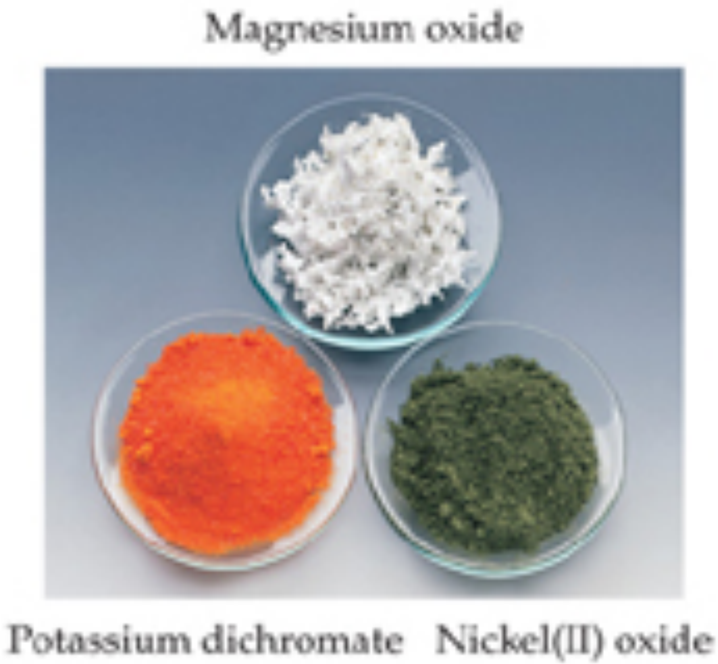
Chapter 8
Concepts of Chemical Bonding

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

Metals: lose electrons easy, low ionization energy (I.E.)

Nonmetals: Gain electrons easy. More negative Electron Affinity (E.A.).

Energetics of Ionic Bonding

$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$

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

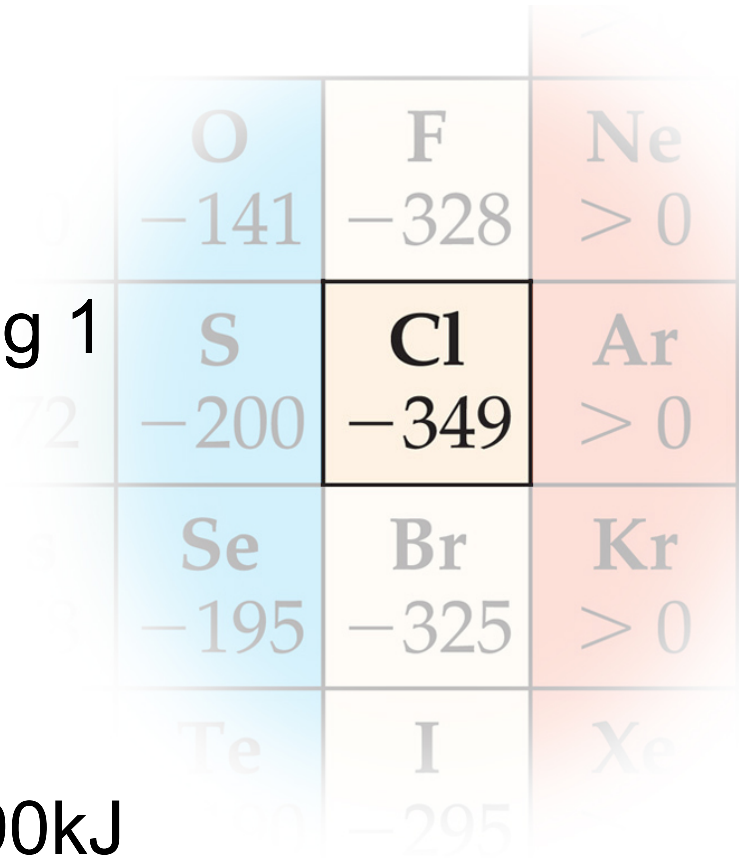
It takes another 240 kJ/mole to:

Cl_2 -→ 2Cl

We get **349 kJ/mol** back by giving 1 electron each to 2 moles of Cl. (Electron affinity of Cl)

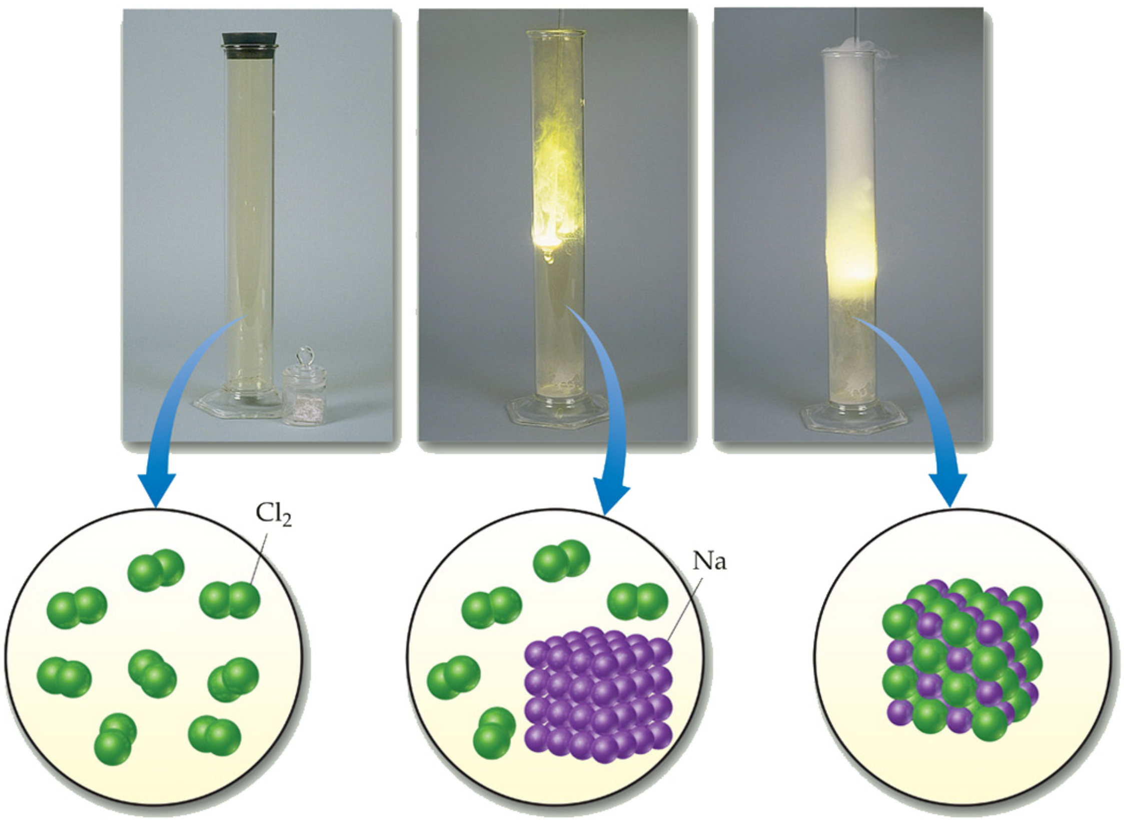
-349x2 = -700 kJ/mol Cl-→ Cl^-

990 kJ/2Na – 700 kJ/Mol Cl^- = 290kJ



Energetics of Ionic Bonding

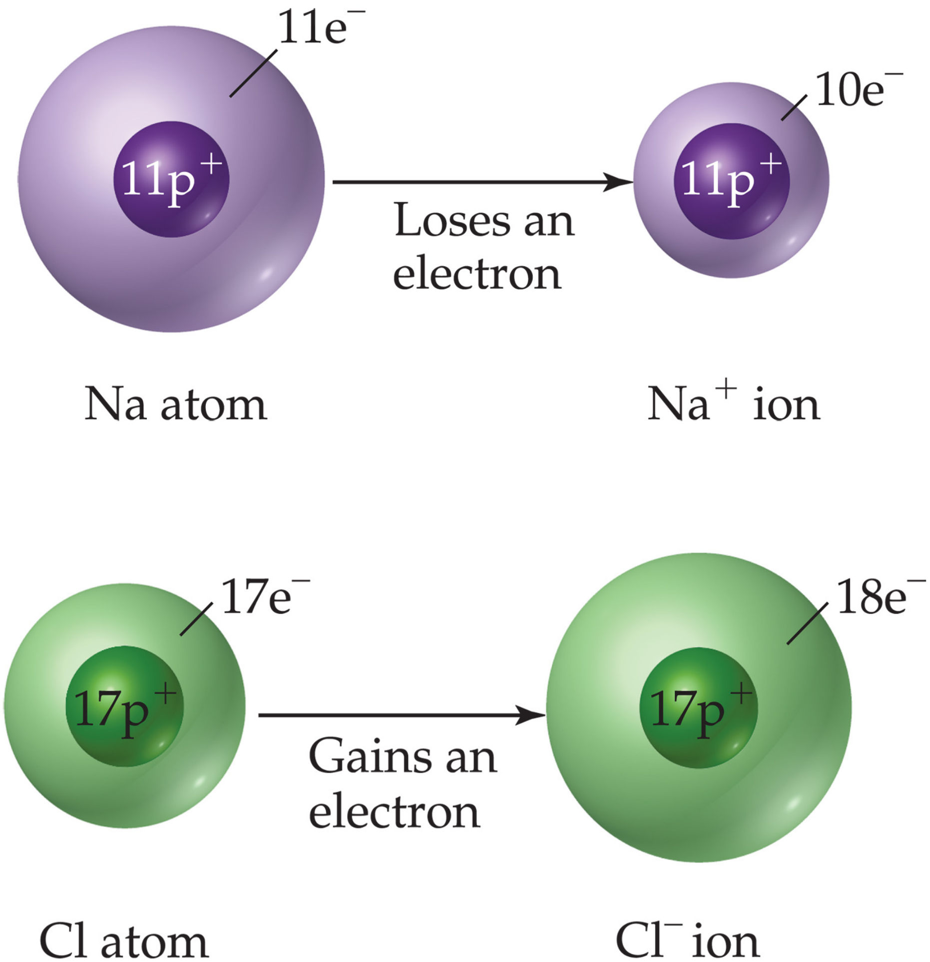
990 kJ/2Na^+ + 240 kJ/mol – 700 kJ/Mol (2Cl^-) = 530kJ



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:

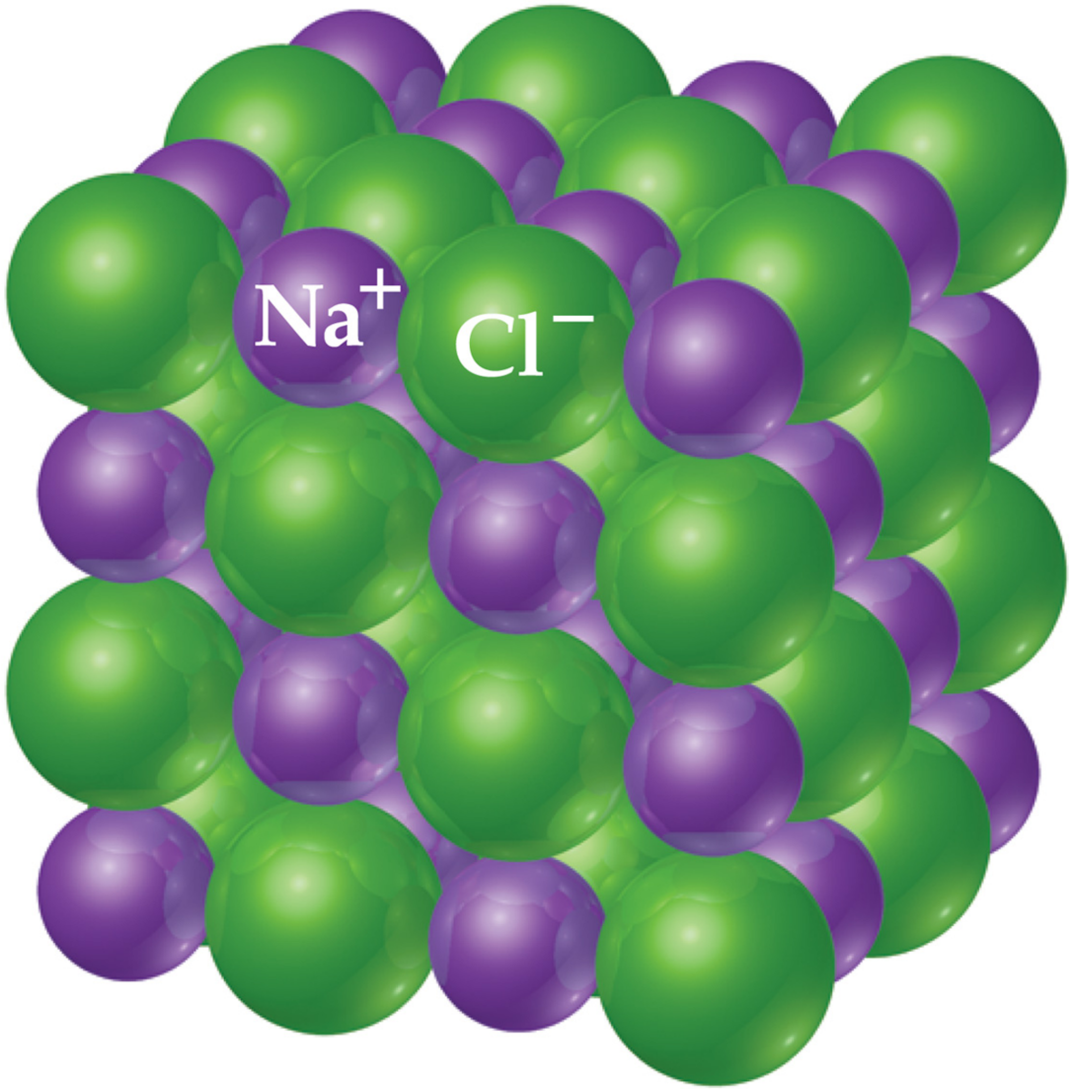
  The energy required to completely separate a mole of a solid ionic compound into its gaseous ions.

- 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

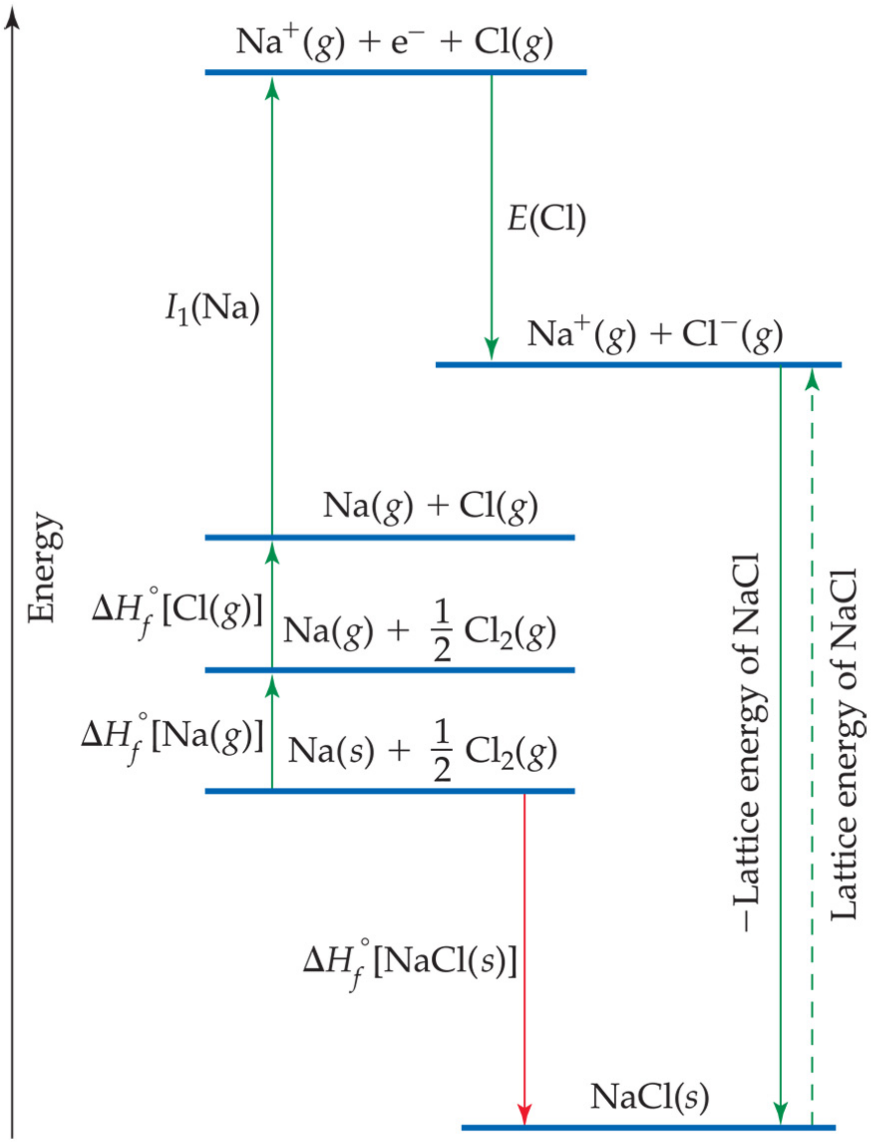
- Lattice energy, then, increases with the charge on the ions.
- It also increases with decreasing size of ions.

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		

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

Energetics of Ionic Bonding

$Na(s) + 1/2Cl_2(g)$ -----> $NaCl(s)$



By accounting for all three energies

ionization energy,
electron affinity,
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	[illegible]
[illegible]	1012	1907	

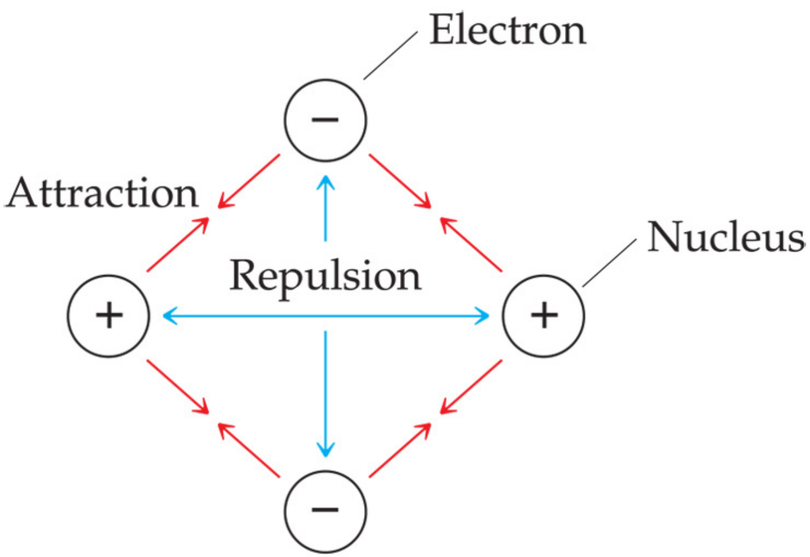
- Why do elements tend to lose or gain electrons only until a shell is filled (noble gas electron configuration)?
  - because at that point the I.E. is too large to be overcome by Lattice Energy
  - Lattice energy gets bigger as charge on ion gets bigger
  - But it can't be big enough to justify the giant I.E. jump.

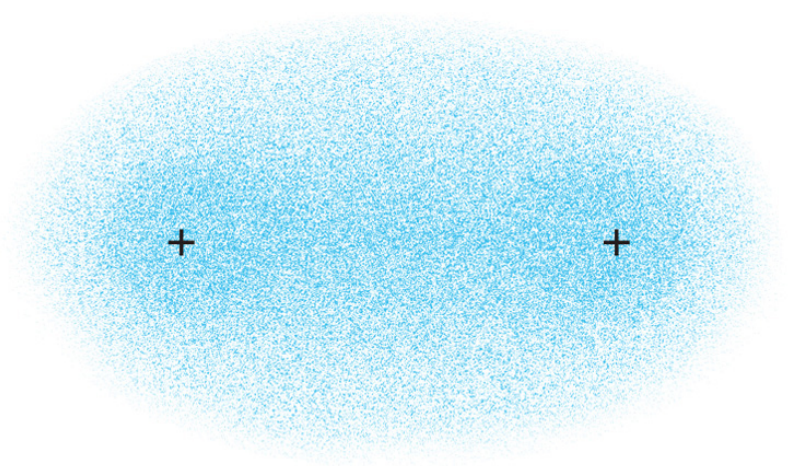
Covalent Bonding

What happens when nonmetals get together

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

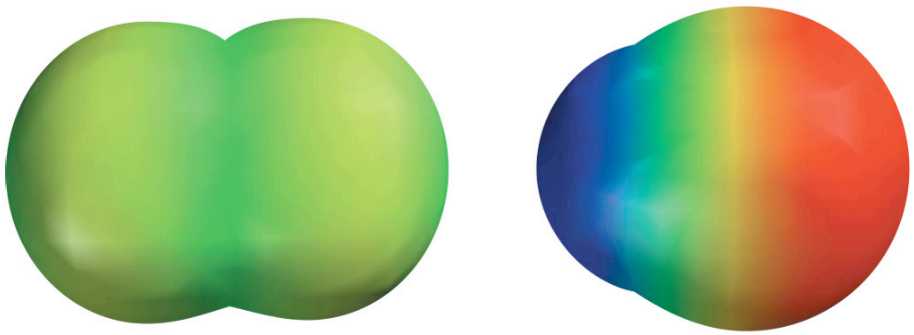
Covalent Bonding





- 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:

Bond strengths:

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 –

H more +

So the ionic component makes bond **stronger.**

Electronegativity:

Developed 1st by Linus Pauling like this:

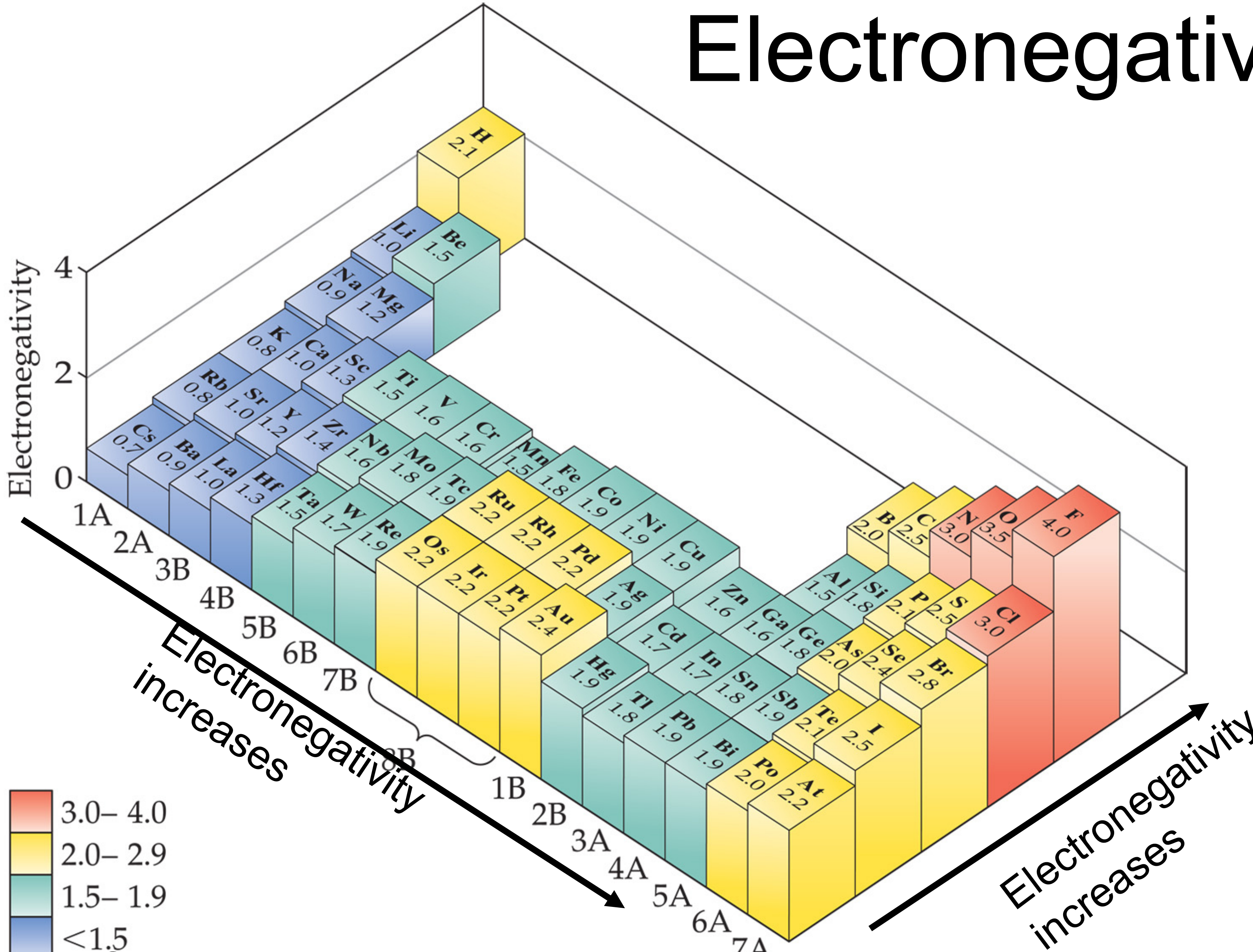
$$EN_A - EN_B = eV^{-1/2}\sqrt{D_{AB} - (D_{AA} + D_{BB})/2}$$

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:



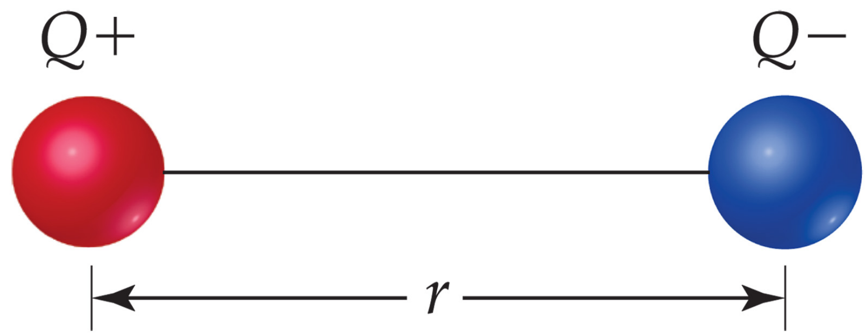
- On the periodic chart, electronegativity increases as you go…
  - …from left to right across a row.
  - …from the bottom to the top of a column.

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:

$$\mu = Qr$$

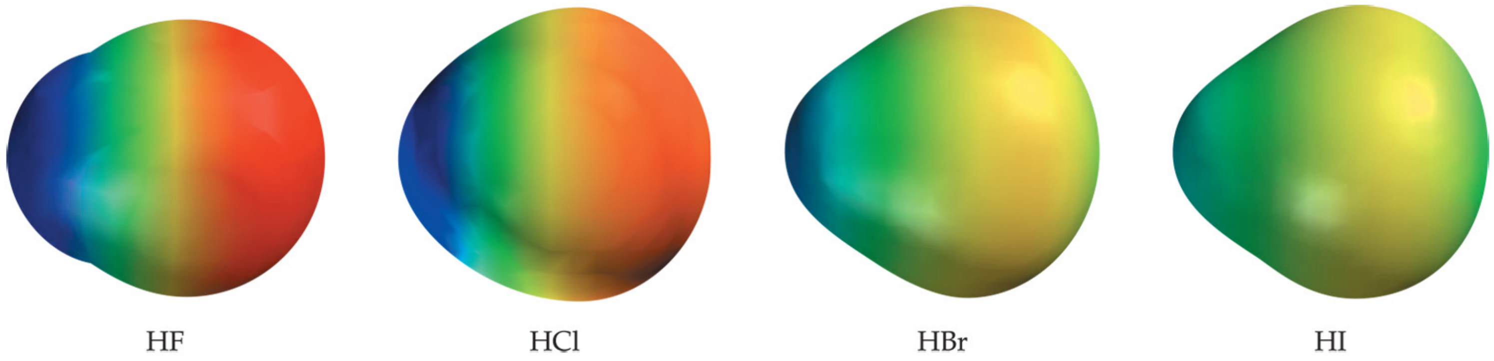
- It is measured in debyes (D).



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 structures

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

Each dot is one valence electron

TABLE 8.1 Lewis Symbols

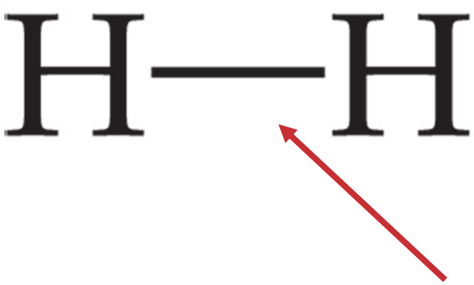
Element	Electron Configuration	Lewis Symbol
Li	[He]$2s^1$	Li·
Be	[He]$2s^2$	·Be·
B	[He]$2s^2 2p^1$	·Ḃ·
C	[He]$2s^2 2p^2$	·Ċ· (4 dots)
N	[He]$2s^2 2p^3$	·Ṅ: (5 dots)
O	[He]$2s^2 2p^4$	:Ȯ: (6 dots)
F	[He]$2s^2 2p^5$	·F̈: (7 dots)
Ne	[He]$2s^2 2p^6$	:N̈e: (8 dots)
Na	[Ne]$3s^1$	Na·
Mg	[Ne]$3s^2$	·Mg·
Al	[Ne]$3s^2 3p^1$	·Ȧl·
Si	[Ne]$3s^2 3p^2$	·Ṡi· (4 dots)
P	[Ne]$3s^2 3p^3$	·Ṗ: (5 dots)
S	[Ne]$3s^2 3p^4$	:Ṡ: (6 dots)
Cl	[Ne]$3s^2 3p^5$	·C̈l: (7 dots)
Ar	[Ne]$3s^2 3p^6$	:Är: (8 dots)

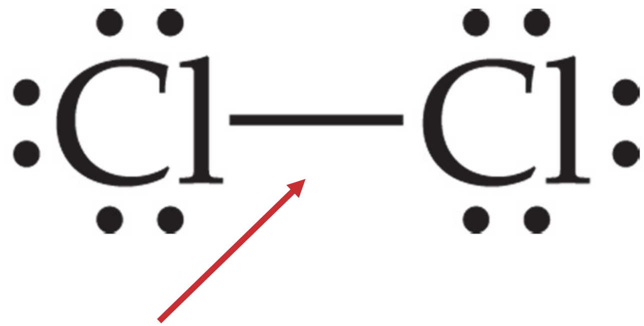
- Lewis structures for 16 elements
- It is rare to use Lewis pictures for other elements (transition metals, etc.)

One dot = 1 electron

Lewis Structures

Most useful for depicting ***molecules***





Lines correspond to 2 electrons in ***covalent*** 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

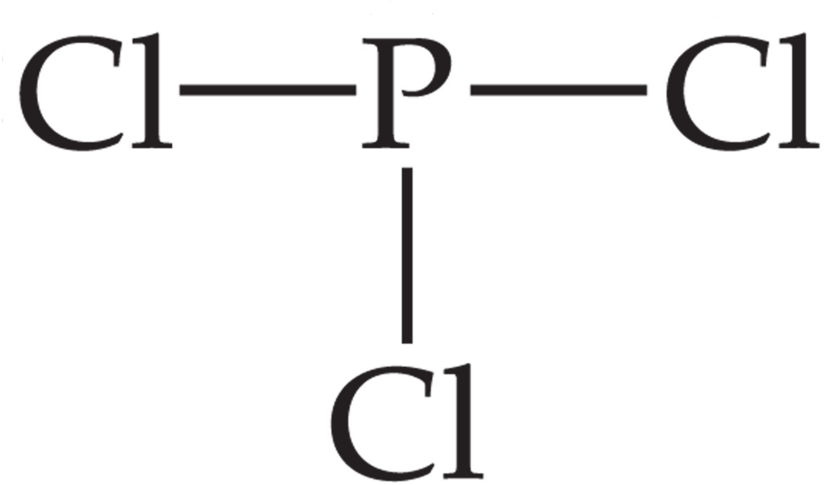
$$PCl_3$$

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

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

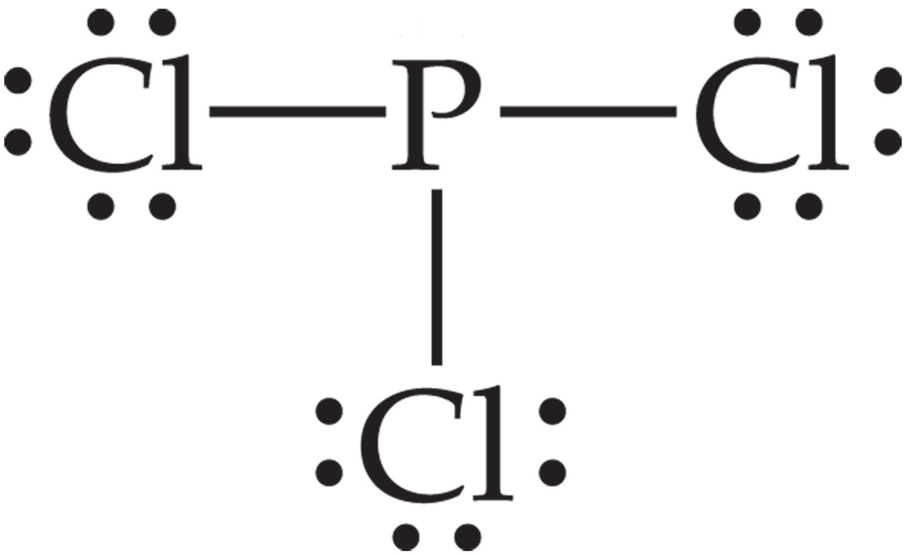


2. The central atom is the *least* electronegative element that isn't hydrogen (why?). Connect the outer atoms to it by single bonds.

Keep track of the electrons:

26 – 6 = 20

Writing Lewis Structures

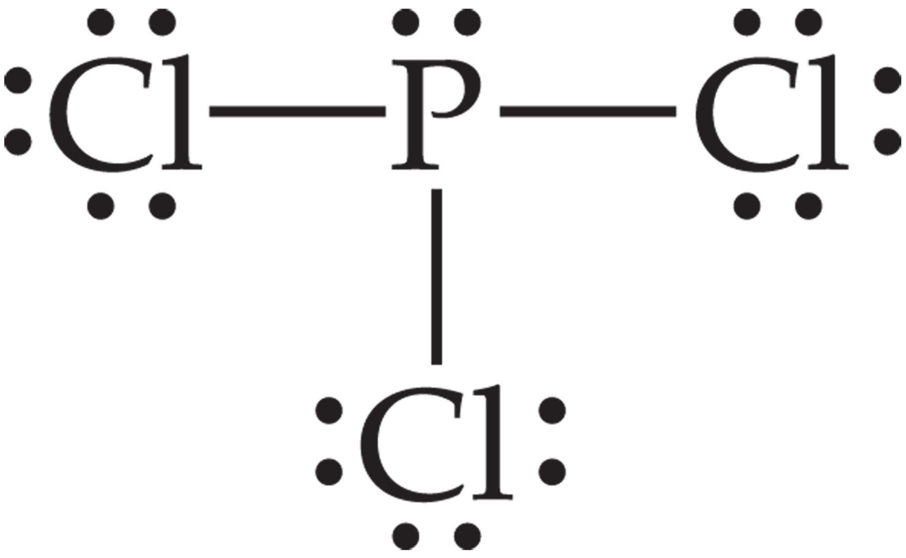


3. Put eight electrons around the outer atoms ("fill their octet"), bonds count 2.

Keep track of the electrons:

26 – 6 = 20 – 18 = 2

Writing Lewis Structures



4. Fill the octet of the central atom.

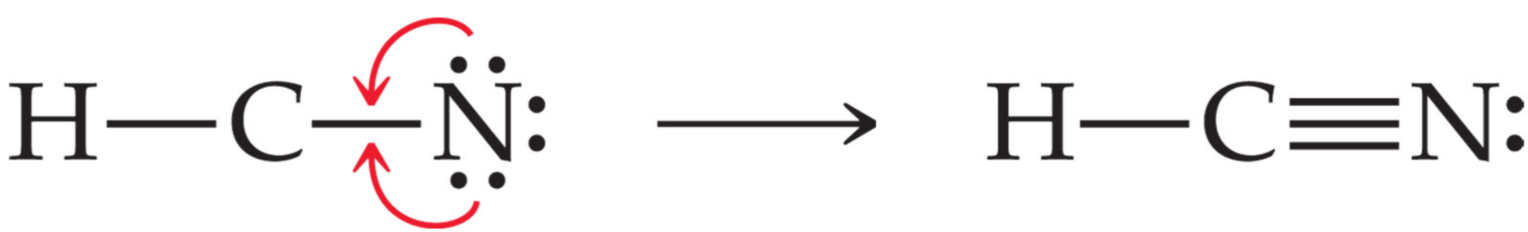
Keep track of the electrons:

26 – 6 = 20 – 18 = 2 – 2 = 0

Writing Lewis Structures

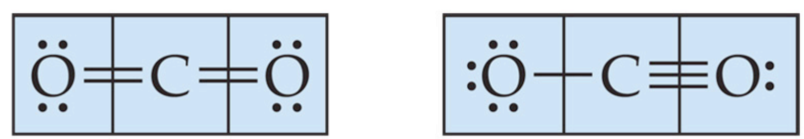
5. If you run out of electrons before the central atom has an octet…

…form multiple bonds until it does.



Writing Lewis Structures

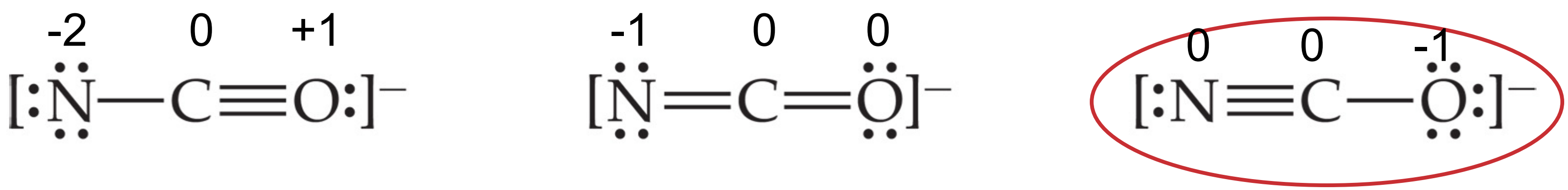
- Then assign formal charges.
  - For each atom, count the electrons in lone pairs and half the electrons in it's bonds (dots plus lines).
  - Subtract that from the number of valence electrons for that atom: The difference is its formal charge.



	O	C	O	O	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

Writing Lewis Structures

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



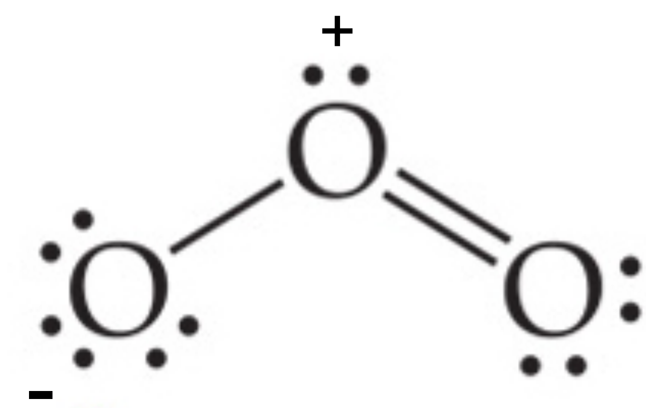
Resonance

Draw the Lewis structure for ozone, O_3.

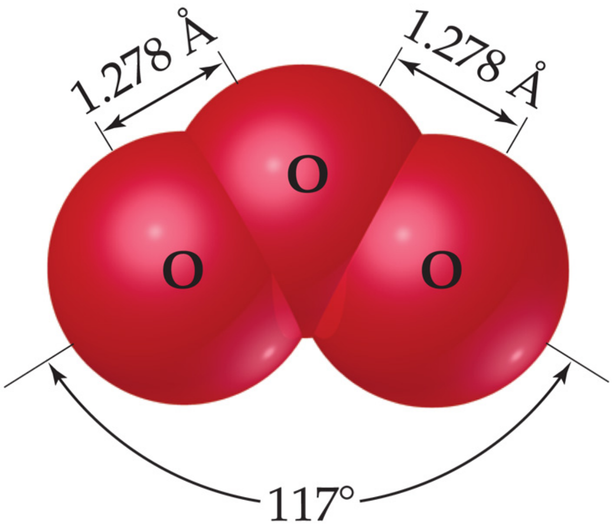
Resonance

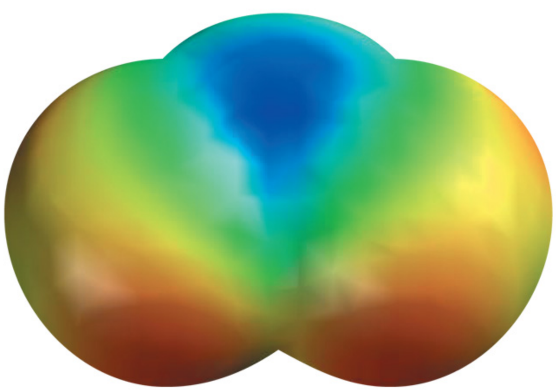
Draw the Lewis structure for ozone, O_3.

But why should one O be different from the other?



Resonance

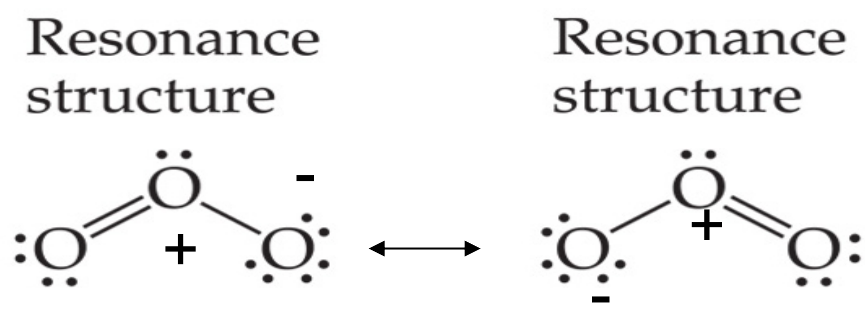




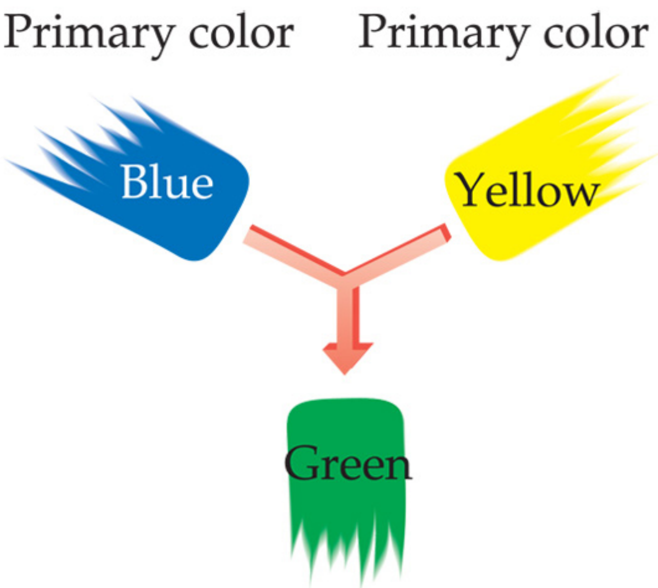
- It is at odds with the true, observed structure of ozone,
  - …both O—O bonds are the same length.
  - …both outer oxygens have a charge of −1/2.

Resonance

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

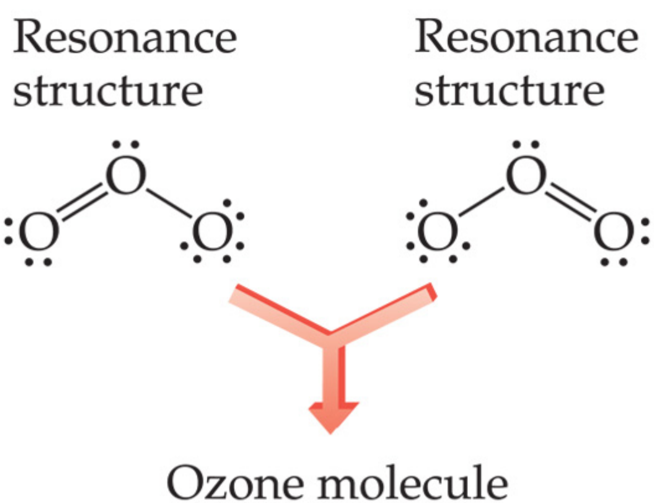


Resonance



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 Lewis structure for:

HCO_2^-

Resonance

Draw Lewis structure for:

HCO_2^-

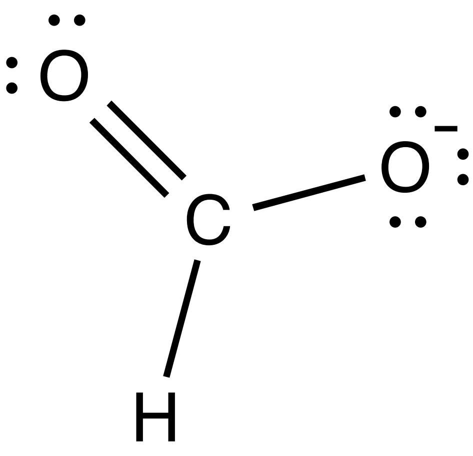
Valence Electrons: 1 + 4 +2(6) +1 = 18

H C O -

Resonance

Draw Lewis structure for:

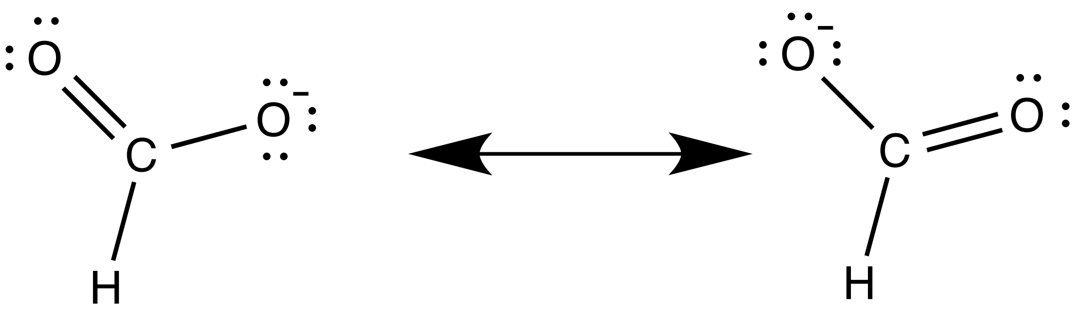
HCO_2^-



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

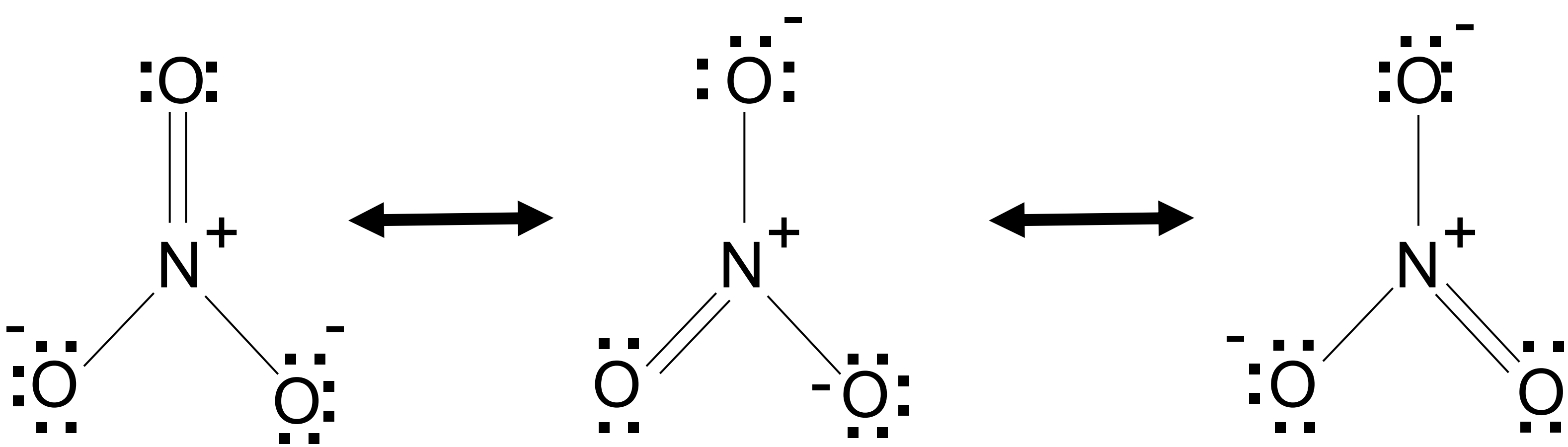
- Draw the Lewis structure of NO_3^-

Resonance

- Draw the Lewis structure of NO_3^-
- Valence Electrons: 5 + 3(6) + 1 = 24

Resonance

- Draw the Lewis structure of NO_3^-



More than one central atom

- Many molecules 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

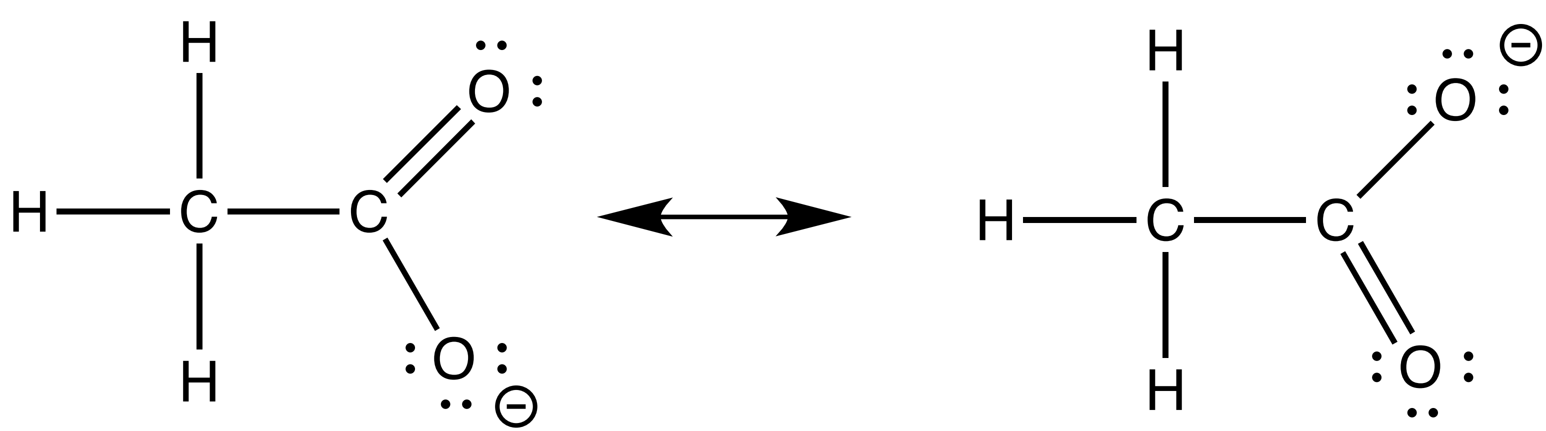
- Lewis structure for acetate:
- $CH_3CO_2^-$

Note: this means:

3 H attached to one C,

2 O attached to the other C and

the 2 C's are attached.

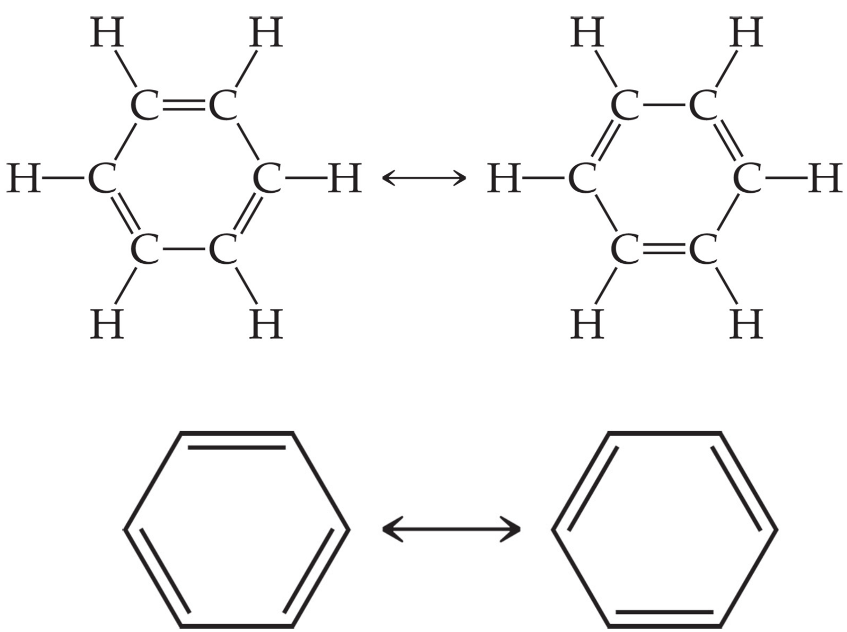


More than 1 central atom

- benzene, C_6H_6 is a hexagon of carbon atoms with 6 H's,
  - one attached to each C.
- Draw the Lewis structure for benzene.

More than 1 central atom

- benzene, C_6H_6, has two resonance structures.



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*** an octet (an expanded octet).

Odd Number of Electrons

Relatively rare

Often unstable

Odd Number of Electrons

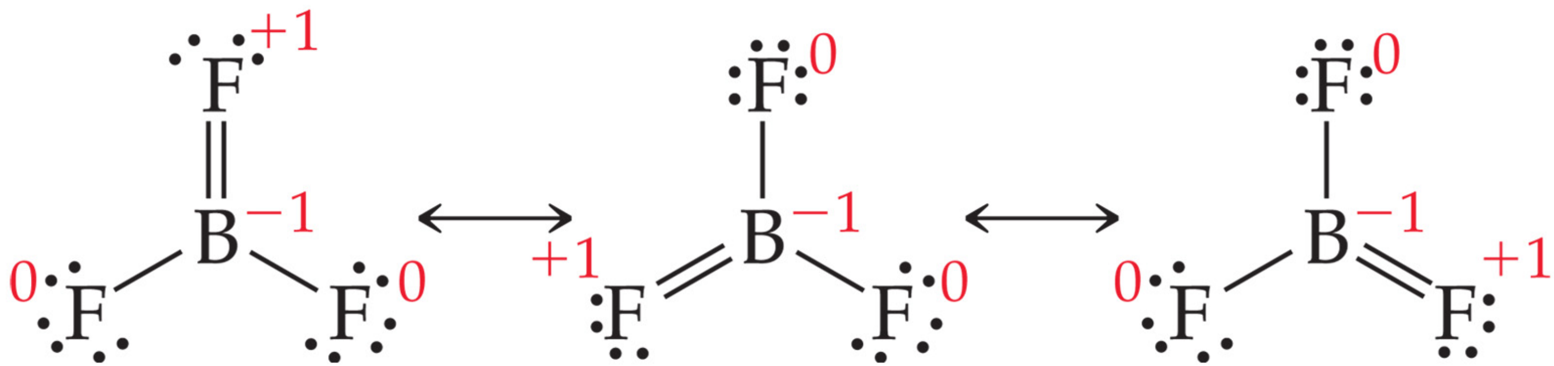
- Example: NO

What's nitric oxide good for?

Fewer Than Eight Electrons

Draw the Lewis structure for BF_3:

Fewer Than Eight Electrons

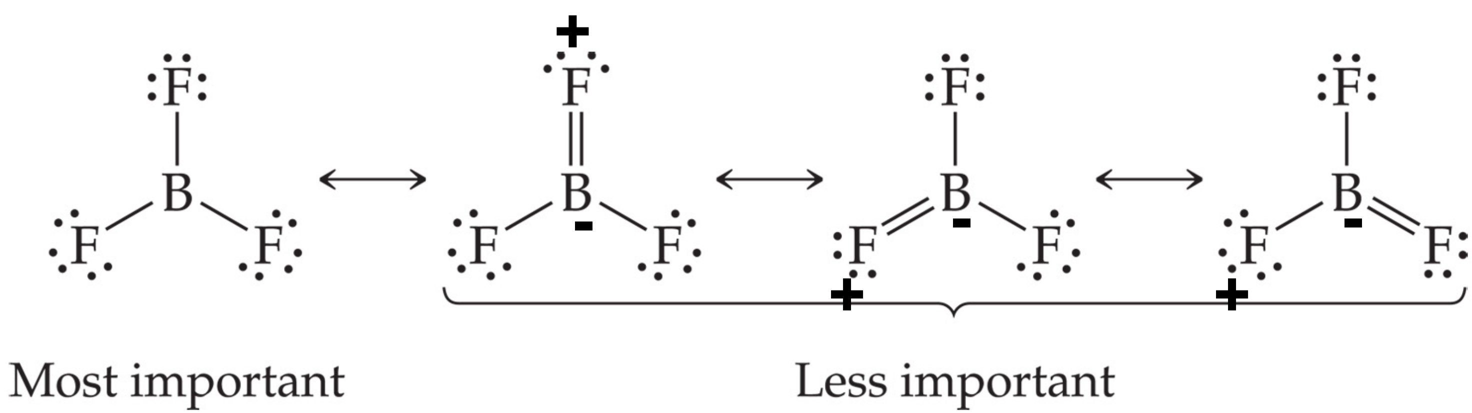


- Consider BF_3:
  - Giving boron a filled octet places ***a negative*** charge on the boron and ***a positive*** charge on fluorine.
  - Not right for BF_3.
  - Halides don’t make double bonds (gives + formal charge)

Fewer Than Eight Electrons

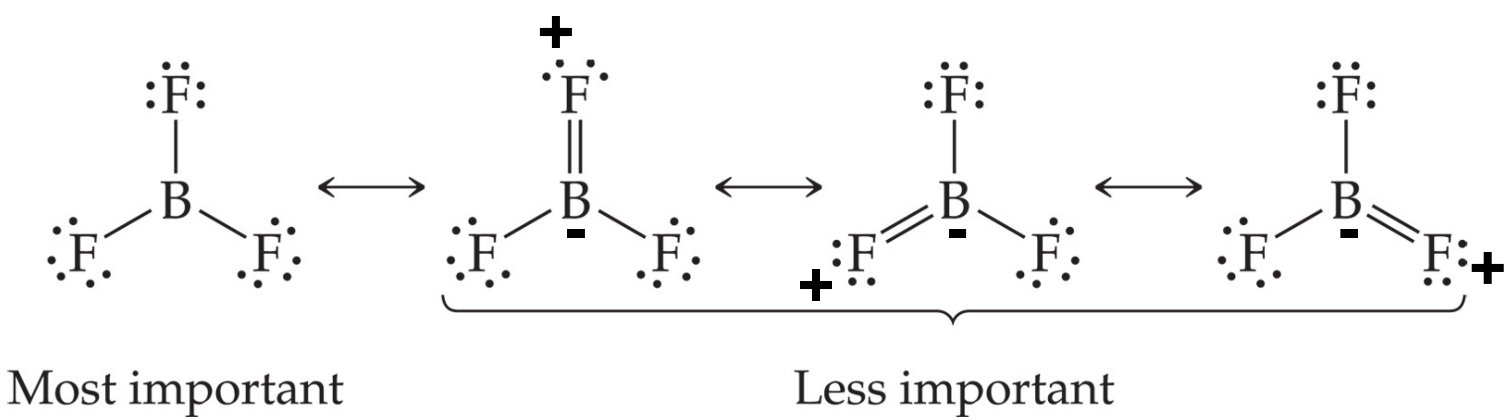
Therefore, structures that put a double bond between boron and fluorine are much less important than the one that leaves boron with only 6 valence electrons.

Double bonds to halogens are less favored.



Fewer Than Eight Electrons

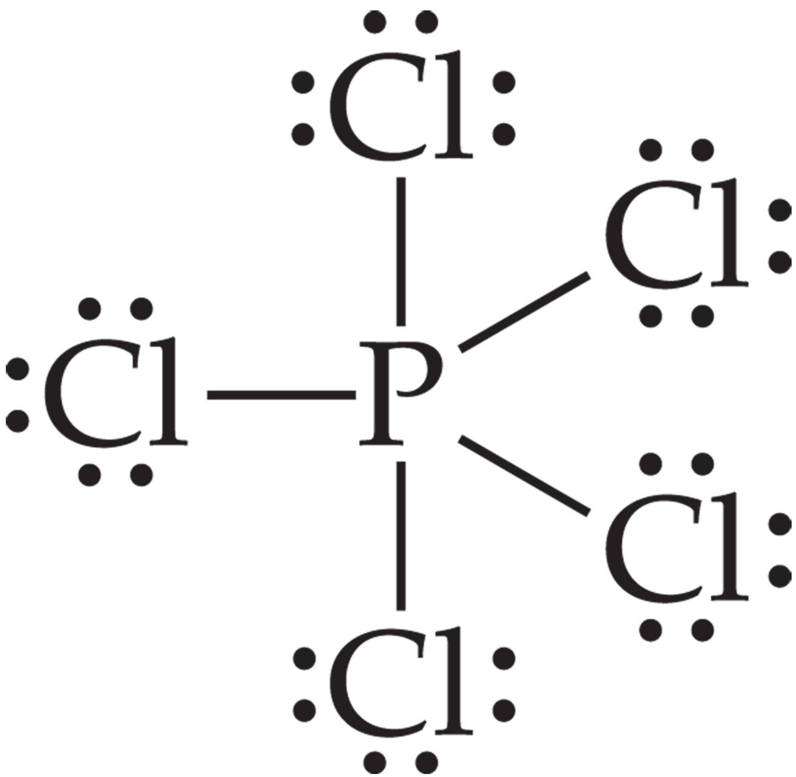
The lesson: If filling the octet of the central atom results in a negative charge on the central atom and a positive charge on the more electronegative outer atom, don't fill the octet of the central atom.



More Than Eight Electrons

Draw the Lewis structure for PCl_5

More Than Eight Electrons



- PCl_5 has to have 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.

But, only break octet

if you have to!!!!

More Than Eight Electrons

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

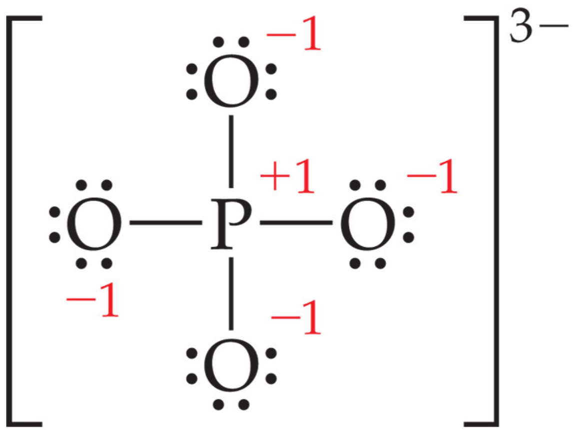
More Than Eight Electrons

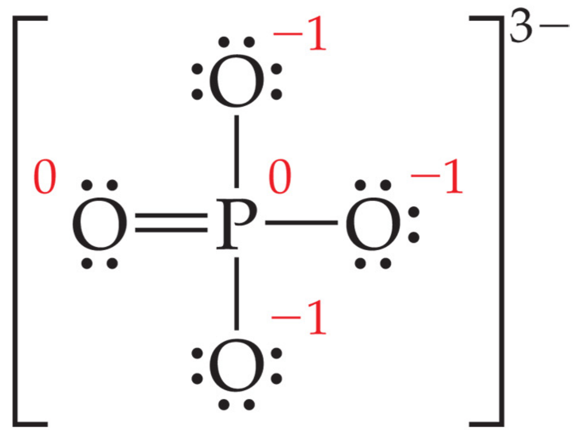
Best Lewis structure

Octet rule.

Minimizes formal charge

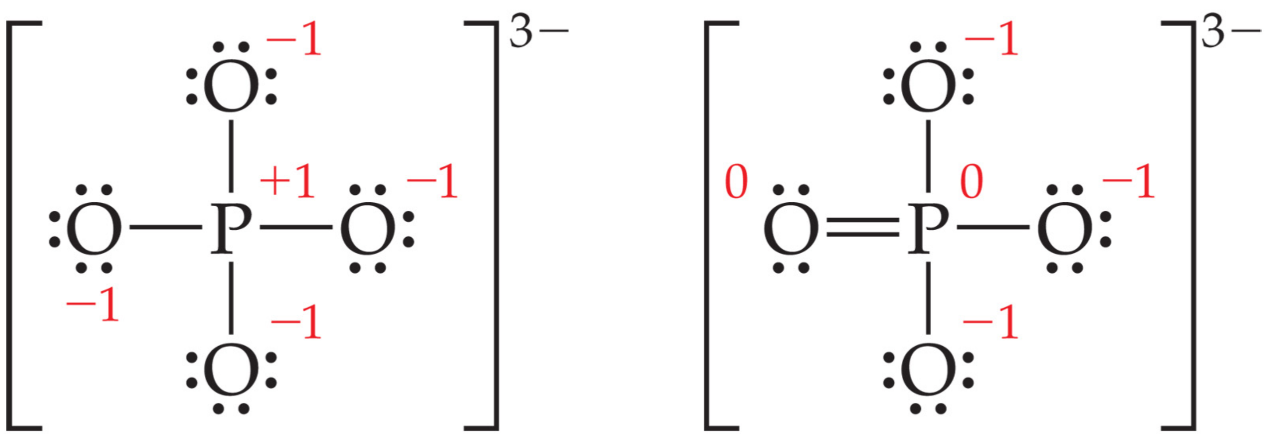
Often seen.





More Than Eight Electrons

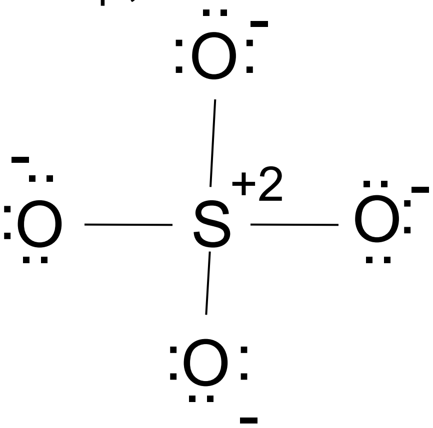
- This eliminates the charge on the phosphorus and the charge on one of the oxygens.
- The lesson is: When the central atom is on the 3rd row or below and expanding its octet eliminates some formal charges, you *can* do so.
- ***But, you don't have to.***

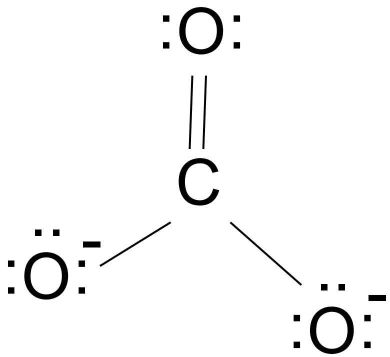


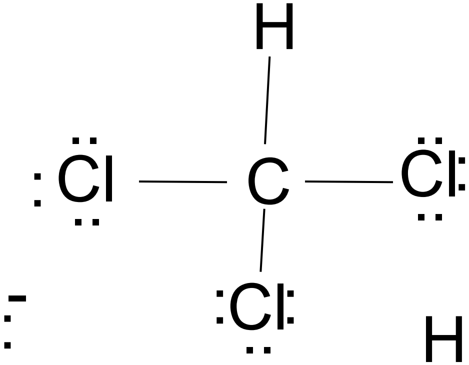
More Practice

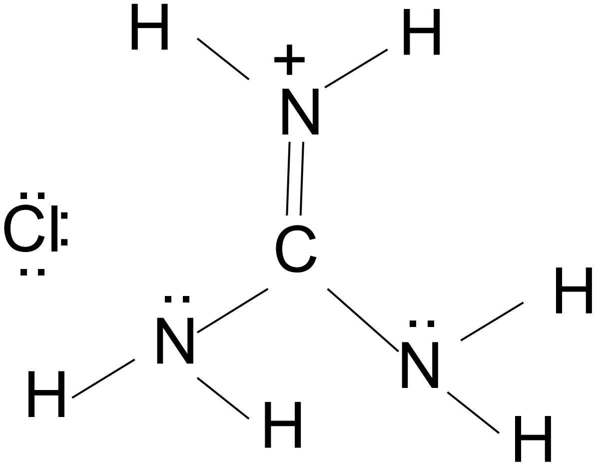
- Draw lewis structures for:
- SO_4^{-2}, CO_3^{-2}, $CHCl_3$, $CN_3H_6^+$ (H’ s are attached to the N’ s). SO_2, PO_3^{3-}, NO_2^{-1}, BrO_3^-, ClO_4^-,

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^-,



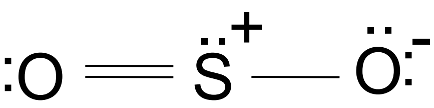




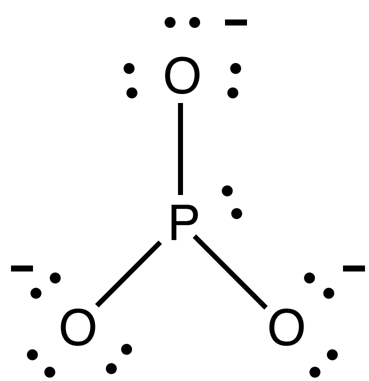


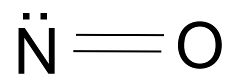
+ 2 resonance.

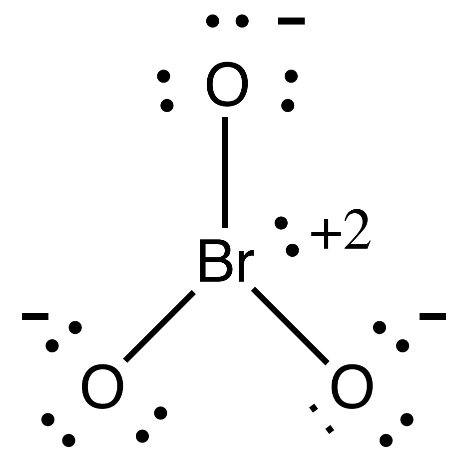
+2 resonance

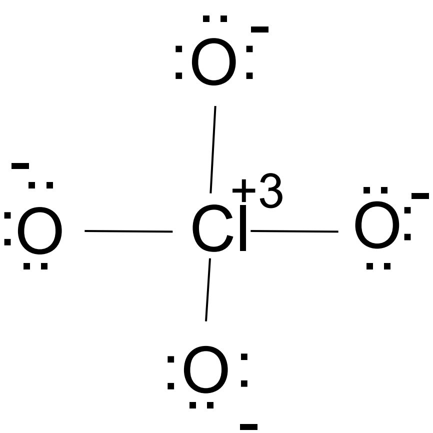


+ 1 resonance.









Covalent Bond Strength

ΔH = 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, $CHCl_3$.

Single Bonds

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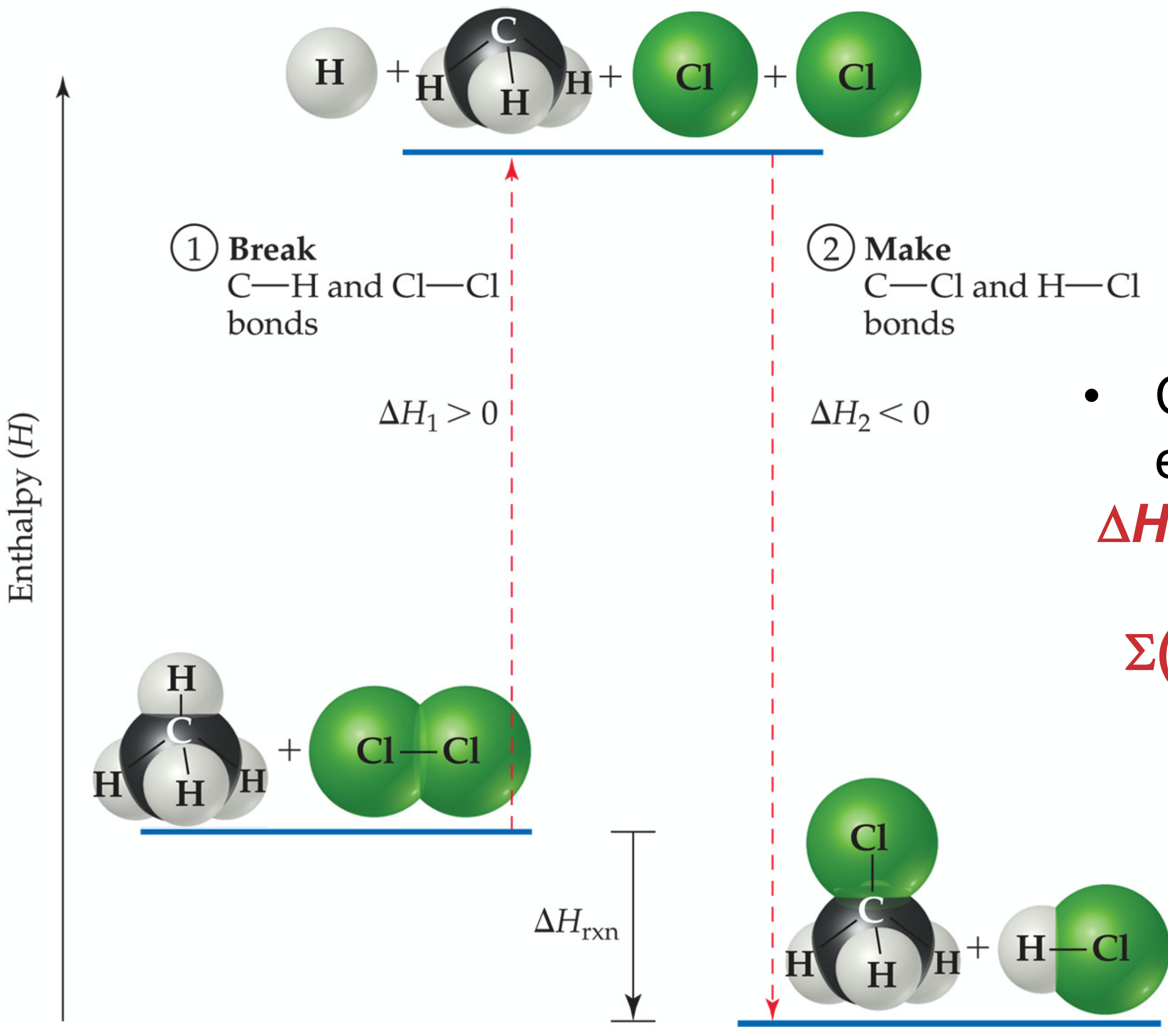
Enthalpies of Reaction



- Can use bond enthalpies to estimate ΔH for a reaction

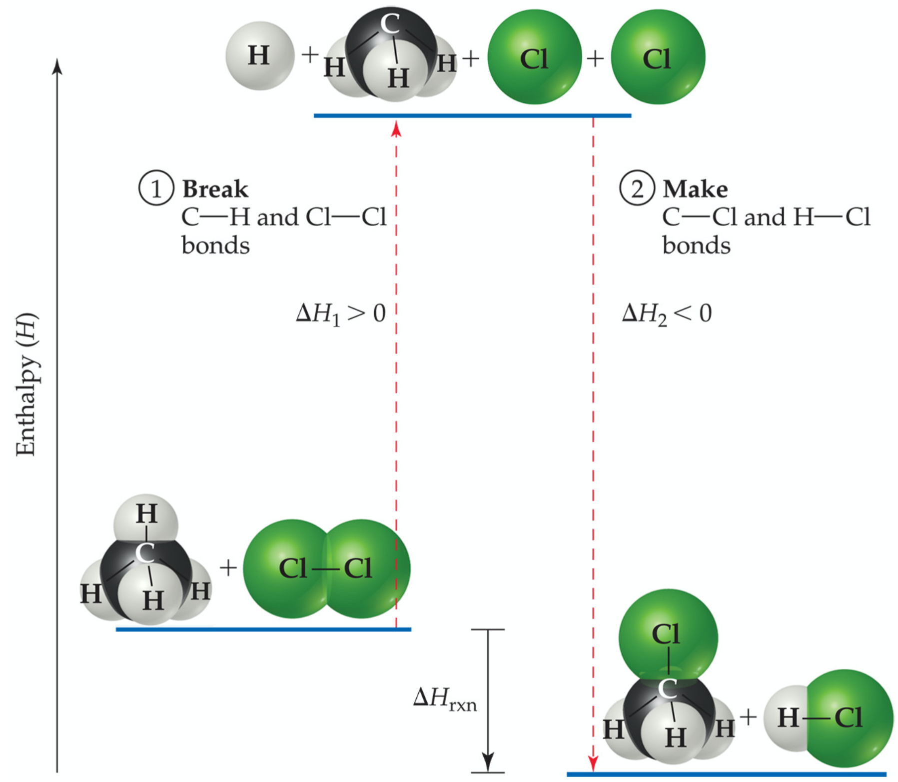
ΔH_{rxn} = Σ(bond enthalpies of bonds broken) – Σ(bond enthalpies of bonds formed)

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,

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

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

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

$$= -104\ \text{kJ}$$

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:

Sulfurous acid

The perchlorate ion

Quiz

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

HOFO

NCO^-