

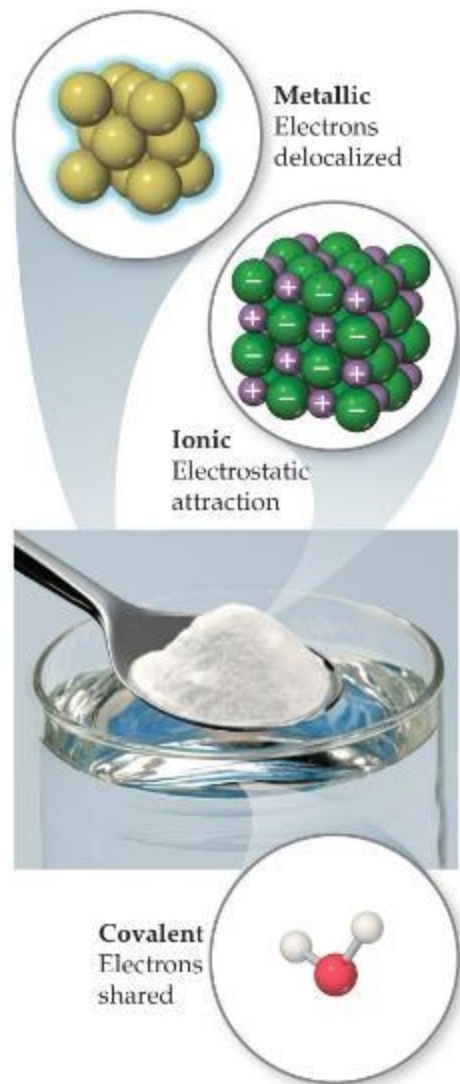
CHEM 103 CHEMISTRY I



CHAPTER 8 BASIC CONCEPTS OF CHEMICAL BONDING

Inst. Dr. Dilek IŞIK TAŞGIN
Inter-Curricular Courses Department
Çankaya University

Chemical Bonds



- Three basic types of bonds
 - Ionic
 - Electrostatic attraction between ions.
 - Covalent
 - Sharing of electrons.
 - Metallic
 - Metal atoms bonded to several other atoms.

Lewis Symbols

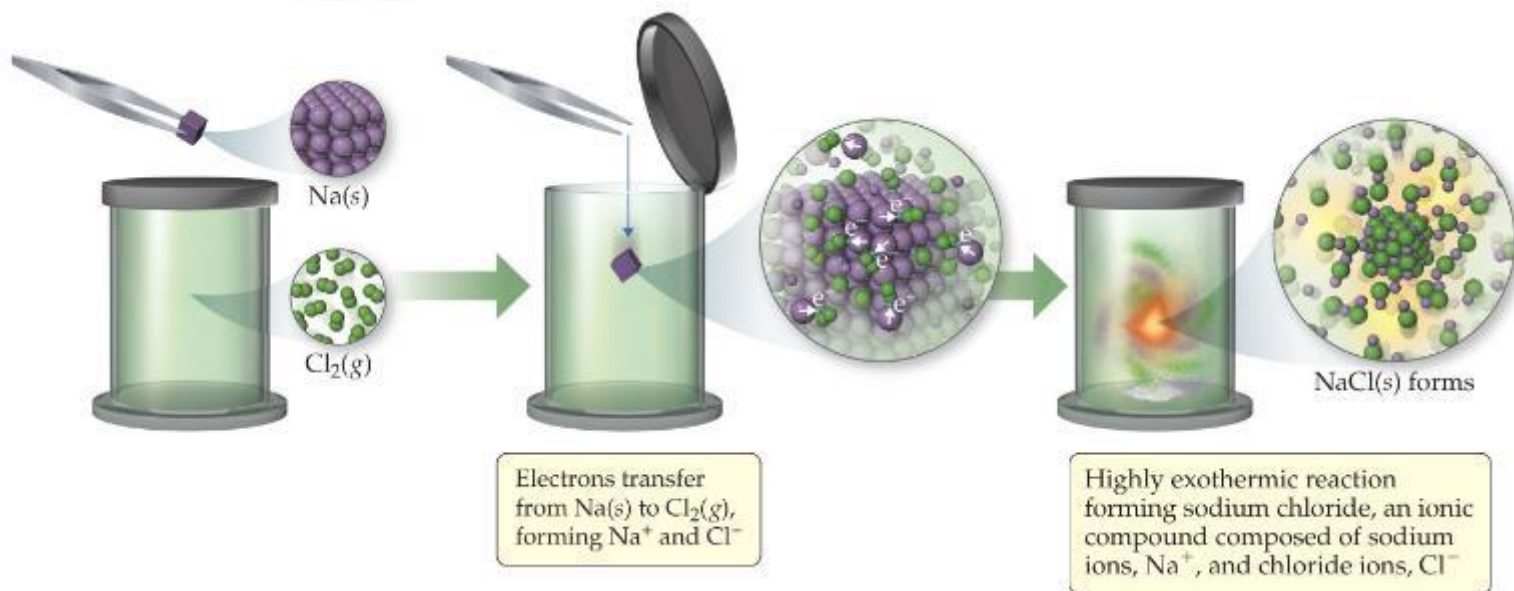
Table 8.1 Lewis Symbols

Group	Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
1A	Li	[He]2s ¹	Li·	Na	[Ne]3s ¹	Na·
2A	Be	[He]2s ²	·Be·	Mg	[Ne]3s ²	·Mg·
3A	B	[He]2s ² 2p ¹	·B·	Al	[Ne]3s ² 3p ¹	·Al·
4A	C	[He]2s ² 2p ²	·C·	Si	[Ne]3s ² 3p ²	·Si·
5A	N	[He]2s ² 2p ³	·N·	P	[Ne]3s ² 3p ³	·P·
6A	O	[He]2s ² 2p ⁴	:O:	S	[Ne]3s ² 3p ⁴	:S:
7A	F	[He]2s ² 2p ⁵	·F·	Cl	[Ne]3s ² 3p ⁵	·Cl·
8A	Ne	[He]2s ² 2p ⁶	:Ne:	Ar	[Ne]3s ² 3p ⁶	:Ar:

- G. N. Lewis developed a method to denote potential bonding electrons by using one dot for every valence electron around the element symbol.
- When forming compounds, atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons (the octet rule).

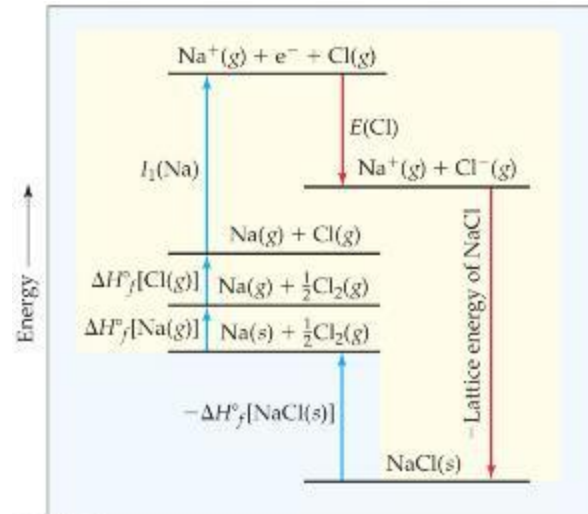
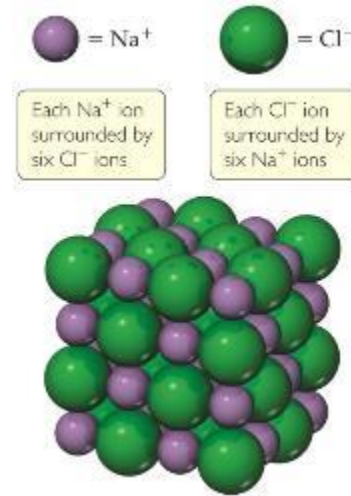
Ionic Formation

- Atoms tend to lose (metals) or gain (nonmetals) electrons to make them isoelectronic to the noble gases.



Energetics of Ionic Bonding— Born-Haber Cycle

- Many factors affect the energy of ionic bonding.
- Start with the metal and nonmetal elements:
 Na(s) and $\text{Cl}_2(\text{g})$.
- Make gaseous atoms:
 Na(g) and Cl(g) .
- Make ions: $\text{Na}^+(\text{g})$ and $\text{Cl}^-(\text{g})$.
- Combine the ions: NaCl(s) .



Energetics of Ionic Bonding

- We already discussed making ions (ionization energy and electron affinity).
- It takes energy to convert the elements to atoms. (endothermic)
- It takes energy to create a cation (endothermic).
- Energy is released by making the anion (exothermic).
- The formation of the solid releases a *huge* amount of energy (exothermic).
- This makes the formation of salts from the elements *exothermic*.

Lattice Energy

- That huge, exothermic transition is the reverse of the **lattice energy**,
 - *the energy required to completely separate a mole of a solid ionic compound into its gaseous ions.*
- The energy associated with electrostatic interactions is governed by Coulomb's law:

$$E_{\text{el}} = \kappa \frac{Q_1 Q_2}{d}$$

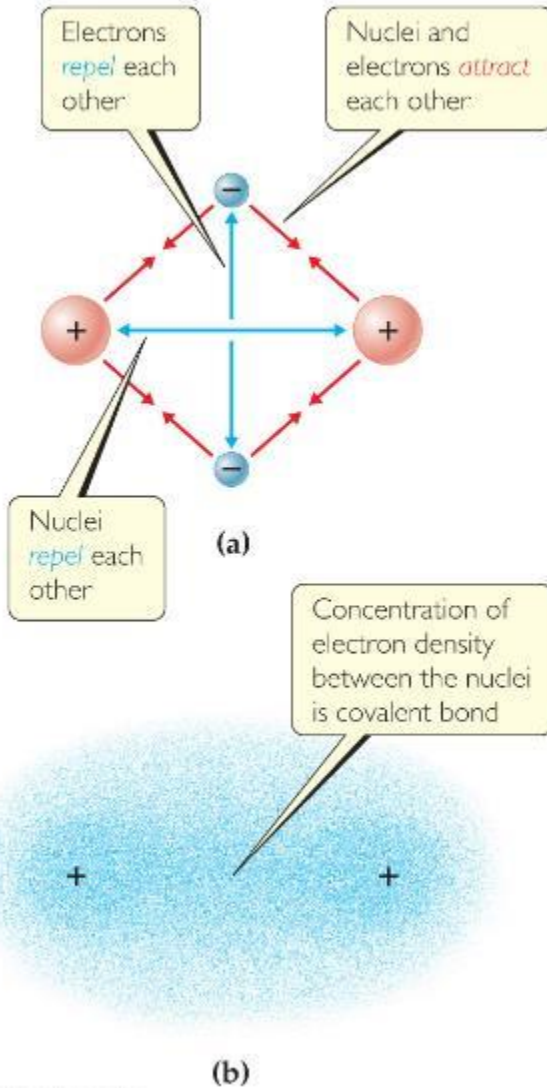
Lattice Energy

- Lattice energy increases with:
 - increasing charge on the ions
 - decreasing size of ions

Table 8.2 Lattice Energies for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	MgCl ₂	2326
LiCl	834	SrCl ₂	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

Covalent Bonding



- In covalent bonds, atoms share electrons.
- There are several electrostatic interactions in these bonds:
 - attractions between electrons and nuclei,
 - repulsions between electrons, and
 - repulsions between nuclei.
- For a bond to form, the attractions must be greater than the repulsions.

Lewis Structures

- Sharing electrons to make covalent bonds can be demonstrated using Lewis structures.
- We start by trying to give each atom the same number of electrons as the nearest noble gas by sharing electrons.
- The simplest examples are for hydrogen, H_2 , and chlorine, Cl_2 , shown below.



Electrons on Lewis Structures

- Lone pairs: electrons located on *only one* atom in a Lewis structure
- Bonding pairs: shared electrons in a Lewis structure; they can be represented by two dots *or* one line

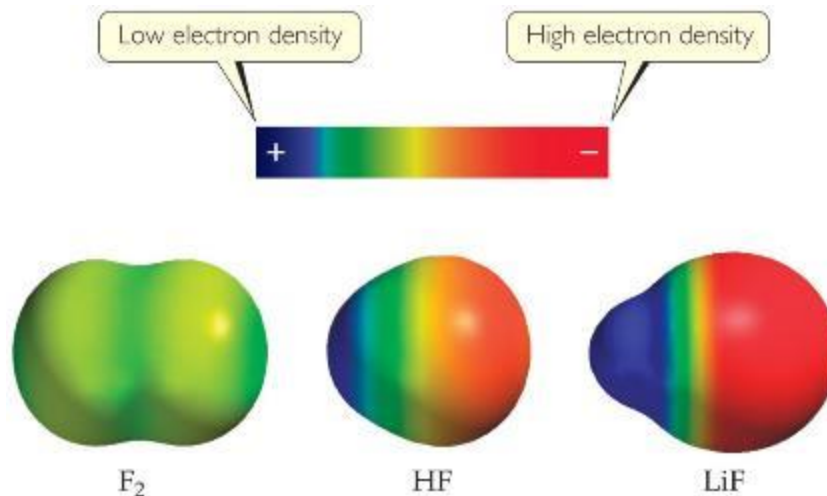
Multiple Bonds

- Some atoms share only one pair of electrons. These bonds are called **single bonds**.
- Sometimes, two pairs need to be shared. These are called **double bonds**.
- There are even cases where three bonds are shared between two atoms. These are called **triple bonds**.



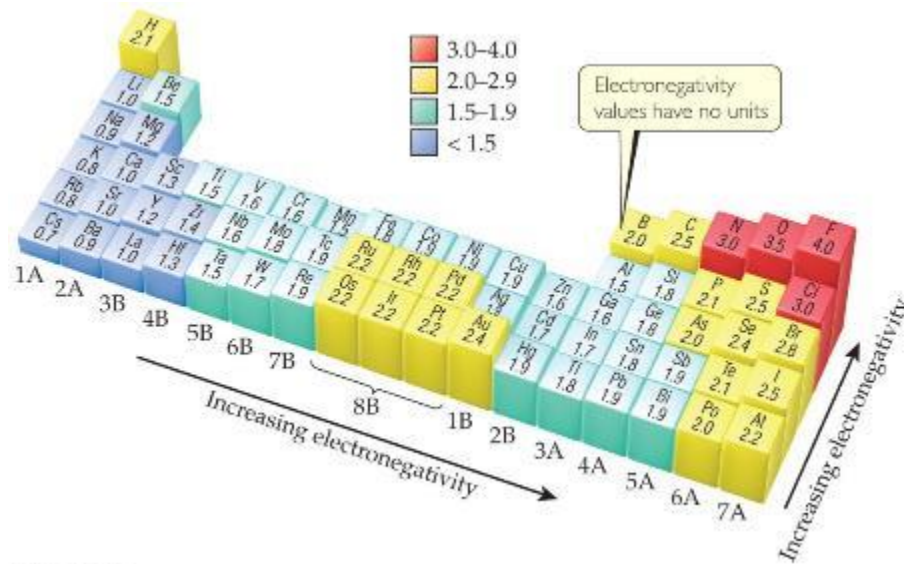
Polar Covalent Bonds

- The electrons in a covalent bond are not always shared equally.
- Fluorine pulls harder on the electrons it shares with hydrogen than hydrogen does.
- Therefore, the fluorine end of the molecule has more electron density than the hydrogen end.



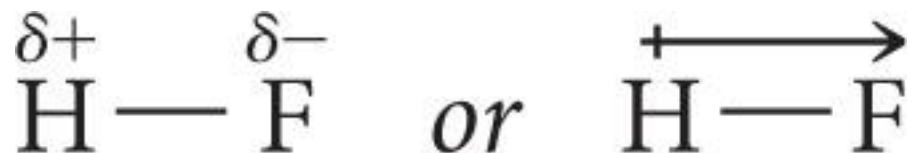
Electronegativity

- Electronegativity is the ability of an atom in a molecule to attract electrons to itself.
- On the periodic table, electronegativity generally increases as you go
 - from left to right across a period.
 - from the bottom to the top of a group.



Electronegativity and Polar Covalent Bonds

- When two atoms share electrons unequally, a **polar covalent bond** results.
- Electrons tend to spend more time around the more electronegative atom. The result is a partial negative charge (*not* a complete transfer of charge). It is represented by δ^- .
- The other atom is “more positive,” or δ^+ .

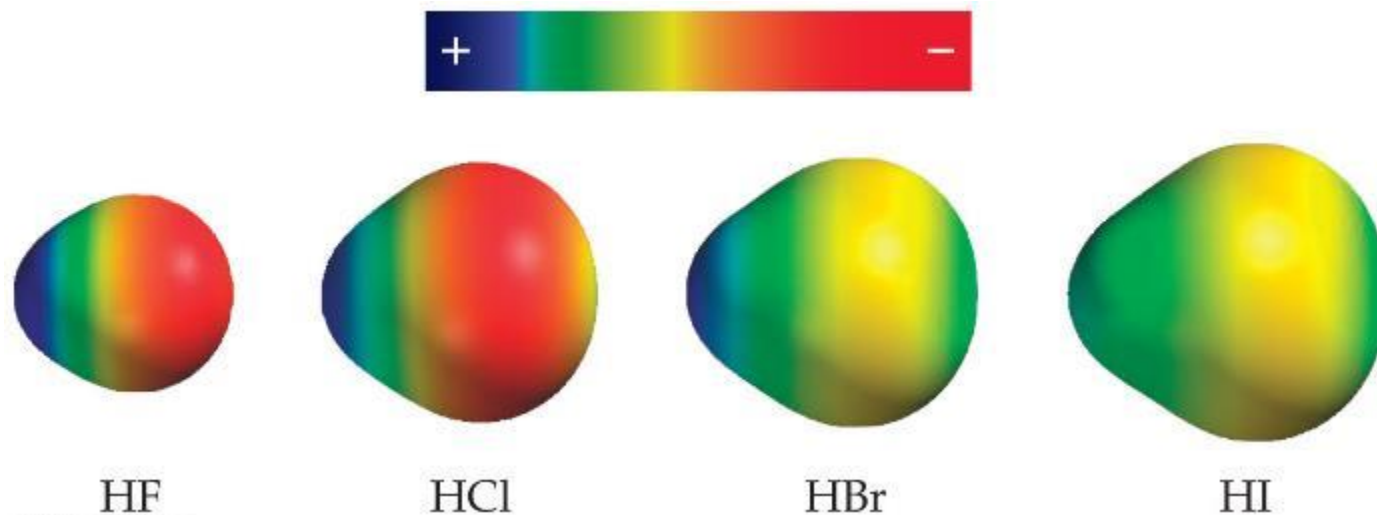


Polar Covalent Bonds

Table 8.3 Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

The greater the difference in electronegativity, the more polar is the bond.

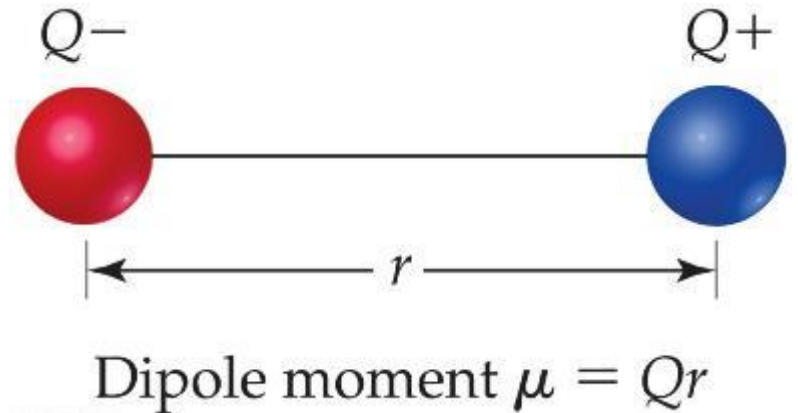


Dipoles

- When two equal, but opposite, charges are separated by a distance, a **dipole** forms.
- A **dipole moment**, μ , produced by two equal but opposite charges separated by a distance, r , is calculated:

$$\mu = Qr$$

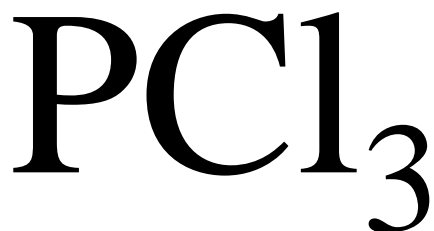
- It is measured in debyes (D).



Is a Compound Ionic or Covalent?

- Simplest approach: Metal + nonmetal is ionic; nonmetal + nonmetal is covalent.
- There are many exceptions: It doesn't take into account oxidation number of a metal (higher oxidation numbers can give covalent bonding).
- Electronegativity difference can be used; the table still doesn't take into account oxidation number.
- Properties of compounds are often best: Lower melting points mean covalent bonding, for example.

Writing Lewis Structures (Covalent Molecules)

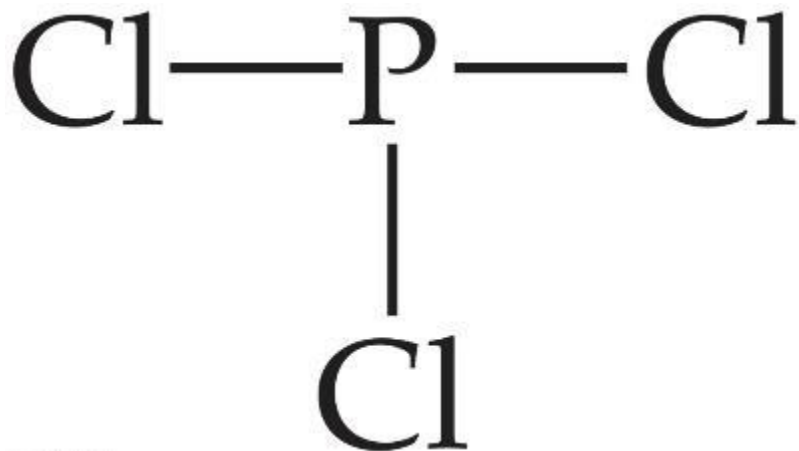


Keep track of the electrons:

$$5 + 3(7) = 26$$

1. Sum the valence electrons from all atoms, taking into account overall charge.
 - If it is an anion, add one electron for each negative charge.
 - If it is a cation, subtract one electron for each positive charge.

Writing Lewis Structures

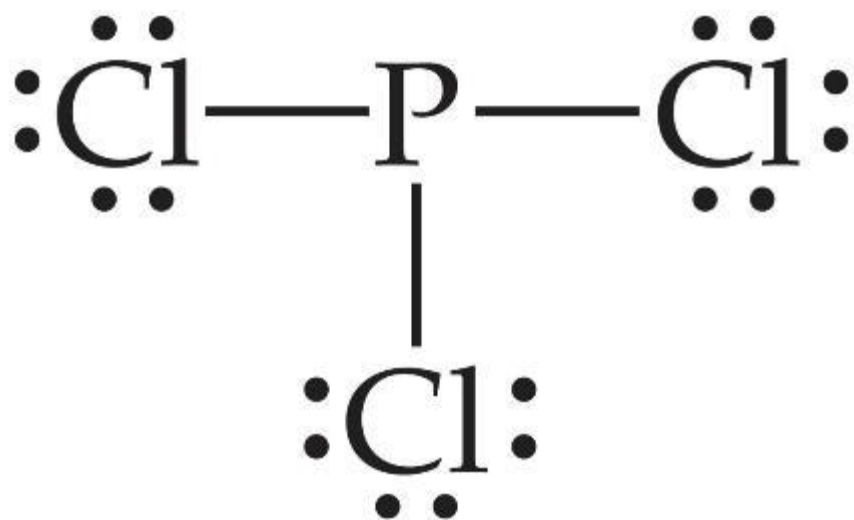


2. Write the symbols for the atoms, show which atoms are attached to which, and connect them with a single bond (a line representing two electrons).

Keep track of the electrons:

$$26 - 6 = 20$$

Writing Lewis Structures

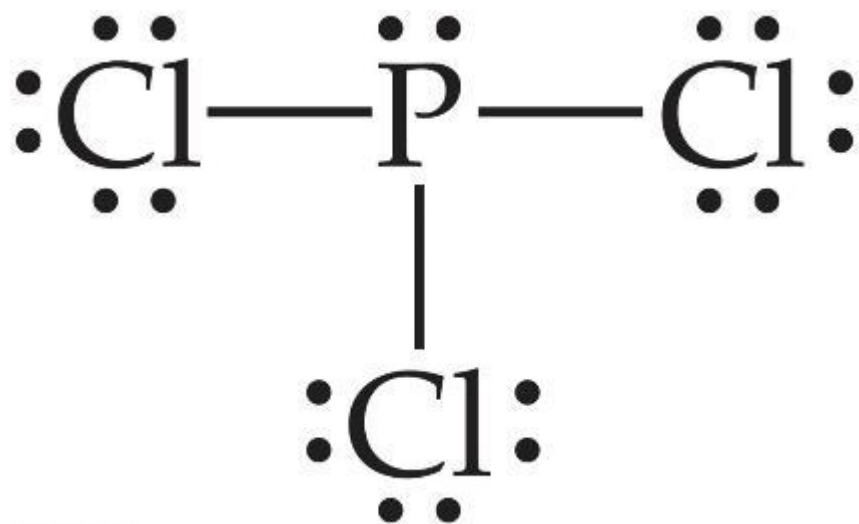


3. Complete the octets around all atoms bonded to the central atom.

Keep track of the electrons:

$$26 - 6 = 20; 20 - 18 = 2$$

Writing Lewis Structures



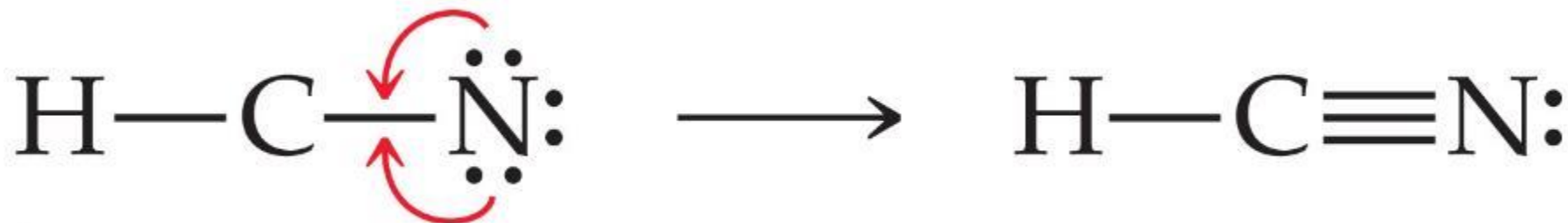
4. Place any leftover electrons on the central atom.

Keep track of the electrons:

$$26 - 6 = 20; 20 - 18 = 2; 2 - 2 = 0$$

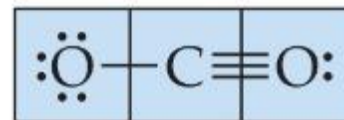
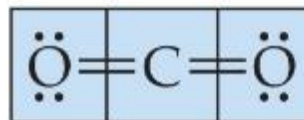
Writing Lewis Structures

5. *If there are not enough electrons to give the central atom an octet, try multiple bonds.*



Writing Lewis Structures

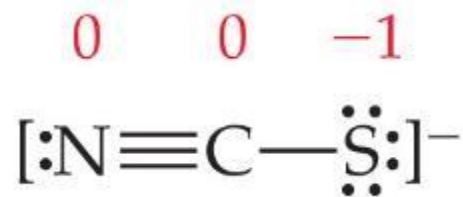
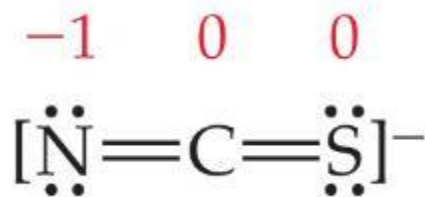
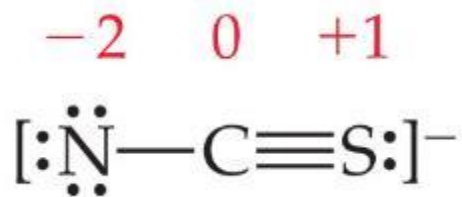
- Then assign formal charges.
- **Formal charge** is the charge an atom would have if all of the electrons in a covalent bond were shared equally.
- Formal charge = valence electrons – $\frac{1}{2}$ (bonding electrons) – *all* nonbonding electrons



Valence electrons:	6	4	6		6	4	6
–(Electrons assigned to atom):	6	4	6		7	4	5
Formal charge:	0	0	0		–1	0	+1

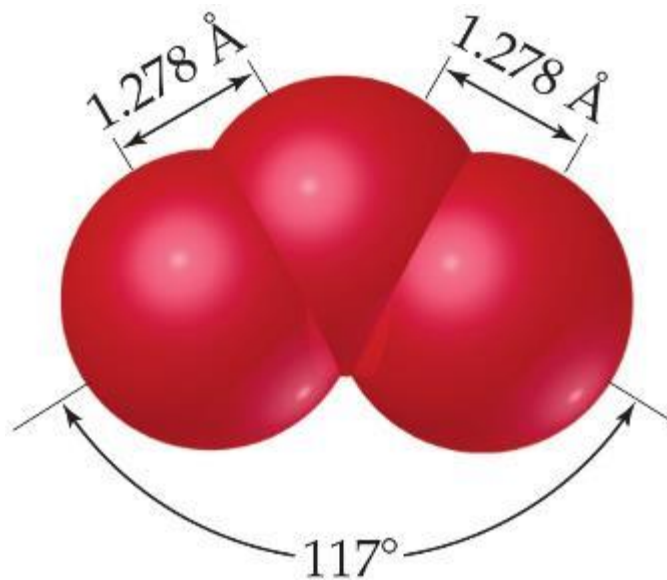
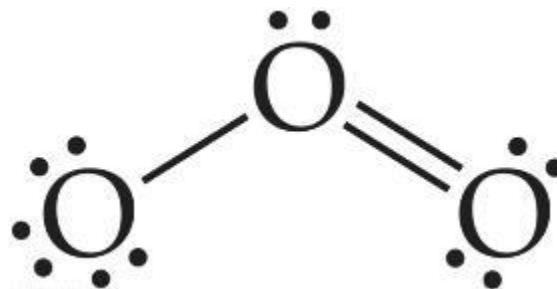
Writing Lewis Structures

- The dominant Lewis structure
 - is the one in which atoms have formal charges closest to zero.
 - puts a negative formal charge on the most electronegative atom.



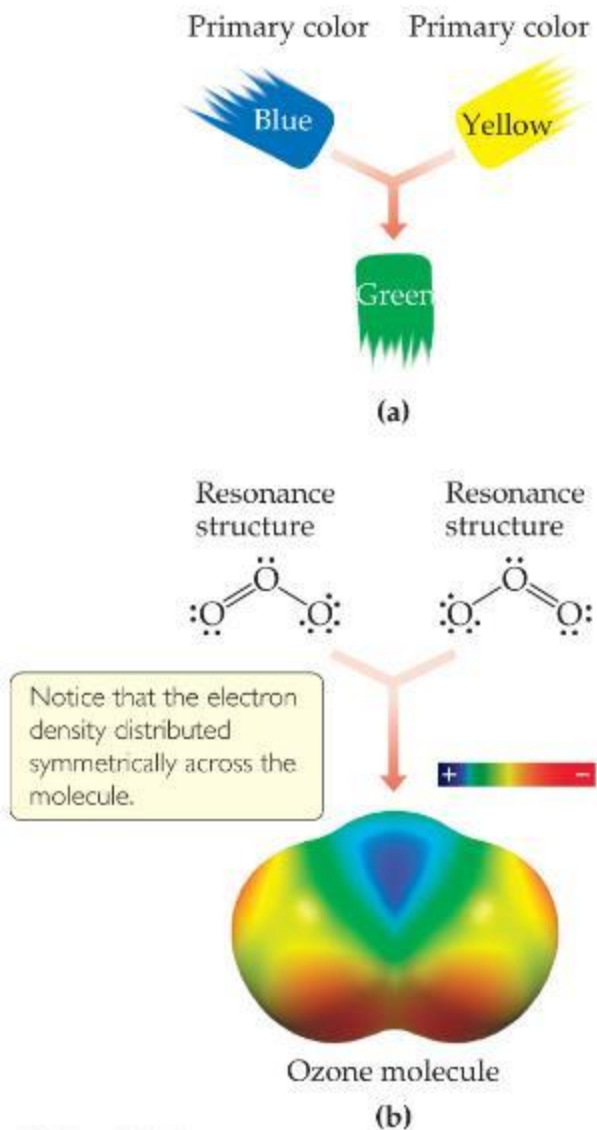
The Best Lewis Structure?

- Following our rules, this is the Lewis structure we would draw for ozone, O_3 .
- However, it doesn't agree with what is observed in nature: Both O to O connections are the same.

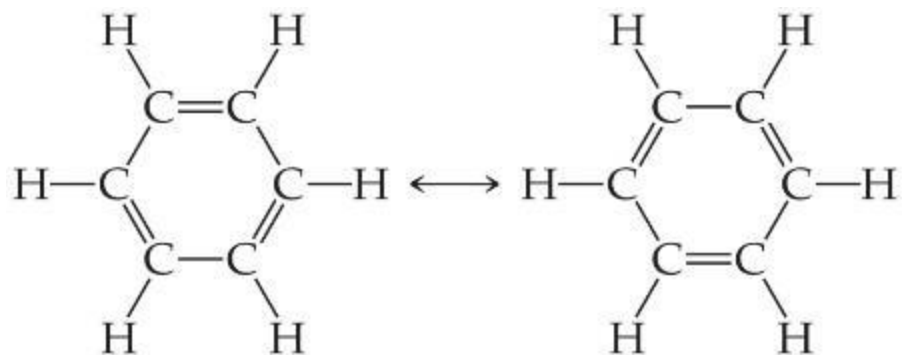


Resonance

- One Lewis structure cannot accurately depict a molecule like ozone.
- We use multiple structures, **resonance structures**, to describe the molecule.



Resonance



- The organic compound benzene, C₆H₆, has two resonance structures.
- It is commonly depicted as a hexagon with a circle inside to signify the delocalized electrons in the ring.

Localized electrons are specifically on one atom or shared between two atoms; *Delocalized* electrons are shared by multiple atoms.

Exceptions to the Octet Rule

- There are three types of ions or molecules that do not follow the octet rule:
 - ions or molecules with an odd number of electrons,
 - ions or molecules with less than an octet,
 - ions or molecules with more than eight valence electrons (an expanded octet).

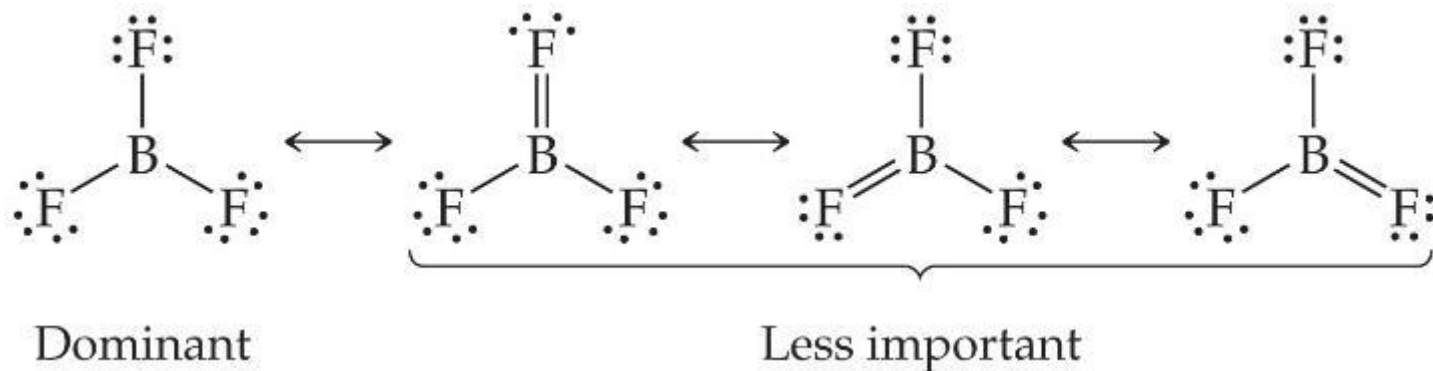
Odd Number of Electrons

Though relatively rare and usually quite unstable and reactive, there are ions and molecules with an odd number of electrons.



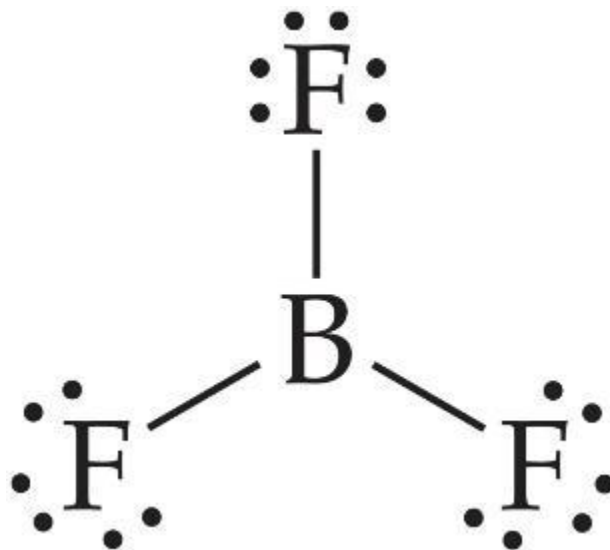
Fewer Than Eight Electrons

- Elements in the second period *before* carbon can make stable compounds with fewer than eight electrons.
- Consider BF_3 :
 - Giving boron a filled octet places a *negative* charge on the boron and a *positive* charge on fluorine.
 - This would not be an accurate picture of the distribution of electrons in BF_3 .



Fewer Than Eight Electrons

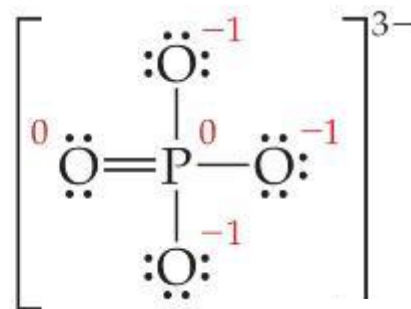
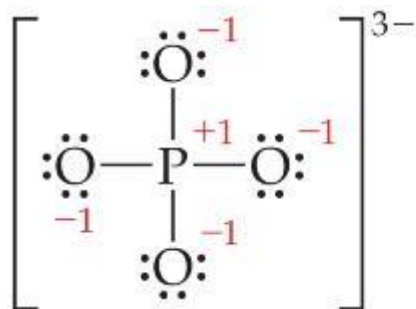
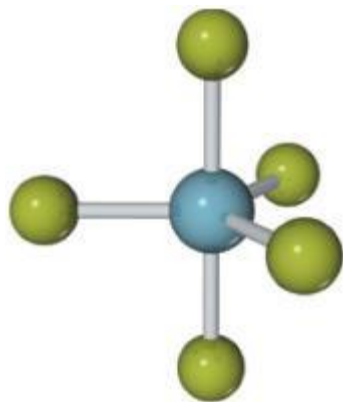
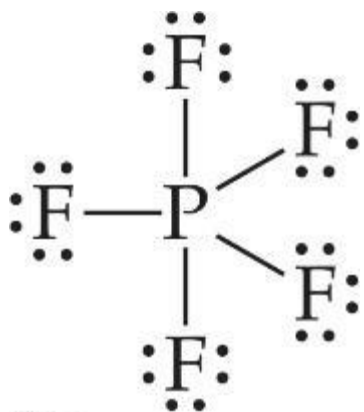
The lesson is: If filling the octet of the central atom results in a negative charge on the central atom and a positive charge on the more electronegative outer atom, don't fill the octet of the central atom.



More Than Eight Electrons

- When an element is in period 3 or below in the periodic table (e.g., periods 3, 4, 5, etc.), it can use *d*-orbitals to make *more* than four bonds.
- Examples: PF_5 and phosphate below

(Note: Phosphate will actually have four resonance structures with five bonds on the P atom!)



Covalent Bond Strength

- Most simply, the strength of a bond is measured by determining how much energy is required to break the bond.
- This is called the **bond enthalpy**.
- The bond enthalpy for a Cl—Cl bond, $D(\text{Cl—Cl})$, is measured to be 242 kJ/mol.
- We write out reactions for breaking *one mole* of those bonds:
– $\text{Cl—Cl} \rightarrow 2 \text{Cl}\cdot$

Average Bond Enthalpies

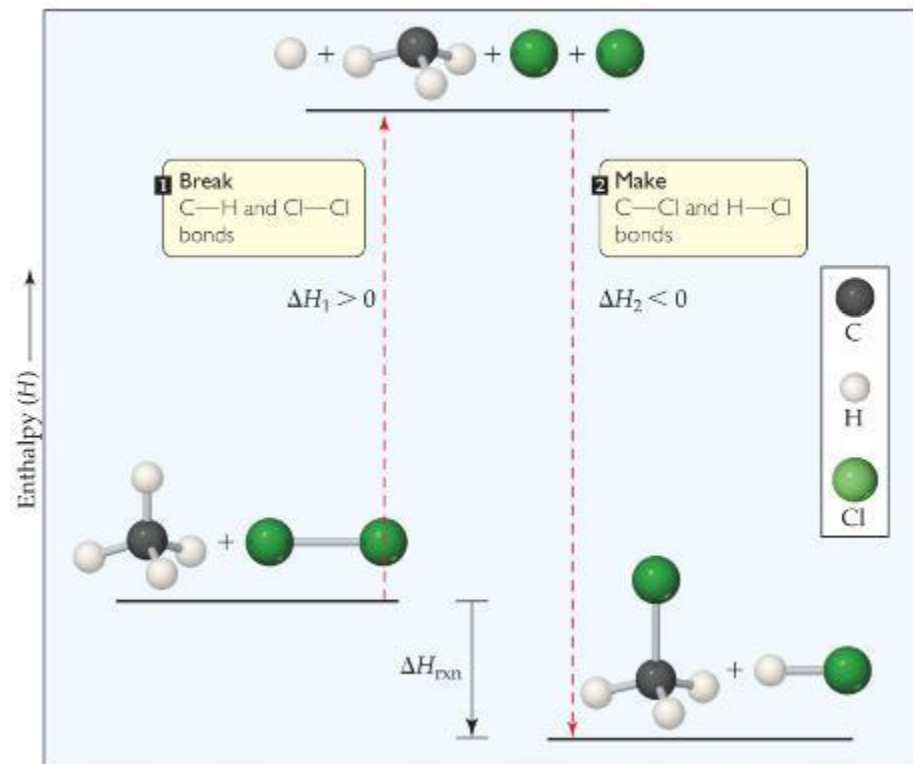
- Average bond enthalpies are positive, because bond breaking is an endothermic process.
- Note that these are *averages* over many different compounds; not every bond in nature for a pair of atoms has exactly the same bond energy.

Table 8.4 Average Bond Enthalpies (kJ/mol)

Single Bonds							
C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						
Multiple Bonds							
C=C	614	N=N	418	O=O	495		
C≡C	839	N≡N	941				
C=N	615	N=O	607	S=O	523		
C≡N	891			S=S	418		
C=O	799						
C≡O	1072						

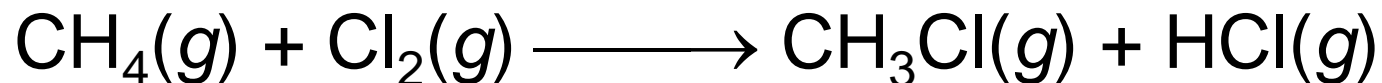
Using Bond Enthalpies to Estimate Enthalpy of Reaction

- One way to *estimate* ΔH for a reaction is to use the bond enthalpies of bonds broken and the new bonds formed.
- Energy is added to break bonds and released when making bonds.
- In other words, $\Delta H_{rxn} = \Sigma(\text{bond enthalpies of all bonds broken}) - \Sigma(\text{bond enthalpies of all bonds formed})$.



Example

From the figure on the last slide



- In this example, one C—H bond and one Cl—Cl bond are broken; one C—Cl and one H—Cl bond are formed.

Answer

$$\begin{aligned}\Delta H &= [D(\text{C—H}) + D(\text{Cl—Cl})] - [D(\text{C—Cl}) + \\ &\quad D(\text{H—Cl})] \\ &= [(413 \text{ kJ}) + (242 \text{ kJ})] - [(328 \text{ kJ}) + (431 \text{ kJ})] \\ &= (655 \text{ kJ}) - (759 \text{ kJ}) \\ &= -104 \text{ kJ}\end{aligned}$$

Bond Enthalpy and Bond Length

- We can also measure an average bond length for different bond types.
- As the number of bonds between two atoms increases, the bond length decreases.

Table 8.5 Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		