

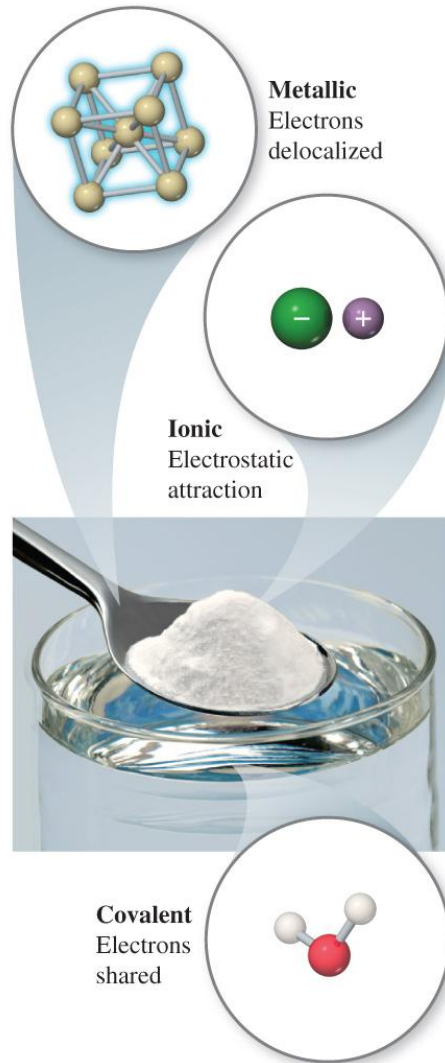
# Lecture Presentation

## Chapter 8

### Basic Concepts of Chemical Bonding

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St. Charles Community College  
Cottleville, MO

# Chemical Bonds



- Three basic types of bonds

- Ionic

- Electrostatic attraction between ions.

- Covalent

- Sharing of electrons.

- Metallic

- Metal atoms bonded to several other atoms.

Basic Concepts  
of Chemical  
Bonding

# Lewis Symbols

TABLE 8.1 • Lewis Symbols

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

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- G.N. Lewis pioneered the use of chemical symbols surrounded with dots to symbolize the valence electrons around an atom.
- When forming compounds, atoms tend to add or subtract electrons until they are surrounded by eight valence electrons (the octet rule).

# Ionic Bonding

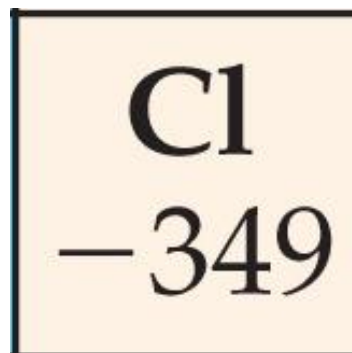
# Energetics of Ionic Bonding

Element	$I_1$
Na	496

As we saw in the last chapter, it takes 496 kJ/mol to remove electrons from sodium.

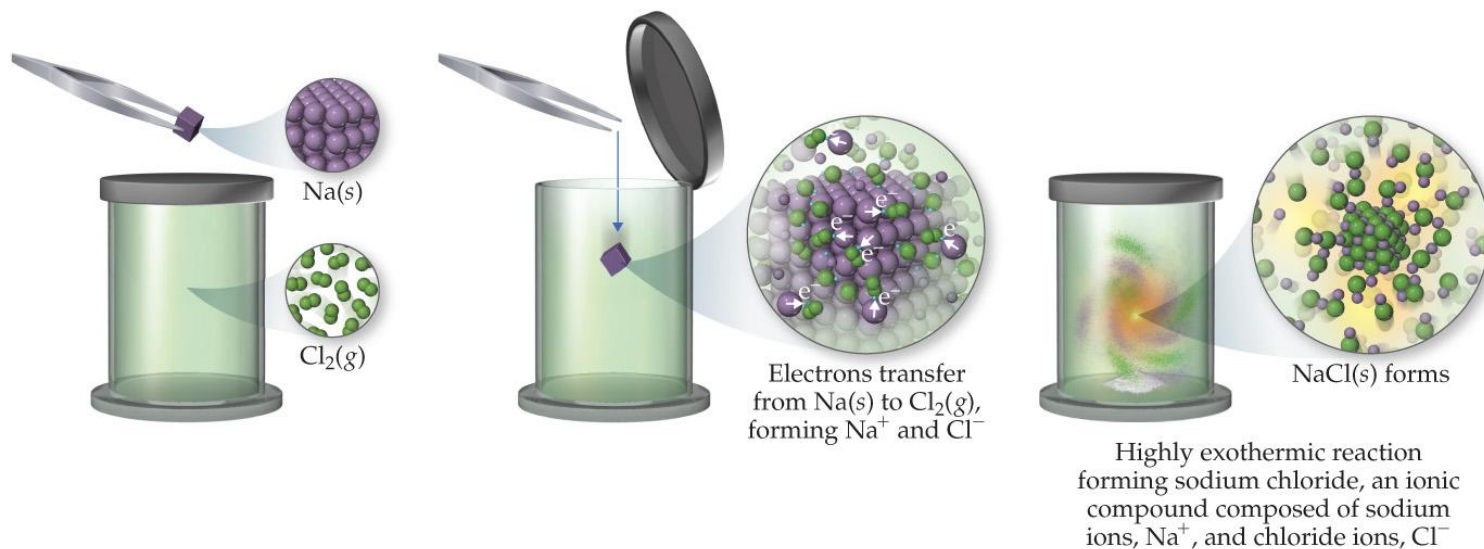
# Energetics of Ionic Bonding

We get 349 kJ/mol  
back by giving  
electrons to  
chlorine.



# Energetics of Ionic Bonding

But these numbers don't explain why the reaction of sodium metal and chlorine gas to form sodium chloride is so exothermic!

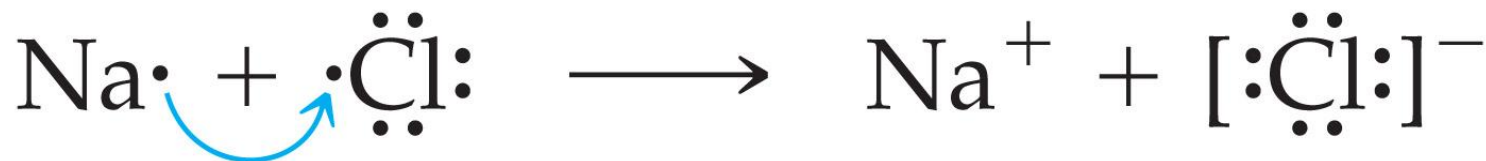


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# Energetics of Ionic Bonding



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- There must be a third piece to the puzzle.
- What is as yet unaccounted for is the electrostatic attraction between the newly formed sodium cation and chloride anion.



# Lattice Energy

- This third piece of the puzzle is 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

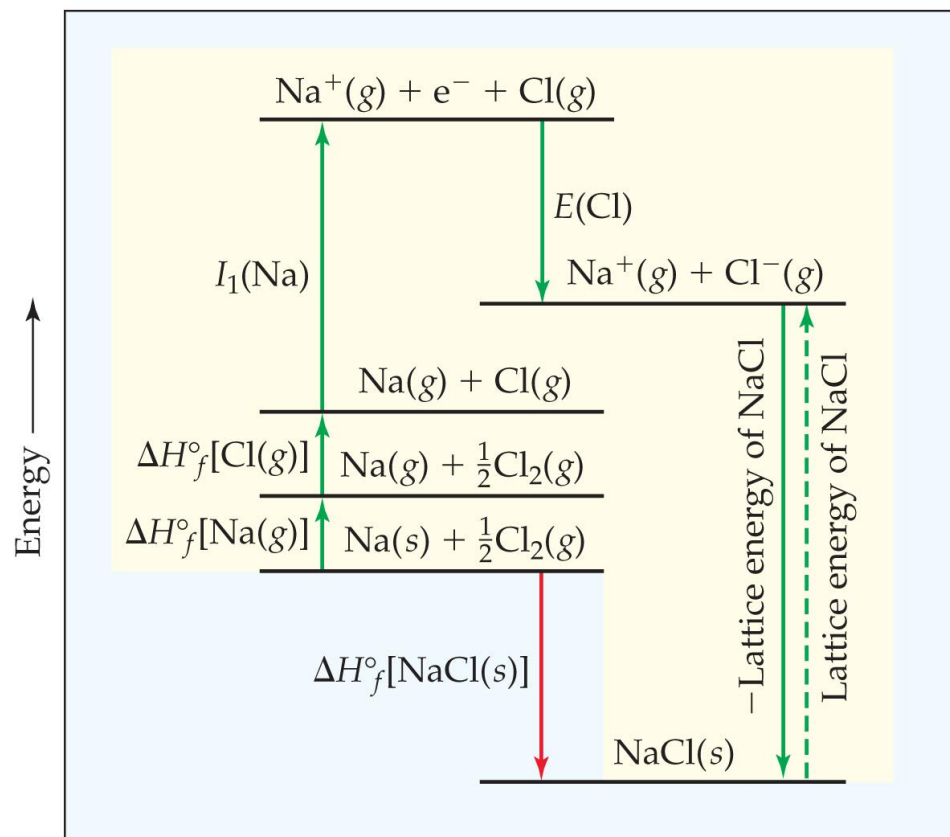
- Lattice energy, then, increases with the charge on the ions.
- It also increases with decreasing size of ions.

**TABLE 8.2 • Lattice Energies for Some Ionic Compounds**

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	MgCl <sub>2</sub>	2326
LiCl	834	SrCl <sub>2</sub>	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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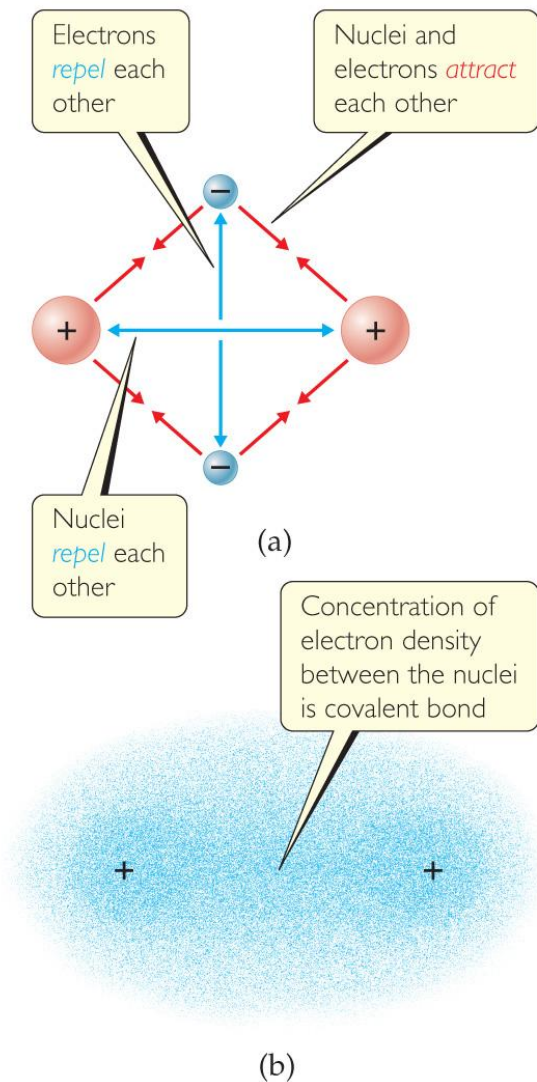
# Energetics of Ionic Bonding



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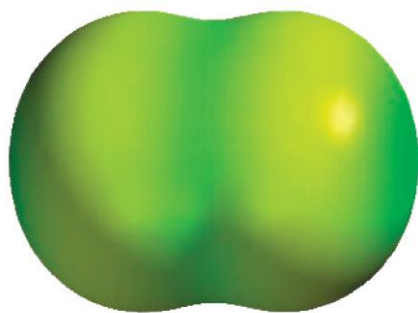
By accounting for all three energies (ionization energy, electron affinity, and lattice energy), we can get a good idea of the energetics involved in such a process.

# Covalent Bonding



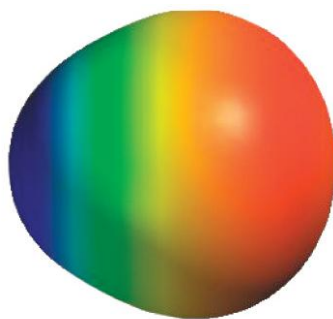
- In covalent bonds, atoms share electrons.
- There are several electrostatic interactions in these bonds:
  - Attractions between electrons and nuclei,
  - Repulsions between electrons,
  - Repulsions between nuclei.

# Polar Covalent Bonds



F<sub>2</sub>

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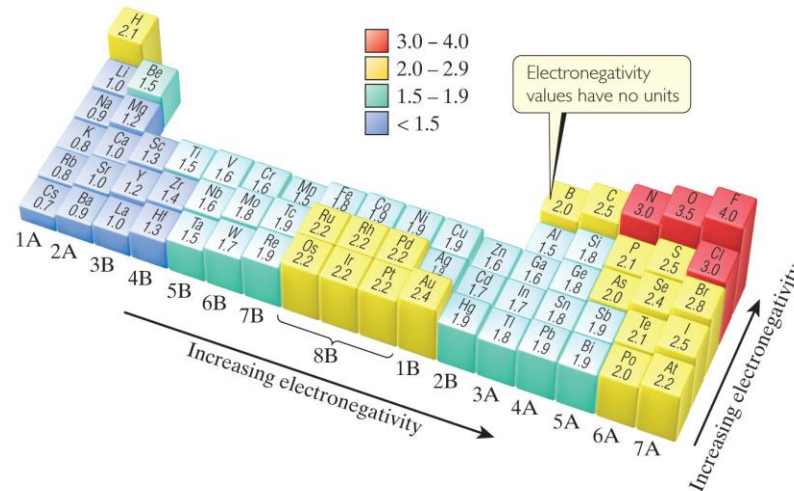
HF

- Though atoms often form compounds by sharing electrons, the electrons 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 atoms in a molecule to attract electrons to themselves.*
- On the periodic chart, electronegativity increases as you go...
  - ...from left to right across a row.
  - ...from the bottom to the top of a column.

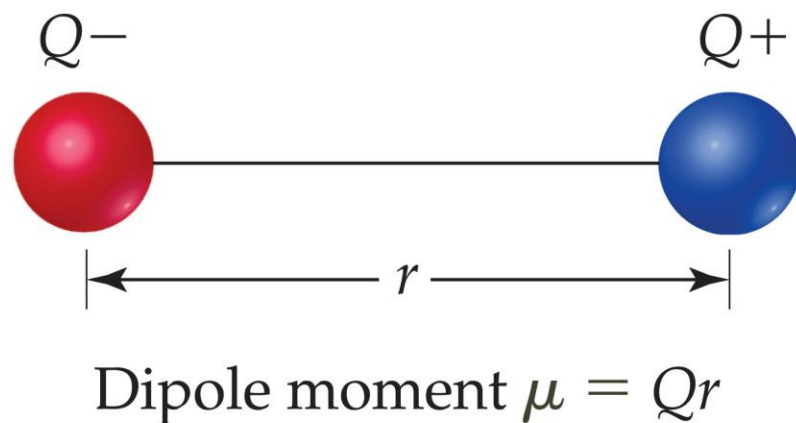


# Polar Covalent Bonds

- When two atoms share electrons unequally, a **bond dipole** results.
- The **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).



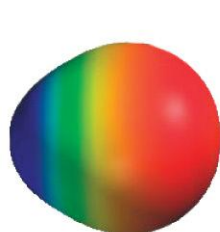
# Polar Covalent Bonds

**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

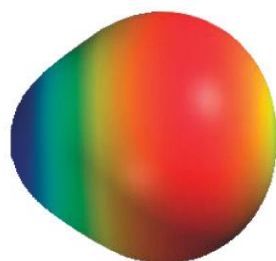
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The greater the difference in electronegativity, the more polar is the bond.

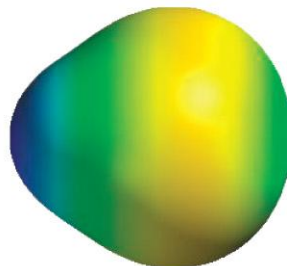


HF

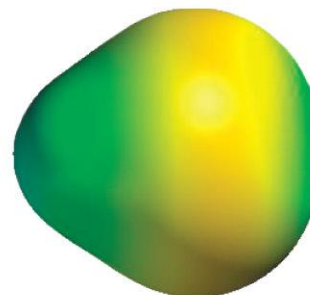
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HCl



HBr



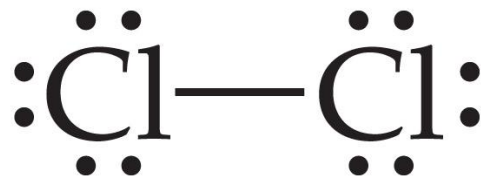
HI



# Lewis Structures

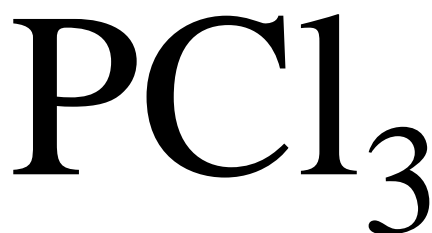


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Lewis structures are representations of molecules showing all electrons, bonding and nonbonding.

# Writing Lewis Structures

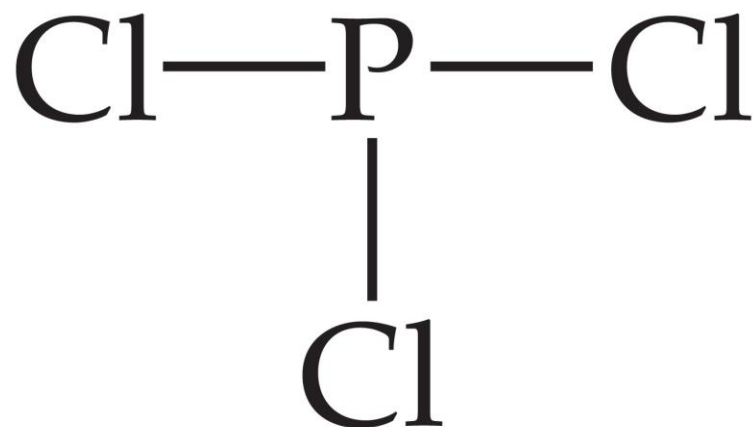


Keep track of the electrons:

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

1. Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.
  - 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

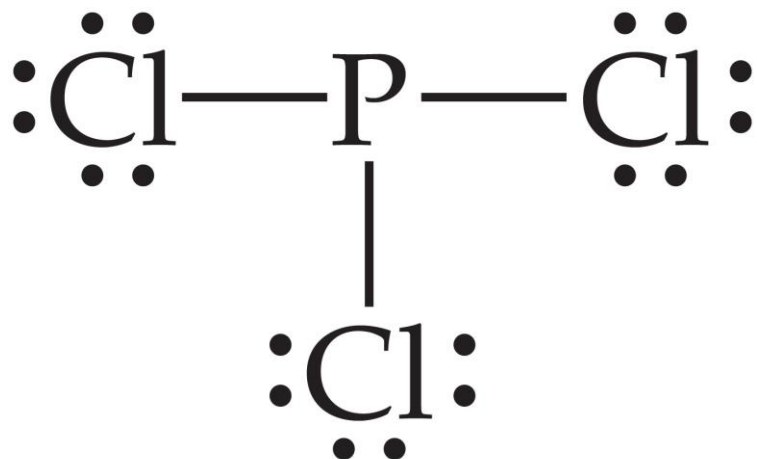


2. The central atom is the *least* electronegative element that isn't hydrogen. Connect the outer atoms to it by single bonds.

Keep track of the electrons:

$$26 - 6 = 20$$

# Writing Lewis Structures

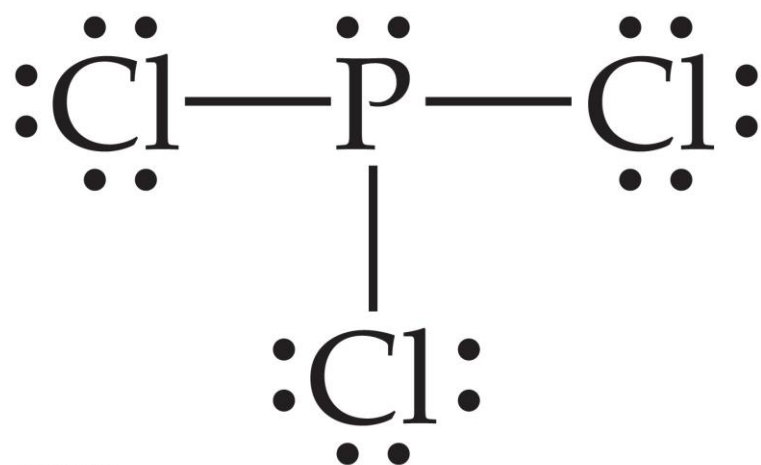


3. Fill the octets of the outer atoms.

Keep track of the electrons:

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

# Writing Lewis Structures



4. Fill the octet of the central atom.

Keep track of the electrons:

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

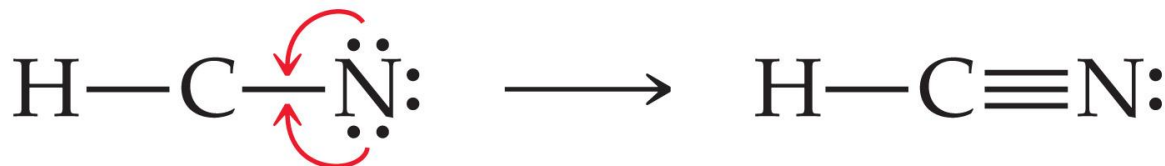
# Writing Lewis Structures



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5. If you run out of electrons before the central atom has an octet...

...form multiple bonds until it does.



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# Writing Lewis Structures

- Then assign formal charges.
  - For each atom, count the electrons in lone pairs and half the electrons it shares with other atoms.
  - Subtract that from the number of valence electrons for that atom: the difference is its **formal charge**.

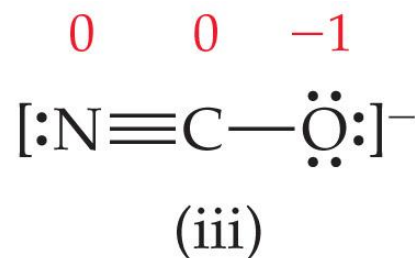
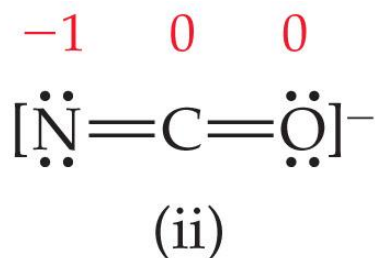
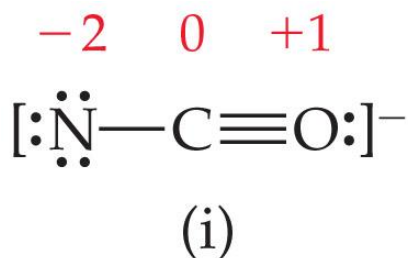
	$\begin{array}{ c c c } \hline \ddot{\text{O}} & =\text{C} & =\ddot{\text{O}} \\ \hline \end{array}$			$\begin{array}{ c c c } \hline :\ddot{\text{O}} & -\text{C} & \equiv \text{O}: \\ \hline \end{array}$		
Valence electrons:	6	4	6	6	4	6
–(Electrons assigned to atom):	6	4	6	7	4	5
Formal charge:	0	0	0	–1	0	+1

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# Writing Lewis Structures

- The best Lewis structure...
  - ...is the one with the fewest charges.
  - ...puts a negative charge on the most electronegative atom.

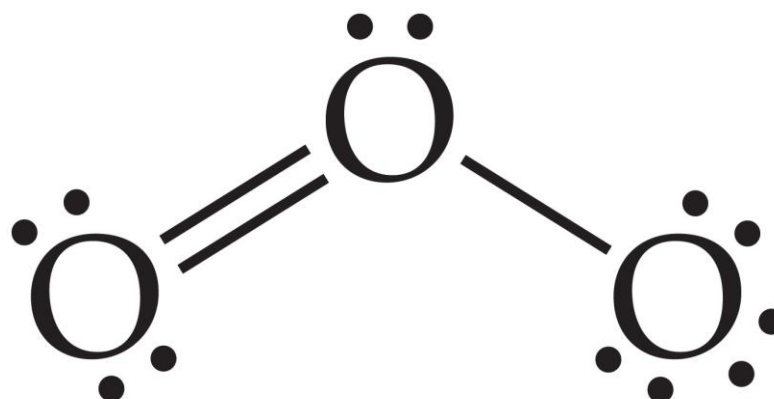


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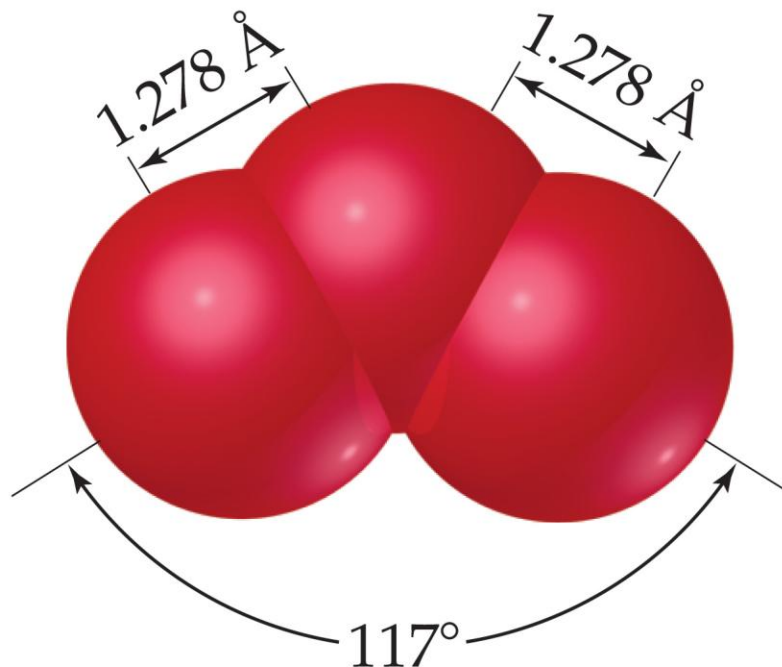
# Resonance

This is the Lewis structure we would draw for ozone,  $O_3$ .



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# Resonance

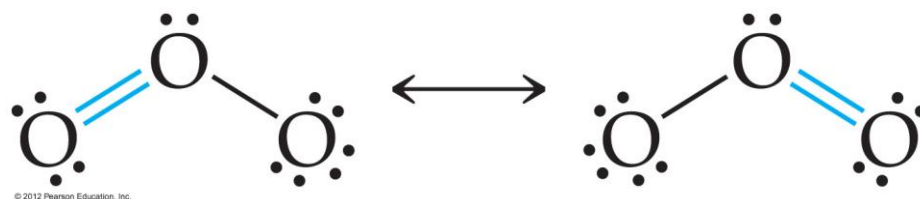


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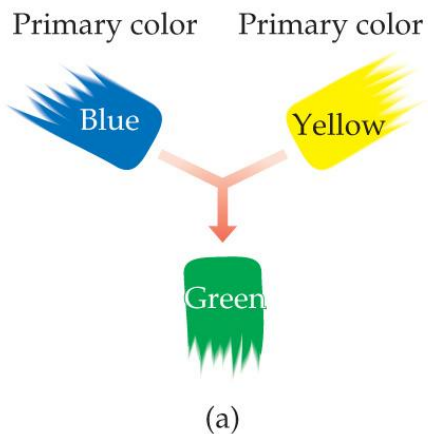
- But this is at odds with the true, observed structure of ozone, in which...
  - ...both O—O bonds are the same length.
  - ...both outer oxygens have a charge of  $-1/2$ .

# Resonance

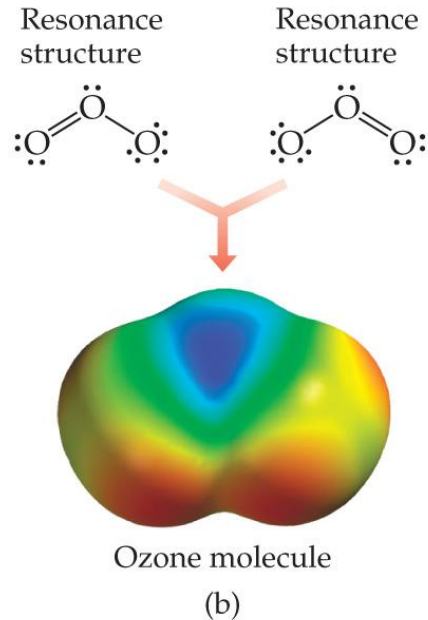
- One Lewis structure cannot accurately depict a molecule like ozone.
- We use multiple structures, resonance structures, to describe the molecule.



# Resonance



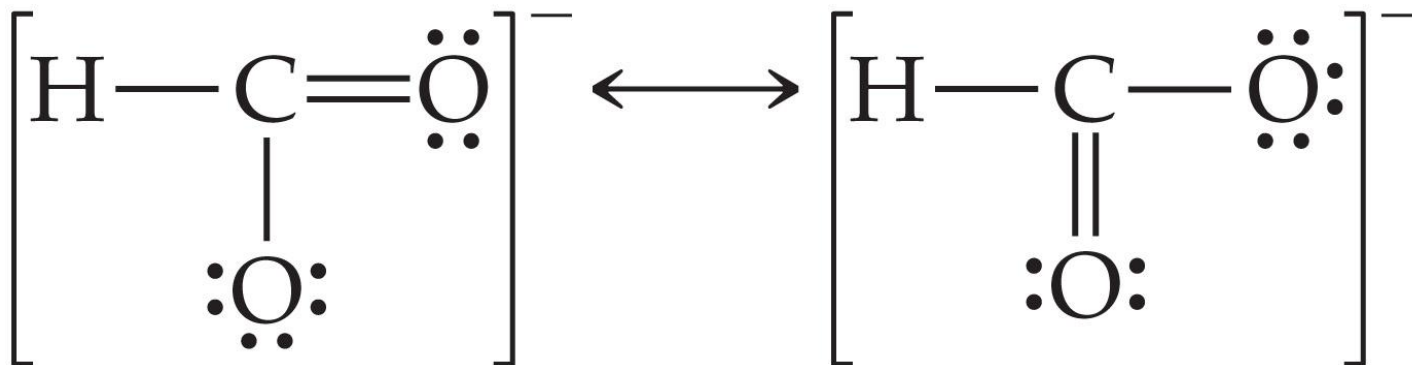
Just as green is a synthesis of blue and yellow...



...ozone is a synthesis of these two resonance structures.

# Resonance

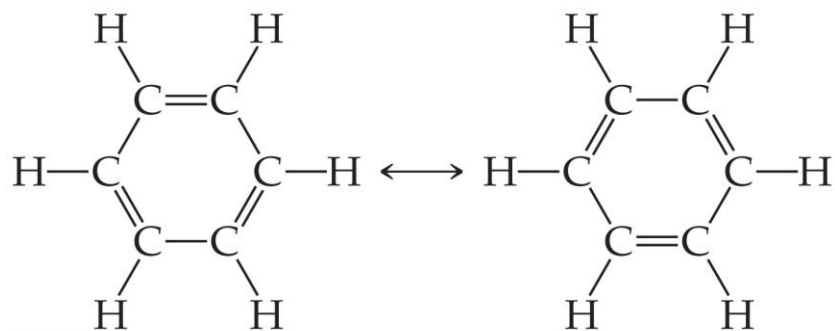
- In truth, the electrons that form the second C—O bond in the double bonds below do not always sit between that C and that O, but rather can move among the two oxygens and the carbon.
- They are not **localized**; they are **delocalized**.



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# Resonance



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- 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.

# 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

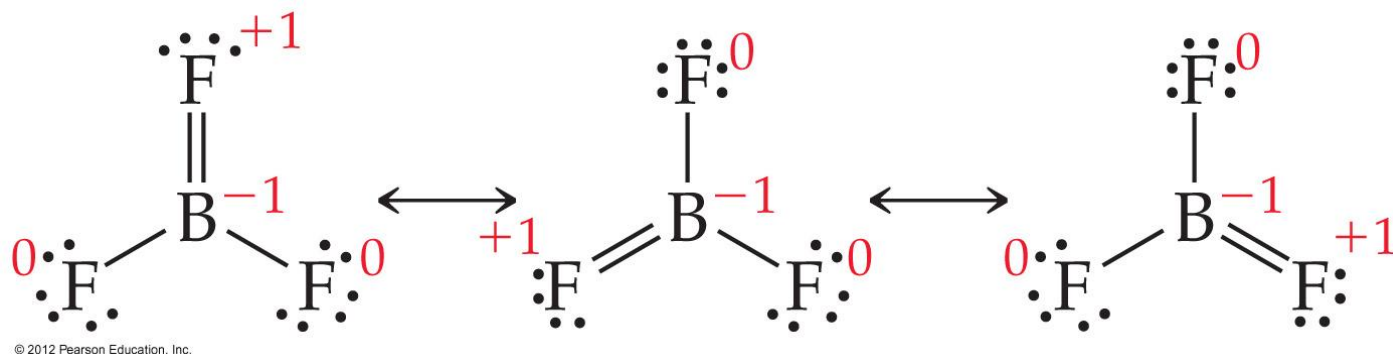
Though relatively rare and usually quite unstable and reactive, there are ions and molecules with an odd number of electrons.



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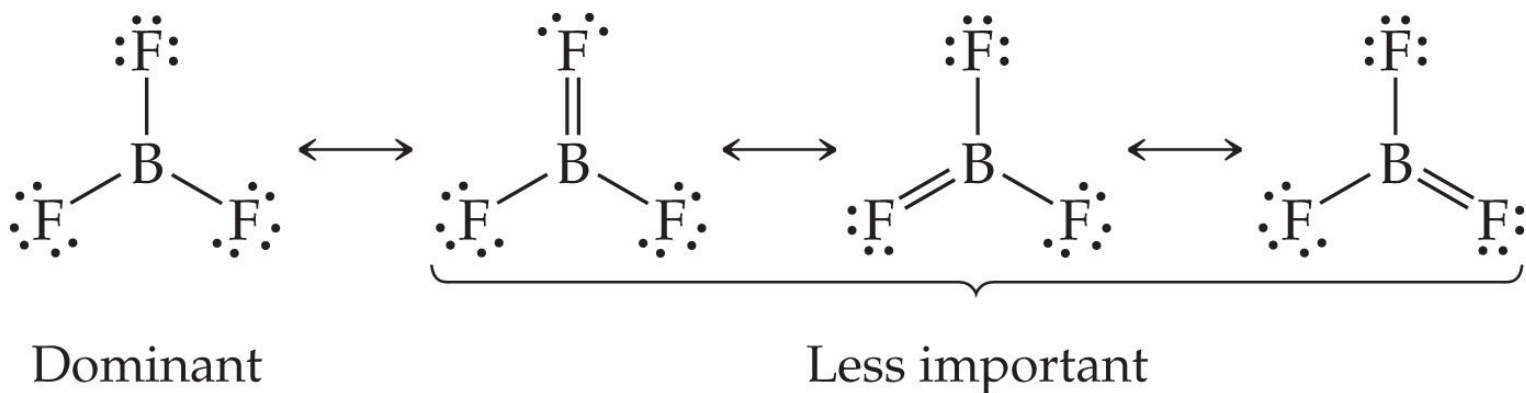
# Fewer Than Eight Electrons



- Consider  $\text{BF}_3$ :
  - 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  $\text{BF}_3$ .

# Fewer Than Eight Electrons

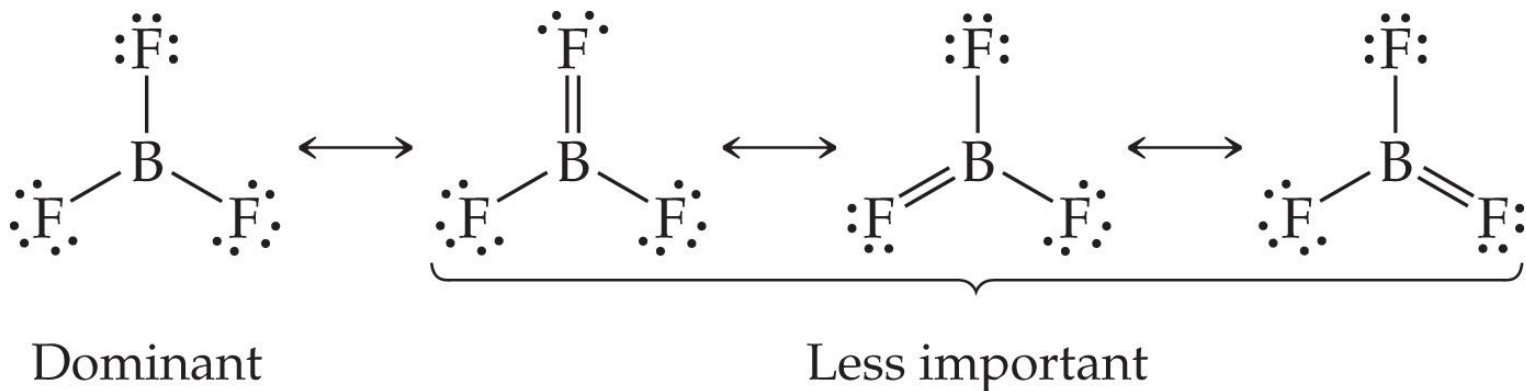
Therefore, structures that put a double bond between boron and fluorine are much less important than the one that leaves boron with only 6 valence electrons.



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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.

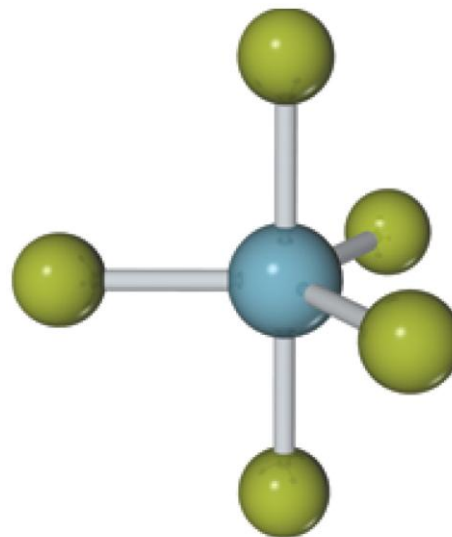
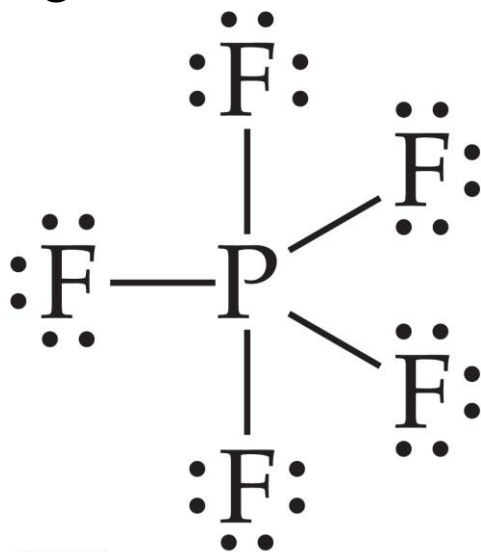


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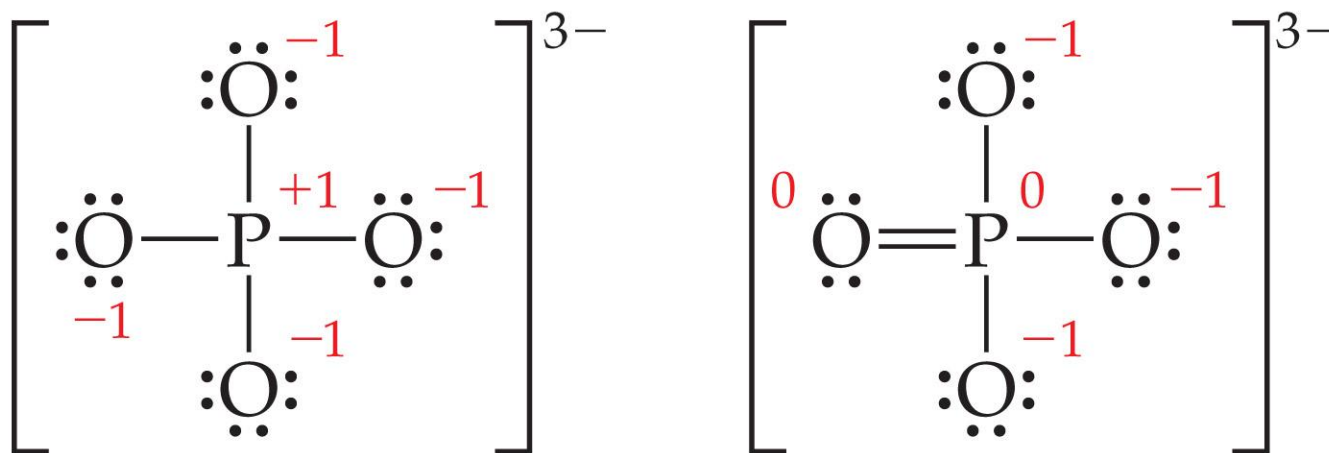
# More Than Eight Electrons

- The only way  $\text{PCl}_5$  can exist is if phosphorus has 10 electrons around it.
- It is allowed to expand the octet of atoms on the third row or below.
  - Presumably *d* orbitals in these atoms participate in bonding.



# More Than Eight Electrons

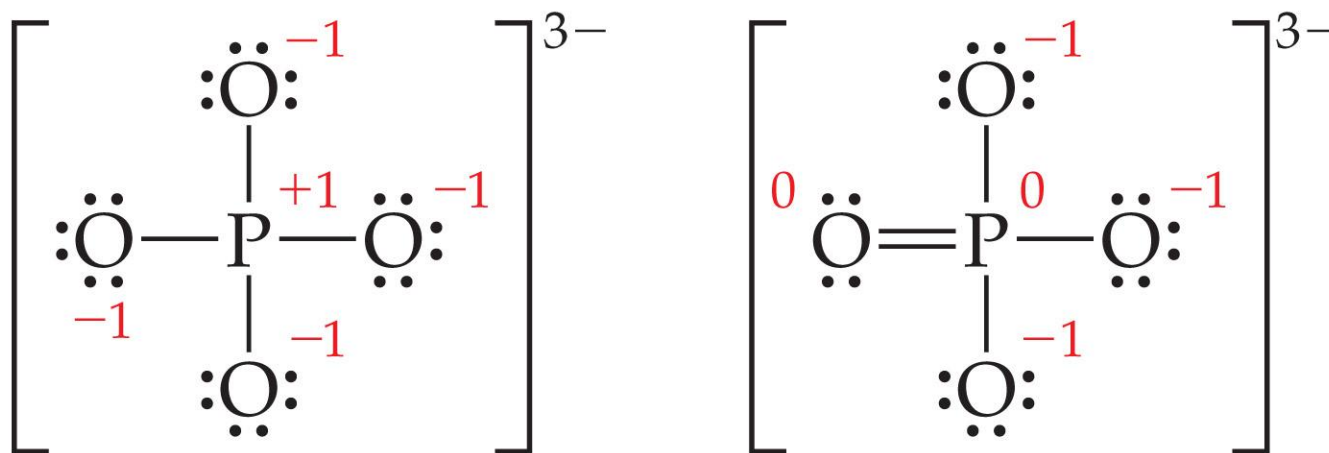
Even though we can draw a Lewis structure for the phosphate ion that has only 8 electrons around the central phosphorus, the better structure puts a double bond between the phosphorus and one of the oxygens.



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# More Than Eight Electrons

- This eliminates the charge on the phosphorus and the charge on one of the oxygens.
- The lesson is: When the central atom is on the third row or below and expanding its octet eliminates some formal charges, do so.



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# Covalent Bond Strength



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- Most simply, the strength of a bond is measured by determining how much energy is required to break the bond.
- This is the **bond enthalpy**.
- The bond enthalpy for a Cl—Cl bond,  $D(\text{Cl—Cl})$ , is measured to be 242 kJ/mol.

# Average Bond Enthalpies

- Table 8.4 lists the average bond enthalpies for many different types of bonds.
- Average bond enthalpies are positive, because bond breaking is an endothermic process.

**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	Cl—F	253
C—N	293	N—O	201	O—F	190	Cl—Cl	242
C—O	358	N—F	272	O—Cl	203		
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 <sub>2</sub>	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				

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# Average Bond Enthalpies

*Note:* These are *average* bond enthalpies, not absolute bond enthalpies; the C—H bonds in methane, CH<sub>4</sub>, will be a bit different than the C—H bond in chloroform, CHCl<sub>3</sub>.

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	Cl—F	253
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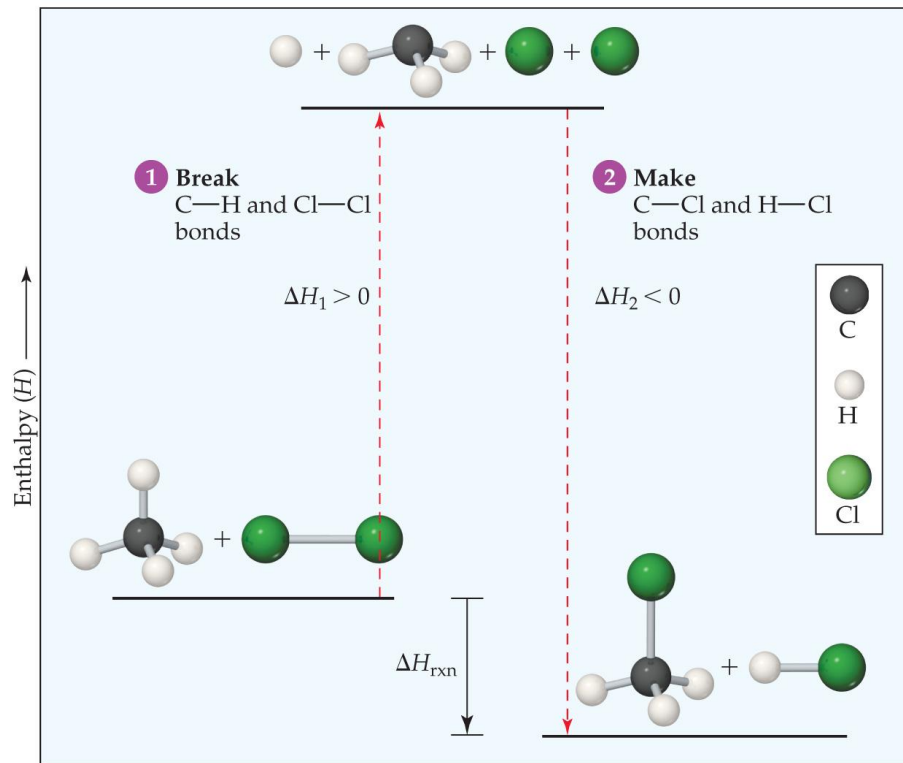
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# Enthalpies of Reaction

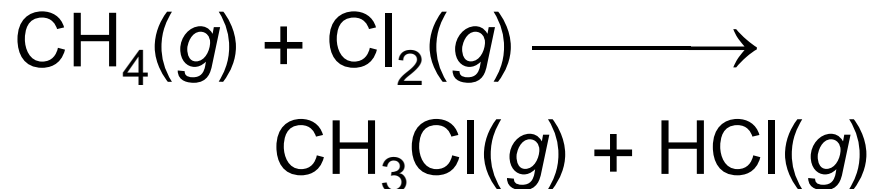
- Yet another way to estimate  $\Delta H$  for a reaction is to compare the bond enthalpies of bonds broken to the bond enthalpies of the new bonds formed.



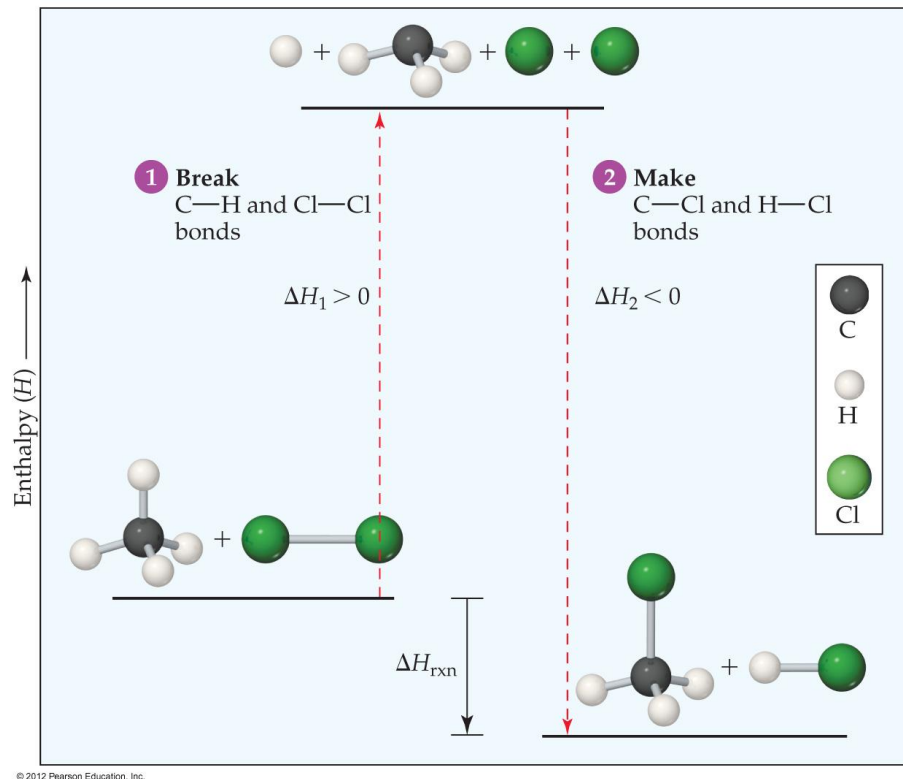
- In other words,

$$\Delta H_{rxn} = \Sigma(\text{bond enthalpies of bonds broken}) - \Sigma(\text{bond enthalpies of bonds formed})$$

# Enthalpies of Reaction



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



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# Enthalpies of Reaction

So,

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

# Bond Enthalpy and Bond Length

**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		

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- 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.