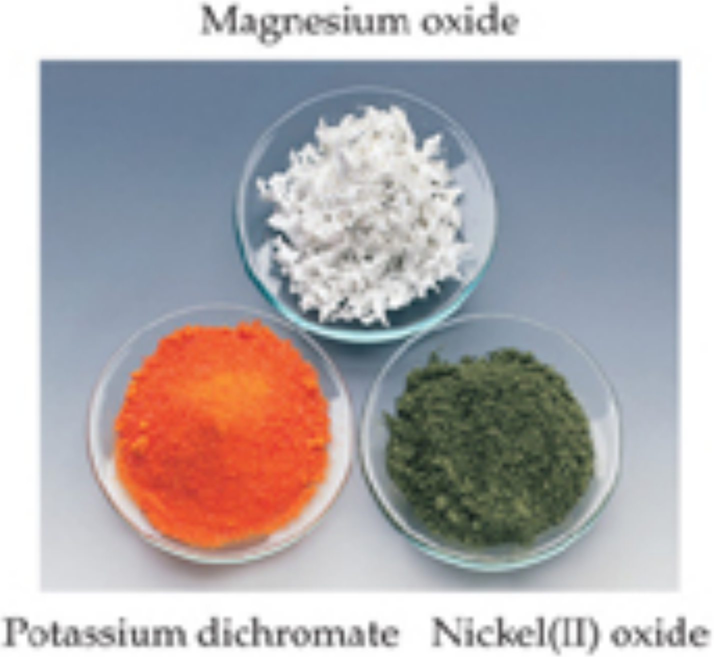
Chapter 8
Concepts of Chemical Bonding

Chemical Bonds

Three types:



- Ionic

  Electrostatic attraction between ions

Covalent

Sharing of electrons

Metallic

Metal atoms bonded to several other atoms

Ionic Bonding

When a metal and a nonmetal get together

Energetics of Ionic Bonding

$2Na(s) + Cl_2(g) \text{ -------> } 2NaCl(s)$

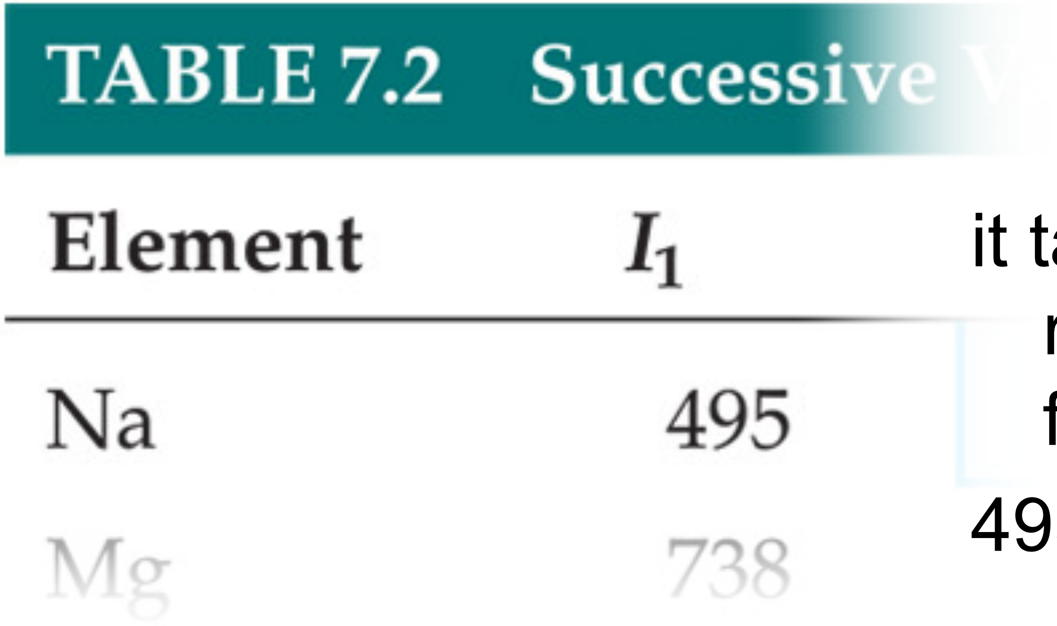


TABLE 7.2 Successive

Element	I_1
Na	495
Mg	738

it takes 495 kJ/mol to remove 1 electron from sodium.

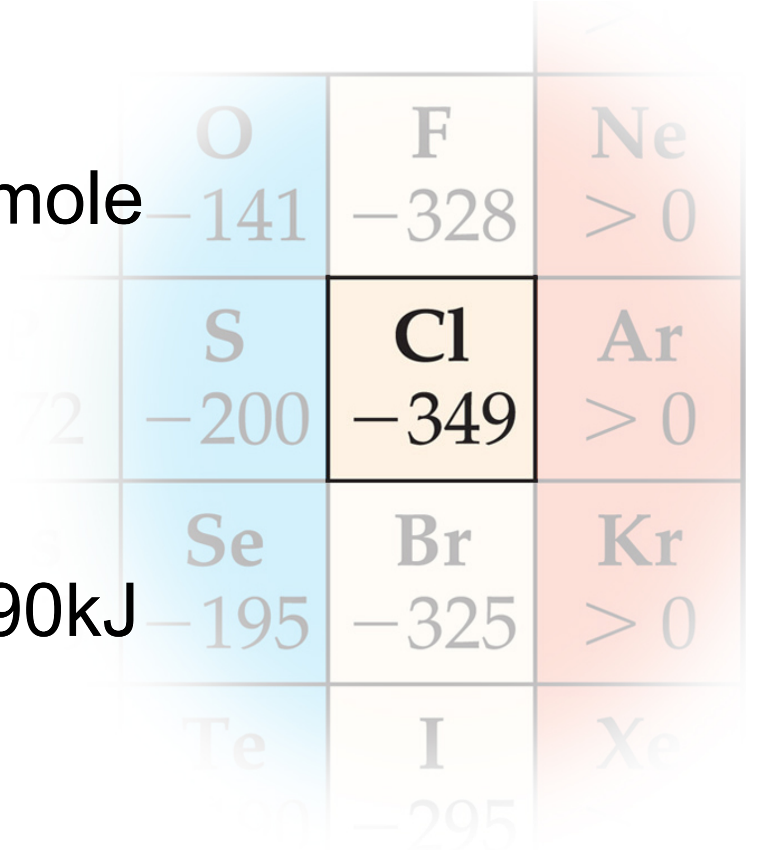
495x2 = 990 kJ/2 Na

Energetics of Ionic Bonding

We get **349 kJ/mol Cl** back by giving 1 electron to each to 1 mole of Cl_2.

$-349 \times 2 = -700$ kJ/mol Cl_2

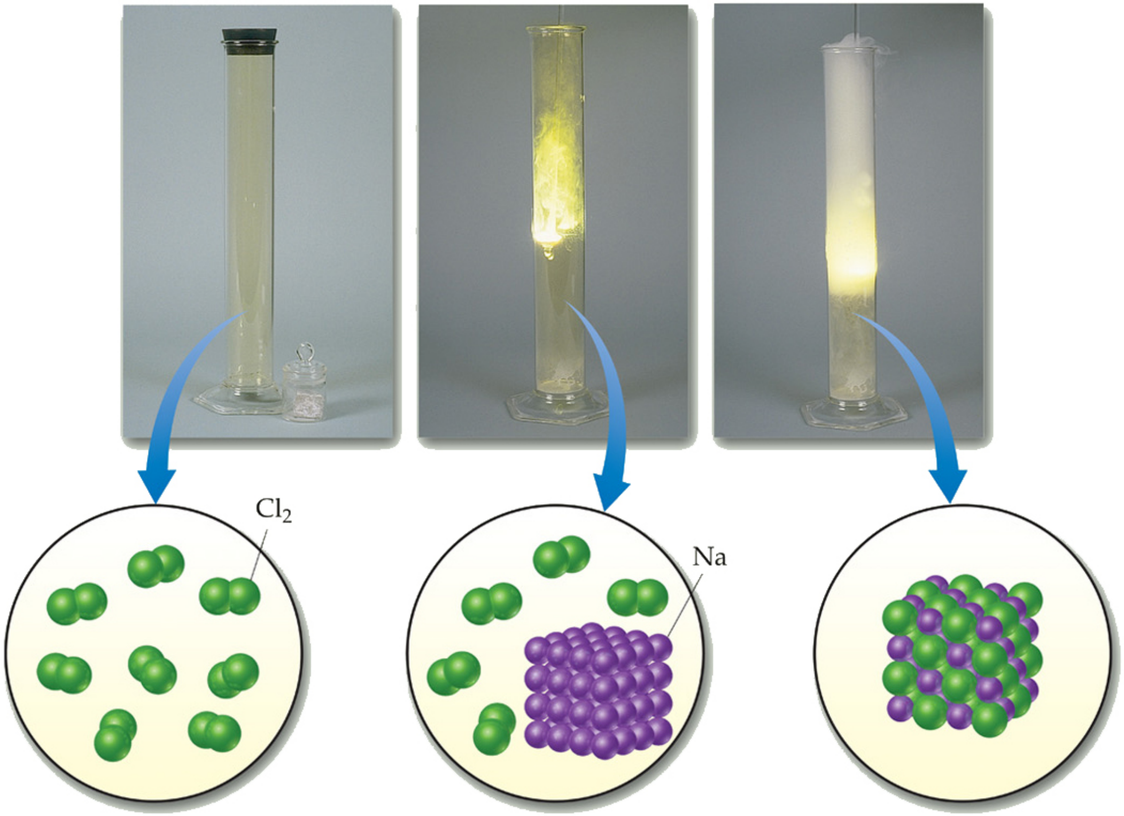
990 kJ/2Na – 700 kJ/Mol Cl_2 = 290kJ



O −141	F −328	Ne > 0
S −200	**Cl** **−349**	Ar > 0
Se −195	Br −325	Kr > 0
Te	I −295	Xe

Energetics of Ionic Bonding

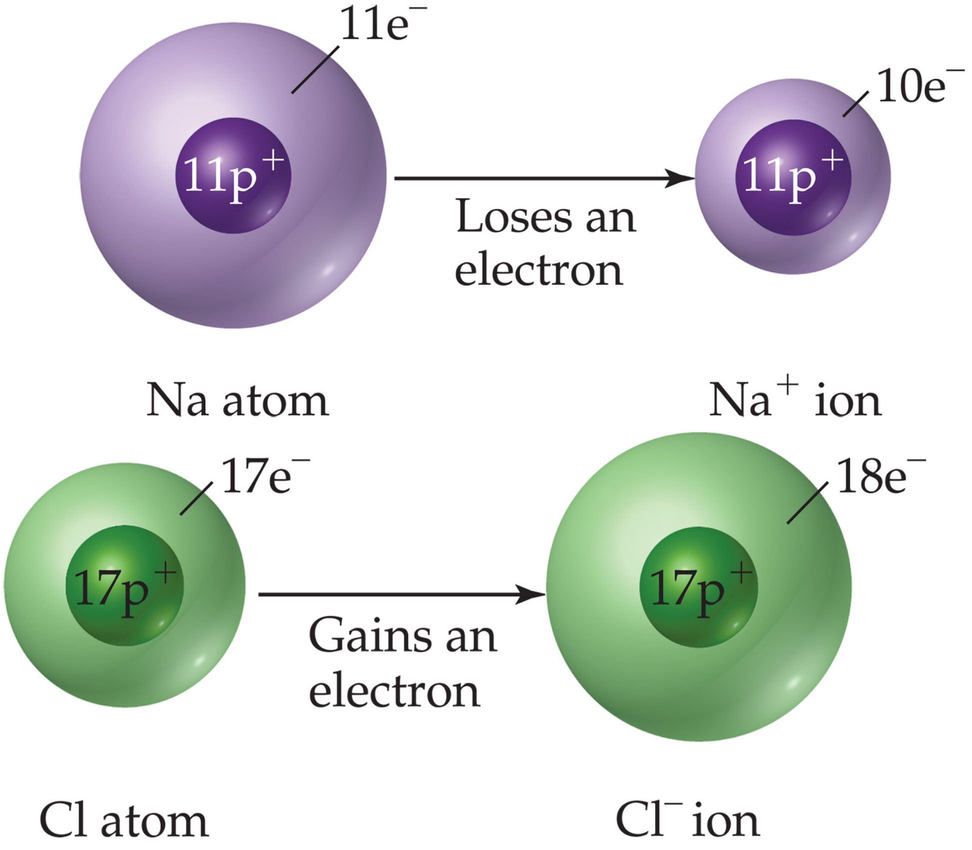
990 kJ/2Na – 700 kJ/Mol Cl_2 = 290kJ



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

Energetics of Ionic Bonding

- There must be a third piece to the puzzle….
- **The electrostatic attraction**
- Between Na^+ and Cl^-.
- ***The ionic Bond!***



Lattice Energy

- This third piece of the puzzle is the lattice energy:

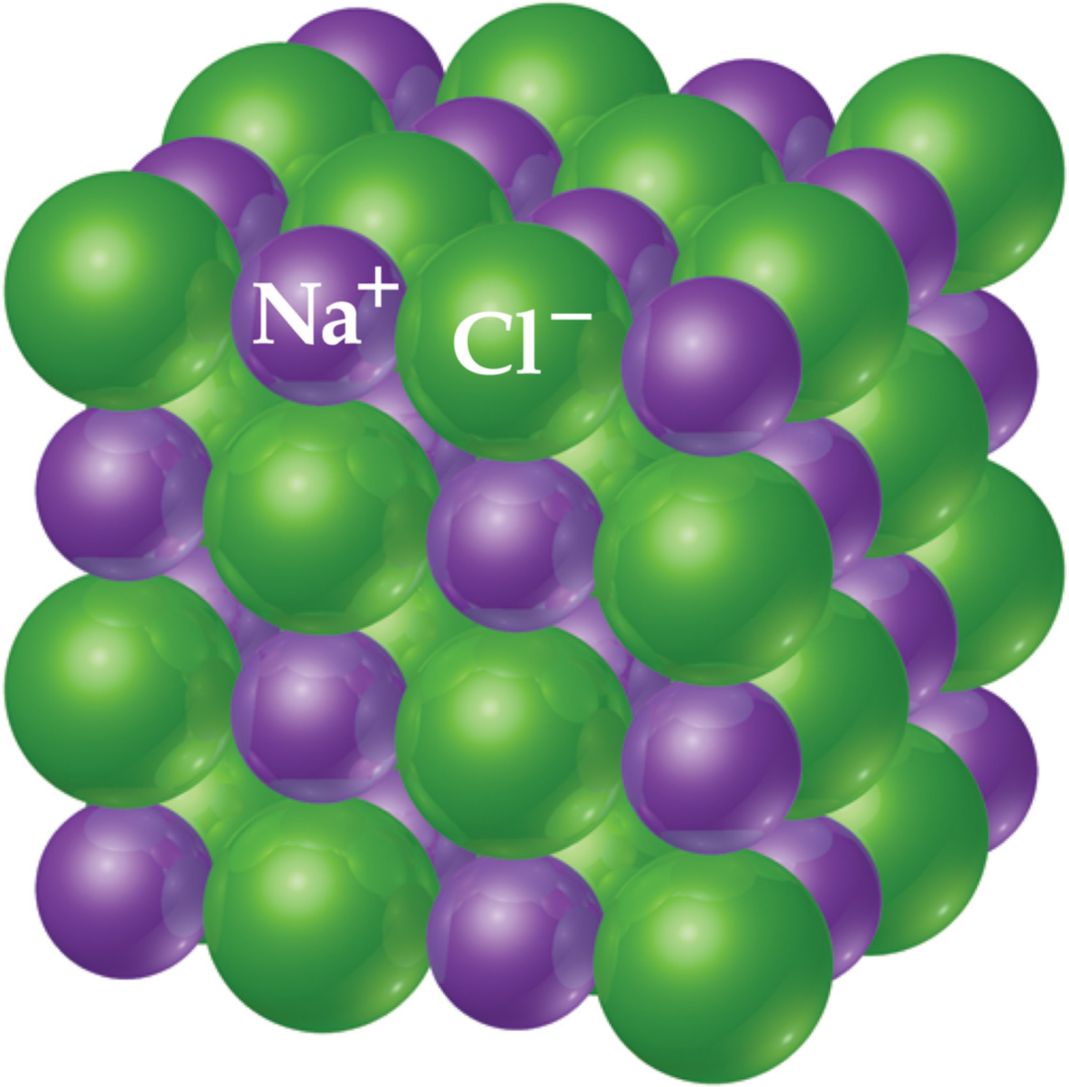
  The energy required to completely separate a mole of a solid ionic compound into its gaseous ions.

- The energy associated with electrostatic interactions is governed by Coulomb's law:

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

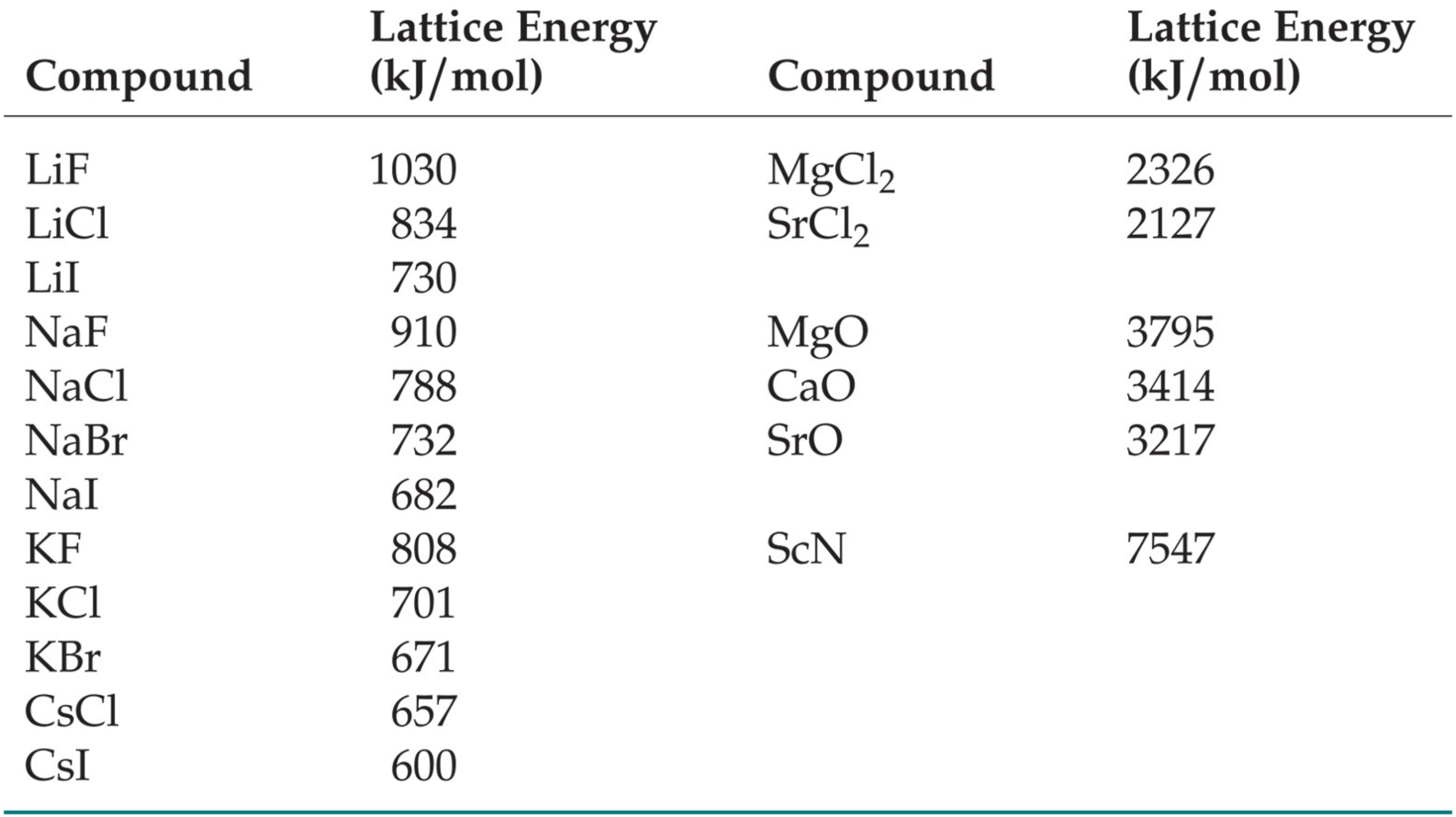
Lattice Energy

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



Lattice Energy

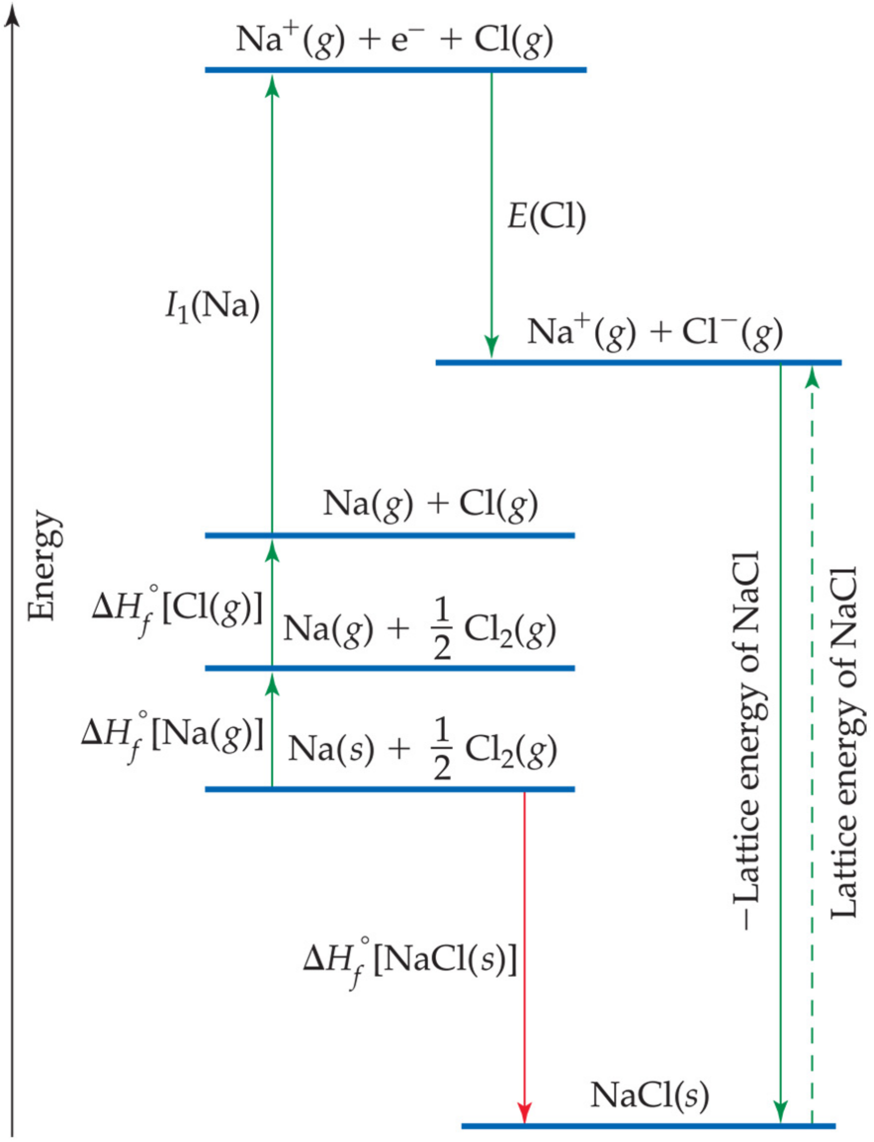
- Lattice energy, then, increases with the charge on the ions.
- It also increases with decreasing size of ions.



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		

Energetics of Ionic Bonding

$Na(s) + 1/2Cl_2(g) \text{ -----> } NaCl(s)$



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.

Energetics of Ionic Bonding

- These phenomena also help explain the “octet rule.”

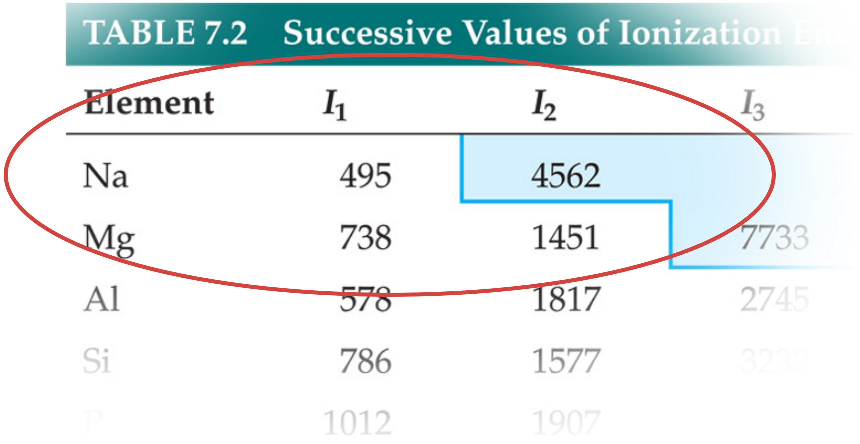


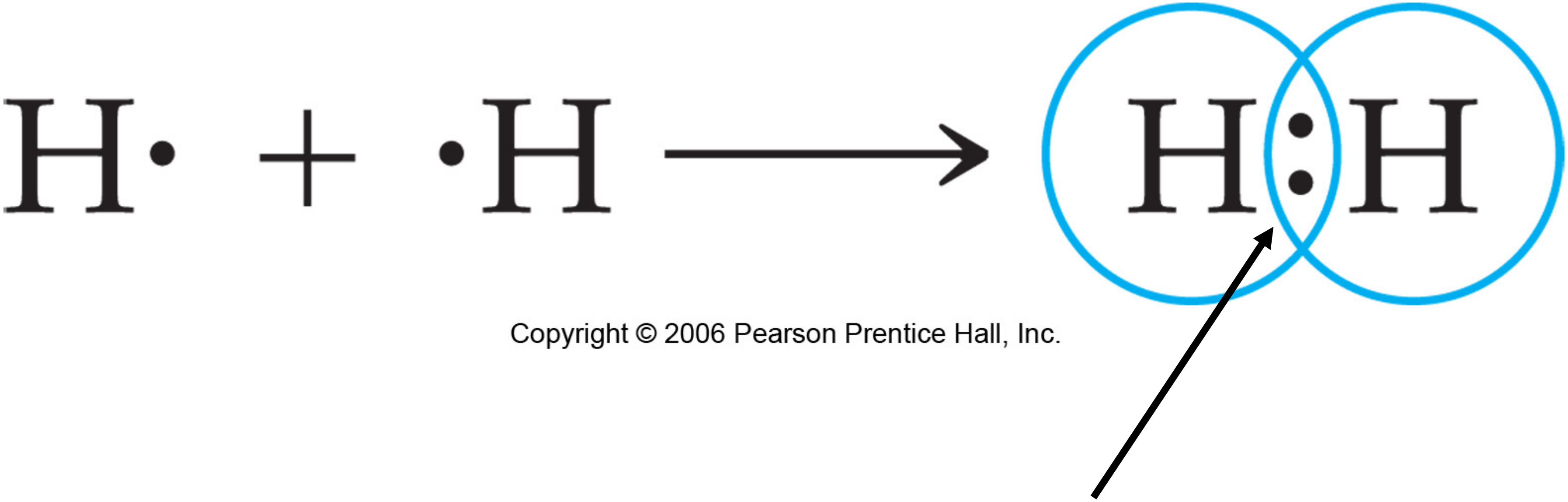
TABLE 7.2 Successive Values of Ionization En

Element	I_1	I_2	I_3
Na	495	4562	
Mg	738	1451	7733
Al	578	1817	2745
Si	786	1577	3232
P	1012	1907	

- Elements tend to lose or gain electrons once they attain a noble gas configuration because energy would be expended that cannot be overcome by lattice energies.

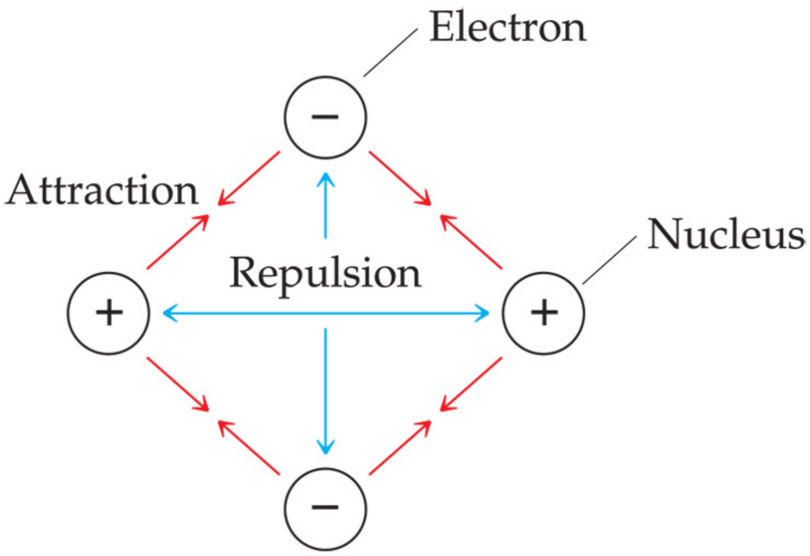
Covalent Bonding

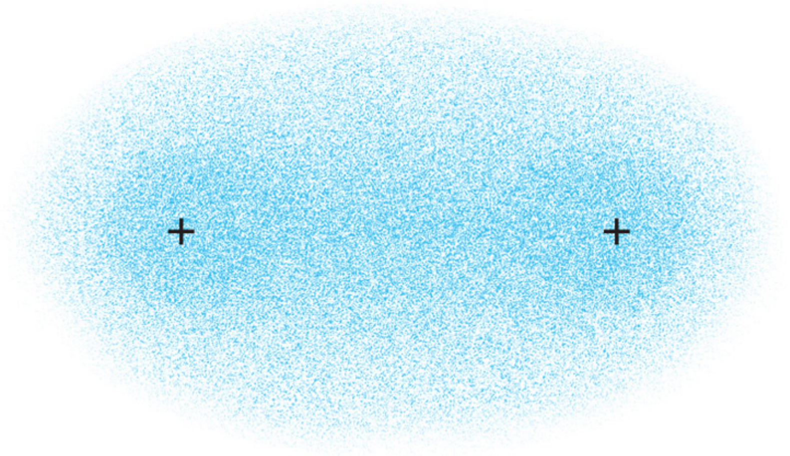
What happens when nonmetals get together



- **In these bonds atoms share electrons.**
- **The electrons that can be shared are the *Valence electrons.***

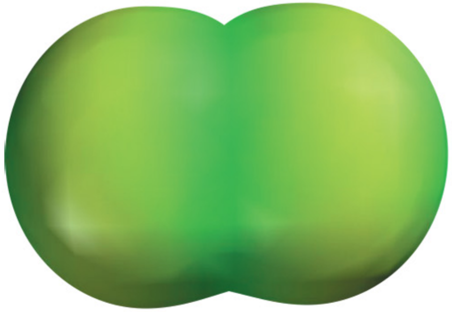
Covalent Bonding





- There are several electrostatic interactions in these bonds:
  - Attractions between electrons and nuclei
  - Repulsions between electrons
  - Repulsions between nuclei

Polar Covalent Bonds



F_2

HF

- Covalent bond, sharing electrons,
- But electron sharing not always equal.

- Fluorine pulls harder on the shared electrons than hydrogen does.
- Therefore, the fluorine end has more electron density than the hydrogen end.
- But how do you know who pulls hardest?

Electronegativity:

Developed 1st by Linus Pauling like this:

H-F -→ H + F >> H-H -→ H + H or F-F → F + F

In other words, H-F bond much stronger than H-H or F-F bond.

Why?

Because there is ***an ionic component*** to attraction in H-F

F more – and H more + so the ionic component makes bond stronger.

Electronegativity:

Developed 1st by Linus Pauling like this:

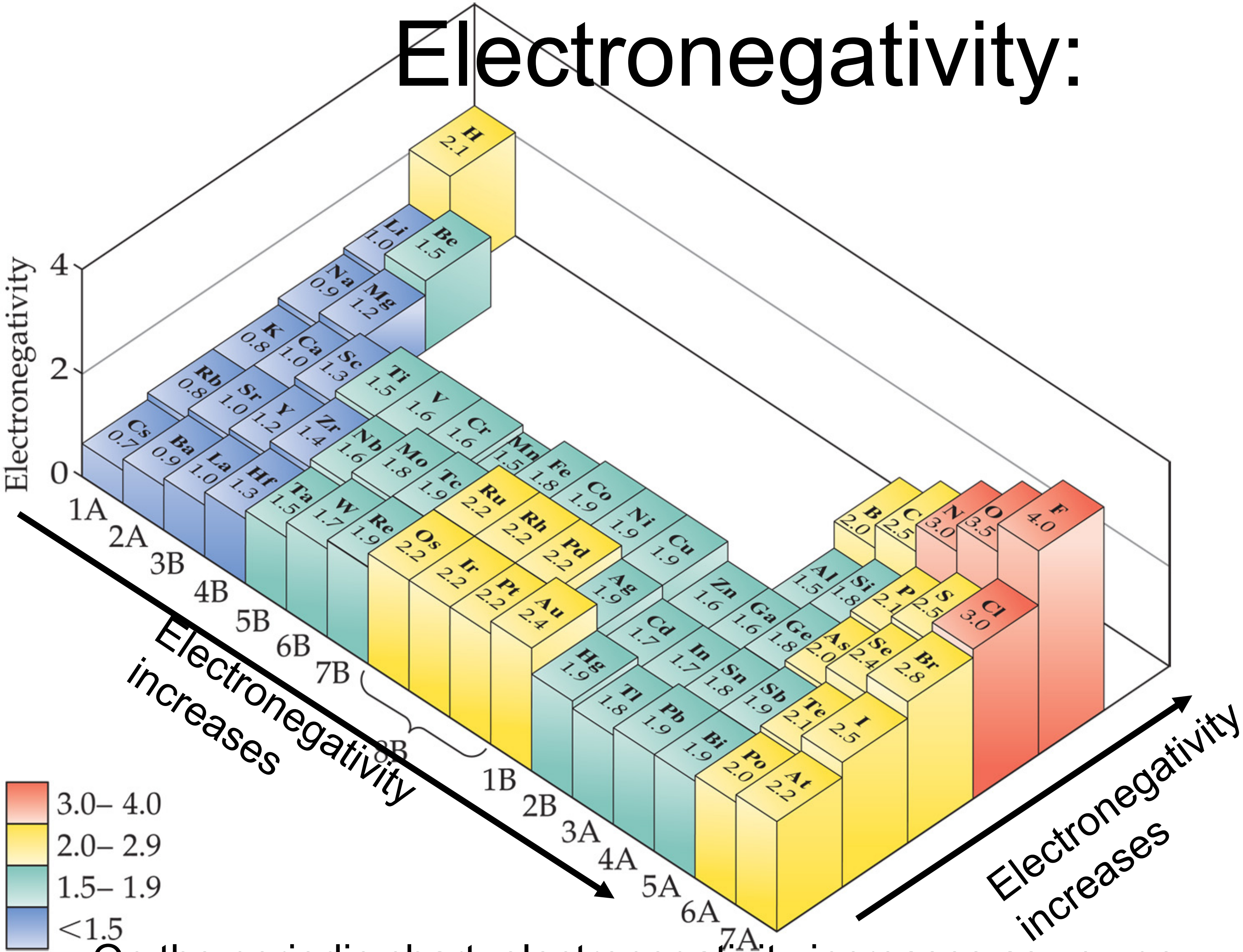
$$EN_A - EN_B = eV^{-1/2}\sqrt{D_{AB} - (D_{AA} + D_{BB})/2}$$

The dissociation energy of the A-B bond versus the A-A And B-B bond gives Pauling electronegativity
A measure of how much an atom attracts electrons *when It is in a molecule.*

Refinements have occurred since, but this is pretty close.

- The ability of atoms in a molecule to attract electrons to itself.
- On the periodic table, electronegativity increases as you go…

Electronegativity:



Electronegativity increases

Electronegativity increases

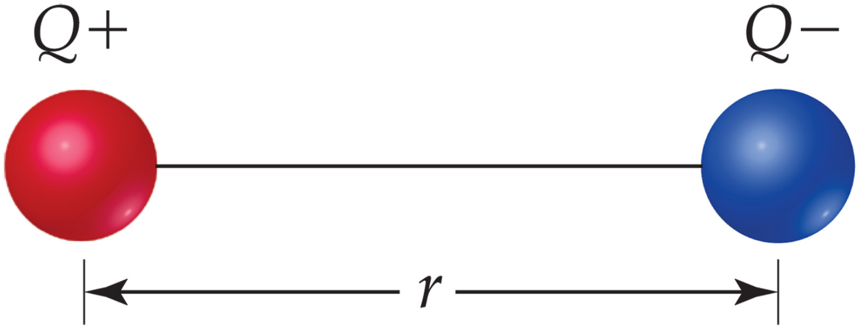
- On the periodic chart, electronegativity increases as you go…
  - …from left to right across a row.
  - …from the bottom to the top of a column.

Polar Covalent Bonds

- When two atoms share electrons unequally, a **bond dipole** results.
- The **dipole moment**, μ, produced by two equal but opposite charges separated by a distance, *r*, is calculated:

$$\mu = Qr$$

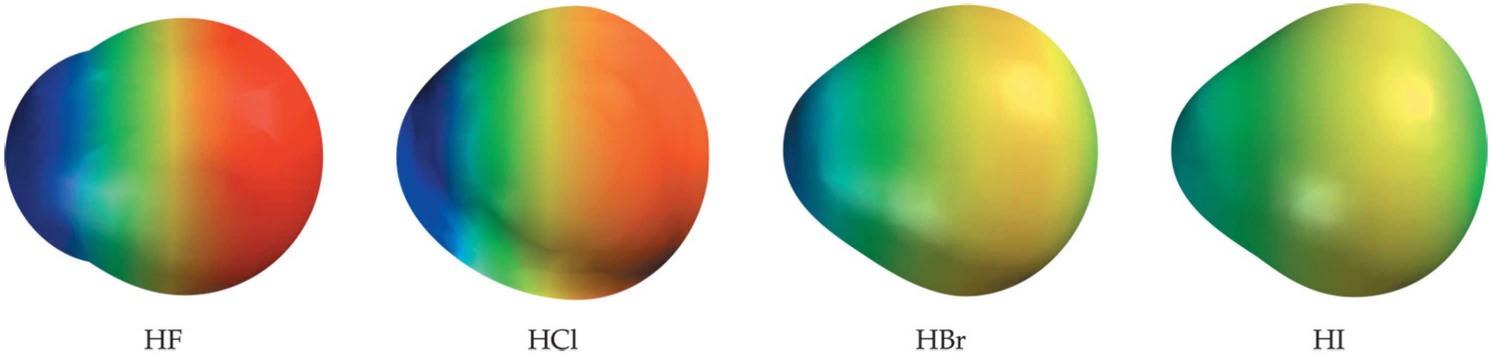
- It is measured in debyes (D).



Polar Covalent Bonds

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.



Lewis symbols

- A convenient way to keep track of the valence electrons in an atom or molecule
- Lewis dot symbol

Each dot is one valence electron

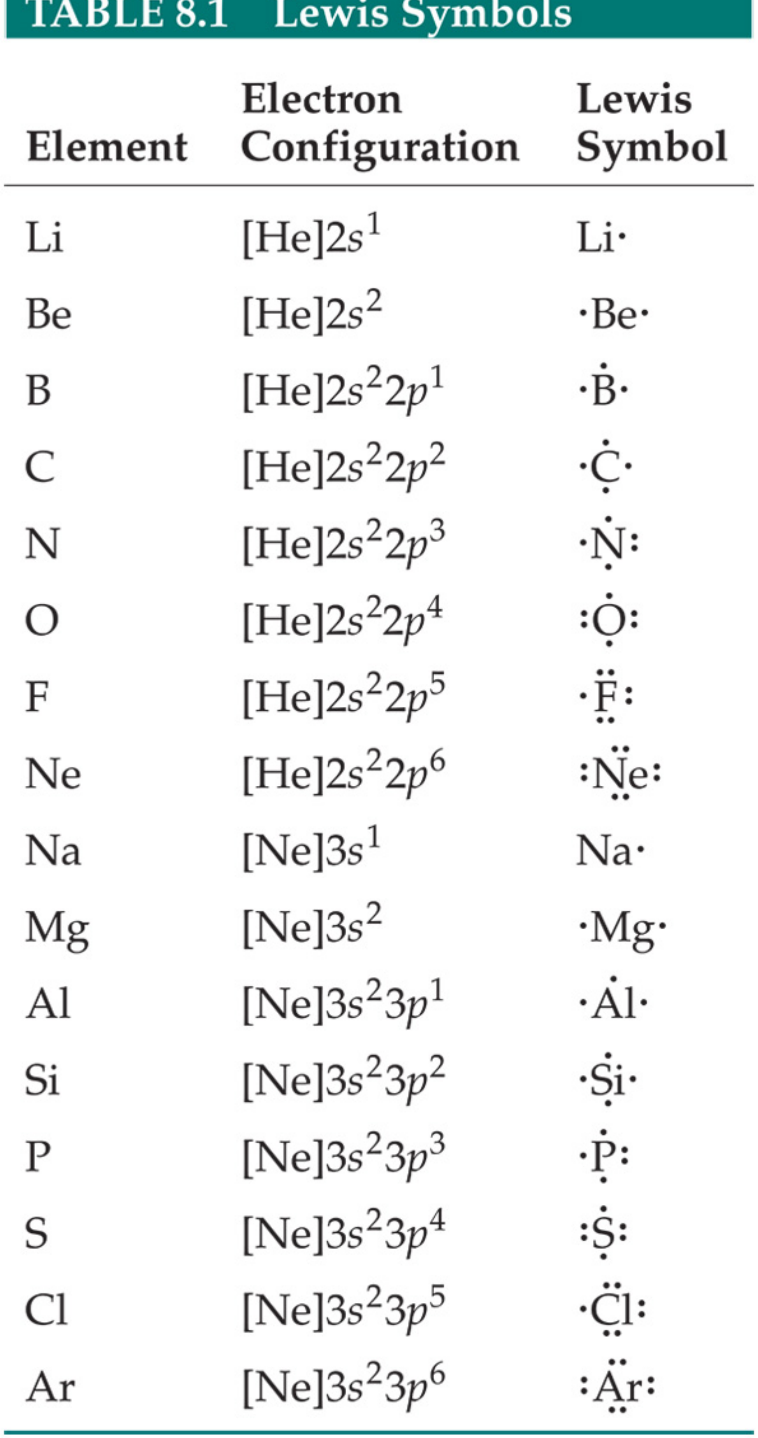


TABLE 8.1 Lewis Symbols

Element	Electron Configuration	Lewis Symbol
Li	$[\text{He}]2s^1$	Li·
Be	$[\text{He}]2s^2$	·Be·
B	$[\text{He}]2s^22p^1$	·Ḃ·
C	$[\text{He}]2s^22p^2$	·Ċ̣·
N	$[\text{He}]2s^22p^3$	·Ṇ̇:
O	$[\text{He}]2s^22p^4$	:Ọ̇:
F	$[\text{He}]2s^22p^5$	·F̤̈:
Ne	$[\text{He}]2s^22p^6$	:N̤̈e:
Na	$[\text{Ne}]3s^1$	Na·
Mg	$[\text{Ne}]3s^2$	·Mg·
Al	$[\text{Ne}]3s^23p^1$	·Ȧl·
Si	$[\text{Ne}]3s^23p^2$	·Ṩi·
P	$[\text{Ne}]3s^23p^3$	·Ṗ̣:
S	$[\text{Ne}]3s^23p^4$	:Ṩ:
Cl	$[\text{Ne}]3s^23p^5$	·C̤̈l:
Ar	$[\text{Ne}]3s^23p^6$	:Ä̤r:

- Lewis structures for 16 elements
- It is rare to use Lewis pictures for other elements (transition metals, etc.)

One dot = 1 electron

Lewis Structures

Diagrams for bonding in molecules

Lines correspond to 2 electrons in bond

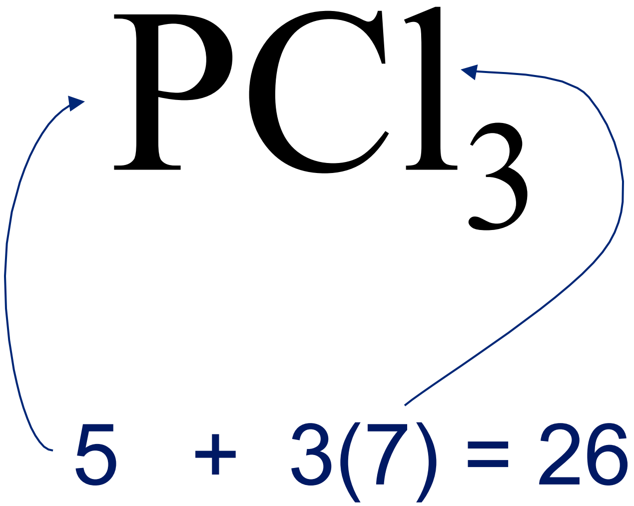
Lewis structures are representations of molecules showing all valence electrons, bonding and nonbonding.

Covalent Bonding

- A bond where electrons from each atom are *shared*
- Each covalent bond has 2 electrons that are shared.
- Only the Valence electrons are involved in these covalent bonds.
- *Why? Why don't electrons in n-1 levels get shared?*

Lewis Structures

A way to keep track of those valence electrons



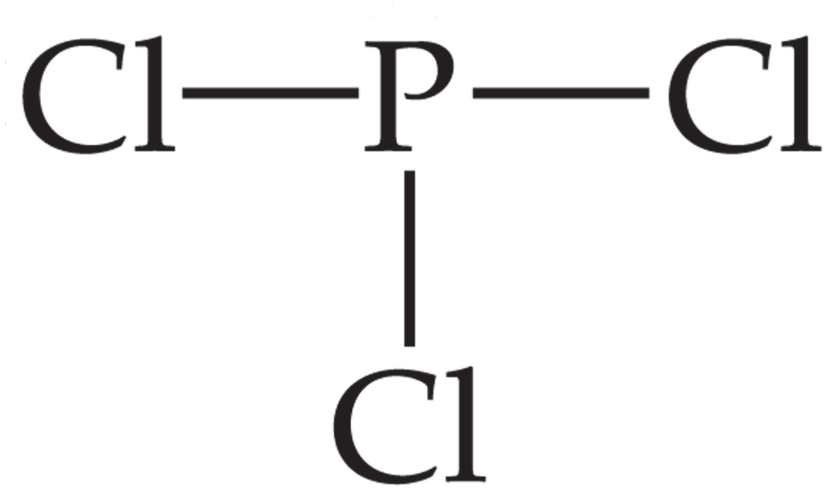
PCl_3

$5 + 3(7) = 26$

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.

Lewis Structures

A way to keep track of those valence electrons

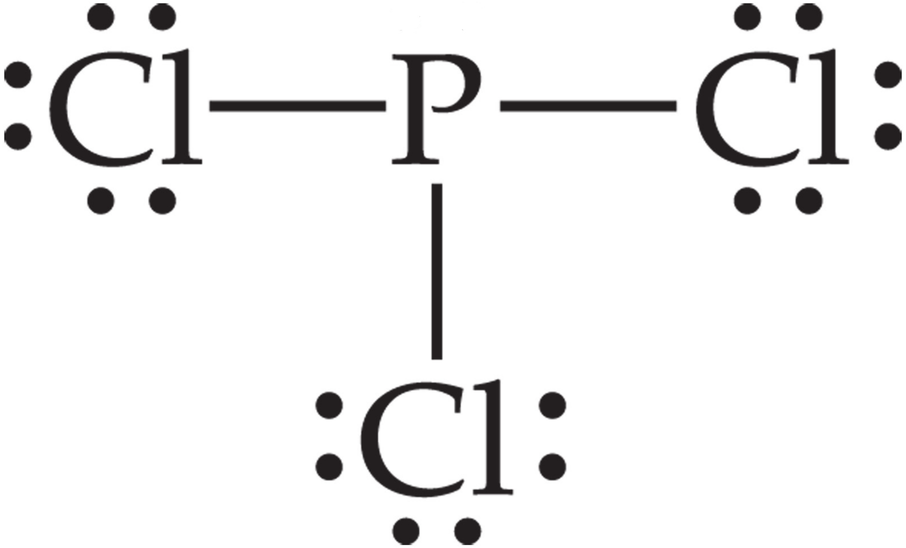


2. The central atom is the *least* electronegative element that isn’t hydrogen (why?). Connect the outer atoms to it by single bonds.

Keep track of the electrons:

26 - 6 = 20

Writing Lewis Structures

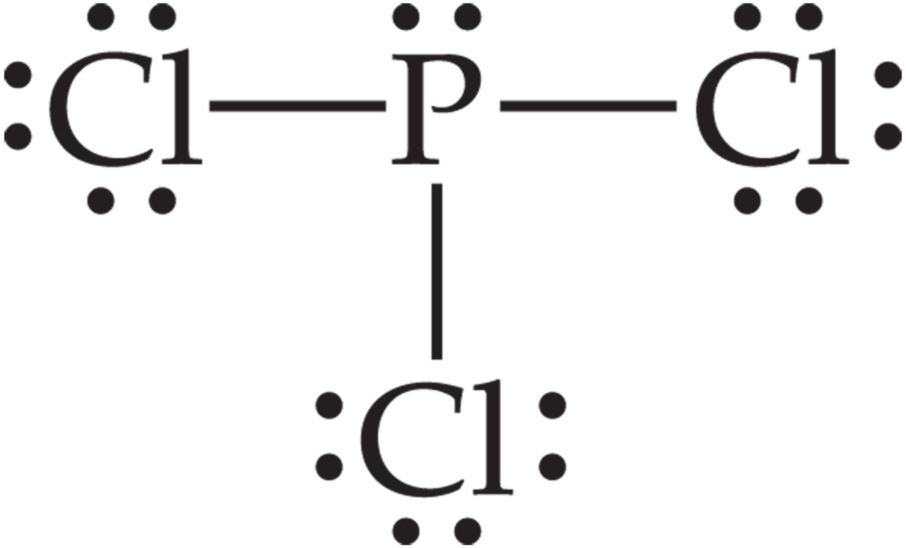


3. Put eight electrons around the outer atoms (“fill their octet”)

Keep track of the electrons:

26 - 6 = 20 - 18 = 2

Writing Lewis Structures



4. Fill the octet of the central atom.

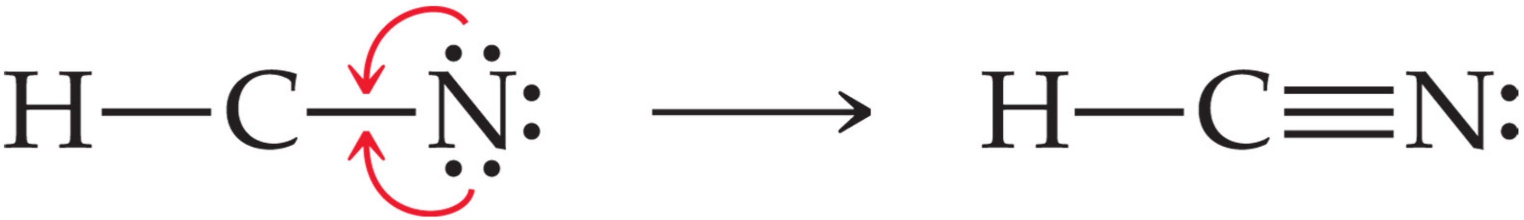
Keep track of the electrons:

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

Writing Lewis Structures

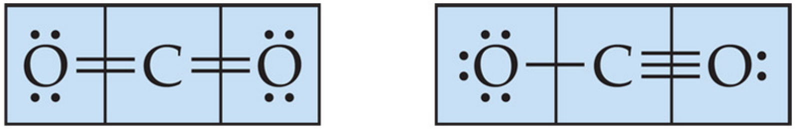
5. If you run out of electrons before the central atom has an octet…

…form multiple bonds until it does.



Writing Lewis Structures

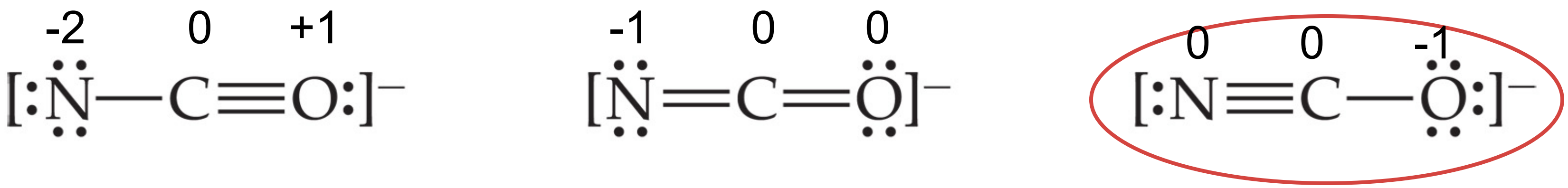
- Then assign formal charges.
  - For each atom, count the electrons in lone pairs and half the electrons it shares with other atoms.
  - Subtract that from the number of valence electrons for that atom: The difference is its formal charge.



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



$[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}-\mathrm{C}\equiv\mathrm{O}:]^-$ $[\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}=\mathrm{C}=\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}]^-$ $[:\mathrm{N}\equiv\mathrm{C}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:]^-$

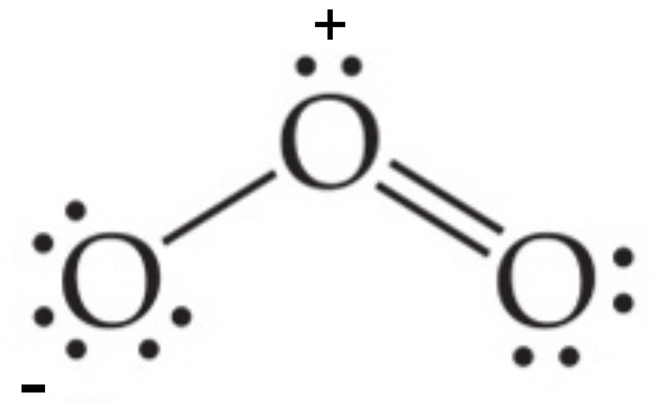
Resonance

Draw the Lewis structure for ozone, O_3.

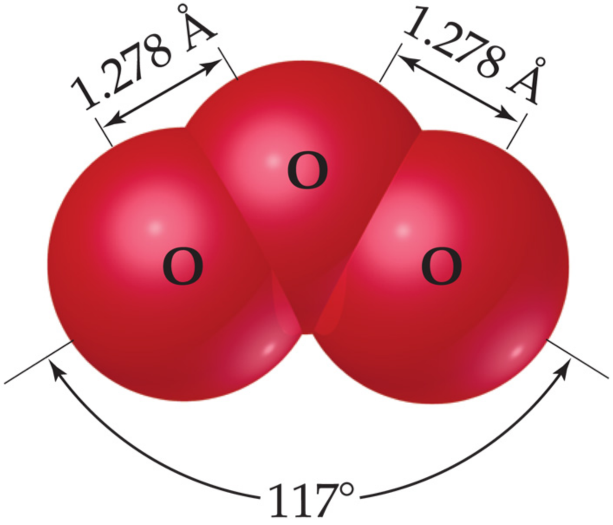
Resonance

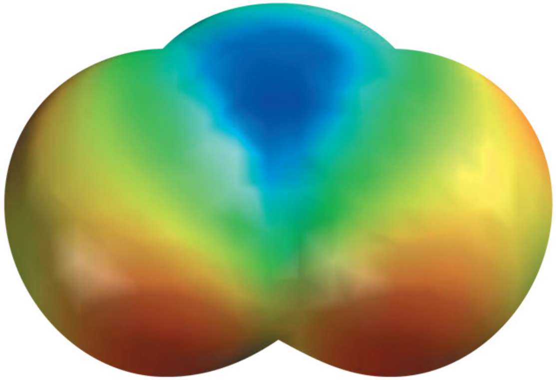
Draw the Lewis structure for ozone, O_3.

But why should one O be different from the other?



Resonance

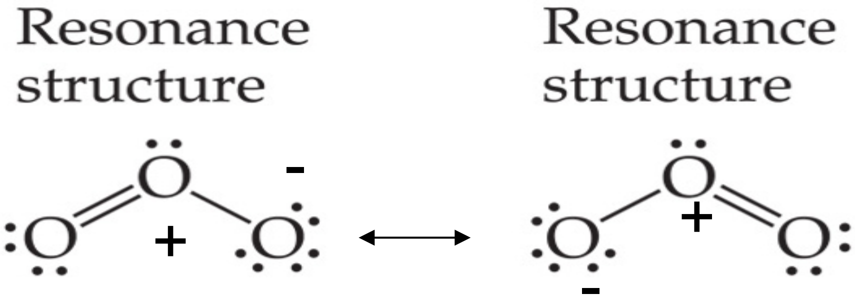




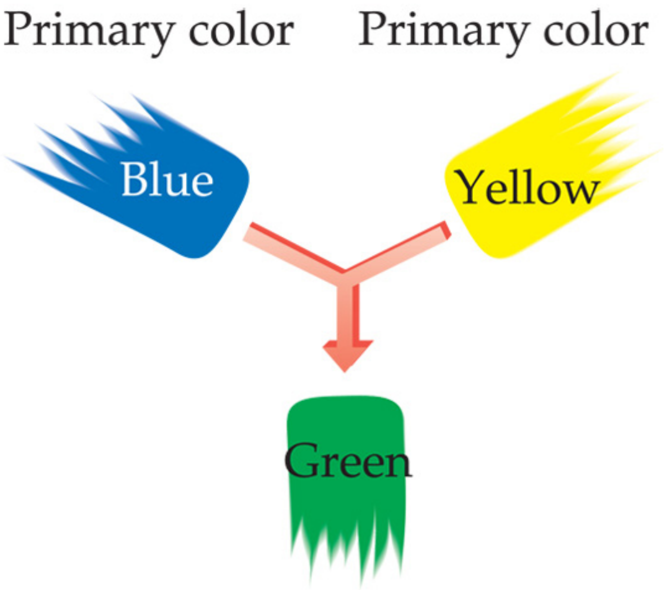
- It is at odds with the true, observed structure of ozone,
  - …both O—O bonds are the same length.
  - …both outer oxygens have a charge of -1/2.

Resonance

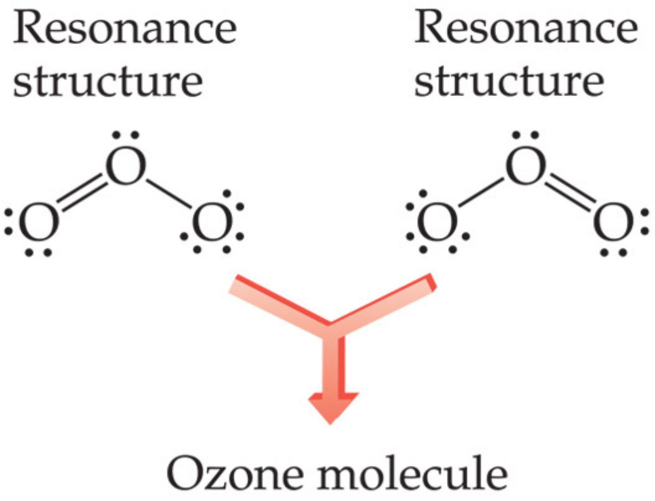
- One Lewis structure cannot accurately depict a molecule such as ozone.
- We use multiple structures, resonance structures, to describe the molecule.



Resonance



Just as green is a synthesis of blue and yellow…



…ozone is a synthesis of these two resonance structures.

It is not jumping between the two.

Resonance

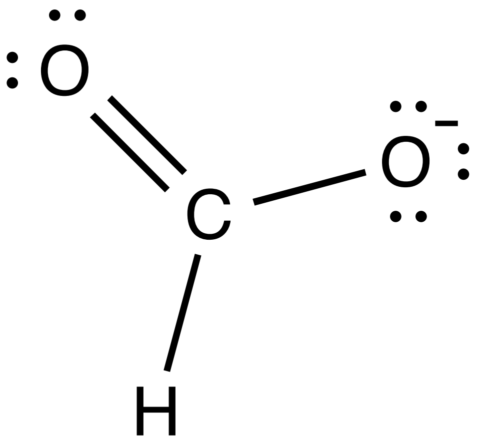
Draw resonance structure for:

HCO_2^-

Resonance

Draw Lewis structure for:

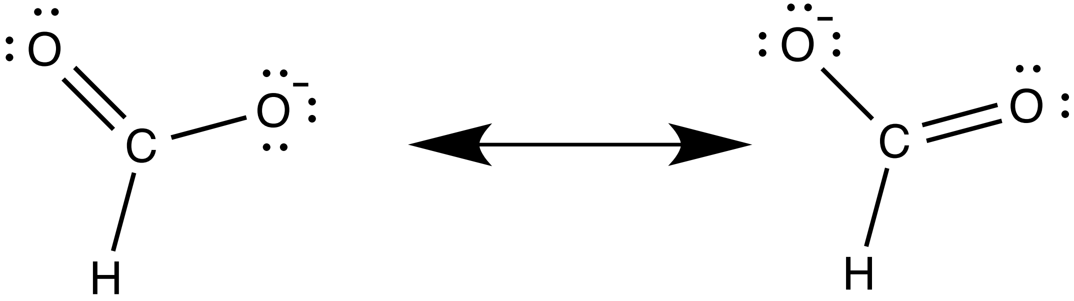
HCO_2^-



But why would the two oxygens be different?

Resonance

- In truth the electrons that make up the double bond are not localized, but rather are delocalized.

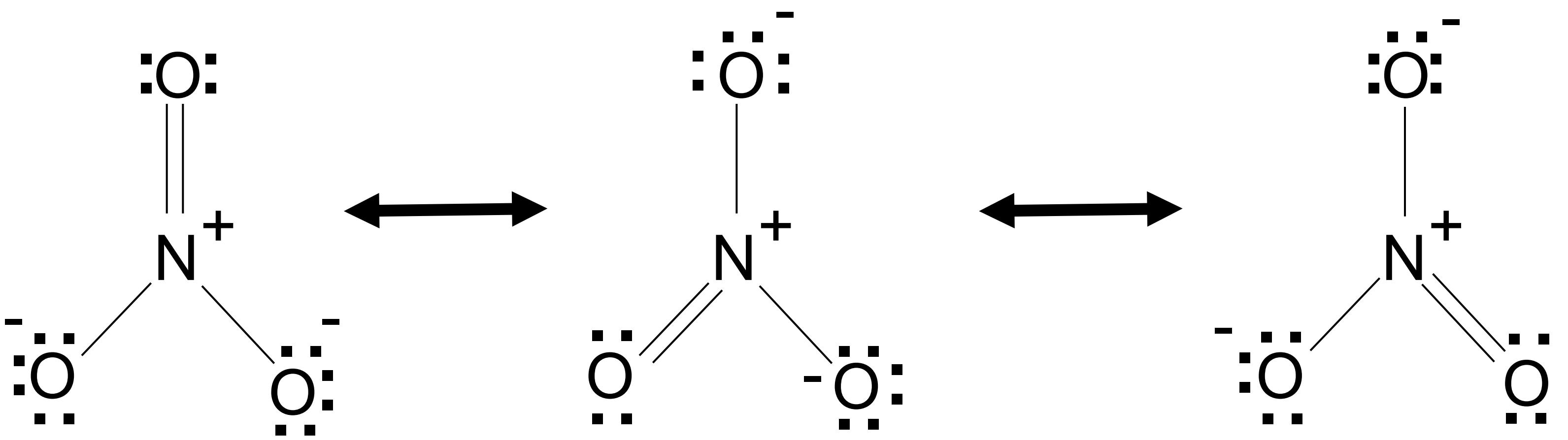


Resonance

- Draw the Lewis structure of NO_3^-

Resonance

- Draw the Lewis structure of NO_3^-

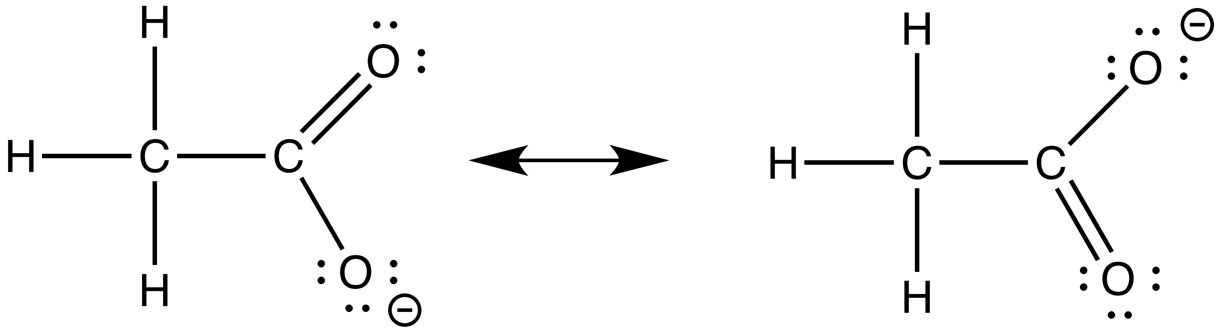


More than one central atom

- Many atoms have more than 1 central atom
- You just deal with each separately
- Example:
- Lewis structure for acetate:
- $CH_3CO_2^-$

More than one central atom

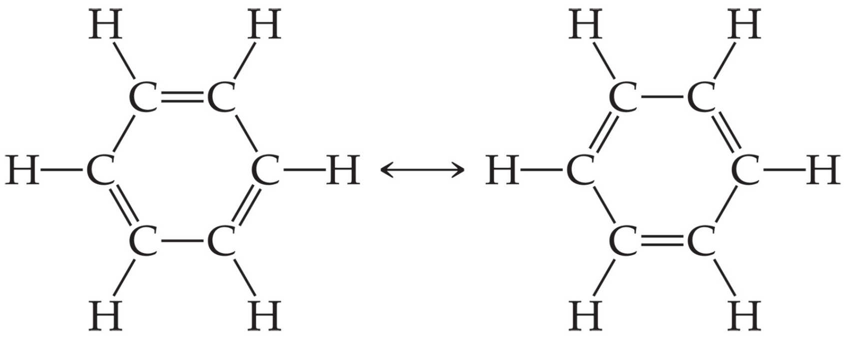
- Lewis structure for acetate:
- $CH_3CO_2^-$



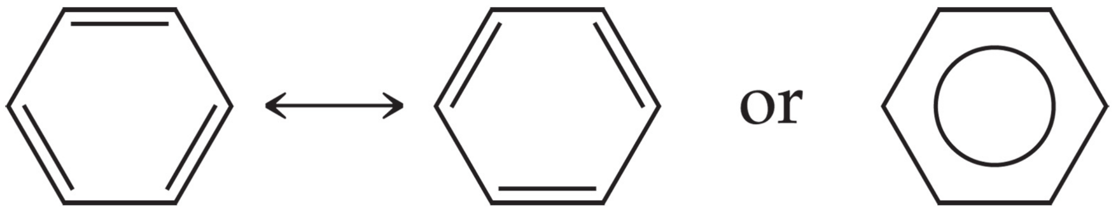
More than 1 central atom

- The organic compound benzene, C_6H_6 is a hexagon of carbon atoms with 6 H/s Draw the Lewis structure for benzene.

More than 1 central atom



- 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.

Odd Number of Electrons

- Example: NO

What’s nitric oxide good for?

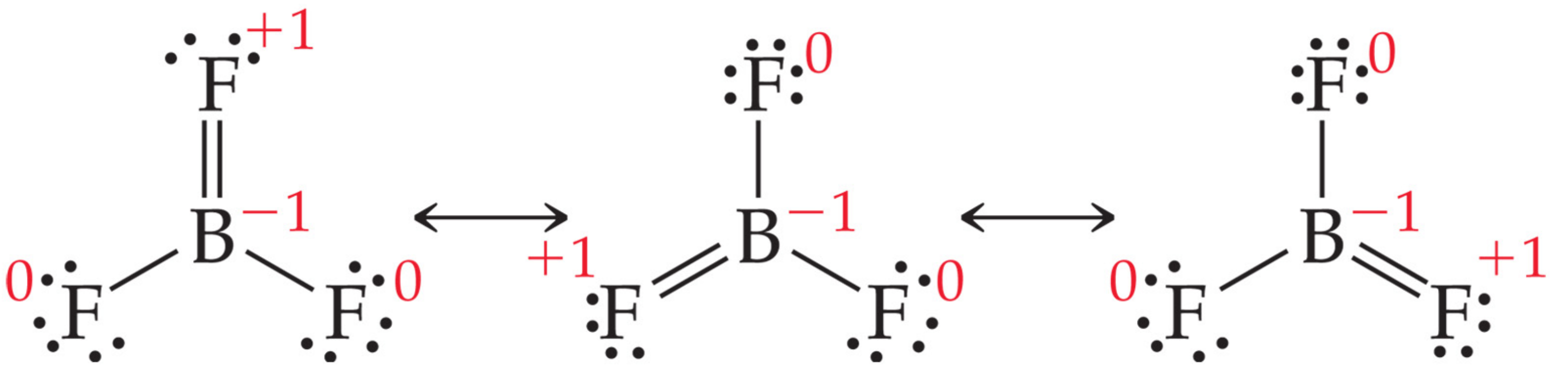
Fewer Than Eight Electrons

Draw the Lewis structure for BF_3

Fewer Than Eight Electrons

Draw the Lewis structure for BF_3:

Fewer Than Eight Electrons

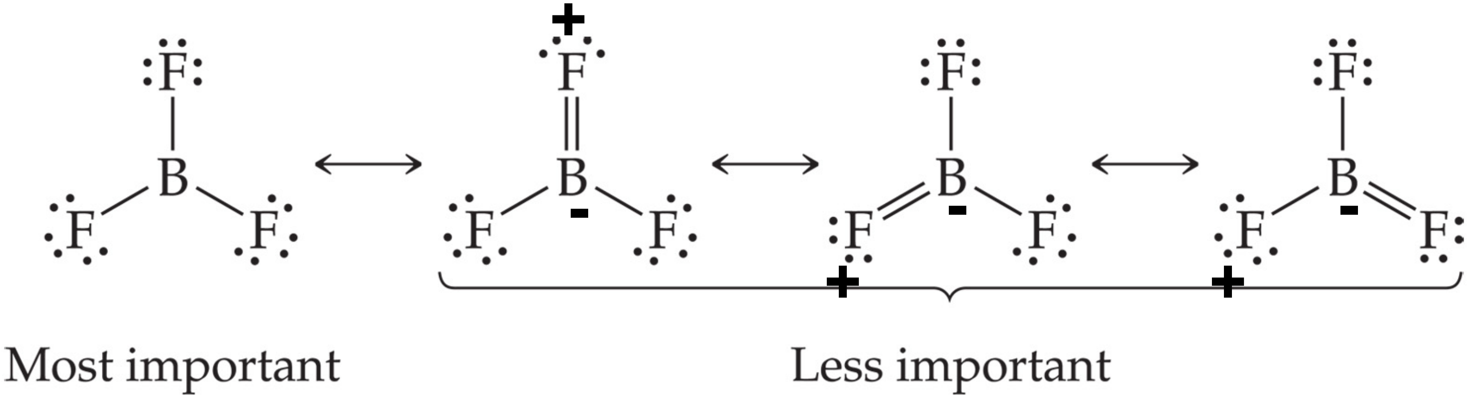


- Consider BF_3:
  - Giving boron a filled octet places a *negative* charge on the boron and a *positive* charge on fluorine.
  - This would not be an accurate picture of the distribution of electrons in BF_3.

Fewer Than Eight Electrons

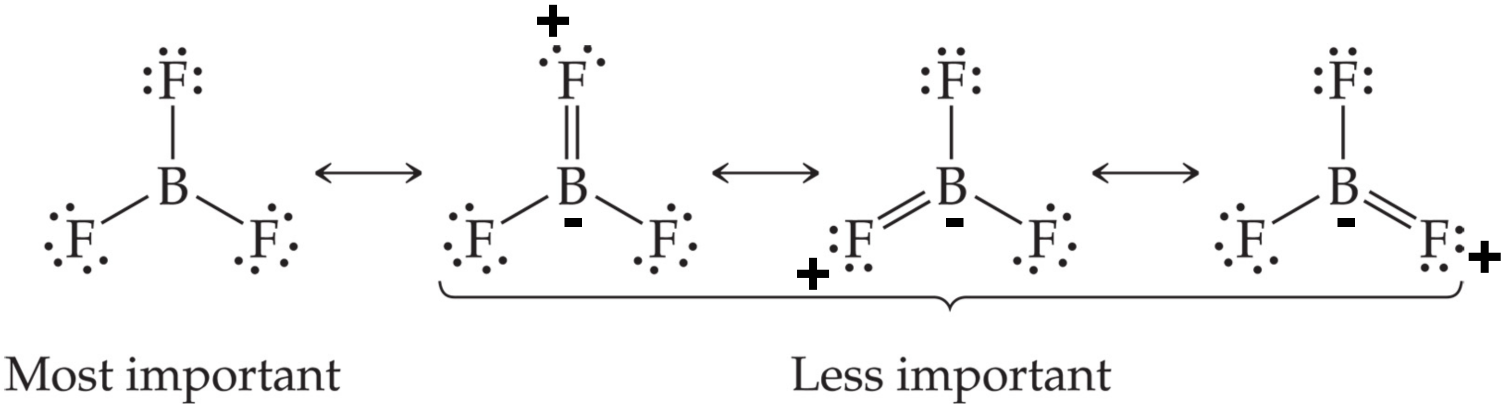
Therefore, structures that put a double bond between boron and fluorine are much less important than the one that leaves boron with only 6 valence electrons.

Double bonds to halogens don’t happen.



Fewer Than Eight Electrons

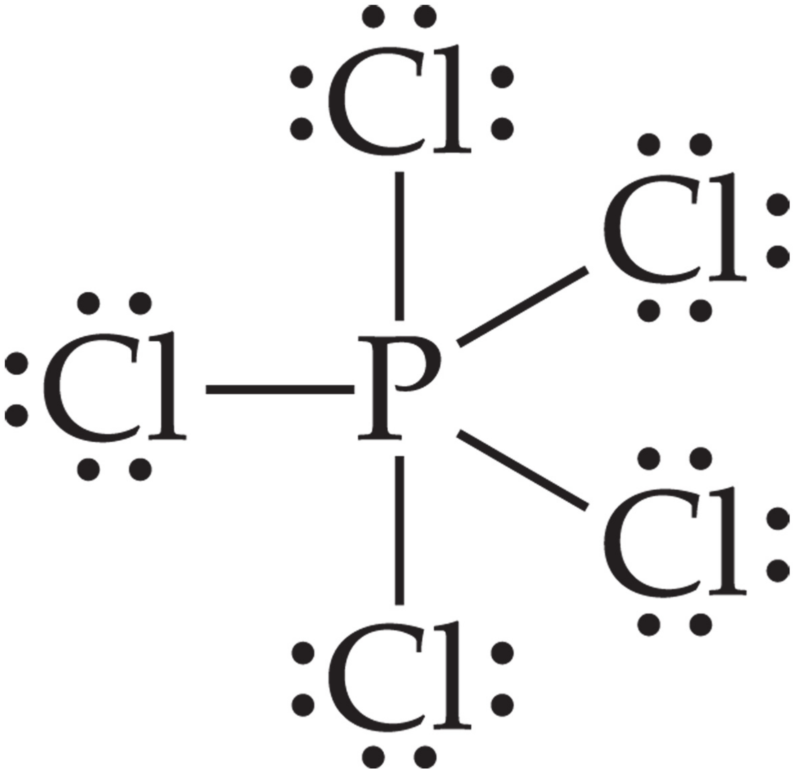
The lesson is: If filling the octet of the central atom results in a negative charge on the central atom and a positive charge on the more electronegative outer atom, don’t fill the octet of the central atom.



More Than Eight Electrons

Draw the Lewis structure for PCl_5

More Than Eight Electrons



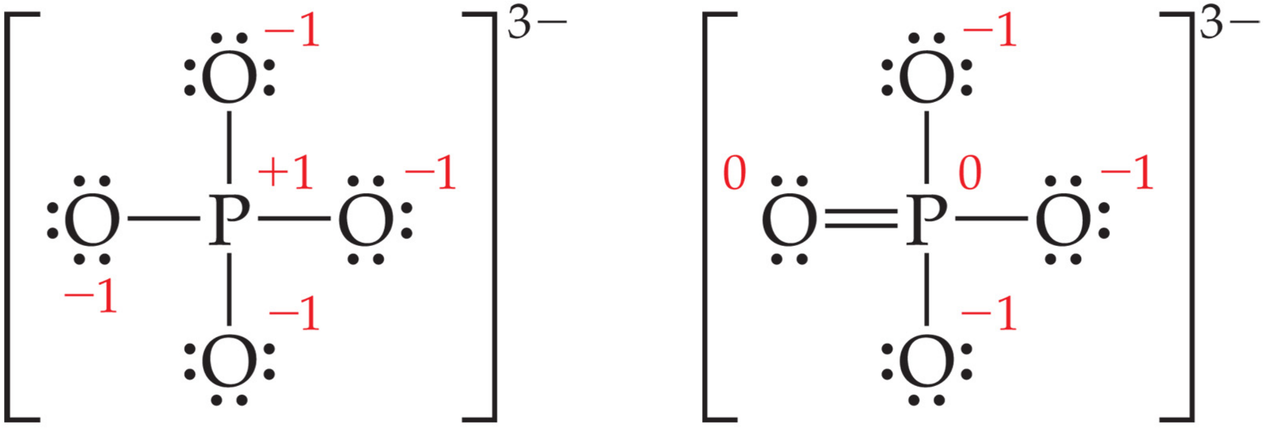
- The only way PCl_5 can exist is if phosphorus has 10 electrons around it.
- atoms on the 3rd row or below can go over an octet of electrons
  - Presumably *d* orbitals in these atoms participate in bonding.

More Than Eight Electrons

- Draw the Lewis structure for phosphate
- PO_4^{-3}

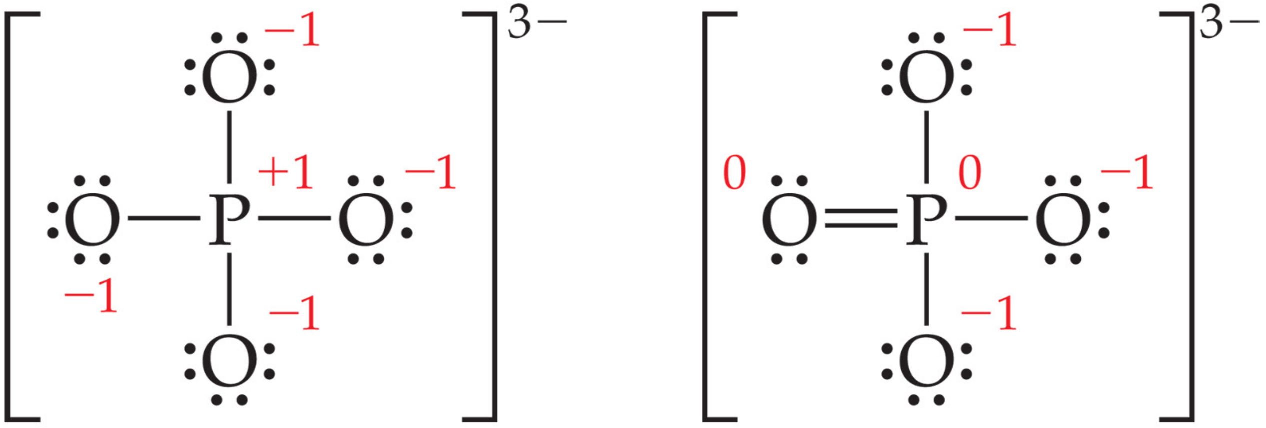
More Than Eight Electrons

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



More Than Eight Electrons

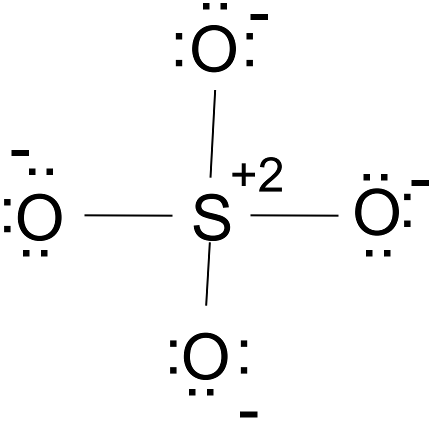
- This eliminates the charge on the phosphorus and the charge on one of the oxygens.
- The lesson is: When the central atom is on the 3rd row or below and expanding its octet eliminates some formal charges, you *can* do so.
- But, you don’t have to.

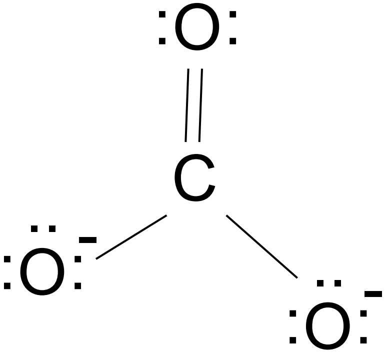


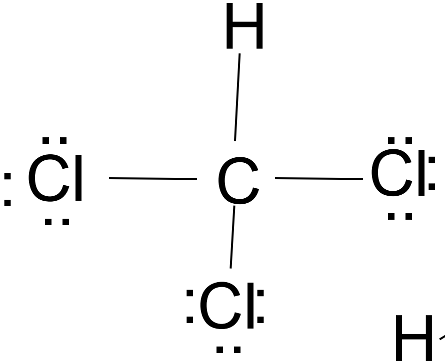
More Practice

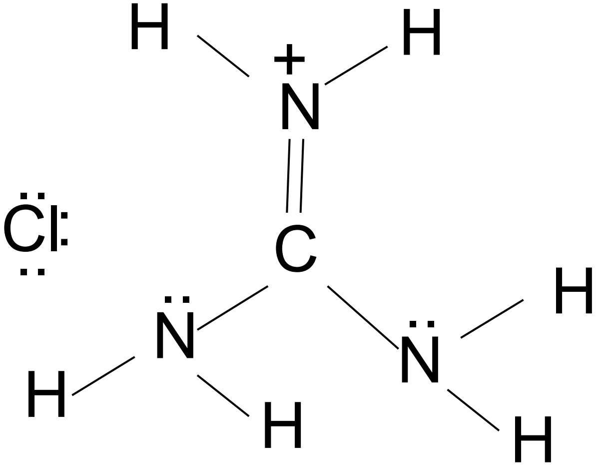
- Draw lewis structures for:
- SO_4^{-2}, CO_3^{-2}, $CHCl_3$, $CN_3H_6^+$ (H’s are attached to the N’s). SO_2, PO_3^{3-}, NO_2^{-1}, BrO_3^-, ClO_4^-,

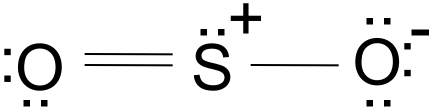
SO_4^{-2}, CO_3^{-2}, $CHCl_3$, $CN_3H_6^+$ (H’s on N’s). SO_2, PO_3^{1-}, NO, BrO_3^-, ClO_4^-,

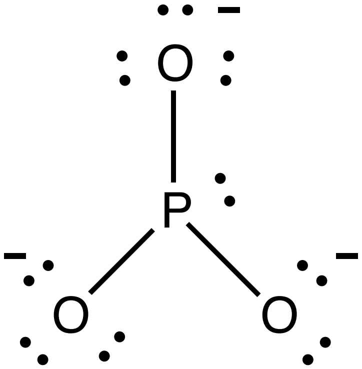


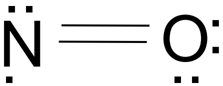


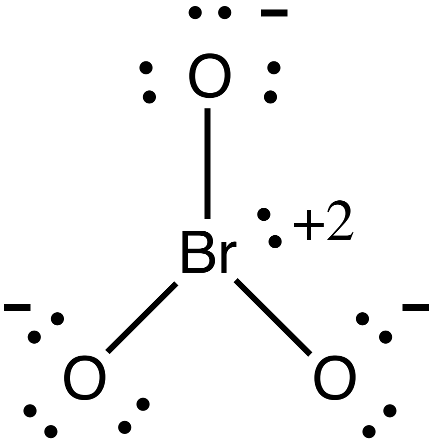


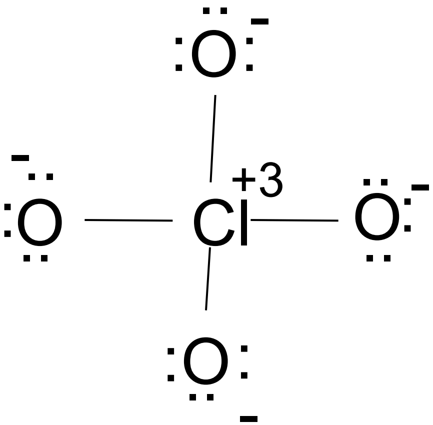




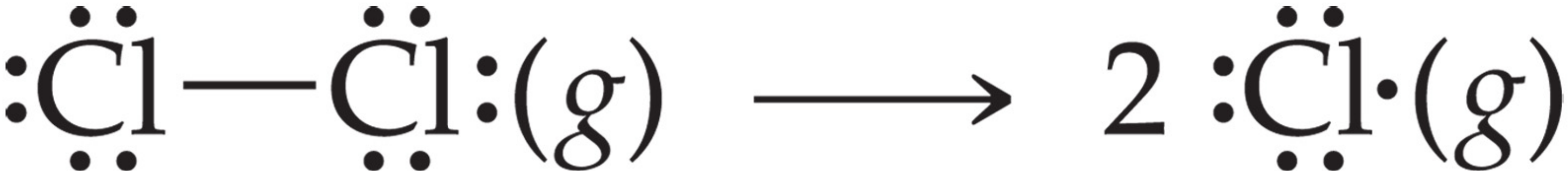








Covalent Bond Strength

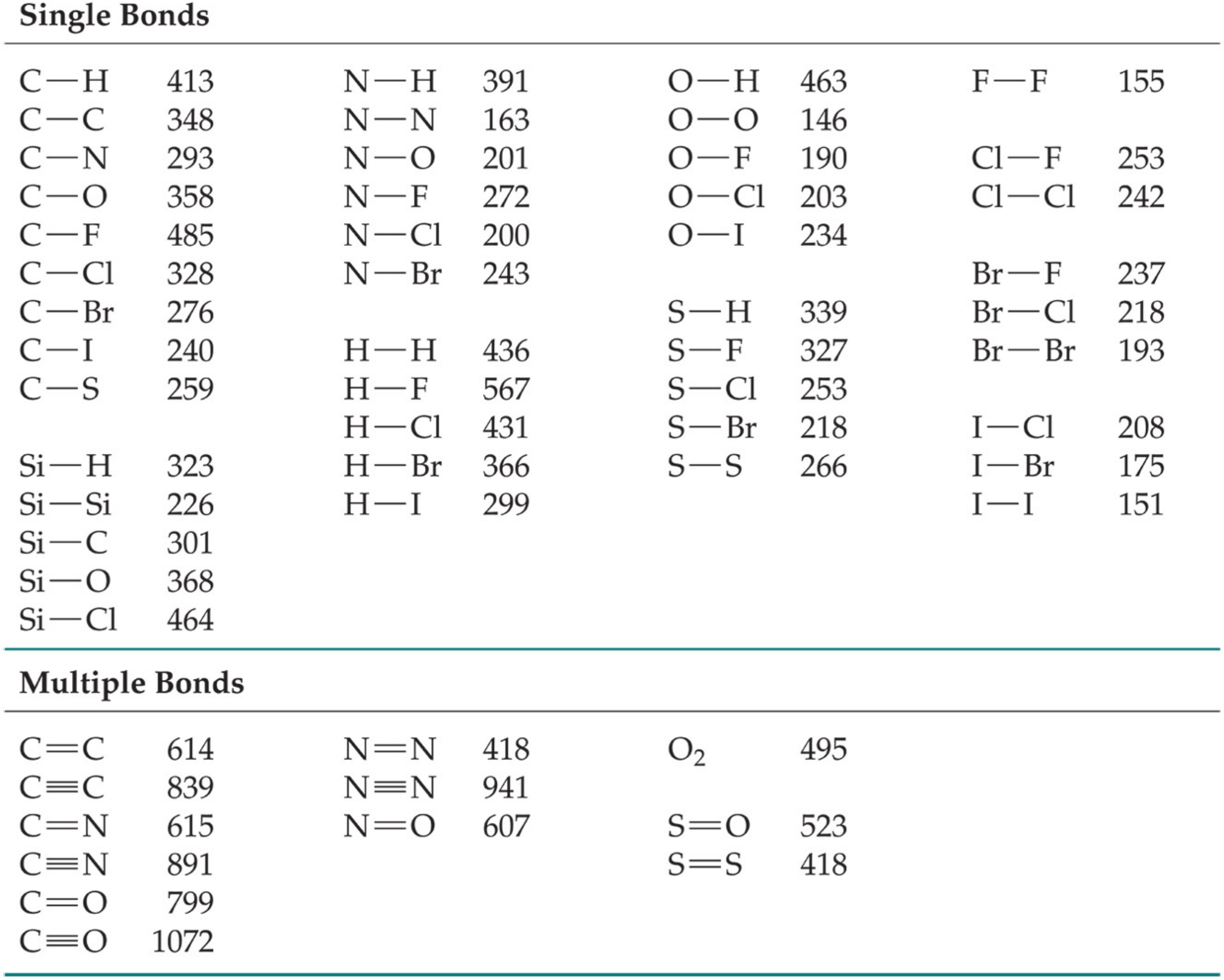


$$:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}-\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:(g) \longrightarrow 2\,:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot(g)$$

$\Delta H = 242$ kJ/mol

- 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*(Cl—Cl), is 242 kJ/mol.

Average Bond Enthalpies



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						

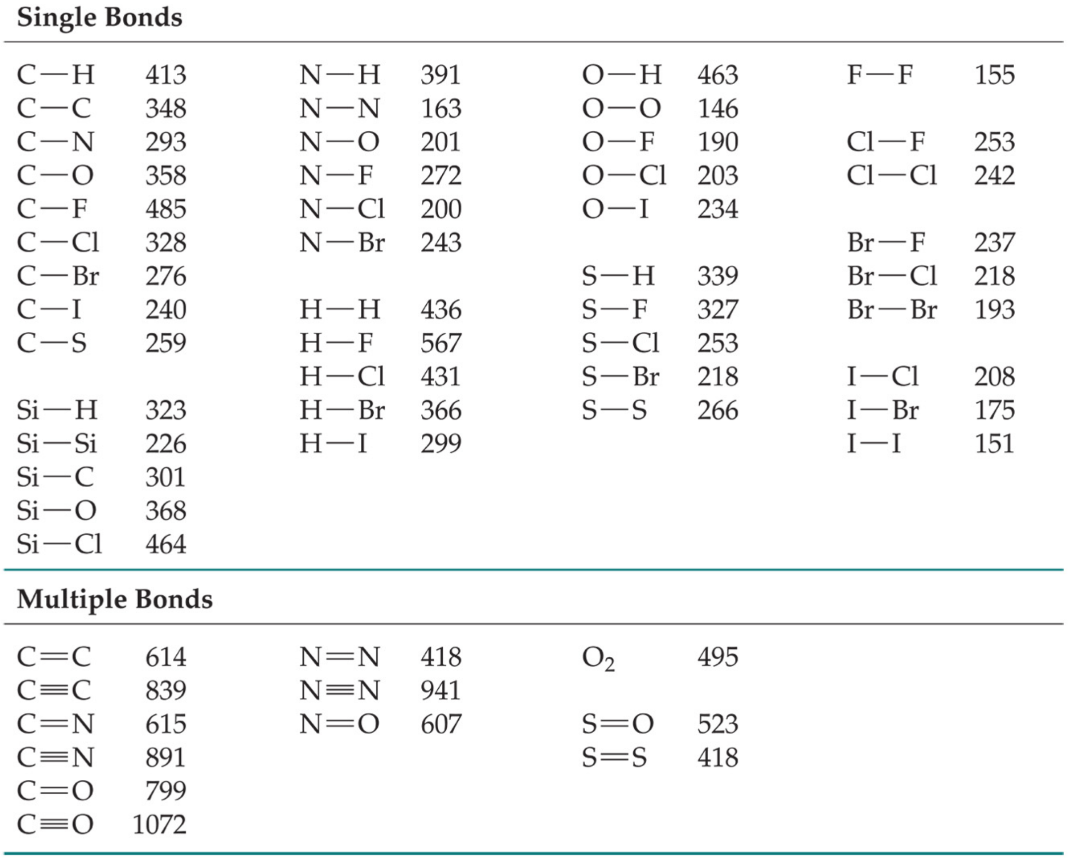
Multiple Bonds

C=C	614	N=N	418	O_2	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				

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

Average Bond Enthalpies

NOTE: These are *average* bond enthalpies, not absolute bond enthalpies; the C—H bonds in methane, CH_4, will be a bit different than the C—H bond in chloroform, $CHCl_3$.



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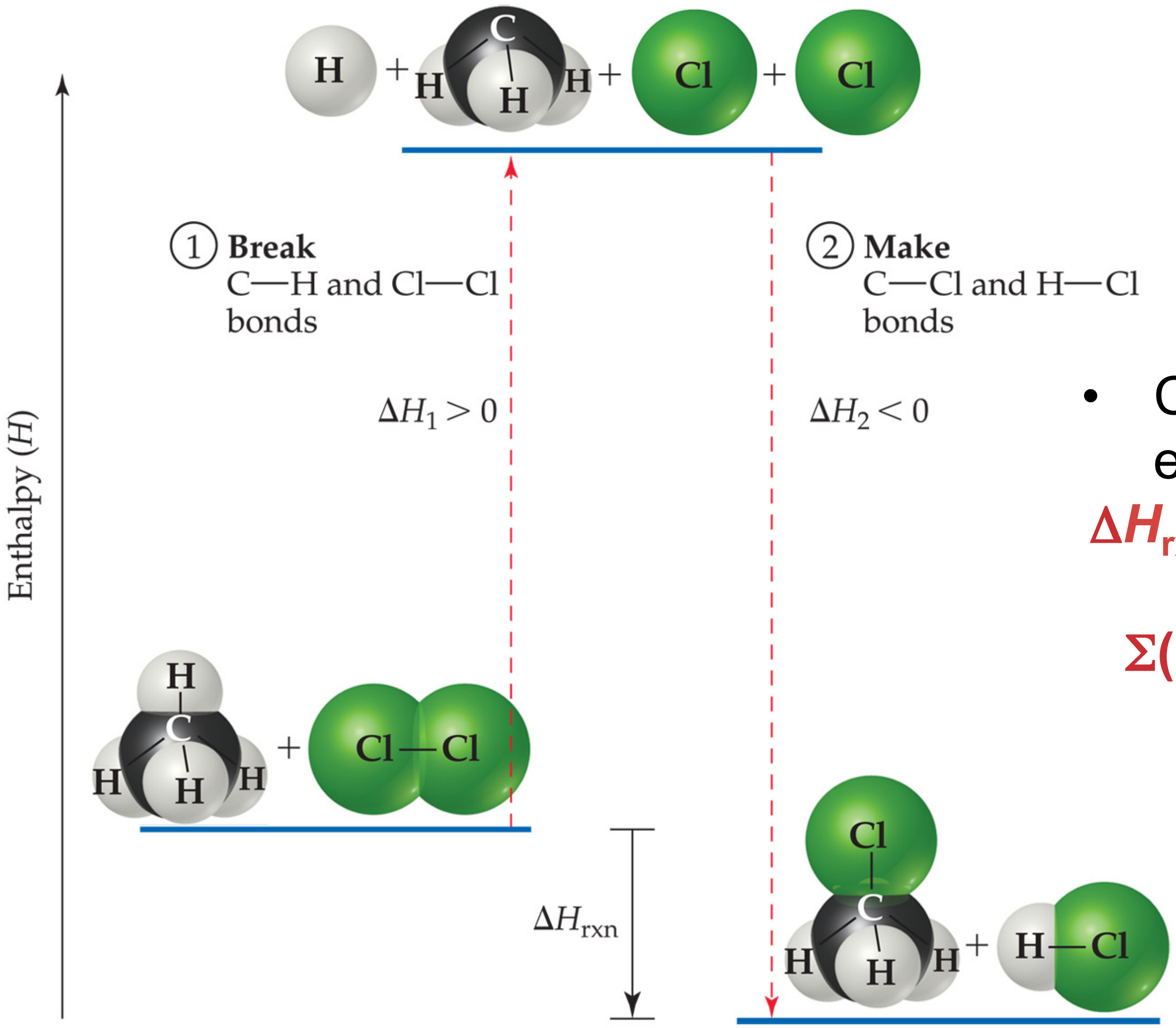
Enthalpies of Reaction



- Can use bond enthalpies to estimate ΔH for a reaction

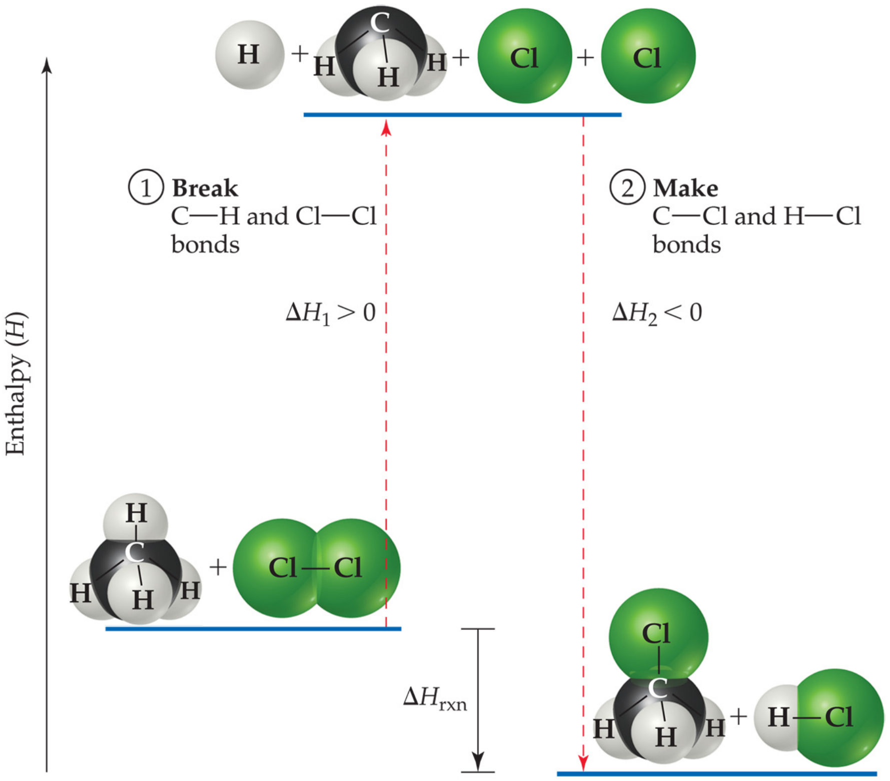
ΔH_{rxn} = Σ(bond enthalpies of bonds broken) - Σ(bond enthalpies of bonds formed)

This is a fundamental idea in chemical reactions. The heat of a reaction comes from breaking bonds and remaking bonds.

Enthalpies of Reaction

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

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



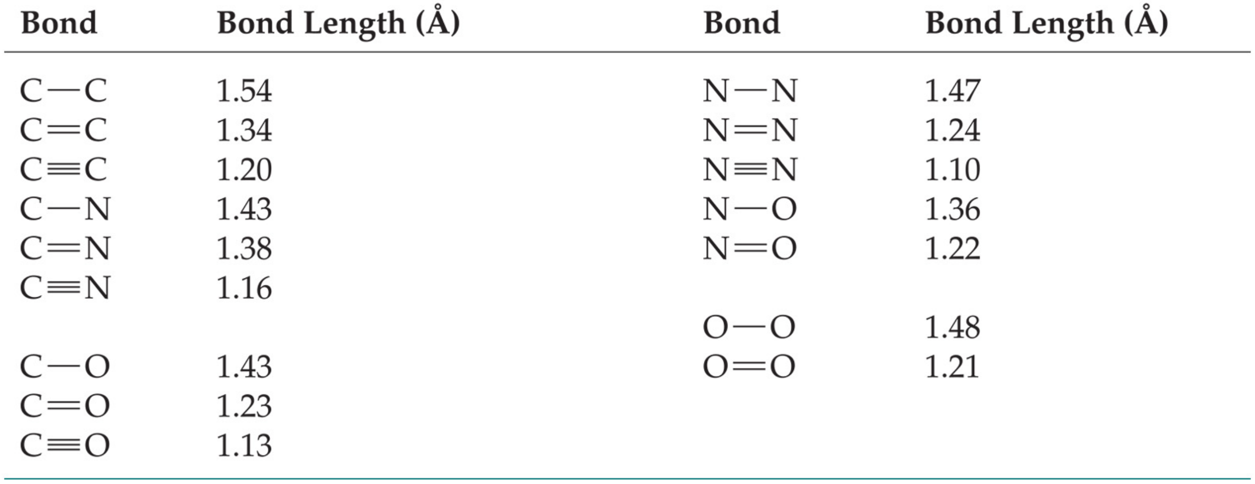
Enthalpies of Reaction

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

So,

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

Bond Enthalpy and Bond Length



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		

- 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.

Enthalpy problem:

- Calculate the enthalpy of reaction for:
- $CH_4 + O_2$ ---> $CO_2 + H_2O$

- $HC\equiv CH + O_2$ ------> $CO_2 + H_2O$

Enthalpy problem:

- Calculate the enthalpy of reaction for:
- $CH_4 + 3/2O_2$ ---> $CO_2 + 2H_2O$
- 4(C--H) + 3/2(O==O) - 2(C==O) - 4(OH)
- 4(413) + 3/2(495) - 2(800) - 4(463) = -563 kJ

- $HC\equiv CH + 5/2O_2$ ------> $2CO_2 + H_2O$

- 1(CC) + 2CH + 5/2(O=O) - 4(C==O) - 2(OH)
- 1(834) + 2(413) +5/2(495) - 4(800) - 2(463) = -1229 kJ

Quiz

Draw the Lewis structure (include resonance and formal charges) for:

HOFO

NCO^-