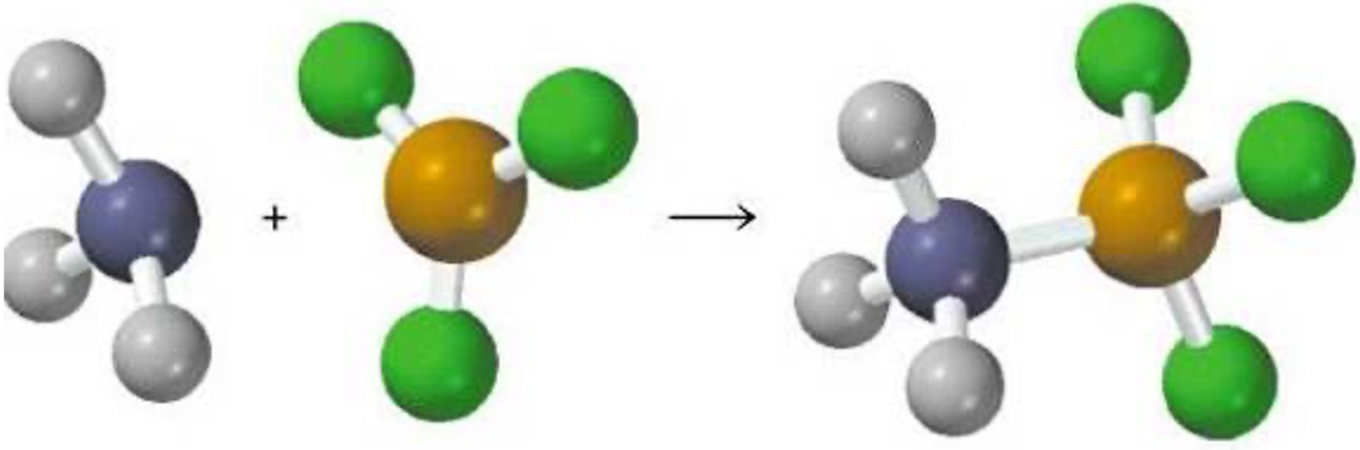
Chapter Six

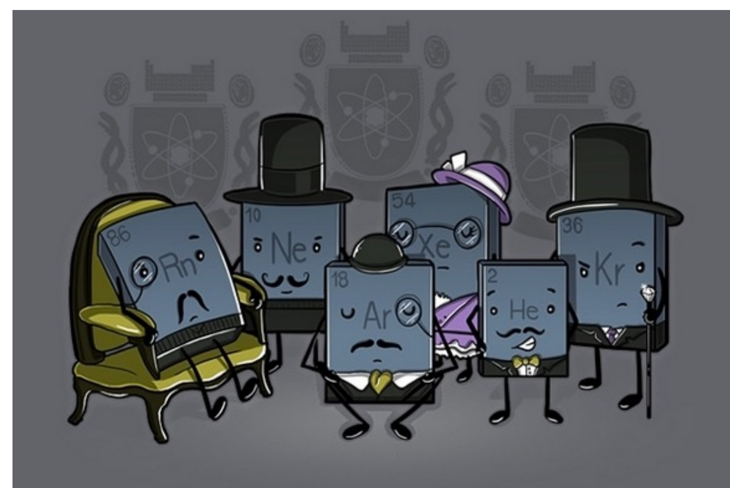
Representing Molecules



Effect of Valence Electrons on Elements

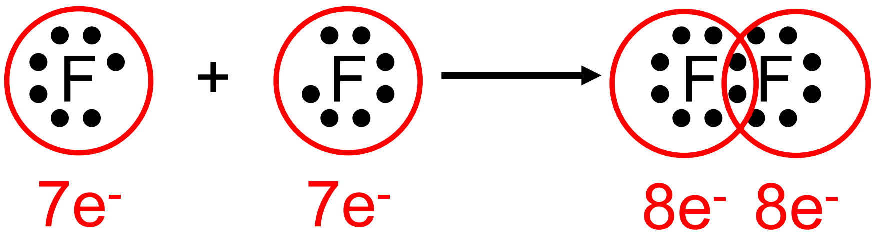
Octet Rule:

- Elements most stable with 8 valence electrons (2s + 6p)
- Noble gases have 8 valence electrons
  - No e^- want to be added or removed
  - Why they are so unreactive
- Main group elements form ions to become isoelectronic with the noble gases
  - Same electron configuration
- He & H follow duet rule
  - 2 e^-; too small for 8e^-



Lewis Structures

Lewis structures represent covalent bond formation



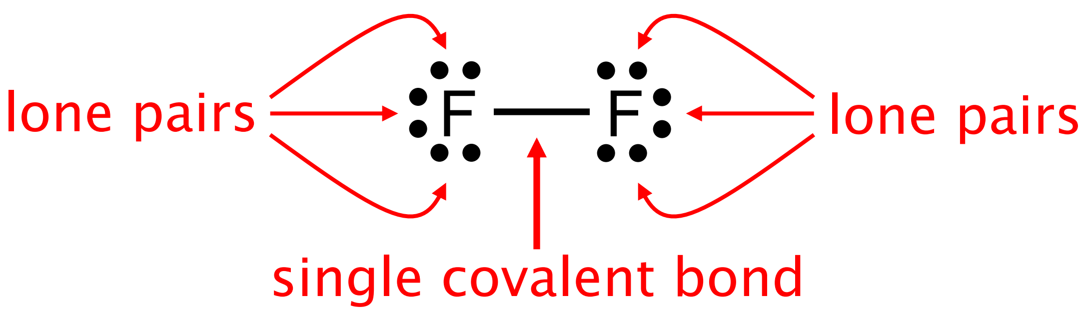
$1s^22s^22p^5 \rightarrow 1s^22s^22p^6$

Bonding Pairs: Electrons shared by both atoms

- Represented by a dash (-) between bonded atoms

Lone Pairs: Non-shared electrons count for 1 atom

- Represented by a pair of dots (••) around atom

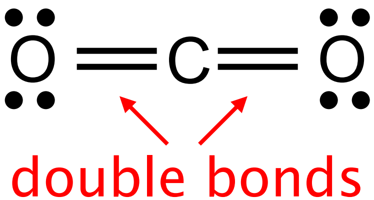


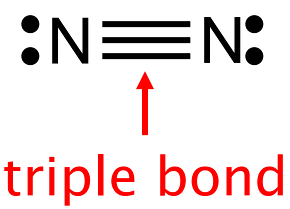
Multiple Bonds

More than one pair of electrons is shared between atoms so each atom can form an octet.

Single Bond:	1 shared pair:	1 dash	(-)
Double bonds:	2 shared pairs:	2 dashes	(=)
Triple bonds:	3 shared pairs:	3 dashes	(≡)

Allows atoms in a molecule to share extra e$^-$ if there are not enough for the central atom





Multiple Bonds

The number of electrons shared impacts the length and strength of a covalent bond

In general:

Single Bond:	longest	weakest (lowest bond energy)
Double bonds:	shorter	medium strength
Triple bonds:	shortest	strongest (highest bond energy)

Bond length is measured as the distance between the nuclei of two bonded atoms

N_2
Bond length 1.10 Å

CO
Bond length 1.13 Å

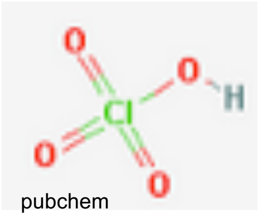
Writing Lewis Structures: Hints & Tips

Electronegativity

- Central atom usually has the **lowest** electronegativity
  (atom lower or to the left in periodic table)
- Terminal atoms (except H) have **higher** electronegativities

Terminal Atoms

- Bonded to only one other atom
- Hydrogen atoms are terminal atoms
- Halogens (col 17) are often terminal atoms



Oxoacids

- Hydrogen atoms are bonded to oxygen atoms in oxoacids

Hints & Tips for Drawing Lewis Structures Con't

- Final structure must include same number of valance e^- as sum of valance e^- from all atoms in the molecule
- Final structure must satisfy octet rule (unless it is an exception)
- Start with single bonds, try double then triple if necessary
- **Hydrogen** only wants one more e^-
  - forms ONE SINGLE BOND
  - will not be between two atoms
- **Carbon** usually does not have lone pairs
  - all 8 e^- must come from single, double, or triple bonds
- **Halogens** only want one more e^-
  - generally only form <u>one single bond</u>
- Molecules are often symmetrical
  - try single atom in middle with other atoms around it

Example: Write the Lewis Structure of HNO

1. Add up the valence electrons in the structure

   1(H) + 5(N) + 6(O) = 12 valence electrons

2. Arrange the atoms & place bonding electrons

   H–N–O nitrogen less electronegative, put in center

3. Place e- pairs around terminal atoms to get 8

   H – N – O:

4. Place remaining electron pairs on central atom

   H – N – O:

5. Add double bond to finish nitrogen octet (8)

   H – N = O

Drawing Lewis Structures:

CH_4

N_2

CO_2

NF_3

Drawing Lewis Structures: Polyatomic ions & simple organic molecules

CO_3^{2-}

C_2H_6

$C_2H_2I_2$

C_2H_6O

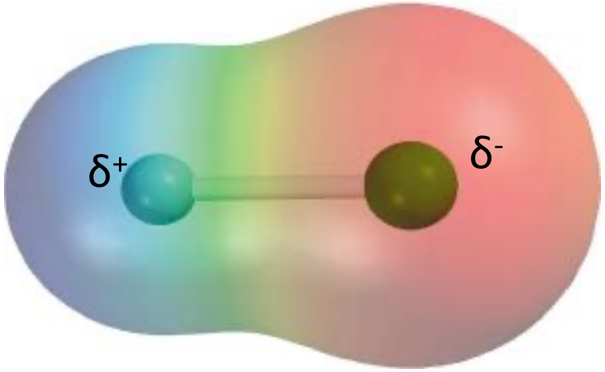
C_3H_6O

Orgo – degrees of unsaturation:
C_nH_{2n+2} – all single bonds
C_nH_{2n} – one double bond (or ring)
C_nH_{2n-2} – 1 triple bond, 2 double bonds, 2 rings, double bond + ring

– 2 for each double bond/ring
– 4 for each triple bond

Electronegativity & Polar Covalent Bonds

Electronegativity



- The ability of an atom to attract e^-
- F is the most electronegative atom
- Nonmetals - high electronegativities

Polar Covalent Bonds

- Differences in electronegativity result in unequal sharing of electrons between atoms
- More electronegative atom has a partial neg. charge (δ^-)
- More electropositive atoms has a partial pos. charge (δ^+)

Percent Ionic Character

- Measure of polarity of bond
  - 100% ionic is full transfer of electron, no sharing
  - 100% covalent is equal sharing, H_2, Cl_2, etc.

Electronegativities of Common Elements

Increasing electronegativity

Increasing electronegativity

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
H 2.1																	
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.0-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9																

Electronegativity difference helps determine bond type

0 – 0.4	0.4 – 1.7	1.7 – 4
Nonpolar	Polar	Ionic

Use to make sure that a metal-nonmetal bond is ionic and to determine if a covalent bond is polar or non-polar.

F & Na: 4.0 – 0.9 = 3.1 = ionic

C & H: 2.5 – 2.1 = 0.4 = nonpolar covalent

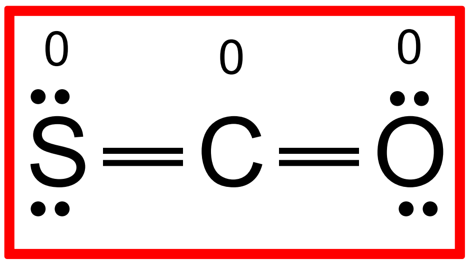
Formal Charge

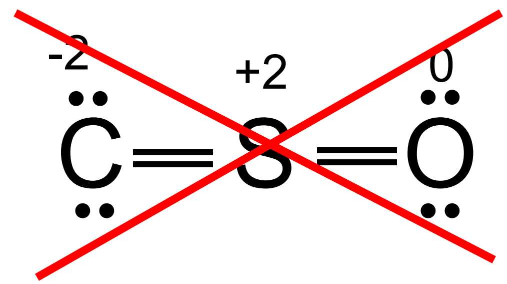
Difference between the # of valence e^- in a free atom & the # of e^- assigned to that atom in a Lewis structure.

F.C. = # ve^- - (# of lone e- + # bonds)

Get #ve^- from group #

Molecule is most stable if formal charge is 0 for each atom.





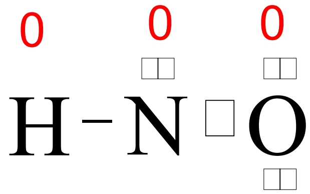
- Most likely Lewis structure has lowest formal charges
- Negative F.C. must be on more electroneg. atom
- Sum of formal charges:

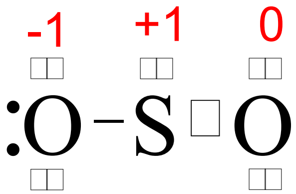
  Molecules = 0

  Polyatomic ions = charge

Calculating formal charge

F.C. = # ve$^-$ - (# of lone e- + # bonds)

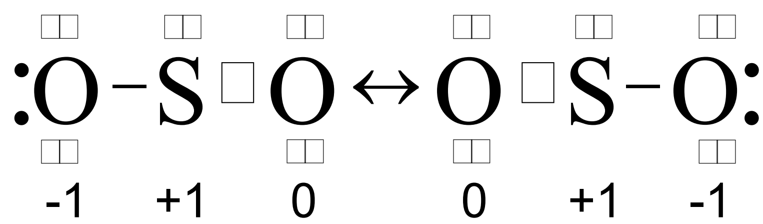




Resonance

If a molecule or ion can be represented by 2 or more Lewis structures that differ only in electron location, the true structure is a blend of those structures.

- Electrons are moving around the molecule
- Neither bond is completely single or double (1.5)



Resonance Structures

- Equivalent Lewis structures for a single molecule
- Formal charges will usually be present

Delocalization

- Electrons are shared by more than two atoms
- Stabilizes the molecule

Exceptions to the Octet Rule: Incomplete Octet

Not enough electrons for central atom to have 8

BeH_2

$$\begin{array}{r} \text{Be} - 2e^- \\ 2\text{H} - 2\text{x}1e^- \\ \hline 4e^- \end{array}$$

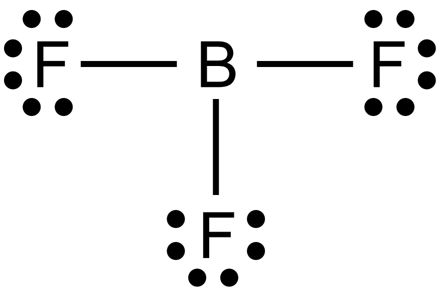
H—Be—H

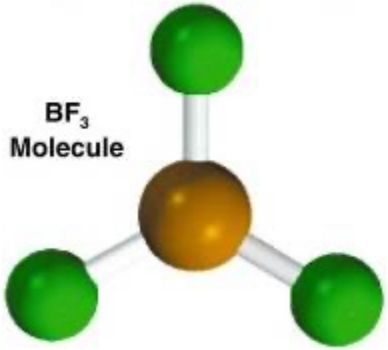
Terminal atoms unwilling to donate more electrons

- Would destabilize terminal atoms & create formal charge

BF_3

$$\begin{array}{r} \text{B} - 3e^- \\ 3\text{F} - 3\text{x}7e^- \\ \hline 24e^- \end{array}$$

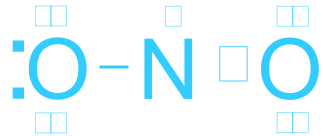




Free Radicals and Expanded Octets

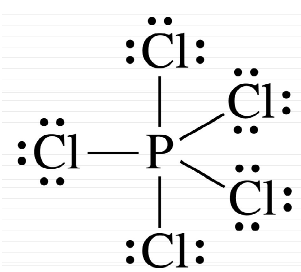
Free Radicals:

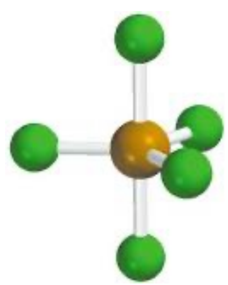
- Molecules with an odd number of valence electrons (N)
- Extremely reactive, odd electron wants to be part of a pair

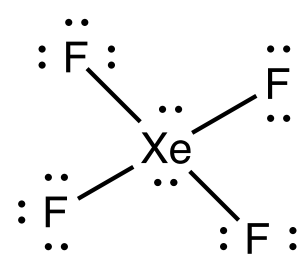


Compounds with expanded valence shells

- Central atom has more than eight electrons
- May have lone pair electrons as well as bonding pairs
- Must be in third row on periodic table or higher (3rd, 4th, 5th, etc.) – have empty d orbitals to put electrons in
- Often occurs when expanded octet minimizes formal charge







Drawing Lewis Structures: Exceptions to the Octet Rule

$XeCl_2$

H_2SO_4

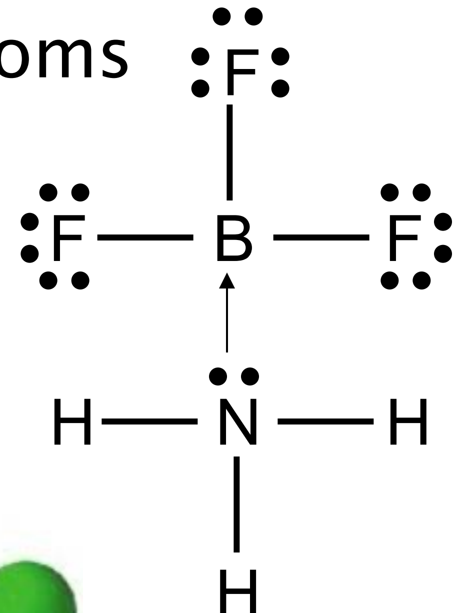
PI_5

BeF_2

Coordinate Covalent Bonds

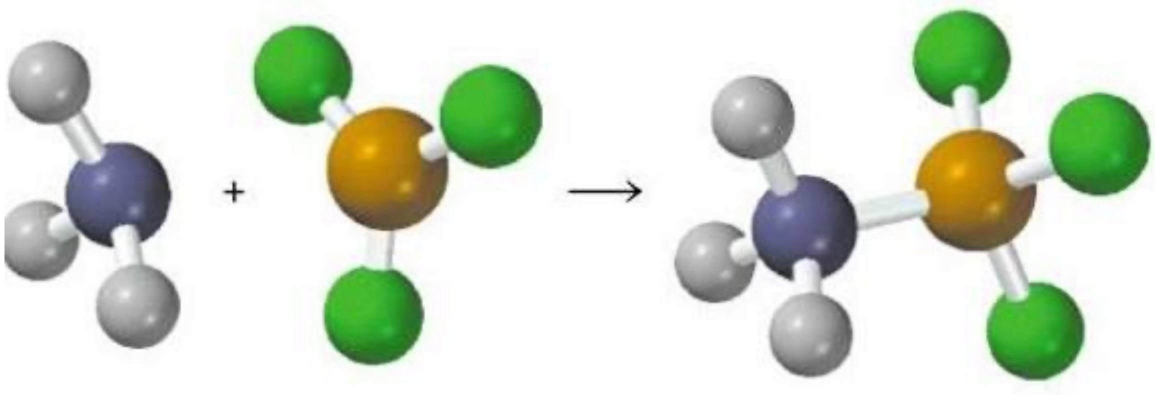
1 atom provides both electrons

- Electrons are then shared between 2 atoms



Ex: BF_3 and NH_3

- B needs 2 electrons to fill octet
- N has a lone pair to share



Seen often with transition metals – can accept electrons into empty d-orbitals