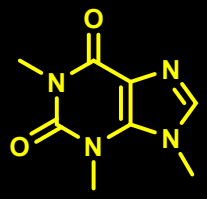
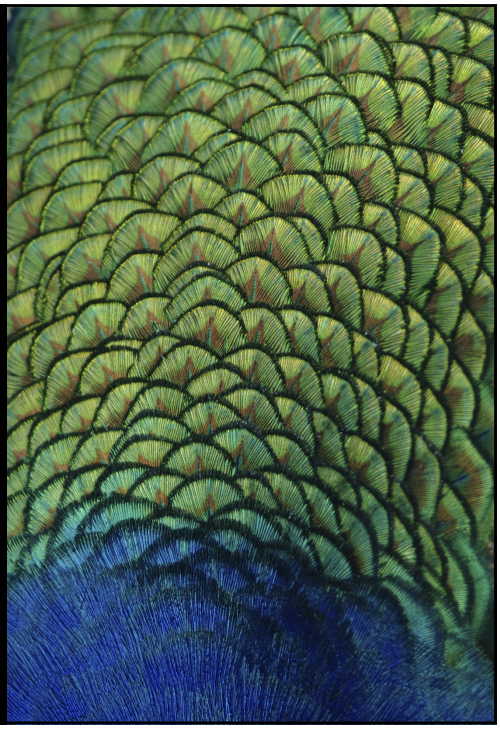
Chem 130, Elementary Organic Chemistry





CHAPTER ONE

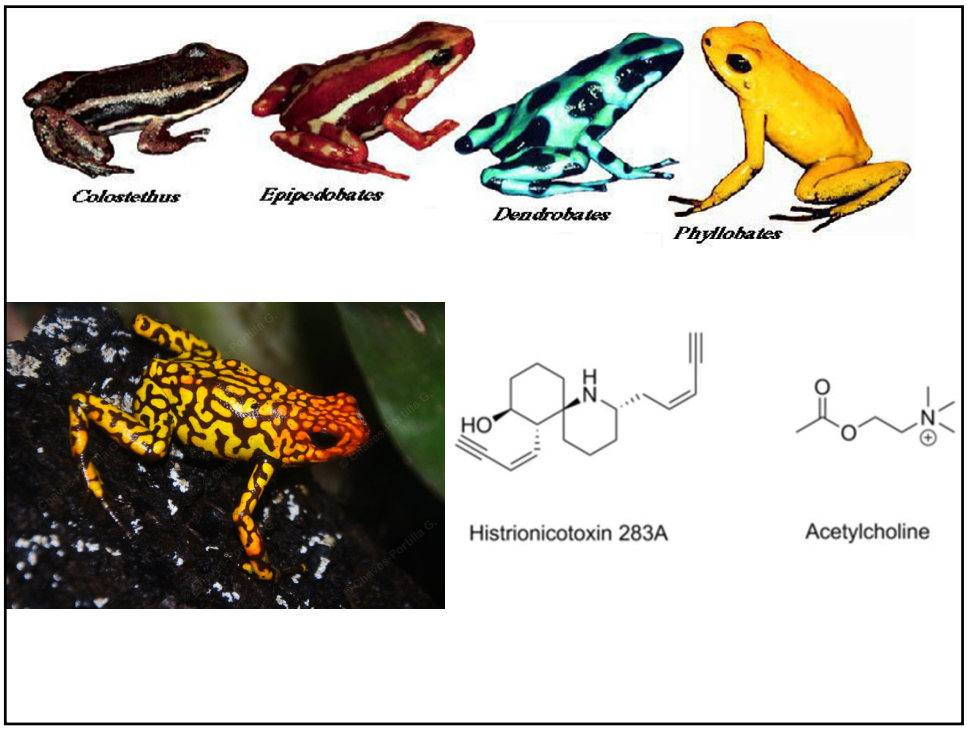
Covalent Bonding and Shapes of Molecules

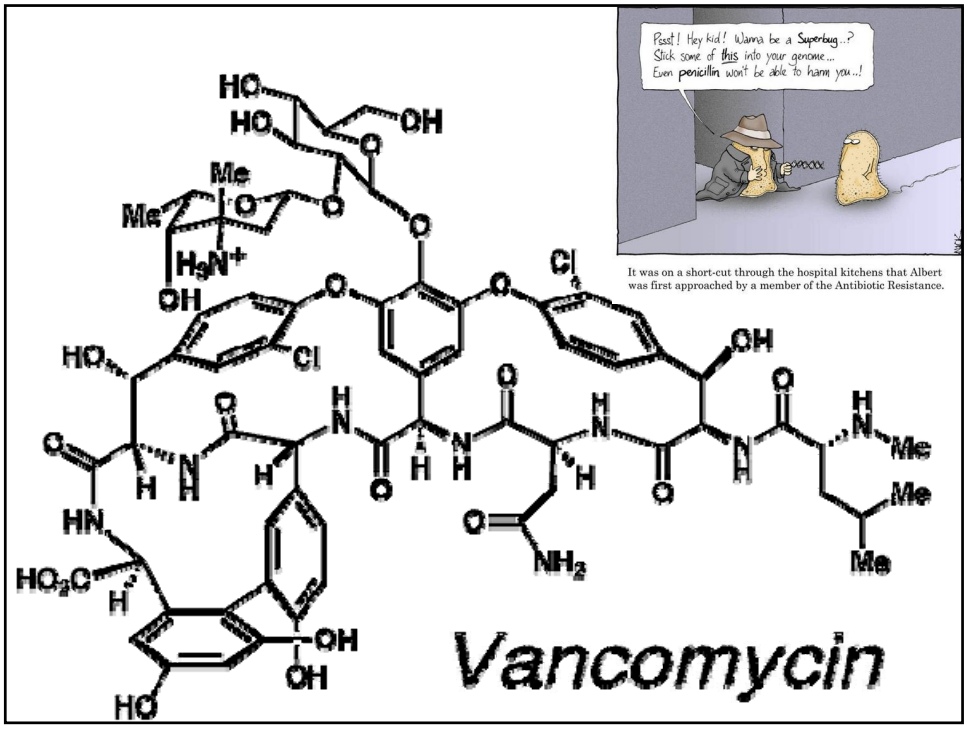
Table of Contents

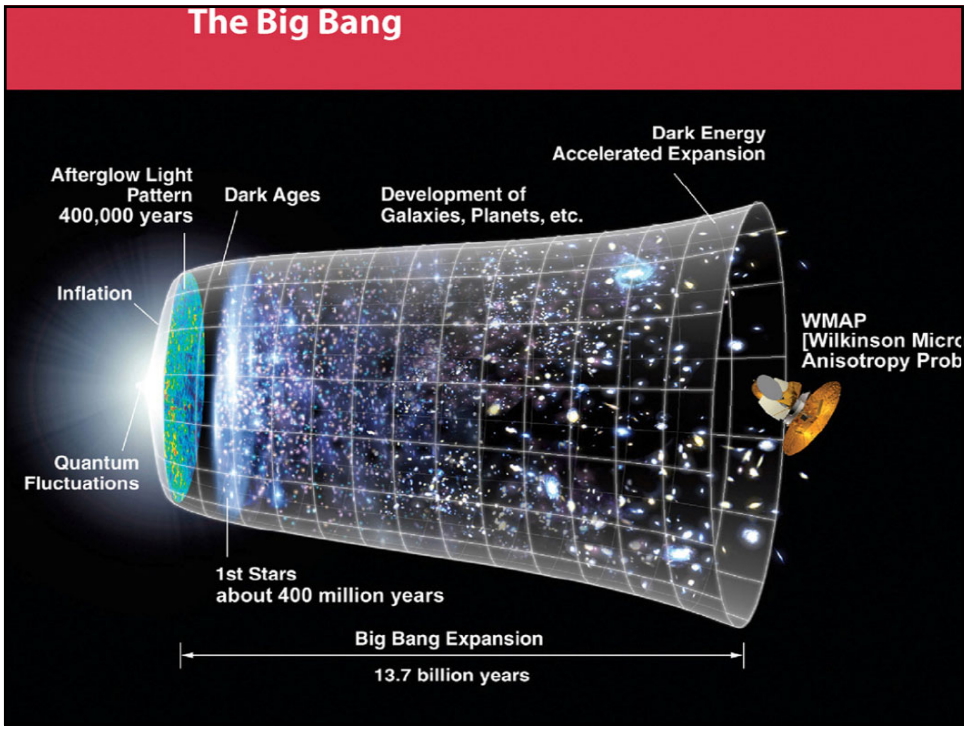

HN
Me
Breaking
Bad


Ph
N
O
HN
OH


Ph
N
O
HN
OH
HO
H_2N
LEGO


Colostethus
Epipedobates
Dendrobates
Phyllobates
Histrionicotoxin 283A
Acetylcholine


Psst! Hey kid! Wanna be a Superbug..? Stick some of this into your genome... Even penicillin won't be able to harm you..!
It was on a short-cut through the hospital kitchens that Albert was first approached by a member of the Antibiotic Resistance.
Vancomycin

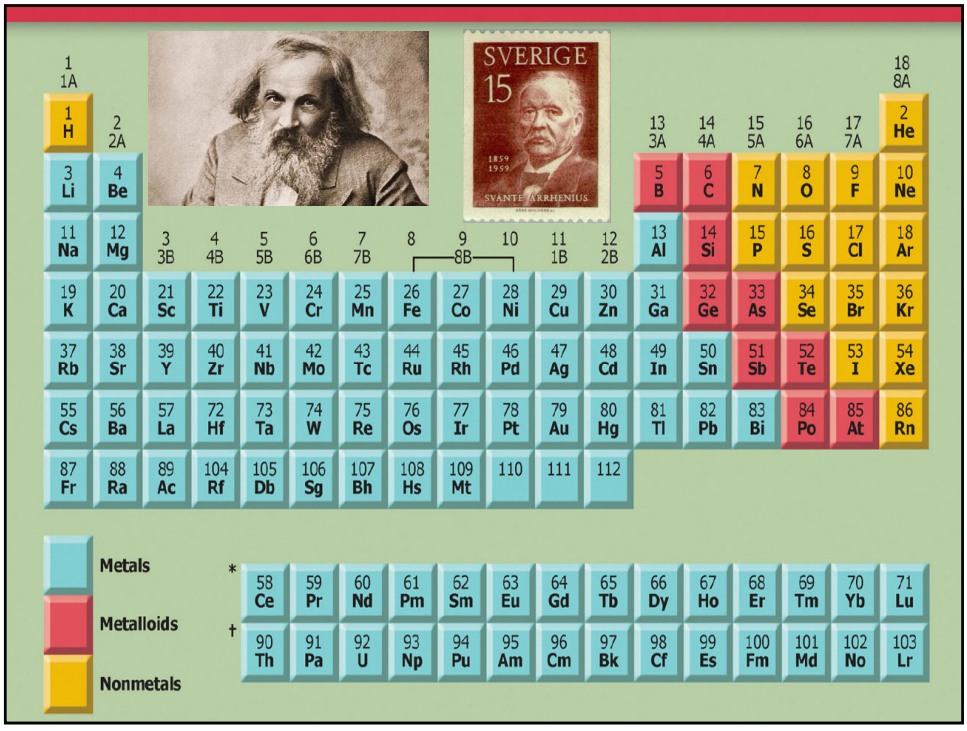

The Big Bang
Afterglow Light Pattern 400,000 years
Dark Ages
Development of Galaxies, Planets, etc.
Dark Energy Accelerated Expansion
Inflation
Quantum Fluctuations
1st Stars about 400 million years
Big Bang Expansion
13.7 billion years
WMAP
[Wilkinson Micro
Anisotropy Prob

Atoms are born

Carbon, Oxygen, Nitrogen, Iron, Hydrogen

Small molecules are born:

Methane, Ammonia, Hydrogen, Oxygen, Water



Electronic Structure of Atoms

TABLE 1.2 Ground-State Electron Configurations for Elements 1–18*

First Period	H	1	$1s^1$	
	He	2	$1s^2$	
Second Period	Li	3	$1s^2 s^1$	[He] $2s^1$
	Be	4	$1s^2 2s^2$	[He] $2s^2$
	B	5	$1s^2 2s^2 2p_x^1$	[He] $2s^2 2p_x^1$
	C	6	$1s^2 2s^2 2p_x^1 2p_y^1$	[He] $2s^2 2p_x^1 2p_y^1$
	N	7	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	[He] $2s^2 2p_x^1 2p_y^1 2p_z^1$
	O	8	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	[He] $2s^2 2p_x^2 2p_y^1 2p_z^1$
	F	9	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$	[He] $2s^2 2p_x^2 2p_y^2 2p_z^1$
	Ne	10	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$	[He] $2s^2 2p_x^2 2p_y^2 2p_z^2$
Third Period	Na	11	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^1$	[Ne] $3s^1$
	Mg	12	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2$	[Ne] $3s^2$
	Al	13	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^1$	[Ne] $3s^2 3p_x^1$
	Si	14	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^1 3p_y^1$	[Ne] $3s^2 3p_x^1 3p_y^1$
	P	15	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^1 3p_y^1 3p_z^1$	[Ne] $3s^2 3p_x^1 3p_y^1 3p_z^1$
	S	16	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^1 3p_z^1$	[Ne] $3s^2 3p_x^2 3p_y^1 3p_z^1$
	Cl	17	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^2 3p_z^1$	[Ne] $3s^2 3p_x^2 3p_y^2 3p_z^1$
	Ar	18	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^2 3p_z^2$	[Ne] $3s^2 3p_x^2 3p_y^2 3p_z^2$

*Elements are listed by symbol, atomic number, ground-state electron configuration, and shorthand notation for the ground-state electron configuration, in that order.

Rule 1. Orbitals in these elements fill in the order 1*s*, 2*s*, 2*p*, 3*s*, and 3*p*.

Rule 2. Notice that each orbital contains a maximum of two electrons. In neon, there are six additional electrons after the 1*s* and 2*s* orbitals are filled. These are written as $2p_x^2 2p_y^2 2p_z^2$. Alternatively, we can group the three filled 2*p* orbitals and write them in a condensed form as $2p^6$.

Rule 3. Because the p_x, p_y, and p_z orbitals are equal in energy, we fill each with one electron before adding a second electron. That is, only after each 3*p* orbital contains one electron do we add a second electron to the $3p_x$ orbital.

Lewis Structures

- **Gilbert N. Lewis**
- **Valence shell**: The outermost electron shell of an atom.
- **Valence electrons**: Electrons in the valence shell of an atom. These electrons are used in forming chemical bonds.
- **Lewis structure of an atom**
  - The symbol of the atom represents the nucleus and all inner shell electrons.
  - Dots represent electrons in the valence shell of the atom.

Lewis Structures

the valence shell of 1st period elements contain only *s* orbitals

the valence shell of 2nd period elements contains *s* and *p* orbitals

TABLE 1.3 Lewis Structures for Elements 1–18 of the Periodic Table

1A	2A	3A	4A	5A	6A	7A	8A
H·							He:
Li·	Be:	·B:	·C:	·N:	:O:	:F:	:Ne:
Na·	Mg:	:Al:	·Si:	·P:	:S:	:Cl:	:Ar:

the valence shell of 3rd period elements contains *s*, *p*, and *d* orbitals. The *d* orbitals allow for expanded covalent bonding opportunities for 3rd period elements

600 million tons of hydrogen is consumed via fusion per second in the sun to give Helium. Takes about 4 billion years… then what?

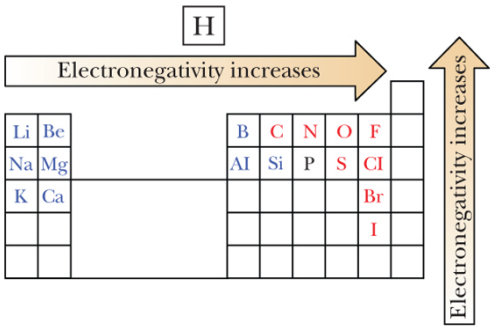
Lewis Model of Bonding

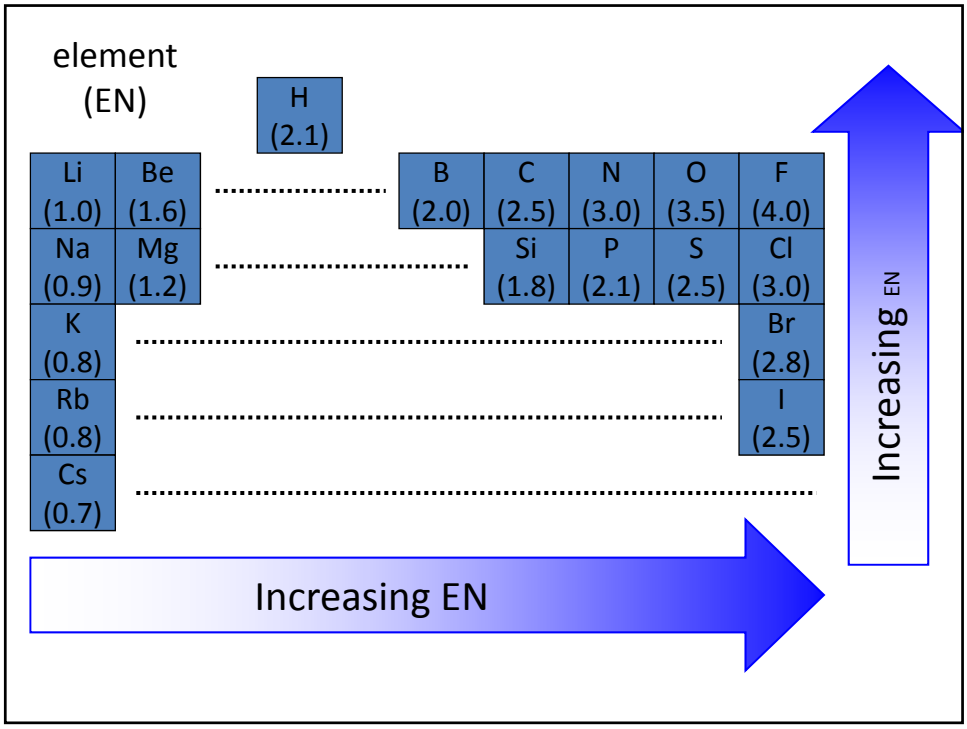
- Atoms bond together so that each atom in the bond acquires the electron configuration of the noble gas nearest it in atomic number.
  - An atom that gains electrons becomes an **anion**.
  - An atom that loses electrons becomes a **cation**.
  - **Ionic bond**: A chemical bond resulting from the electrostatic attraction of an anion and a cation.
  - **Covalent bond**: A chemical bond resulting from two atoms sharing one or more pairs of electrons.
- We classify chemical bonds as ionic, polar covalent, and nonpolar covalent based on the difference in electro-negativity between the bonded atoms.

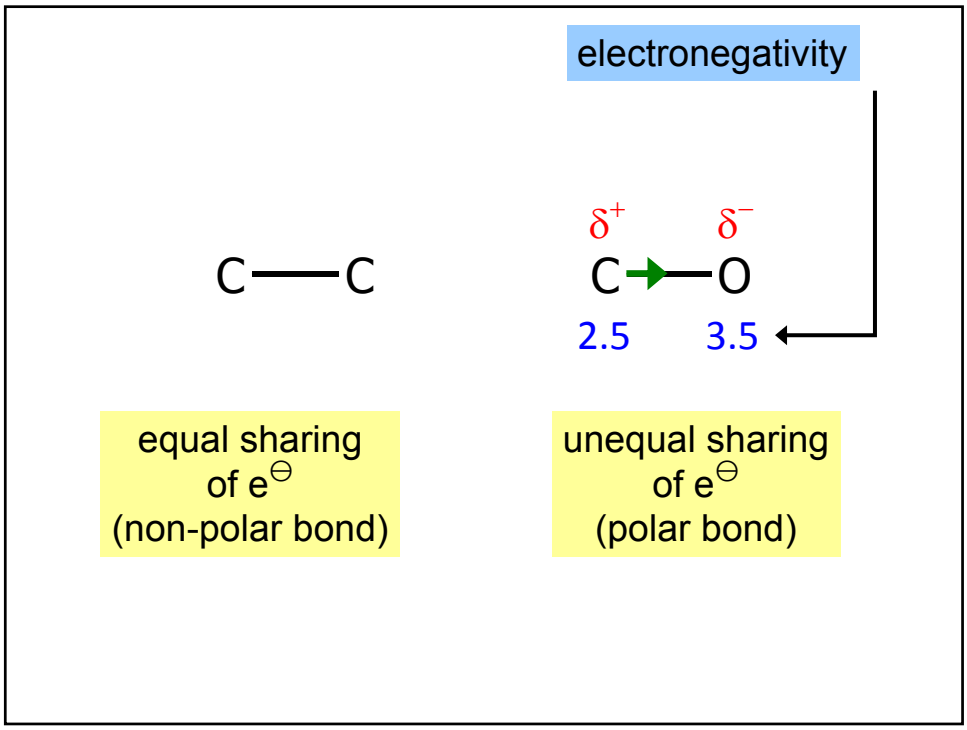
- Electronegativity (EN)
  - The intrinsic ability of an atom to attract the shared electrons in a covalent bond
  - Electronegativities are based on an arbitrary scale, with F the most electronegative (EN = 4.0) and Cs the least (EN = 0.7)

Electronegativity

- **Electronegativity**: A measure of the force of an atom's attraction for the electrons it shares in a chemical bond with another atom.
- **Pauling scale**
  - Increases from left to right within a period.
  - Increases from bottom to top in a group.



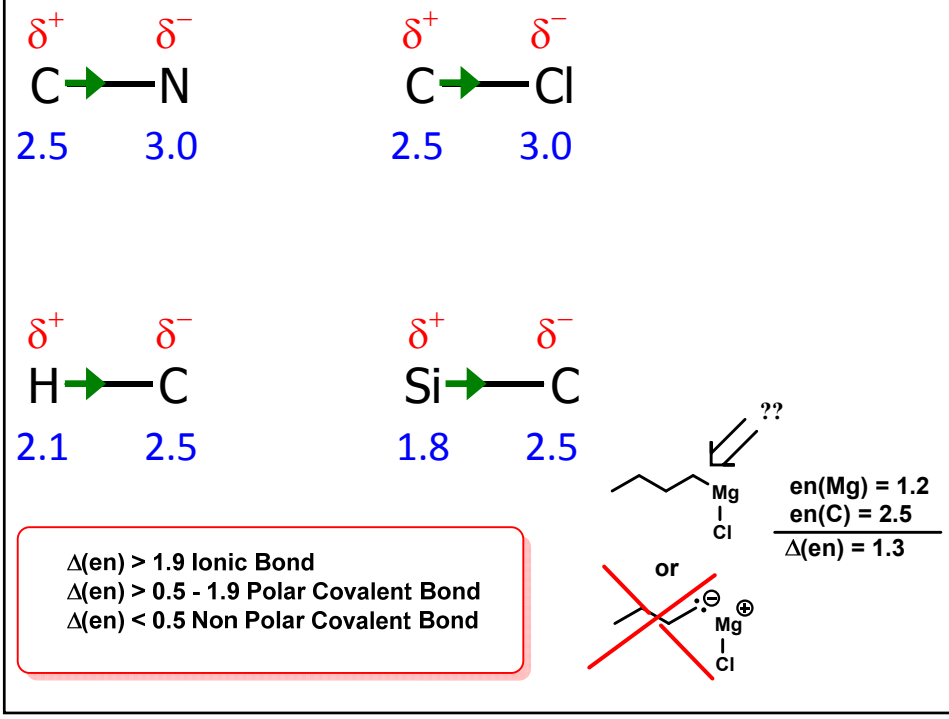

element
(EN)
H
(2.1)
Li
(1.0)
Be
(1.6)
B
(2.0)
C
(2.5)
N
(3.0)
O
(3.5)
F
(4.0)
Na
(0.9)
Mg
(1.2)
Si
(1.8)
P
(2.1)
S
(2.5)
Cl
(3.0)
K
(0.8)
Br
(2.8)
Rb
(0.8)
I
(2.5)
Cs
(0.7)
Increasing EN
Increasing EN


electronegativity
C—C
δ+ δ−
C—O
2.5
3.5
equal sharing
of e⊖
(non-polar bond)
unequal sharing
of e⊖
(polar bond)

Electronegativity

TABLE 1.5 Classification of Chemical Bonds

Difference in Electronegativity between Bonded Atoms	Type of Bond	Most Likely Formed Between
Less than 0.5	Nonpolar covalent	Two nonmetals or a nonmetal and a metalloid
0.5 to 1.9	Polar covalent	
Greater than 1.9	Ionic	A metal and a nonmetal

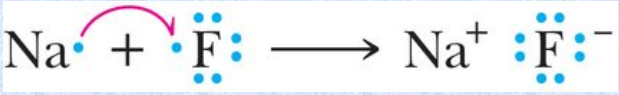


Ionic Bonds

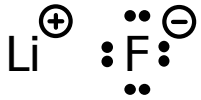
- An ionic bond forms by the transfer of electrons from the valence shell of an atom of lower electronegativity to the valence shell of an atom of higher electronegativity.

$$Na(1s^2\ 2s^2\ 2p^6\ \mathbf{3s^1}) + F(1s^2\ 2s^2\ \mathbf{2p^5}) \longrightarrow Na^+(1s^2 2s^2 2p^6) + F^-(1s^2 2s^2\ \mathbf{2p^6})$$

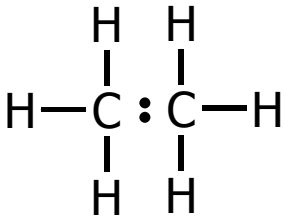
  - We show the transfer of a single electron by a single-headed (barbed) curved arrow.



Polar Covalent Bonds



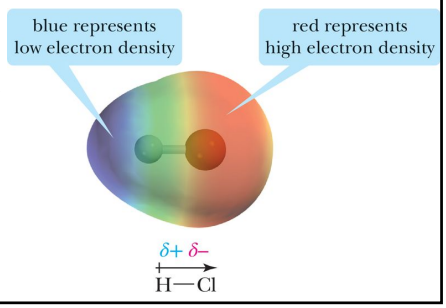
- Lithium fluoride has an ionic bond

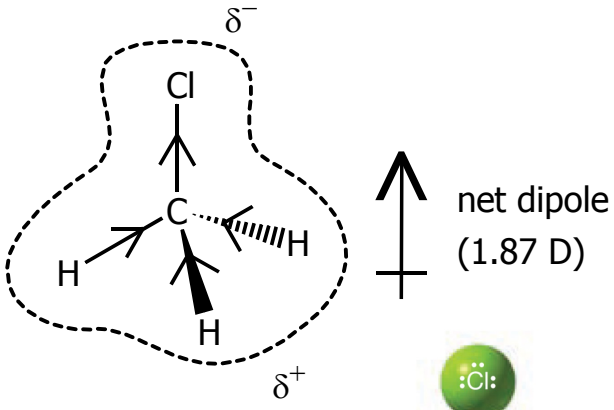


- Ethane has a covalent bond. The electrons are shared equally between the carbon atoms

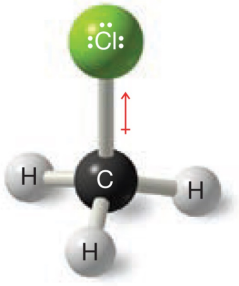
Polar Covalent Bonds

- **In a polar covalent bond**:
  - The more electronegative atom has a partial negative charge, indicated by the symbol δ–.
  - The less electronegative atom has a partial positive charge, indicated by the symbol δ+.
- In an electron density model:
  - Red indicates a region of high electron density.
  - Blue indicates a region of low electron density.



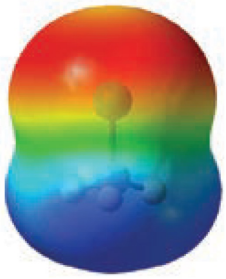


net dipole
(1.87 D)



μ = **1.87 D**

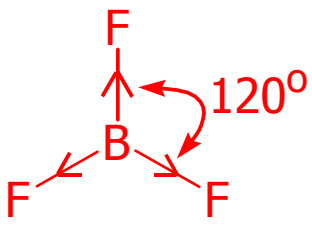
(*a*)



(*b*)

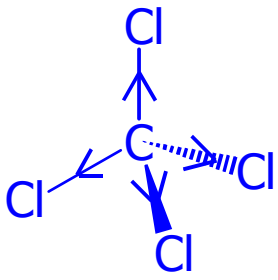
- Molecules containing polar bonds are not necessarily polar as a whole, for example

(1) BF_3 (μ = 0 D)



(trigonal planar)

(2) CCl_4 (μ = 0 D)



(tetrahedral)

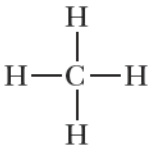
Drawing Lewis Structures

- To draw a Lewis structures:
  - Determine the number of valence electrons in the molecule or ion.
  - Determine the connectivity (arrangement) of atoms.
  - Connect the atoms by single line between atoms.
  - Arrange the remaining electrons so that each atom has a complete valence shell.
  - Show bonding electrons as single lines.
  - Show nonbonding electrons as pairs of dots.
  - Atoms share 1 pair of electrons in a single bond, 2 pairs in a double bond, and 3 pairs in a triple bond.

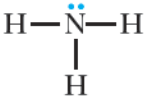
Lewis Structures- Table 1.6

H_2O (8)
Water

HCl (8)
Hydrogen chloride



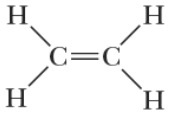
CH_4 (8)
Methane



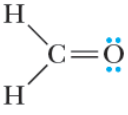
NH_3 (8)
Ammonia

Lewis Structures Table 1.6

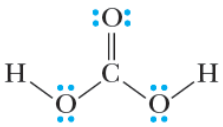
C_2H_2 (10)
Acetylene



C_2H_4 (12)
Ethylene



CH_2O (12)
Formaldehyde



H_2CO_3 (24)
Carbonic acid

Lewis Structures

- In **neutral molecules** containing C, H, N, O, and halogen (X)
  - Hydrogen has one bond.
  - Carbon has 4 bonds and no unshared electrons.
  - Nitrogen has 3 bonds and 1 unshared pair of electrons.
  - Oxygen has 2 bonds and 2 unshared pairs of electrons.
  - Halogen has 1 bond and 3 unshared pairs of electrons.

Formal Charge

- **Formal charge**: the charge on an atom in a molecule or polyatomic ion.
  - Write a Lewis structure for the molecule or ion.
  - Assign each atom all its unshared (nonbonding) electrons and one-half its shared (bonding) electrons.
  - Compare this number with the number of valence electrons in the neutral, unbonded atom.
  - If the number is less than that assigned to the unbonded atom, the atom has a positive formal charge.
  - If the number is greater, the atom has a negative formal charge.

$$\text{Formal charge} = \begin{matrix}\text{Number of valence}\\ \text{electrons in neutral}\\ \text{unbonded atom}\end{matrix} - \left(\begin{matrix}\text{All unshared}\\ \text{electrons}\end{matrix} + \begin{matrix}\text{One-half of all}\\ \text{shared electrons}\end{matrix}\right)$$

Lewis Structures

- **Problem**: Which is an acceptable Lewis structure (formal charges are not shown) for carbon monoxide, CO? For an acceptable structure, assign formal charges as appropriate.

(a) $C \equiv O:$ **(c)** $\ddot{C}=\ddot{O}$

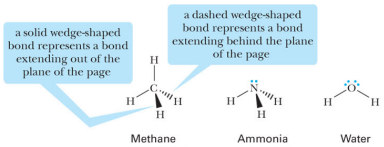
(b) $:C \equiv O:$ **(d)** $:\ddot{C}-\ddot{O}:$

Valence-shell Electron-Pair Repulsion

- VSEPR is based on two concepts.
  - Atoms are surrounded by regions of electron density.
  - Regions of electron density repel each other.

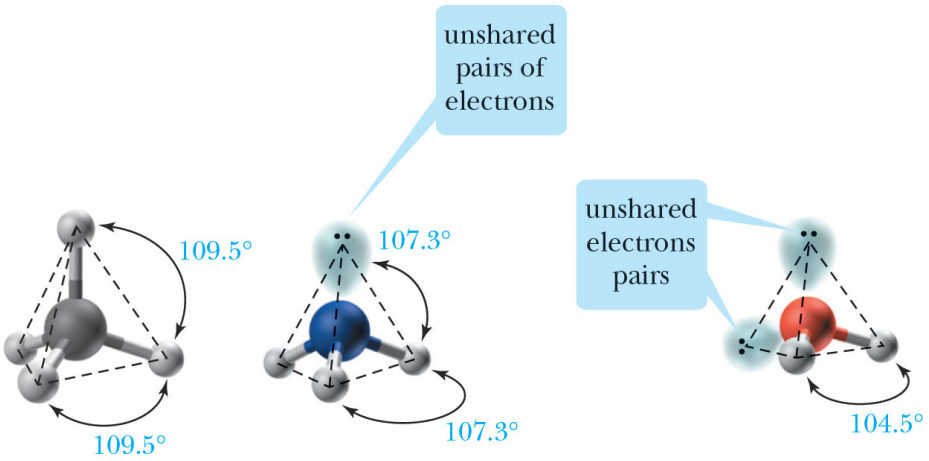
TABLE 1.7 Predicted Molecular Shapes (VSEPR)

Regions of Electron Density around Central Atom	Predicted Distribution of Electron Density about the Central Atom	Predicted Bond Angles	Examples (Shape of the Molecule)
4	Tetrahedral	109.5°	Methane (tetrahedral), Ammonia (pyramidal), Water (bent)
3	Trigonal planar	120°	Ethylene (planar), Formaldehyde (planar)
2	Linear	180°	Carbon dioxide (linear), Acetylene (linear)



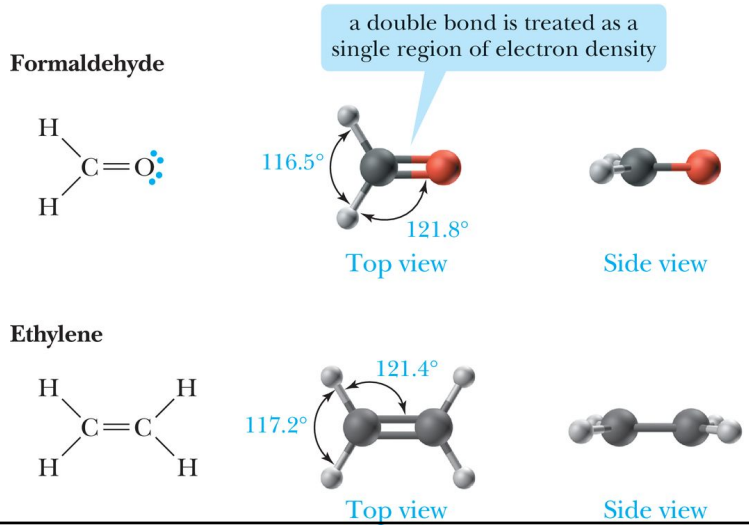
Shapes of Molecules

Methane, Ammonia, and Water molecules. For each, VSEPR predicts tetrahedral distribution of electron density and bond angles of 109.5°



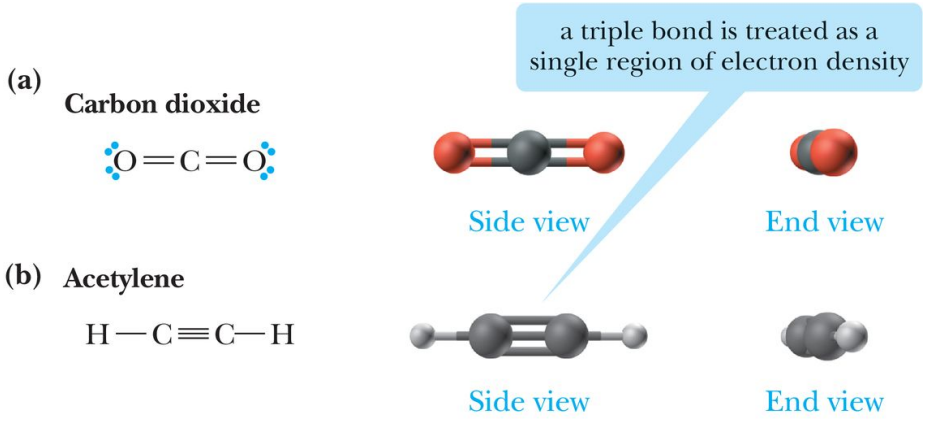
Shapes of Molecules

- **Figure 1.9** Shapes of Formaldehyde and Ethylene. VESPR predicts trigonal planar geometry



Shapes of Molecules

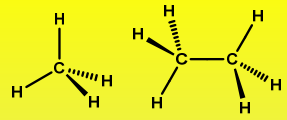
- **Figure 1.10** Shapes of carbon dioxide and acetylene. Both are planar molecules.



Octet Rule and Hybridization. Does the atom in question have a filled octet (8 electrons)?

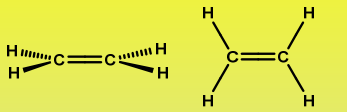
If yes:

No double or triple bonds: sp^3



all ~ 109.5 deg angle
tetrahedral carbons

Double bond : sp^2



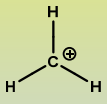
all ~ 120 deg angle
trigonal planar

Triple bond : sp

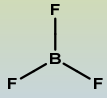
all 180 deg angle
linear

If no:

sp^2



all ~ 120 deg angle
trigonal planar



sp

linear

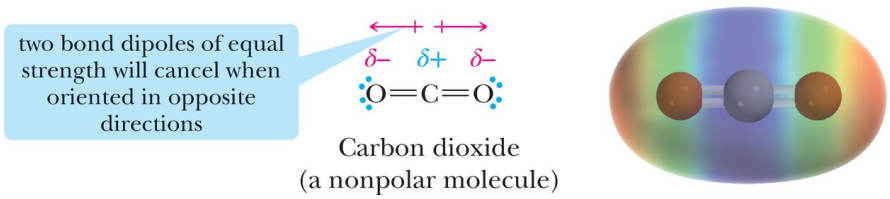
VSEPR

- **Problem**: Draw a Lewis structure and predict all bond angles and all hybridizations for all atoms for these molecules and ions.

(a) NH_4^+	(b) CH_3NH_2	(c) CH_3OH
(d) $CH_3CH{=}CH_2$	(e) H_2CO_3	(f) HCO_3^-
(g) CH_3CHO	(g) CH_3COOH	(h) BF_4^-

Polar and Nonpolar Molecules

- A molecule with polar bonds is nonpolar if:
  - The vector sum of its bonds dipoles is zero (that is, the bond dipoles cancel each other).
  - Carbon dioxide has two polar covalent bonds and because of its geometry, is a nonpolar molecule.

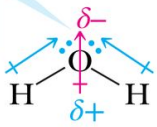


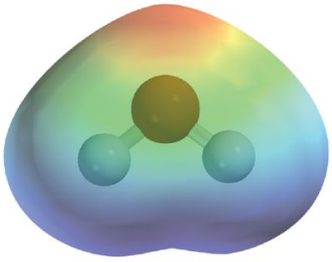
Carbon dioxide
(a nonpolar molecule)

Polar and Nonpolar Molecules

- A water molecule has two polar covalent bonds and, because of its geometry, is a polar molecule.

the vector sum (red) of the bond dipoles (blue) situates the center of partial positive charge (δ^+) in between the two hydrogen atoms



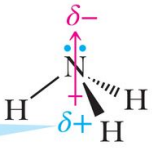


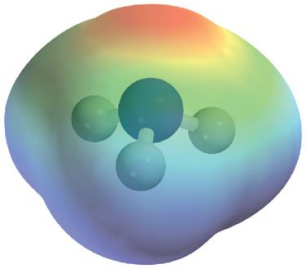
Water
(a polar molecule)

Polar and Nonpolar Molecules

- An ammonia molecule has three polar covalent bonds, and because of its geometry, is a polar molecule

the center of partial positive charge ($\delta+$) is midway between the three hydrogen atoms



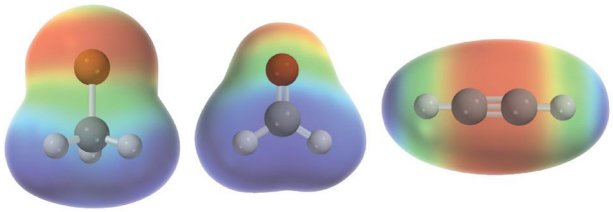


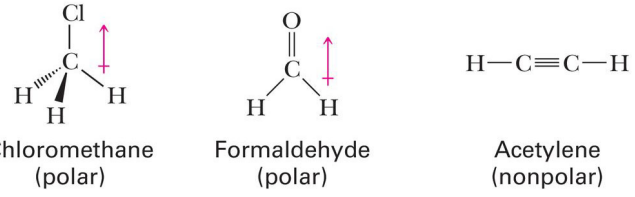
Ammonia
(a polar molecule)

Polar and Nonpolar Molecules

– Chloromethane and formaldehyde are polar molecules.

– Acetylene is a nonpolar molecule.

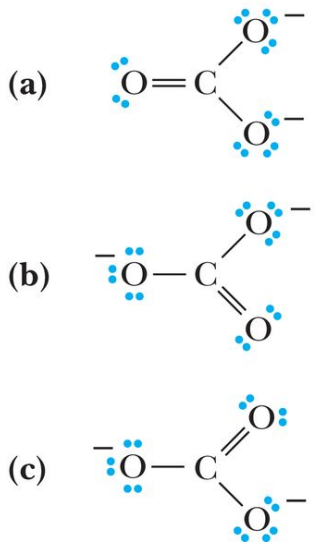




Chloromethane (polar) | Formaldehyde (polar) | Acetylene (nonpolar)

Resonance

- A way to describe molecules and ions for which no single Lewis structure provides a truly accurate representation.
- **Figure 1.11** Three Lewis structures for the carbonate ion. Each implies that one carbon-carbon bond is different from the other two.

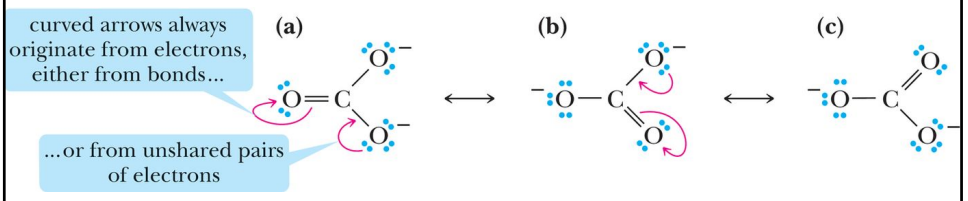


Resonance

- Linus Pauling - 1930s
  - Many molecules and ions are best described by writing two or more Lewis structures.
  - Individual Lewis structures are called **contributing structures**.
  - Connect individual contributing structures by a **double-headed** arrow.
  - The molecule or ion is a **hybrid** of the various contributing structures.

Resonance

- **Figure 1.12** The carbonate ion as a hybrid of three equivalent contributing structures. Curved arrows show the redistribution of valence electrons between one contributing structure and the next.



Resonance

- **Curved arrow**: A symbol used to show the redistribution of valence electrons.
- In using curved arrows, there are only two allowed types of electron redistribution:
  - from a bond to an adjacent atom.
  - from an atom to an adjacent bond.
- Electron pushing by the use of curved arrows is a survival skill in organic chemistry.
  - learn it well!

Resonance

- All acceptable contributing structures must:

1. Have the same number of valence electrons.
2. Obey the rules of covalent bonding.
   - No more than 2 electrons in the valence shell of H.
   - No more than 8 electrons in the valence shell of a 2nd period element.
   - 3rd period elements may have up to 12 electrons in their valence shells.
3. Differ only in distribution of valence electrons.
4. Have the same total number of paired and unpaired electrons.

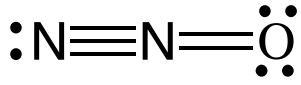
Resonance

- Examples of ions and a molecule best represented as resonance hybrids. Draw contributing structures for each resonance hybrid.

carbonate ion	CO_3^{2-}
acetate ion	CH_3COO^-
acetone	CH_3COCH_3

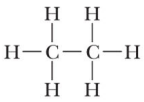
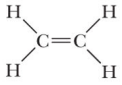
Resonance

- Problem: Nitrous oxide, N_2O, laughing gas, is a colorless, nontoxic, tasteless, and odorless gas. Because it is soluble in vegetable oils (fats), it is used as a propellant in whipped toppings.
  - (a) How many valence electrons are present in nitrous oxide?
  - (b) Write two equivalent contributing structures for this molecule. The connectivity is N—N—O. Be certain to show formal charges, if any are present.
  - (c) Explain why the following is not an acceptable contributing structure.



Hybrid Orbitals

TABLE 1.8 Covalent Bonding of Carbon

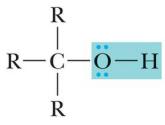
Groups Bonded to Carbon	Orbital Hybridization	Predicted Bond Angles	Types of Bonds to Carbon	Example	Name
4	sp^3	109.5°	four sigma bonds		ethane
3	sp^2	120°	three sigma bonds and one pi bond		ethylene
2	sp	180°	two sigma bonds and two pi bonds		acetylene

Functional Groups

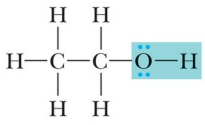
- **Functional Group**: An atom or group of atoms within a molecule that shows a characteristic set of physical and chemical properties.
- Functional groups are important for three reasons, they are:
  - The units by which we divide organic compounds into classes.
  - The sites of characteristic chemical reactions.
  - The basis for naming organic compounds.

Functional Groups

- **Alcohol**: A compound that contains an –OH (**hydroxyl group**) bonded to a tetrahedral carbon atom.



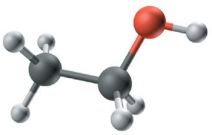
Functional group (R=H or carbon group)



Structural formula

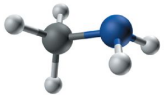
CH_3CH_2OH

Condensed structural formula



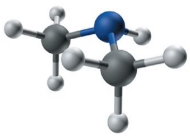
Functional Groups

- **Amine**: A compound that contains an amino group: a nitrogen atom bonded to one, two, or three carbon atoms.
  - Amines are classified as 1°, 2°, and 3° according to the number of carbon atoms bonded directly to the nitrogen atom.



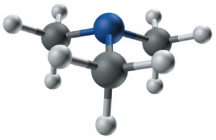
CH_3NH_2

Methylamine (a 1° amine)



CH_3NH or $(CH_3)_2NH$
CH_3

Dimethylamine (a 2° amine)

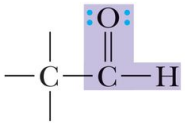


CH_3NCH_3 or $(CH_3)_3N$
CH_3

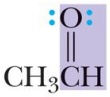
Trimethylamine (a 3° amine)

Functional Groups

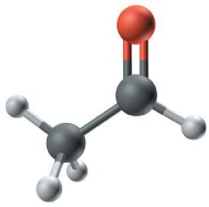
- **Carbonyl group (C=O)** of aldehydes and ketones.

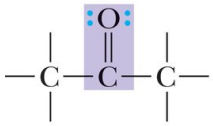


Functional group



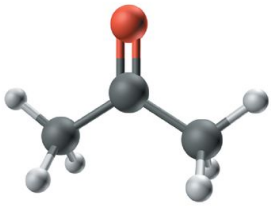
An aldehyde





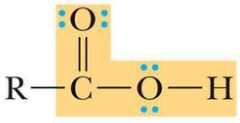
Functional group

A ketone



Functional Groups

- **Carboxyl group** of carboxylic acids.



Functional group

Acetic acid