Lecture Presentation

**Chapter 8**

**Basic Concepts of Chemical Bonding**

# Chemical Bonds



Metallic
Electrons delocalized

Ionic
Electrostatic attraction

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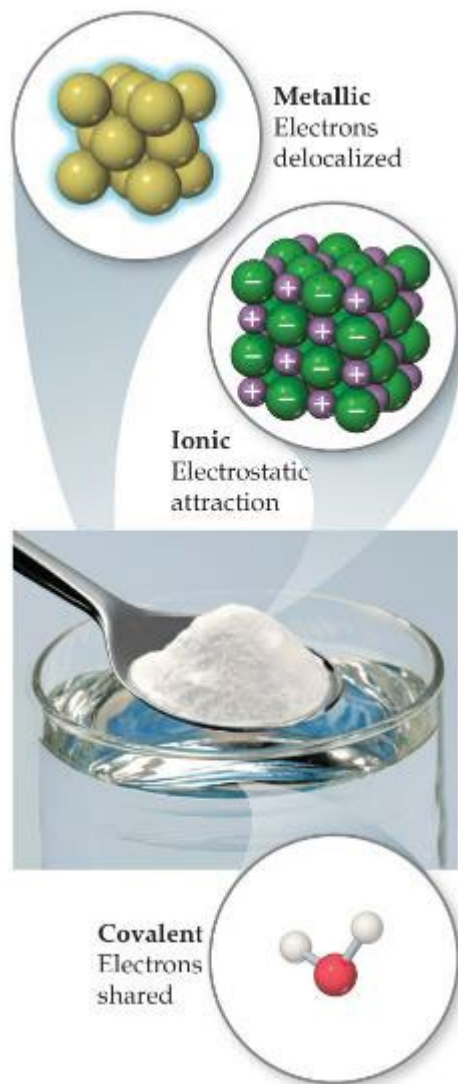
- Three basic types of bonds
  - Ionic
    - Electrostatic attraction between ions.
  - Covalent
    - Sharing of electrons.
  - Metallic
    - Metal atoms bonded to several other atoms.

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# 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 | $[He]2s^2 2p^1$ | ·Ḃ· | Al | $[Ne]3s^2 3p^1$ | ·Ál· |
| 4A | C | $[He]2s^2 2p^2$ | ·Ċ· | Si | $[Ne]3s^2 3p^2$ | ·Ṡi· |
| 5A | N | $[He]2s^2 2p^3$ | ·N̈: | P | $[Ne]3s^2 3p^3$ | ·P̈: |
| 6A | O | $[He]2s^2 2p^4$ | :Ö: | S | $[Ne]3s^2 3p^4$ | :S̈: |
| 7A | F | $[He]2s^2 2p^5$ | :F̈: | Cl | $[Ne]3s^2 3p^5$ | ·C̈l: |
| 8A | Ne | $[He]2s^2 2p^6$ | :N̈e: | Ar | $[Ne]3s^2 3p^6$ | :Är: |

- 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).
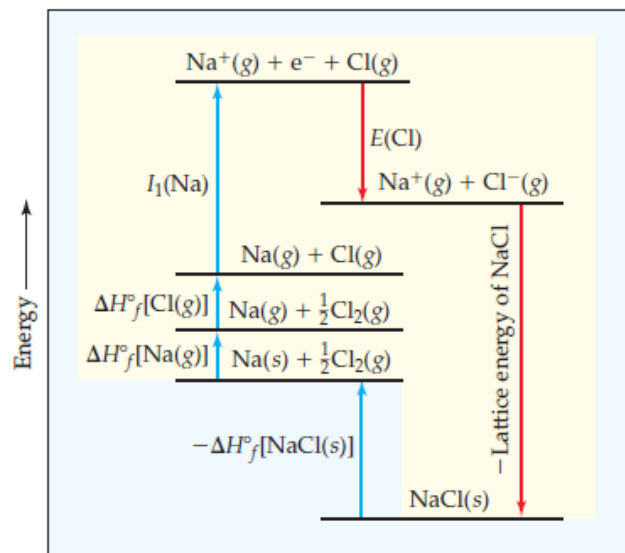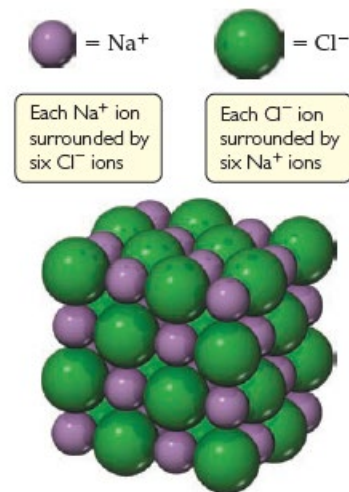
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# Ionic Formation

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

$$Na\cdot + \cdot \ddot{\underset{..}{Cl}}: \longrightarrow Na^+ + [:\ddot{\underset{..}{Cl}}:]^-$$

Na(s)

Cl$_2$(g)

Electrons transfer
from Na(s) to Cl$_2$(g),
forming Na$^+$ and Cl$^-$

Highly exothermic reaction
forming sodium chloride, an ionic
compound composed of sodium
ions, Na$^+$, and chloride ions, Cl$^-$

NaCl(s) forms

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# 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 Cl$_2$($g$).

- Make gaseous atoms: Na($g$) and Cl($g$).

- Make ions: Na$^+$($g$) and Cl$^-$($g$).

- Combine the ions: NaCl($s$).



ic Concepts Chemical Bonding

# 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*.

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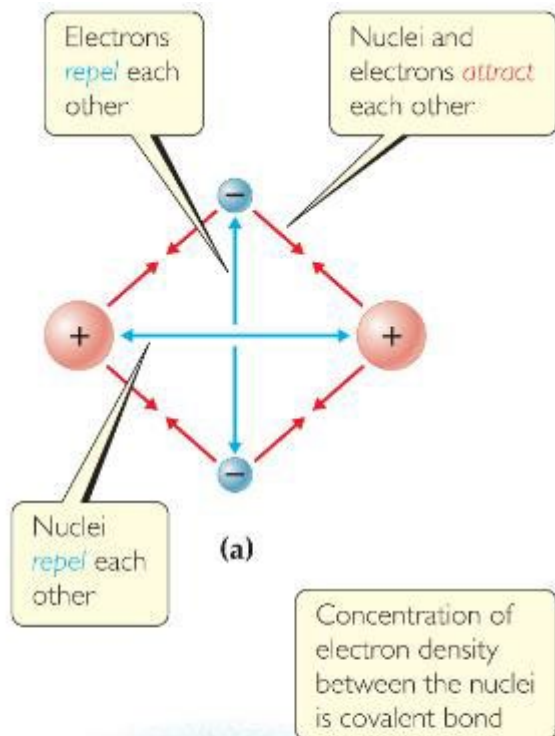
$$E_{\text{el}} = \kappa \frac{Q_1 Q_2}{d}$$

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# 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 | | |

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# Covalent Bonding



Electrons repel each other

Nuclei and electrons attract each other

Nuclei repel each other

(a)

Concentration of electron density between the nuclei is covalent bond

(b)

- 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.

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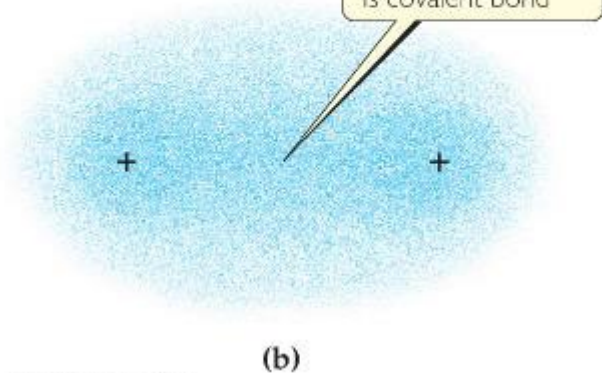
# Lewis Structures

- 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.

$$H-H \qquad \ddot{:Cl}-\ddot{Cl}:$$

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# 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

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# 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**.

$$:\overset{..}{\underset{..}{O}}:\ +\ \cdot\overset{.}{\underset{.}{C}}\cdot\ +\ :\overset{..}{\underset{..}{O}}:\ \longrightarrow\ \overset{..}{\underset{..}{O}}::C::\overset{..}{\underset{..}{O}}\qquad (\text{or}\ \overset{..}{\underset{..}{O}}=C=\overset{..}{\underset{..}{O}})$$

$$:\overset{.}{\underset{.}{N}}\cdot\ +\ \cdot\overset{.}{\underset{.}{N}}:\ \longrightarrow\ :N:::N:\qquad (\text{or}\ :N\equiv N:)$$

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# 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.
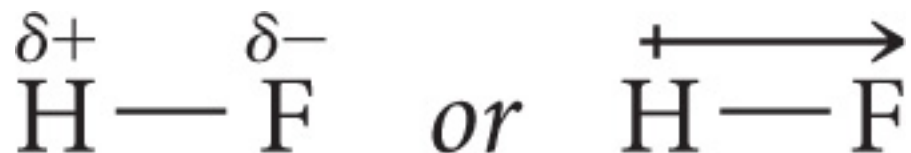
Low electron density

High electron density

+    −

$F_2$         HF         LiF
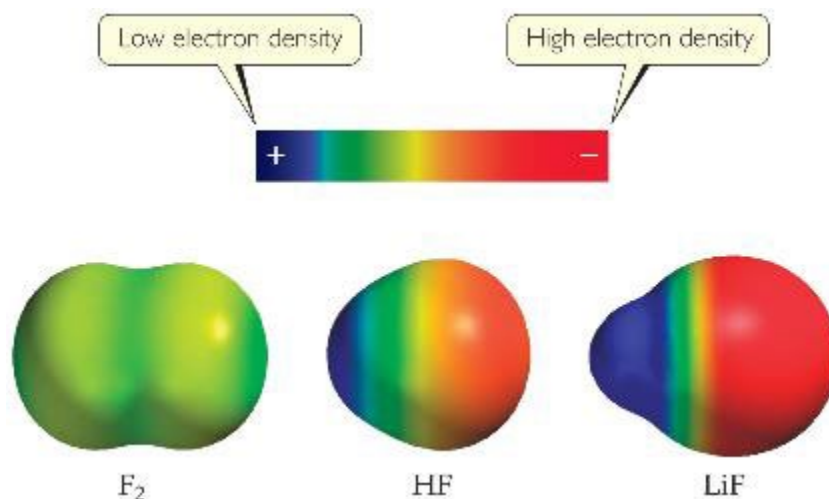
# Electronegativity

- 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.



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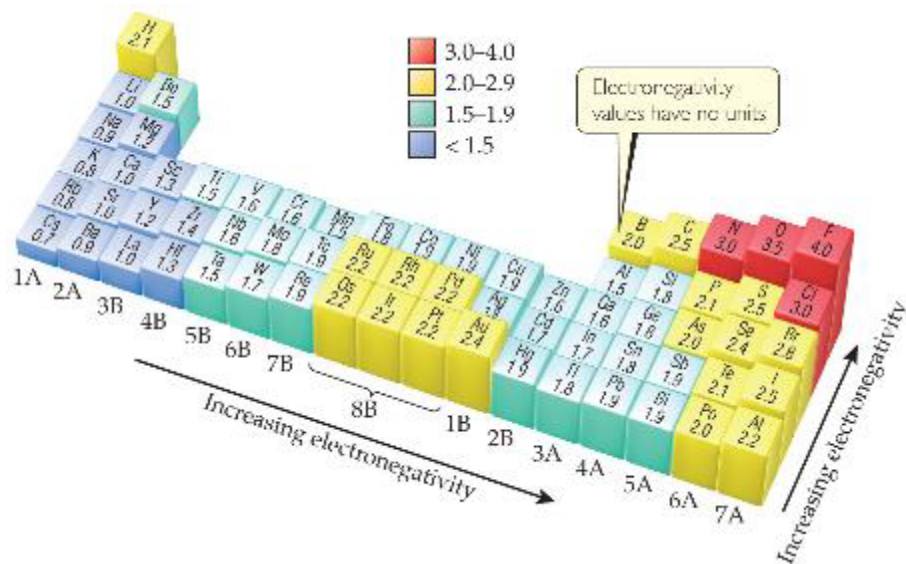
# Electronegativity and Polar Covalent Bonds

- 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 $\delta-$.

- The other atom is "more positive," or $\delta+$.

$$\overset{\delta+}{H} - \overset{\delta-}{F} \quad or \quad \overset{+\longrightarrow}{H - F}$$

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# 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.



HF          HCl          HBr          HI

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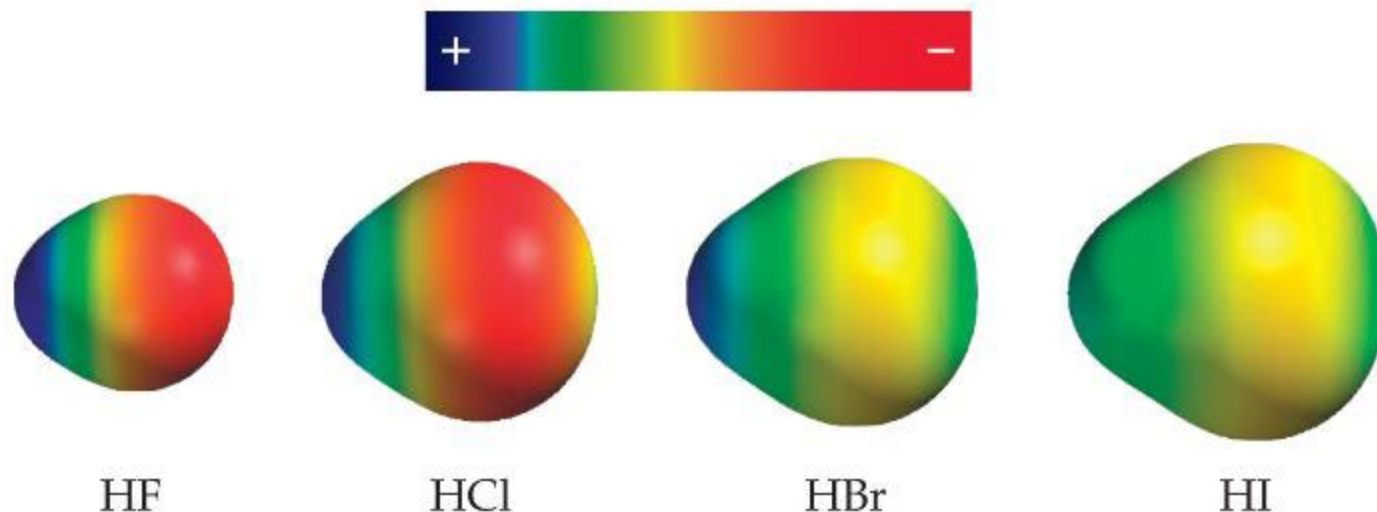
# Dipoles

- When two equal, but opposite, charges are separated by a distance, a **dipole** forms.

- A **dipole moment**, $\mu$, produced by two equal but opposite charges separated by a distance, $r$, is calculated:

$$\mu = Qr$$

- It is measured in debyes (D).



$Q-$      $Q+$

$\leftarrow r \rightarrow$

Dipole moment $\mu = Qr$

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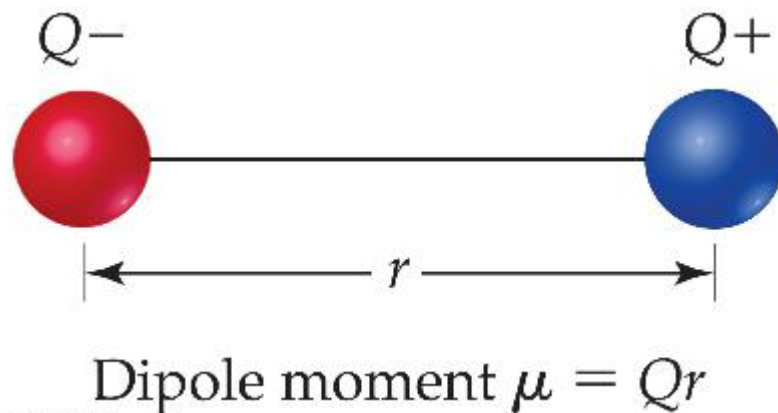
# Is a Compound Ionic or Covalent?

- 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.

Basic Concepts of Chemical Bonding

Which kind of work a chemistry student will do in future?

# Working places of chemistry guys



cepts
ical
Bonding

# Crystal Structure of IDO1-4PI complex
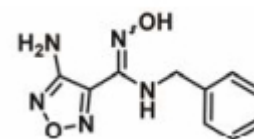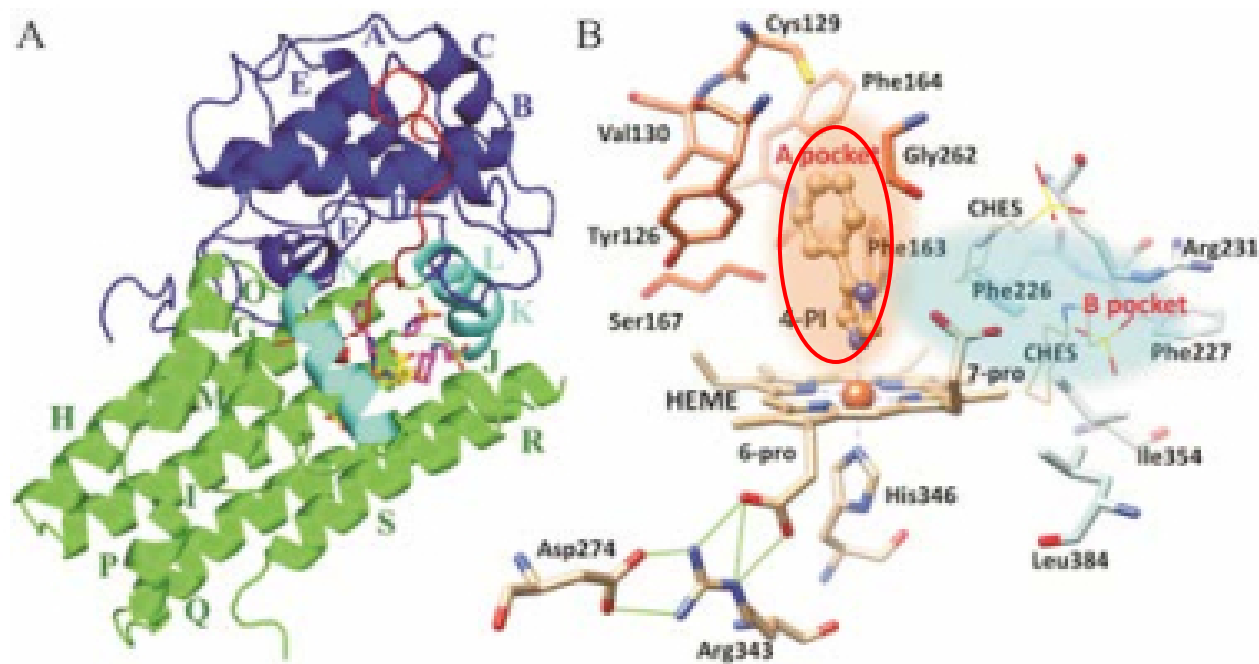


## Inhibitor
## (抑制剂)

IDO1 is an enzyme（酶）that can inhibit immune system (免疫系统) to kill tumor（肿瘤）

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# $457,000,000.00
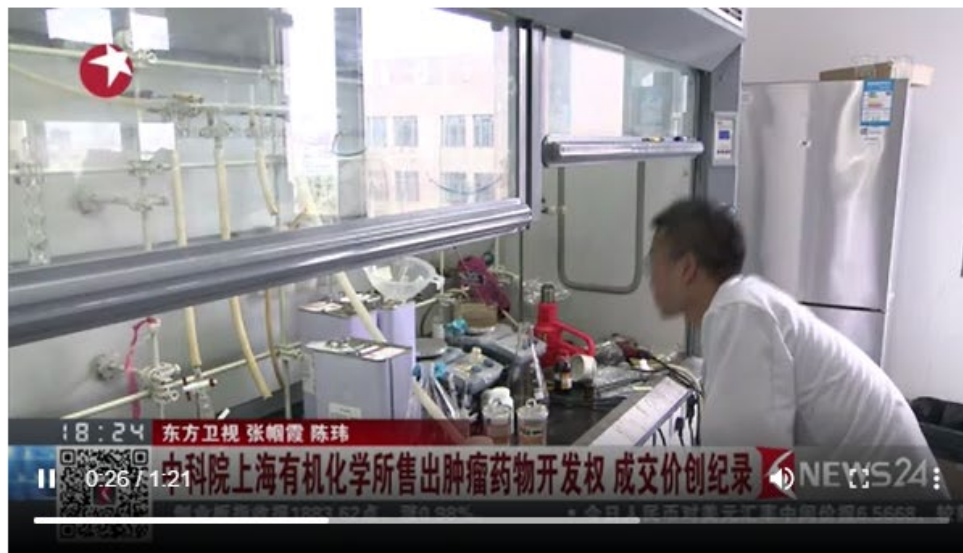


中国科学院上海有机化学研究所与信达生物制药（苏州）有限公司近期就肿瘤免疫靶向小分子药物的授权开发达成了合作协议。信达生物以首付款、研发里程碑和销售里程碑付款共计4.57亿美元另加销售提成的合作方式，获得上海有机所研发的吲哚胺 2,3-双加氧酶（IDO）小分子抑制剂的全球独家开发许可权。这是目前国内科研院所与本土生物制药企业达成的合作金额最高的项目，充分体现了分子创制的价值，有望成为中国院企创新药合作的重大里程碑事件。

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# Writing Lewis Structures (Covalent Molecules)

$PCl_3$
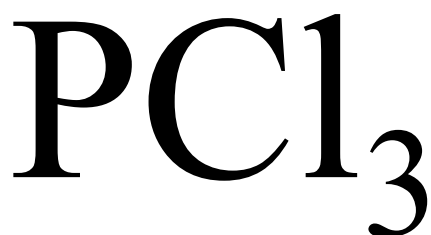
1. Sum the valence electrons from all atoms, taking into account overall charge.

   – If it is an anion, add one electron for each negative charge.

   – If it is a cation, subtract one electron for each positive charge.

Keep track of the electrons:

5 + 3(7) = 26

# Writing Lewis Structures

Cl—P—Cl
|
Cl

**Keep track of the electrons:**
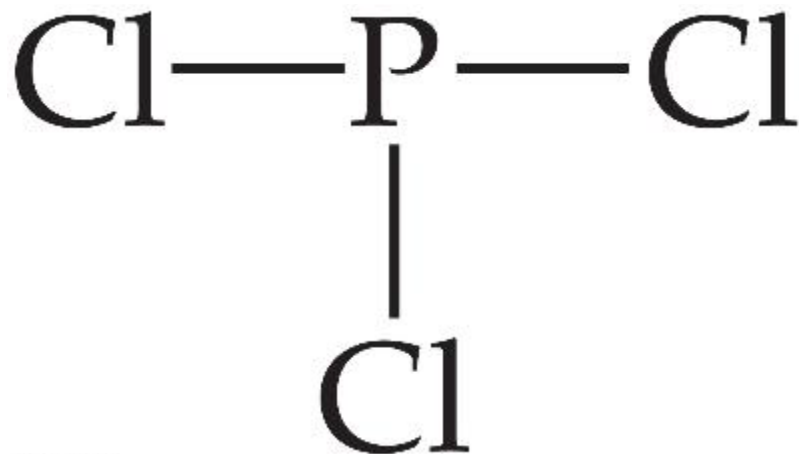
26 − 6 = 20

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).

# Writing Lewis Structures
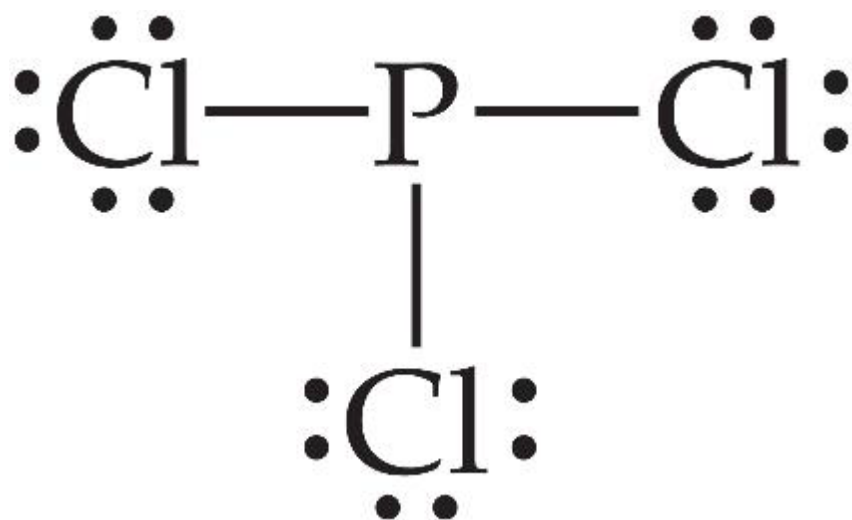


3. Complete the octets around all atoms bonded to the central atom.

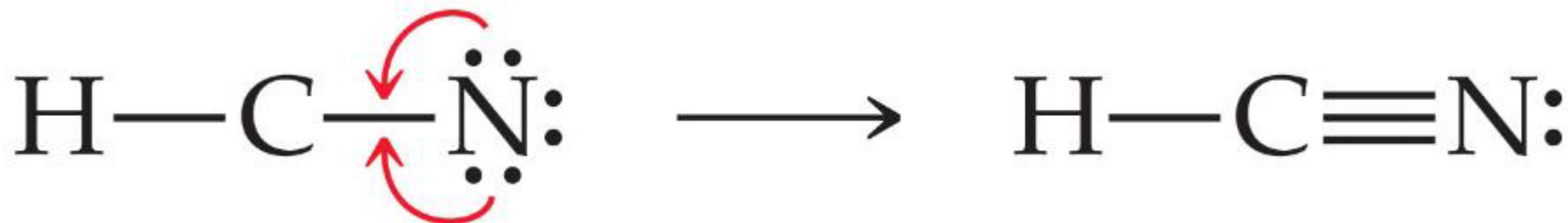Keep track of the electrons:

26 − 6 = 20; 20 − 18 = 2

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# Writing Lewis Structures
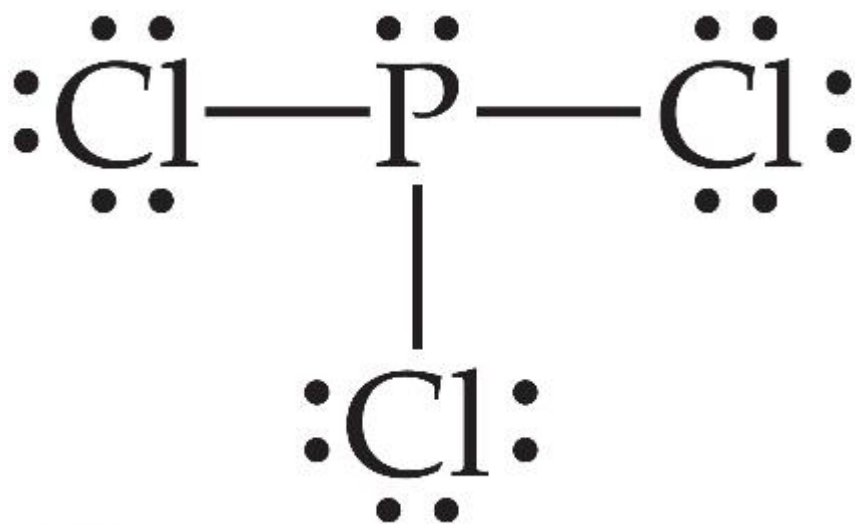


4. Place any leftover electrons on the central atom.

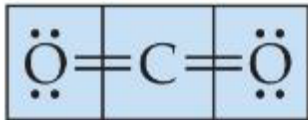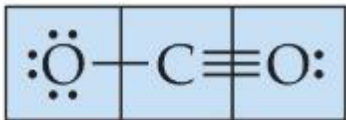Keep track of the electrons:

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

# Writing Lewis Structures

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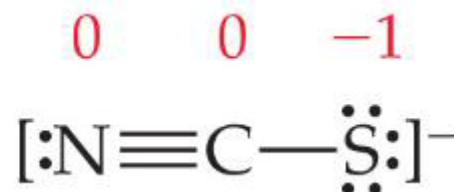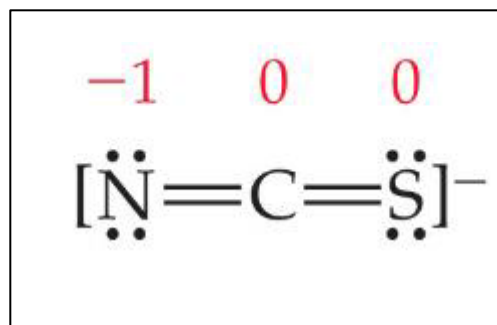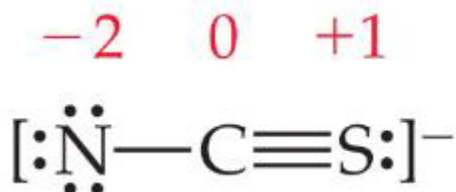
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# Writing Lewis Structures

- 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  –
  ½ (bonding electrons)  –  *all* nonbonding electrons

|  | Ö=C=Ö |  |  | :Ö—C≡O: |  |
|---|---|---|---|---|---|
| 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 |

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# Writing Lewis Structures

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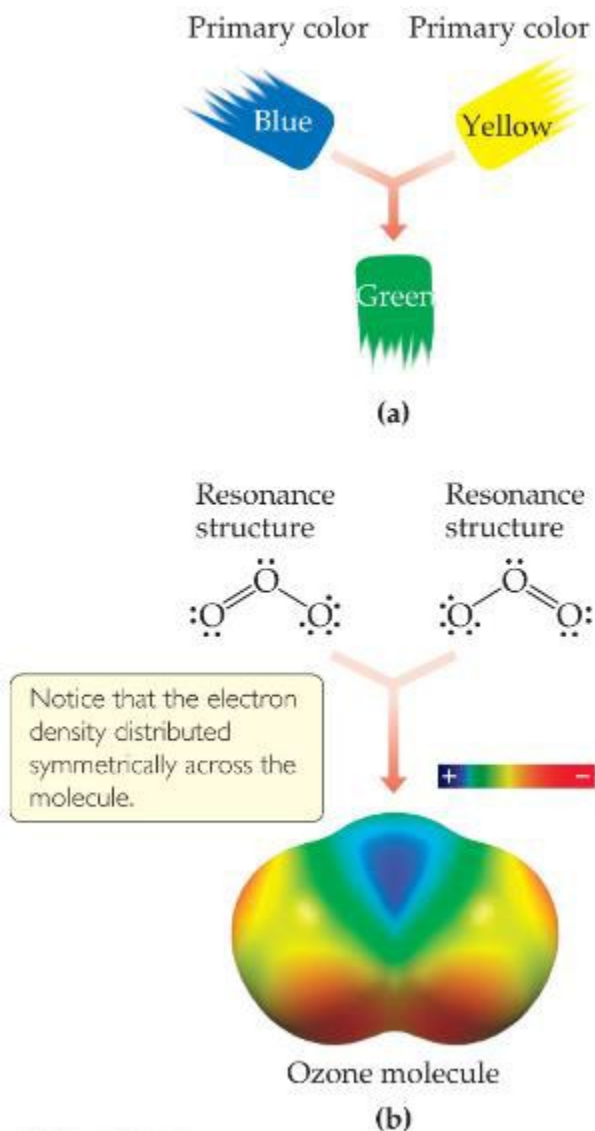  - puts a negative formal charge on the most electronegative atom.

$$-2 \quad 0 \quad +1$$
$$[:\ddot{N}{-}C{\equiv}S:]^-$$

$$-1 \quad 0 \quad 0$$
$$[\ddot{N}{=}C{=}\ddot{S}]^-$$

$$0 \quad 0 \quad -1$$
$$[:N{\equiv}C{-}\ddot{S}:]^-$$

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# 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.



1.278 Å    1.278 Å

117°
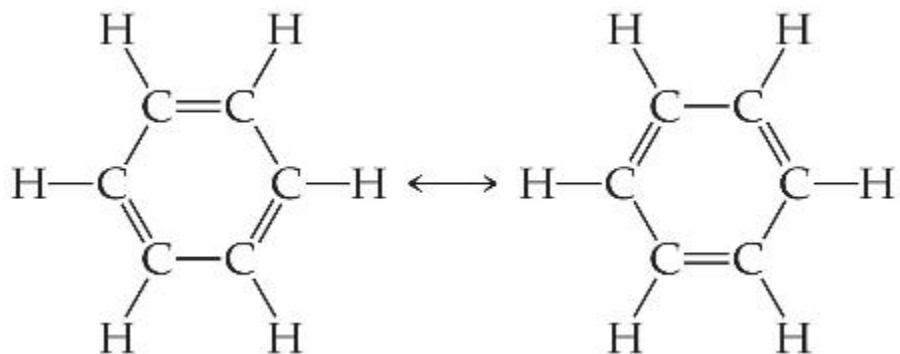
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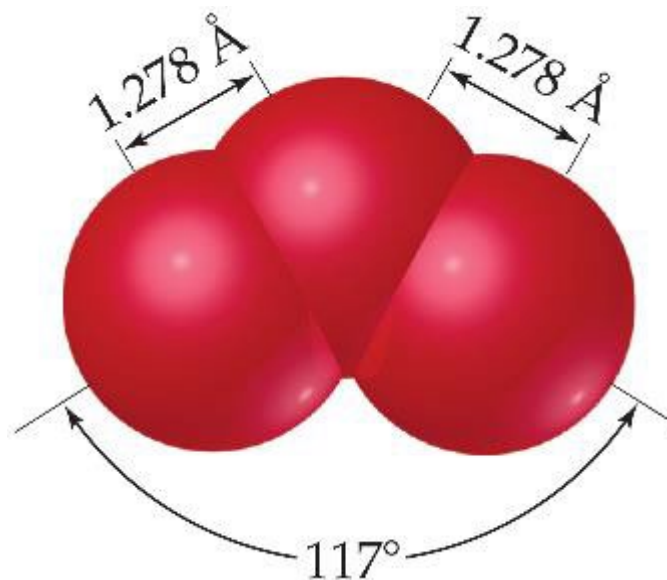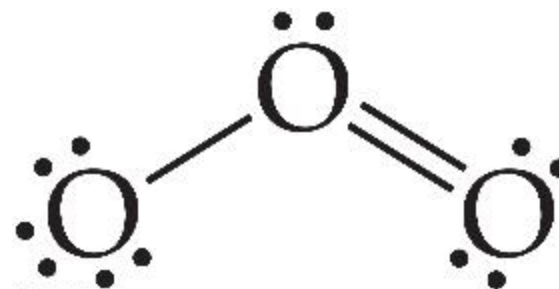
# Resonance

- One Lewis structure cannot accurately depict a molecule like ozone.

- We use multiple structures, **resonance structures**, to describe the molecule.

Primary color    Primary color

Blue    Yellow

Green

(a)

Resonance structure    Resonance structure

Notice that the electron density distributed symmetrically across the molecule.

+    −

Ozone molecule

(b)

Basic Concepts of Chemical Bonding

# Resonance



- The organic compound benzene, $C_6H_6$, 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.

Basic Concepts of Chemical Bonding

# 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 of valence electrons,

  - ions or molecules with more than eight valence electrons (an expanded octet).

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# Odd Number of Electrons

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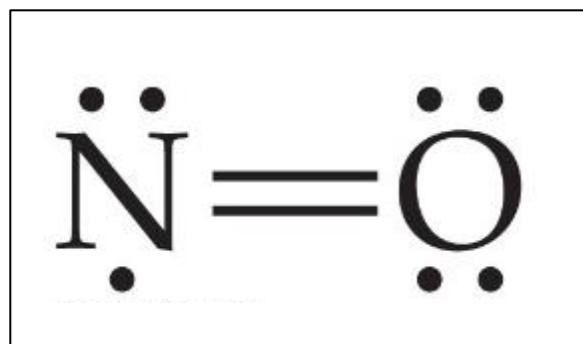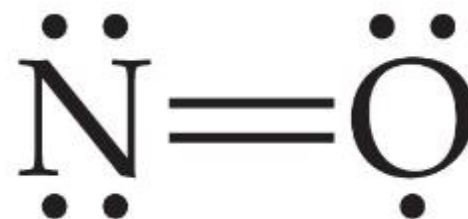


5+6 = 11 valence electrons

# 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 $BF_3$.



Dominant          Less important

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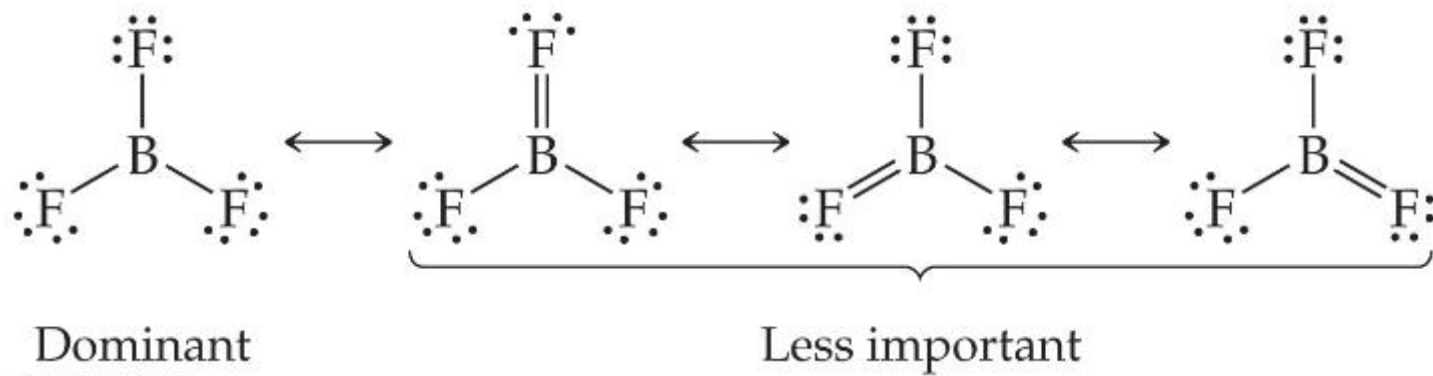
# Fewer Than Eight Electrons

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.
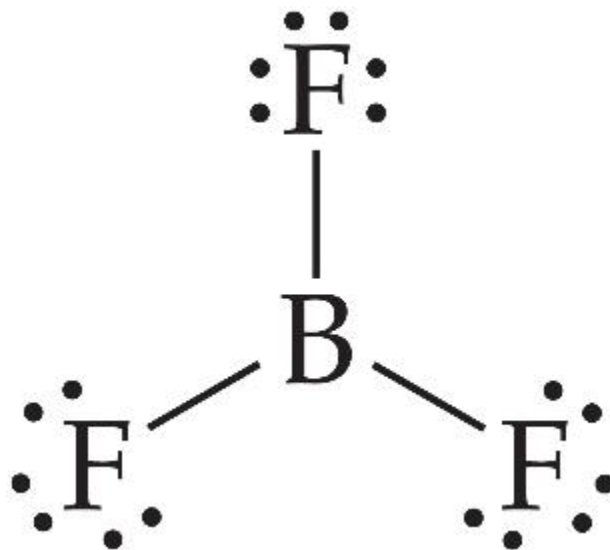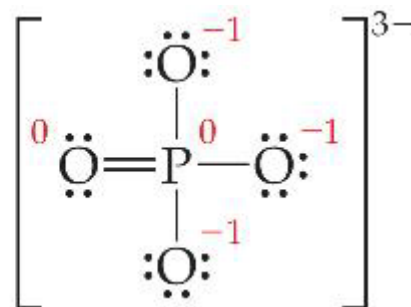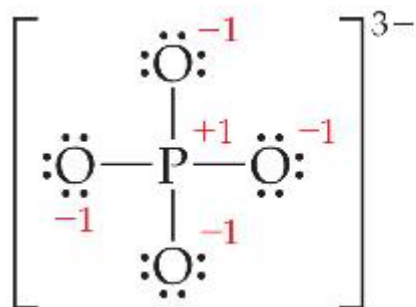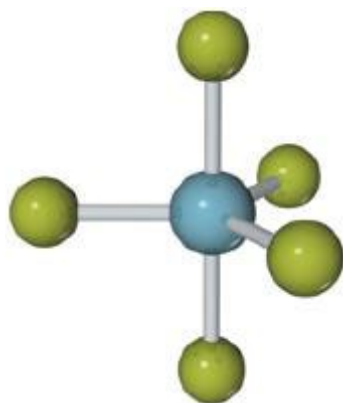
# More Than Eight Electrons

- 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!)

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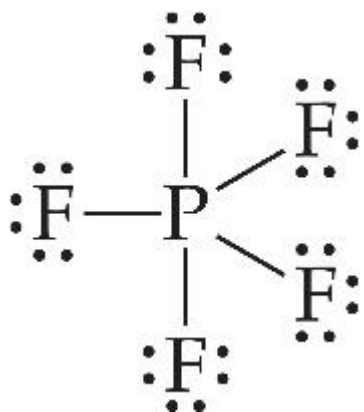
# Covalent Bond Strength

- 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, $D$(Cl— Cl), is measured to be 242 kJ/mol.

- We write out reactions for breaking *one mole* of those bonds:

  Cl—Cl  →  2 Cl•

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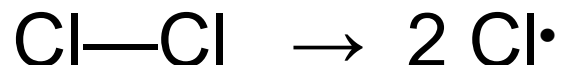
# Average Bond Enthalpies

- Average bond enthalpies are positive, because bond breaking is an endothermic process.

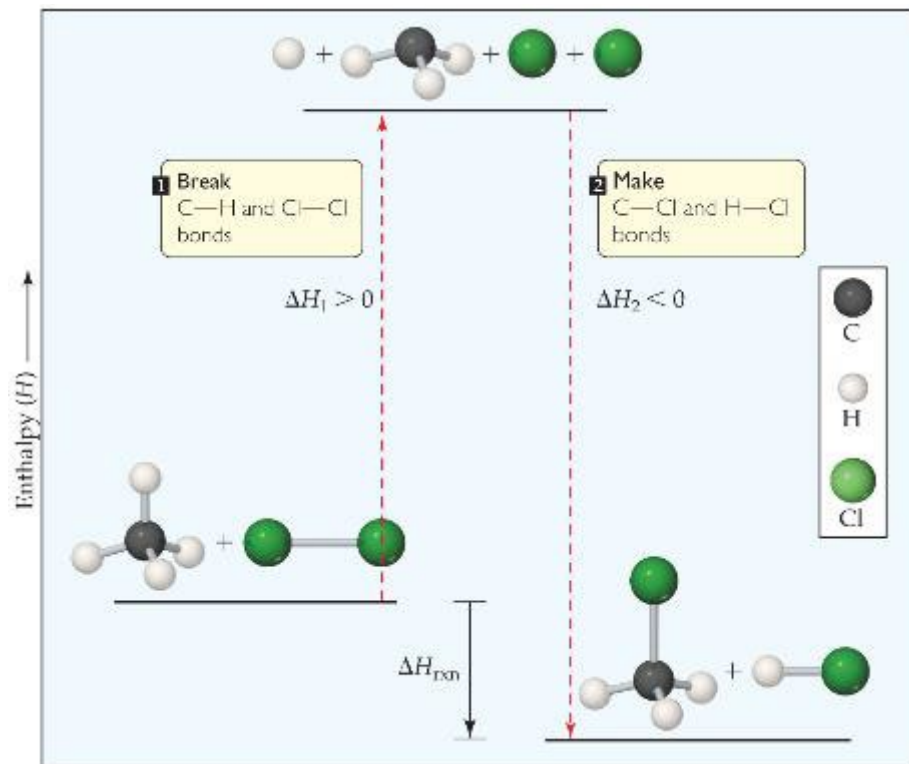- Note that these are *averages* over many different compounds; not every bond in nature for a pair of atoms has exactly the same bond energy.

**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**

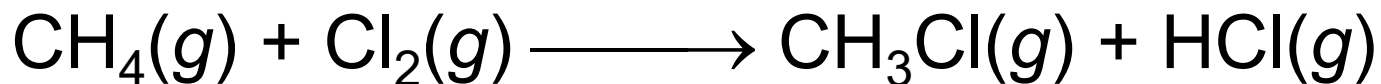| | | | | | |
|---|---|---|---|---|---|
| C=C | 614 | N=N | 418 | O=O | 495 |
| C≡C | 839 | N≡N | 941 | | |
| C=N | 615 | N=O | 607 | S=O | 523 |
| C≡N | 891 | | | S=S | 418 |
| C=O | 799 | | | | |
| C≡O | 1072 | | | | |

Basic Concepts of Chemical Bonding

# Using Bond Enthalpies to Estimate Enthalpy of Reaction

- One way to *estimate* $\Delta H$ 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, $\Delta H_{rxn} = \Sigma$(bond enthalpies of all bonds broken) $- \Sigma$(bond enthalpies of all bonds formed).



1 Break
C—H and Cl—Cl bonds

$\Delta H_1 > 0$

2 Make
C—Cl and H—Cl bonds

$\Delta H_2 < 0$

C
H
Cl

Enthalpy (H)

$\Delta H_{rxn}$

Basic Concepts of Chemical Bonding

# Example

From the figure on the last slide

$$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$$

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

Basic Concepts
of Chemical
Bonding

# Answer

$\Delta H = [D(\text{C—H}) + D(\text{Cl—Cl})] - [D(\text{C—Cl}) +$

$$D(\text{H—Cl})]$$

$= [(413 \text{ kJ}) + (242 \text{ kJ})] - [(328 \text{ kJ}) + (431 \text{ kJ})]$

$= (655 \text{ kJ}) - (759 \text{ kJ})$

$= -104 \text{ kJ}$

Basic Concepts
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Bonding

# 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 | | |

Basic Concepts of Chemical Bonding