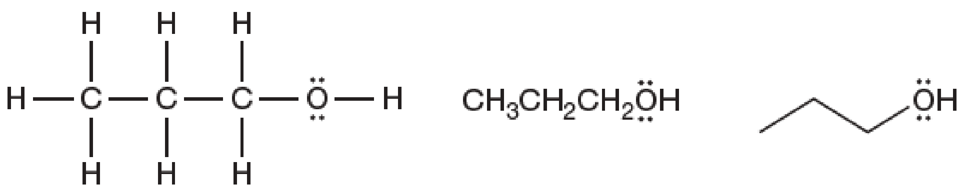
    - Ethanol and dimethyl ether.



1.6 How to Write and Interpret Structural Formulas

➢ Two other important types of formulas are ***condensed formulas*** and ***bond-line formulas*** or ***skeletal formulas***.

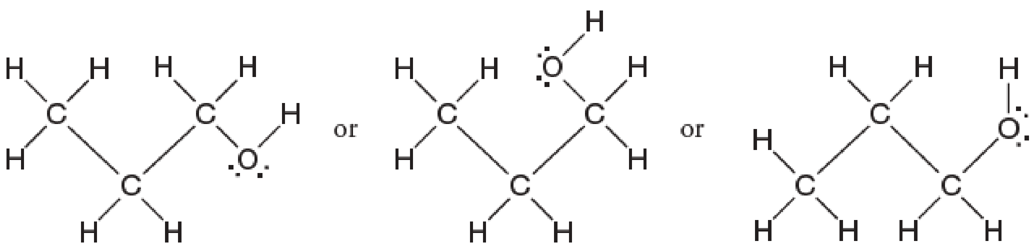
Ball-and-stick model (*a*) Electron-dot formula (*b*)



Dash formula (*c*) Condensed formula (*d*) Bond-line formula (*e*)

1.6A Dash Structural Formulas

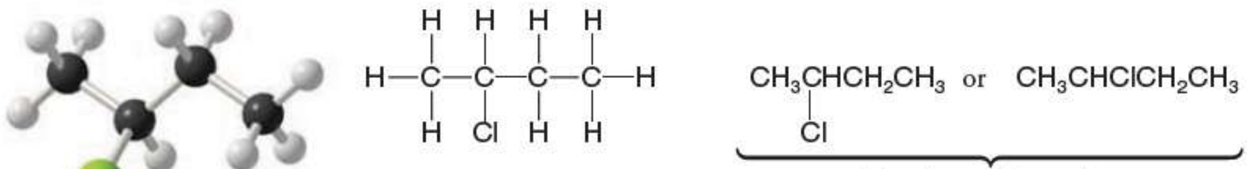
➢ **Dash structural formulas:** have lines that show bonding electron pairs, and include elemental symbols for all of the atoms in a molecule.



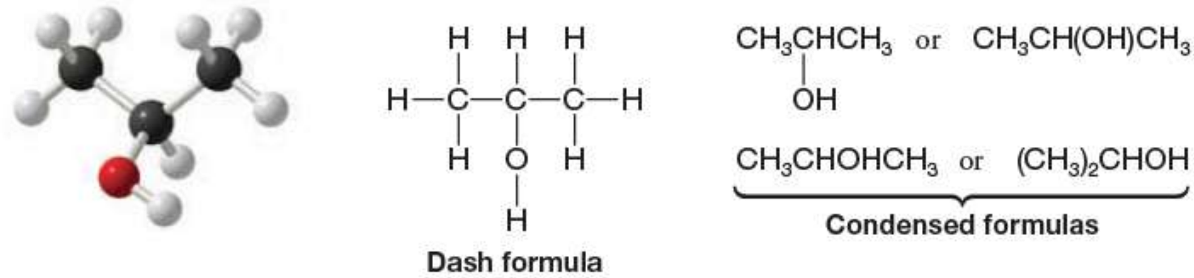
Equivalent dash formulas for propyl alcohol

1.6B Condensed Structural Formulas

➢ In fully condensed formulas, all of the atoms that are attached to the carbon are usually written immediately after that carbon, listing hydrogens first.



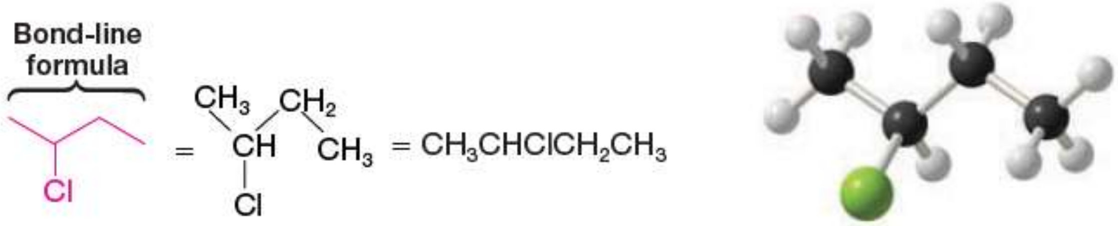
Dash formula **Condensed formulas**

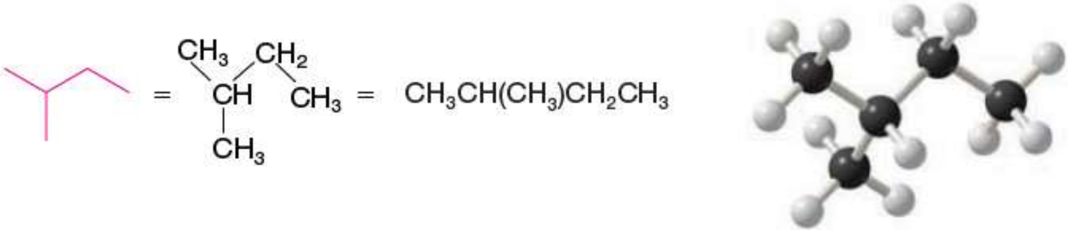


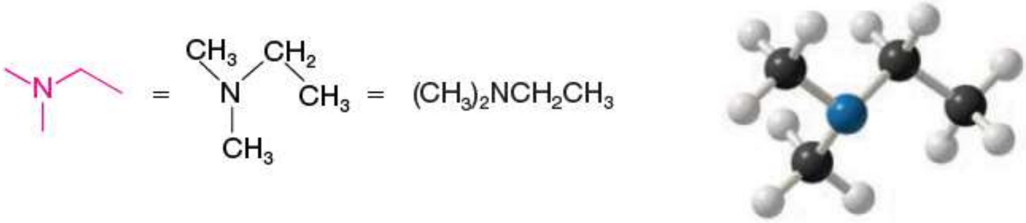
1.6C Bond-Line Formulas

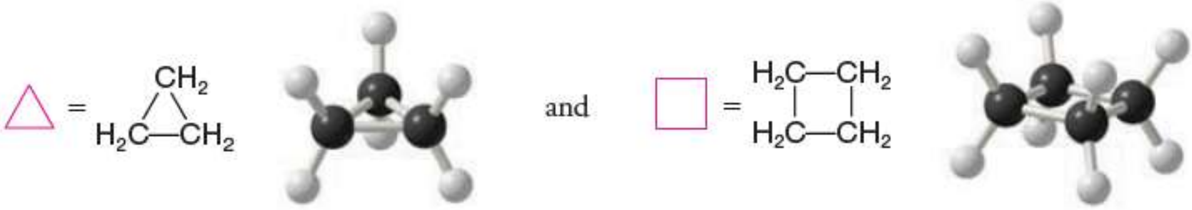
The rules for drawing bond-line formulas:

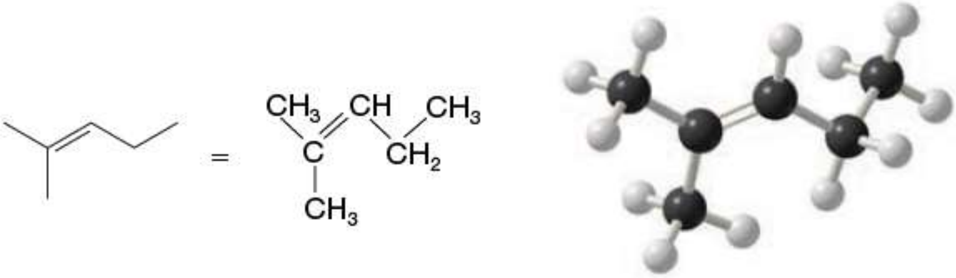
1. Each line represents a bond.
2. Each **bend** in a line or **terminus** of a line represents a carbon atom, unless another group is shown explicitly.
3. No **Cs** are written for carbon atoms, except optionally for CH_3 groups at the end of a chain or branch.
4. No **Hs** are shown for hydrogen atoms, unless they are needed to give a three-dimensional perspective, in which case we use dashed or solid wedges.
5. The number of hydrogen atoms bonded to each carbon is inferred by assuming that as many hydrogen atoms are present as needed to fill the valence shell of the carbon, unless a charge is indicated.
6. When an atom other than carbon or hydrogen is present, the symbol for that element is written at the appropriate location (i.e., in place of a bend or at the terminus of the line leading to the atom).
7. Hydrogen atoms bonded to atoms other than carbon (e.g., oxygen or nitrogen) are written explicitly.

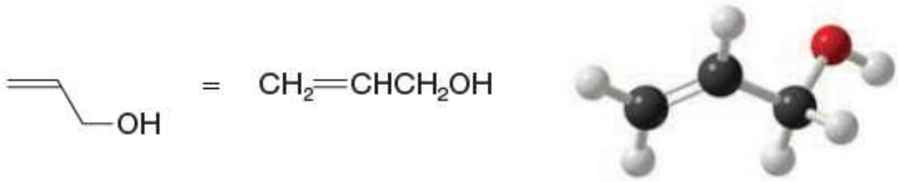


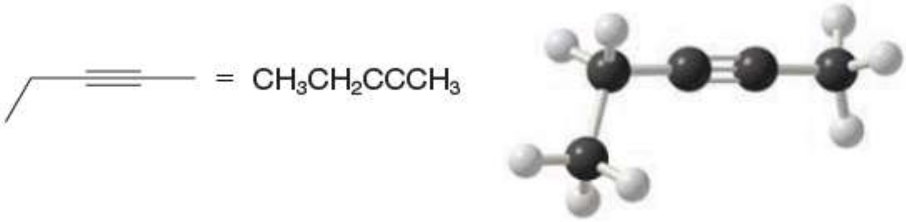

=
$CH_3CH(CH_3)CH_2CH_3$


=
$(CH_3)_2NCH_2CH_3$


and



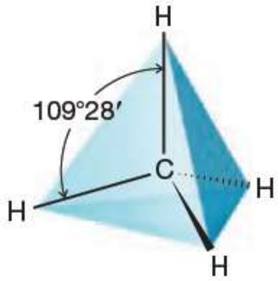

=
$CH_2{=}CHCH_2OH$


=
$CH_3CH_2CCCH_3$

1.7D Three-Dimensional Formulas

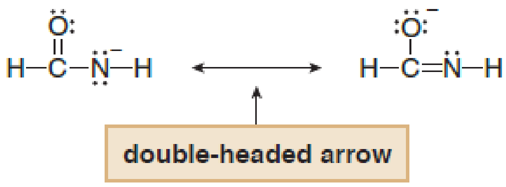
- Molecules exist in three dimensions.
- We can depict three-dimensional geometry in molecules using bonds represented by dashed wedges, solid wedges, and lines.
  1. A **dashed wedge** ( ) represents a bond that projects behind the plane of the paper.
  2. A **solid wedge** ( ) represents a bond that projects out of the plane of the paper.
  3. An **ordinary line** (——) represents a bond that lies in the plane of the paper.


Methane



1.7 Resonance Theory

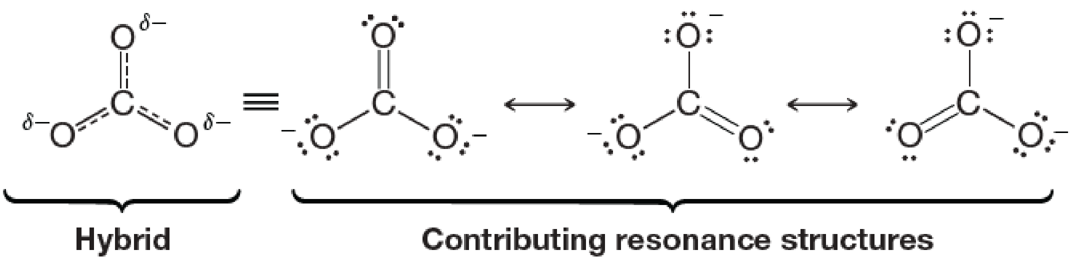
- **Resonance theory:** states that whenever a molecule or ion can be represented by two or more Lewis structures *that differ only in the positions of the electrons*
  - **For example:** two valid Lewis structures can be drawn for the anion $(HCONH)^{-}$.
    - One structure has a negatively charged N atom and a C – O double bond; the other has a negatively charged O atom and a C – N double bond.



    - The true structure is a composite of both resonance forms, and is called a **resonance hybrid**.
    - The hybrid shows characteristics of **both** resonance structures.
- Each resonance structure implies that electron pairs are localized in bonds or on atoms.

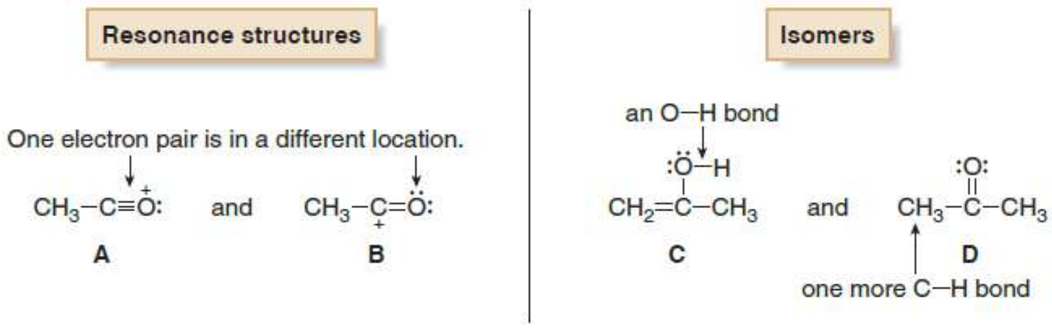
- In actuality, resonance allows certain electron pairs to be *delocalized* over two or more atoms, and this delocalization of electron density adds stability.

➢ A molecule with two or more resonance structures is said to be ***resonance stabilized***.



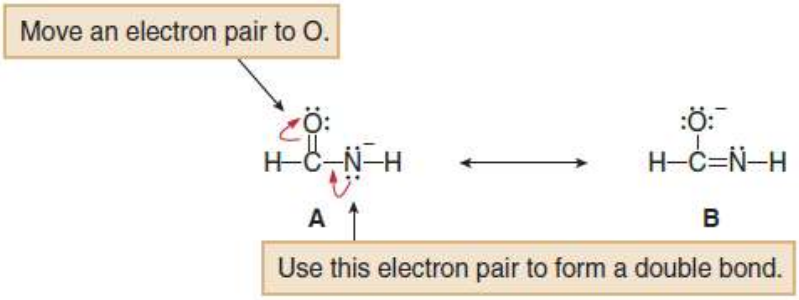
The basic principles of resonance theory:

1. Resonance structures are **not real**.
   - An individual resonance structure does not accurately represent the structure of a molecule or ion. Only the hybrid does.
2. Resonance structures are **not in equilibrium** with each other.
   - There is no movement of electrons from one form to another.
3. Resonance structures are **not isomers**.
   - Two isomers differ in the arrangement of both atoms and electrons, whereas resonance structures differ only in the arrangement of electrons.



1.7A The Use of Curved Arrows

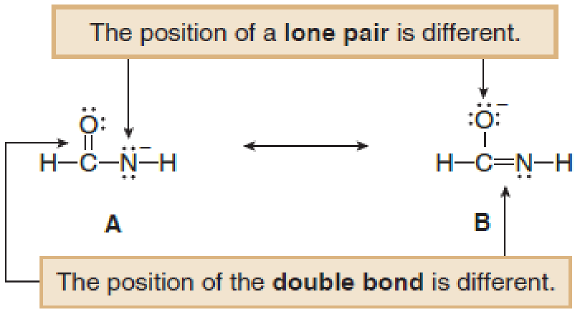
➢ **Curved arrow notation**: *is a convention that shows how electron position differs between the two resonance forms*.
   - Curved arrow notation shows the movement of an electron pair.
     - The tail of the arrow always begins at an electron pair, either in a bond or lone pair.
     - The head points to where the electron pair "moves."



1.7B Rules for Writing Resonance Structures

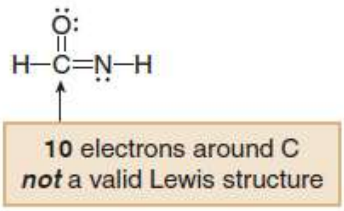
➢ To draw resonance structures, use the three rules that follow:

Rule [1] Two resonance structures differ in the position of multiple bonds and non-bonded electrons. The placement of atoms and single bonds always stays the same.



Rule [2] Two resonance structures must have the same number of unpaired electrons.

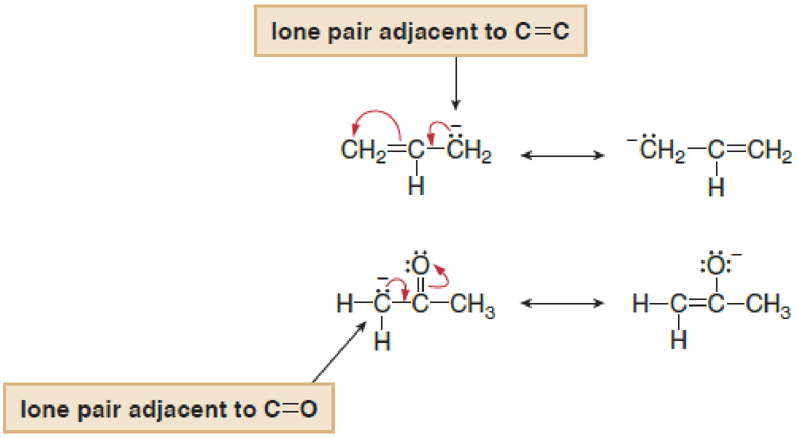
Rule [3] Resonance structures must be valid Lewis structures. Hydrogen must have two electrons and no second-row element can have more than eight electrons.



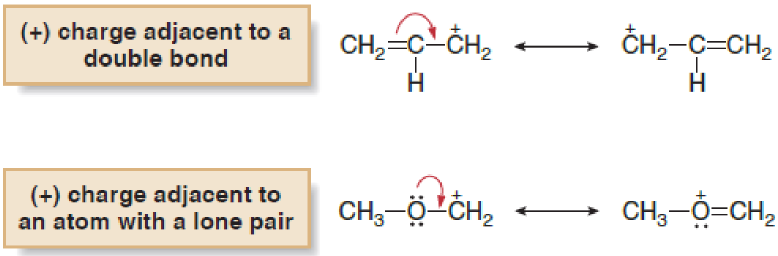
Note

➢ Two different resonance structures can be drawn in the following situations:

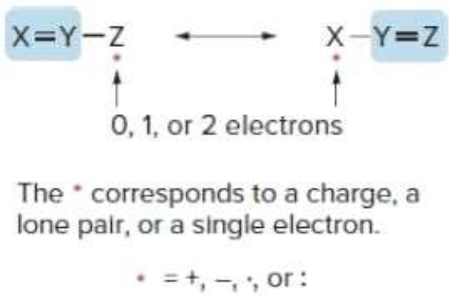
1. When a lone pair is located on an atom directly bonded to a multiple bond.



2. When an atom bearing a (+) charge is bonded to either a multiple bond or an atom with a lone pair.

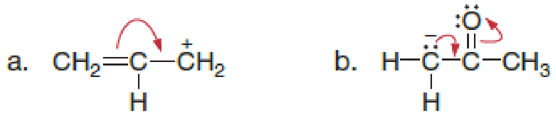


- In a group of three atoms having a multiple bond **X=Y** joined to an atom **Z** having a *p* orbital with zero, one, or two electrons, two resonance structures can be drawn.



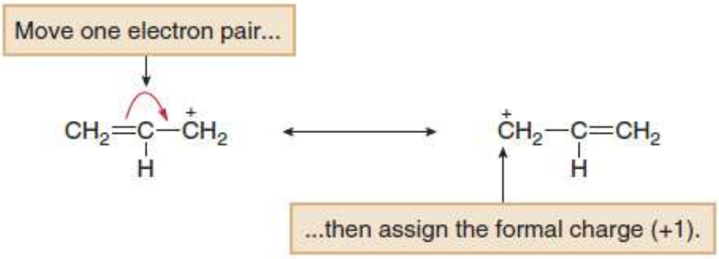
- **The more** stable a structure is (when taken by itself), **the greater** is its contribution to the hybrid.

Sample Problem 1.2 Follow the curved arrows to draw a second resonance structure for each ion.



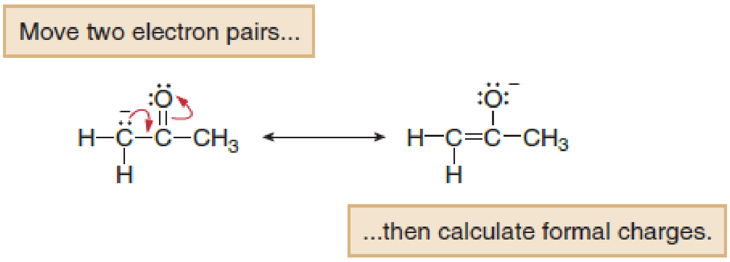
Solution

a. The curved arrow tells us to move **one** electron pair in the double bond to the adjacent C – C bond. Then determine the formal charge on any atom whose bonding is different.



- Positively charged carbon atoms are called **carbocations**.
- **Carbocations** are *unstable intermediates* **<u>because</u>** they contain a carbon atom that is lacking an octet of electrons.

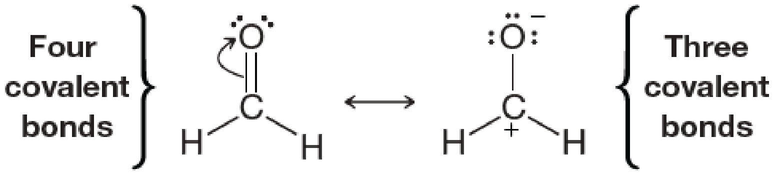
b. **Two** curved arrows tell us to move **two** electron pairs. The second resonance structure has a formal charge of (–1) on O.



- This type of resonance-stabilized anion is called an **enolate anion**.

1.7C How to Decide When One Resonance Structure Contributes More to the Hybrid Than Another

1. The more covalent bonds a structure has, the more stable it is.



A B

More stable Less stable

Resonance structures for formaldehyde

2. Charge separation decreases stability.

- It takes energy to separate opposite charges, and therefore a structure with separated charges is less stable.
- Structure **B** for formaldehyde has separated plus and minus charges; therefore, it is the less stable contributor and makes a smaller contribution to the hybrid.

3. Structures in which all the atoms have a complete valence shell of electrons (i.e., the noble gas structure) are more stable.

- The carbon atom in structure **B** has only six electrons around it, whereas in **A** it has eight, therefore **A** is more stable and makes a larger contribution.