

CHEMISTRY  
XL-14A

CHEMICAL  
BONDS



July 16, 2011

Robert lafe

# Office Hours

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- July 18-July 22
  - Monday: 2:00pm in Room MS-B 3114
  - Tuesday-Thursday: 3:00pm in Room MS-B 3114

# Chapter 2 Overview

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- Ionic Bonds
- Covalent Bonds
- Exceptions to the Octet Rule
- Ionic vs Covalent Bonds
- Strength and Length of Covalent Bonds

# Ionic Bonds

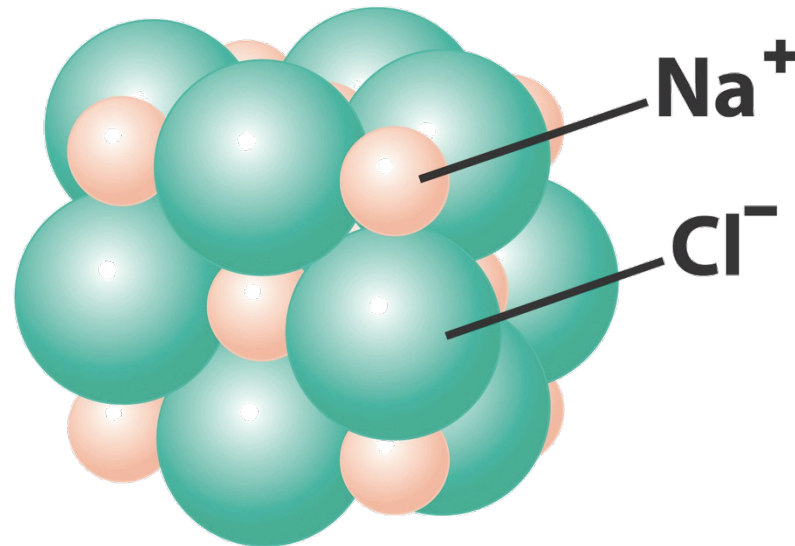
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- Ions that Different Elements Form
- Lewis Symbols
- Energetics of Ionic Bonding
- Interactions between Ions

# Ionic Bonds

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- Ions formed by transfer of electrons are held together by electrostatic interactions
- Ionic Bonds are formed between metals (especially Groups I, II) and nonmetals
- Ionic Solids are crystalline solids: ions stacked together in a regular pattern

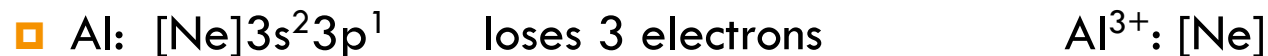


# Ion Formation

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Main Group elements aim for closest noble gas electron configuration

□ Groups I – III lose electrons, leaving core of previous noble gas



□ Groups V - VII gain electrons to complete the valence shell



# Transition Metals

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Periods 4 and below:

Main group metals lose s and p electrons, but not filled d subshell



□ Transition metals (d block elements)

□ 1st lose outermost s electrons, then variable # of d electrons



□ The ability of an element to form different ions is called

**variable valence**

Some Main group elements are variable valence: **Inert-Pair Effect** (Section 1.19)

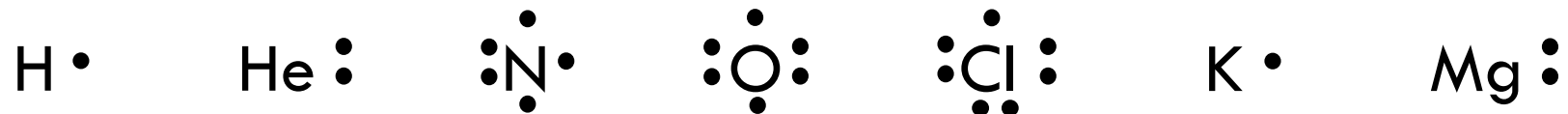
□ Lose either valence p electrons or both valence s and p electrons

# Lewis Symbols

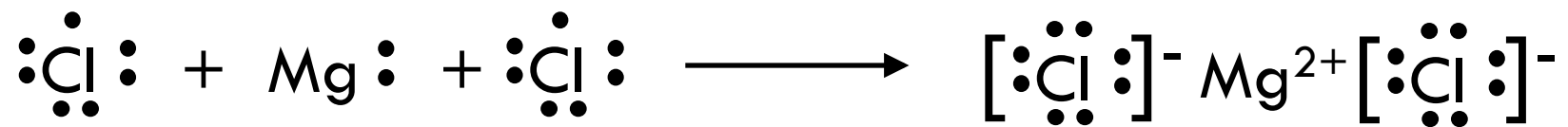
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Lewis symbols: show # of valence electrons of atoms and ions

- Number of dots = Number of valence electrons
- Single dots are unpaired electrons
- Paired dots are electrons paired in an orbital



- Can use Lewis Symbols to determine ionic formulas:



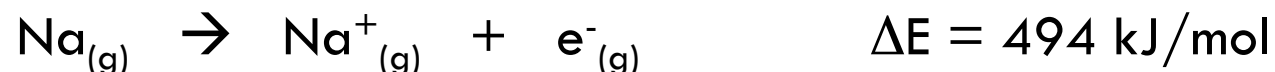
Mg and Cl form  $\text{MgCl}_2$



# Energetics of Ionic Bonding

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Ionization Energy: need energy to pull an electron off an atom



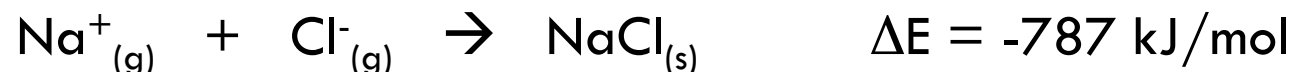
Electron Affinity: Certain elements really want more electrons:



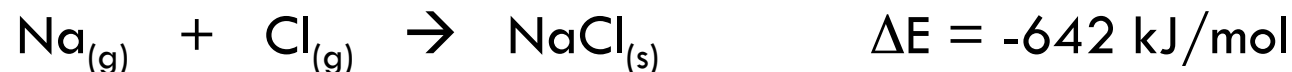
$$494 \text{ kJ/mol} - 349 \text{ kJ/mol} = +145 \text{ kJ/mol}$$

A gas of non-interacting  $\text{Na}^+$  and  $\text{Cl}^-$  ions is high in energy

The attraction of + and - ions results in a release of energy:

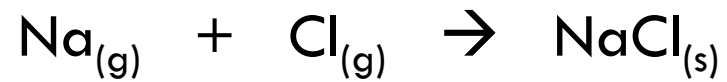
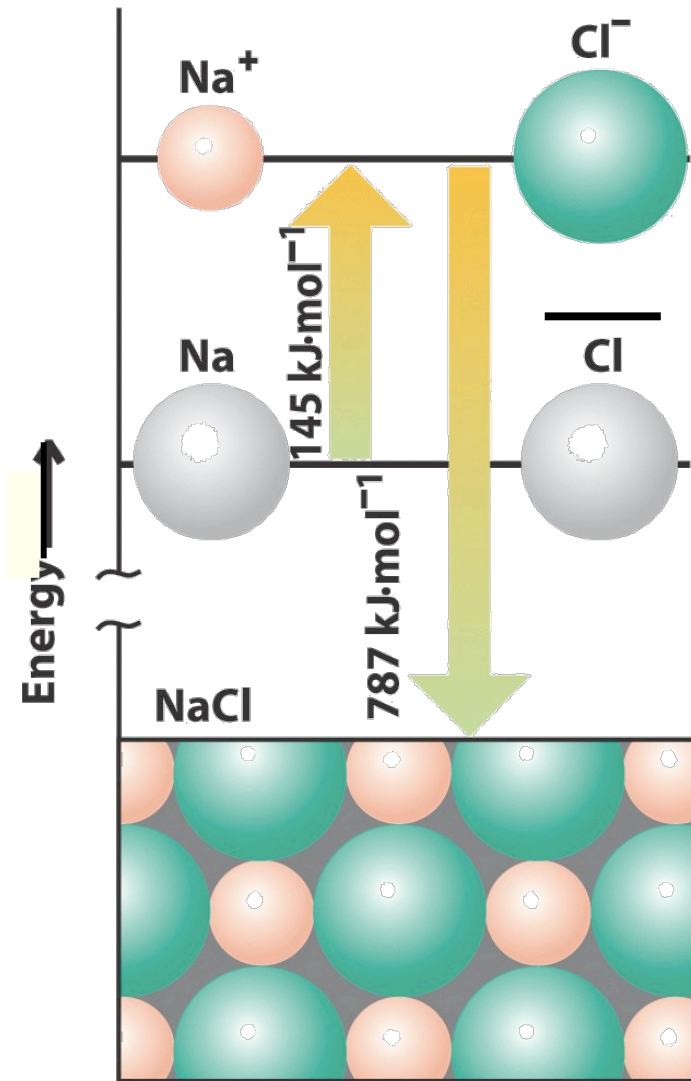


Add this all together to see overall process:

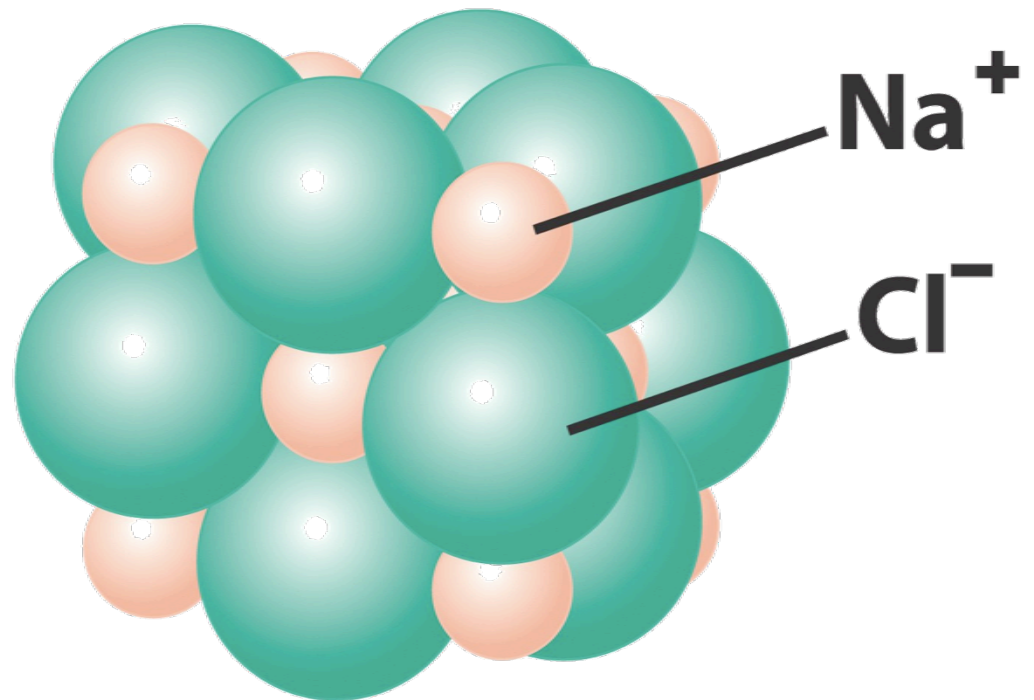


# Energetics of Ionic Bonding

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$$\Delta E = -642 \text{ kJ/mol}$$



# Interactions between Ions

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Typically consider an ionic solid with many cations and many anions

All ions are interacting with each other: repulsion and attraction

Lattice energy of a solid –  $\Delta E$  of ions in gas vs solid

High LE – strong interaction between ions, tightly bonded solid

Start with the CPE of 2 ions with charges  $z_1$  and  $z_2$ :

$$\text{CPE}_{12} = \frac{(z_1 e) \times (z_2 e)}{4\pi\epsilon_0 r_{12}} = \frac{z_1 z_2 e^2}{4\pi\epsilon_0 r_{12}}$$

Total PE of ionic solid is sum of CPE interactions between all ions

# Interactions between Ions

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Consider a line of alternating cations and anions:

CPE of an ion in center:

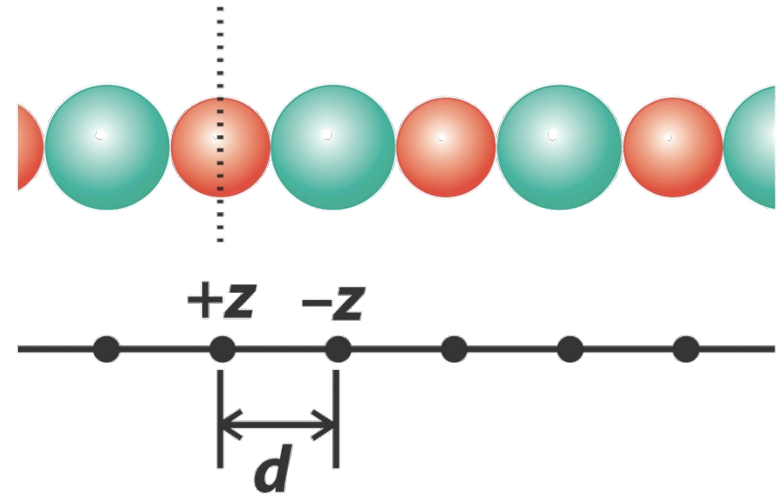
$$E = -A \times \frac{z^2 N_A e^2}{4\pi\epsilon_0 d}$$

$$A = 2 \ln 2$$

CPE is negative, net attraction between the ions

Now expand the model to 3D:

Coefficient  $A$  – Madelung constant – related to arrangement of ions



**TABLE 2.1** Madelung Constants

Structural type*	$A$
cesium chloride	1.763
fluorite	2.519
rock salt	1.748
rutile	2.408

# Interactions between Ions

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As ions are separated, the attraction decreases

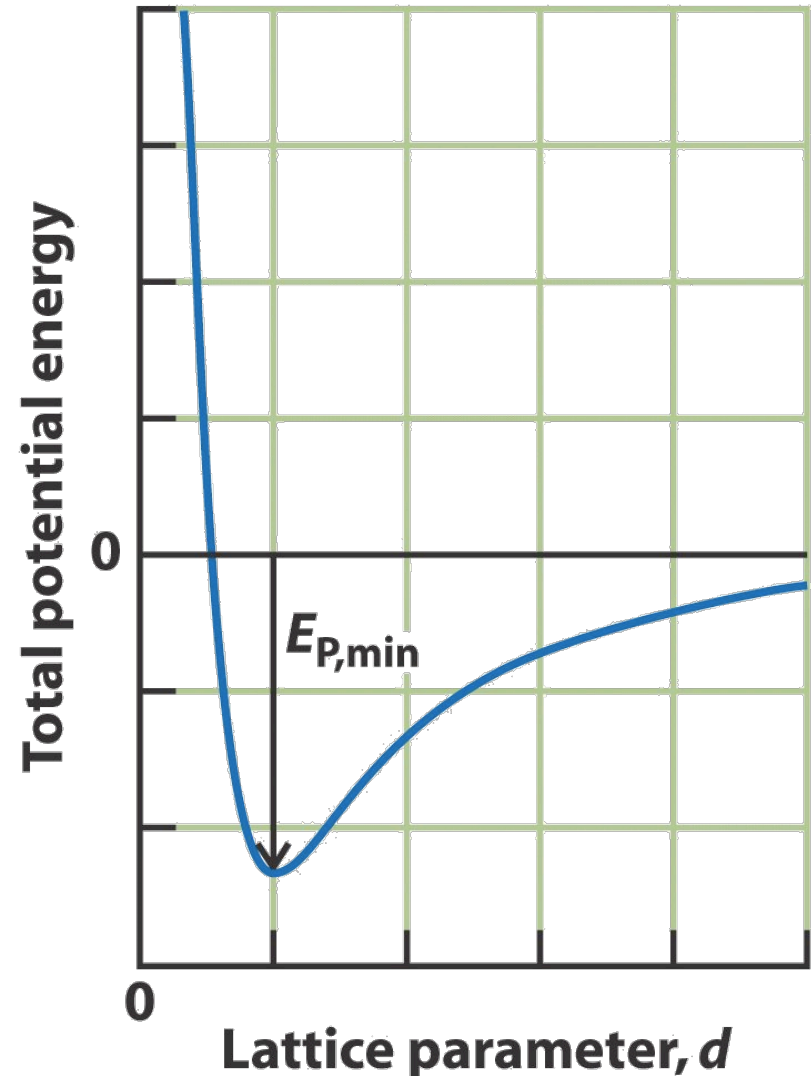
If ions are too close, past the point of contact, they repel each other

There is an ideal separation between ions:

Born-Meyer equation

$$PE_{\min} = -\frac{N_A |z_1 z_2| e^2}{4\pi\epsilon_0 d} \left(1 - \frac{d^*}{d}\right) A$$

$$d^* = 34.5 \times 10^{-12} \text{ m}$$



# Covalent Bonds

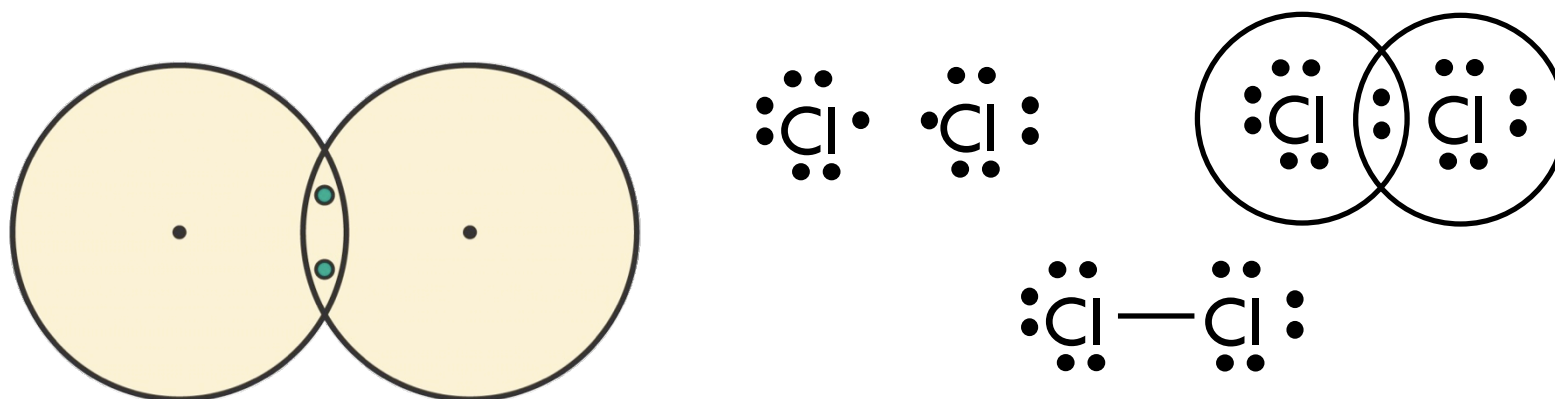
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- Lewis Structures of Diatomic Molecules
- Lewis Structures of Polyatomics
- Resonance
- Formal Charge

# Lewis Structures

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1916: **Covalent bond** – pair of electrons shared between 2 atoms...



Atoms try to get octets by sharing electron pairs

**Valence** of an element is the max # of bonds it can form

Lewis symbols – dots represent electrons and electron pairs

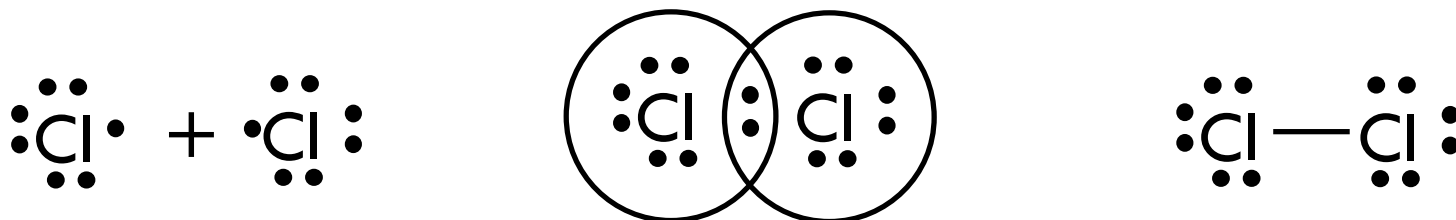
**Lewis Structures** – a line represents a pair of electrons shared in a covalent bond

# Lewis Structures of Diatomic Molecules

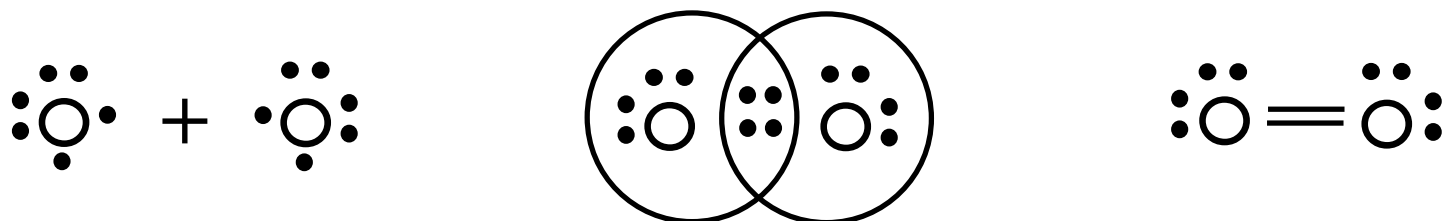
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Lines represent shared electron pairs in covalent bonds

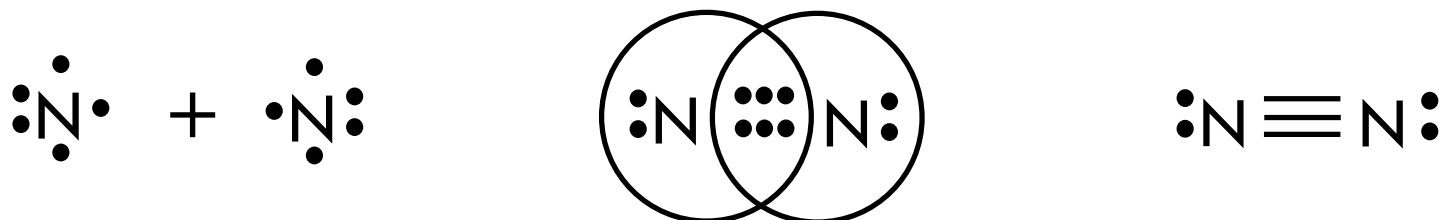
A single line represents a single bond (2 shared electrons)



A double line represents a double bond (4 shared electrons)



A triple line represents a triple bond (6 shared electrons)





# Lewis Structures of Polyatomic Species

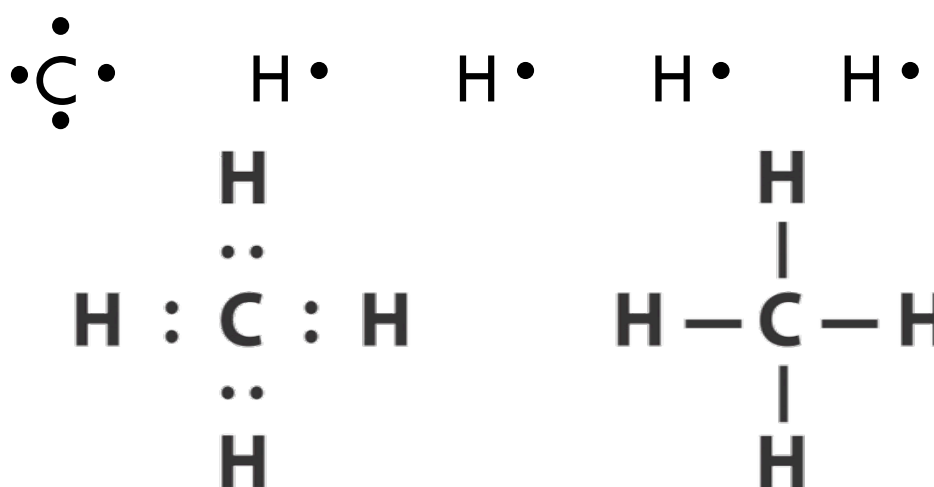
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What about compounds with more than 2 atoms?

Each atom in a polyatomic molecule completes its octet

(or duplet, in the case of Hydrogen)

Consider methane, CH<sub>4</sub>:



**Terminal atom** – bonded to only 1 other atom (H always terminal)

**Central atom** – bonded to more than one atom

# Lewis Structures 'How to'

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1. Count total number of valence electrons. Divide by 2 to get total number of bonds and lone pairs

Electron pairs not involved in bonding – **lone pairs**

2. Arrange the atoms symmetrically around the central atom

Typically listed first in chemical formula

3. Place 1 electron pair between each pair of bonded atoms

4. Complete the octet of each atom using remaining electron pairs

If there are not enough pairs to complete all octets, try double and triple bonds

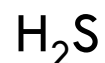
5. Represent each bonded electron pair by a line

\*\*\*If determining Lewis structure of a polyatomic ion, subtract 1 electron per + charge, and add 1 electron per - charge

# Lewis Structures 'How to'

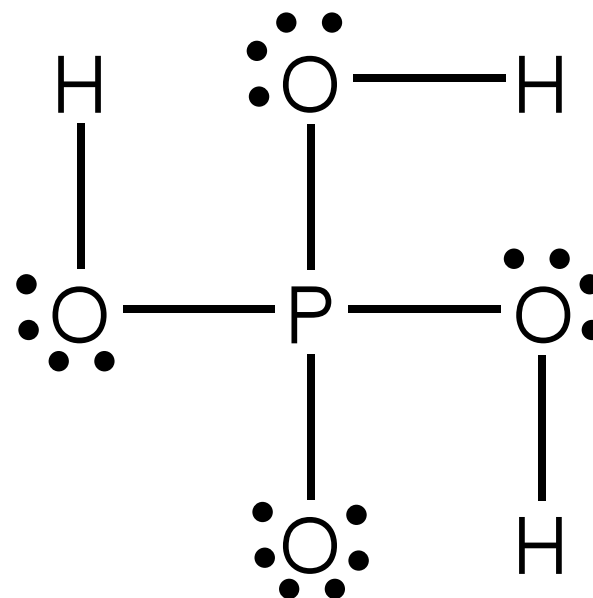
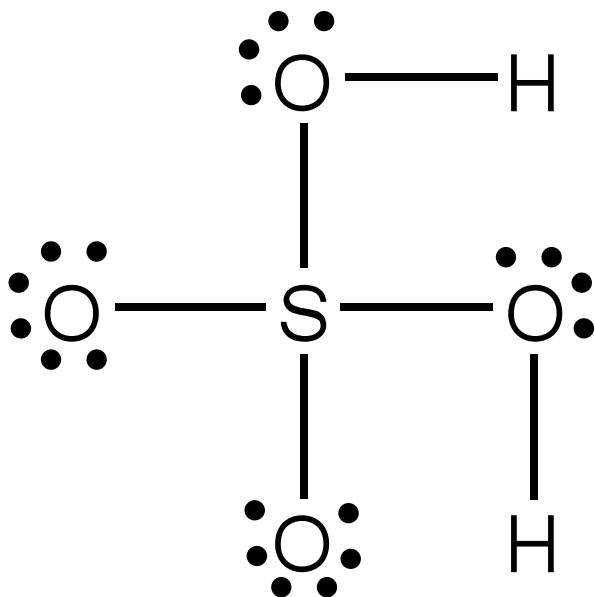
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An exception to rule 1 includes acids where H is typically listed first



H is never a central atom

In oxoacids ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ), H atoms are bonded to O atoms which are in turn bonded to the central atom

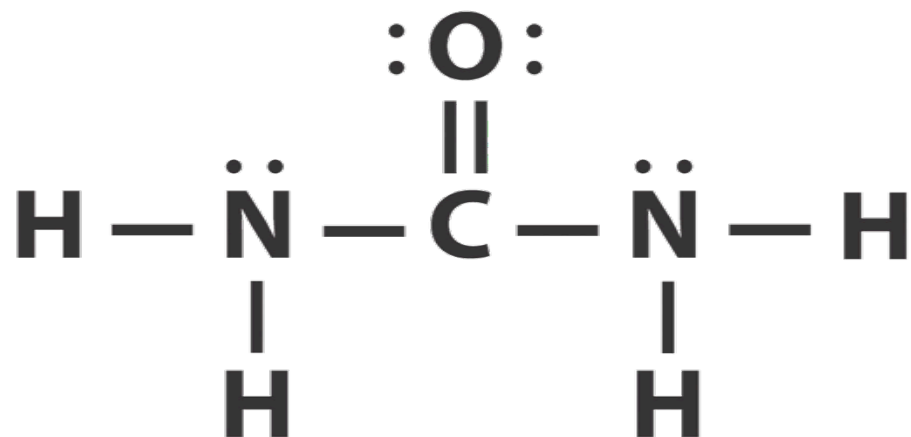


# Lewis Structures 'How to'

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Hints to molecular structure are given in the molecular formula

You will begin to notice patterns which represent certain combinations of atoms



**Urea, (NH<sub>2</sub>)<sub>2</sub>CO**

# Lewis Structures Practice

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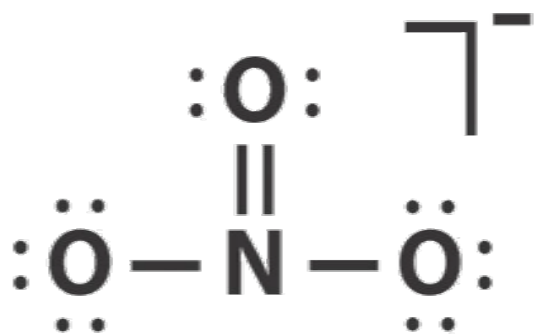
What are the Lewis Structures of:



# Resonance

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Sometimes, a molecule can have several correct Lewis Structures



There are several choices here of where to put the double bonds.

Is there any 'big picture' difference between these?

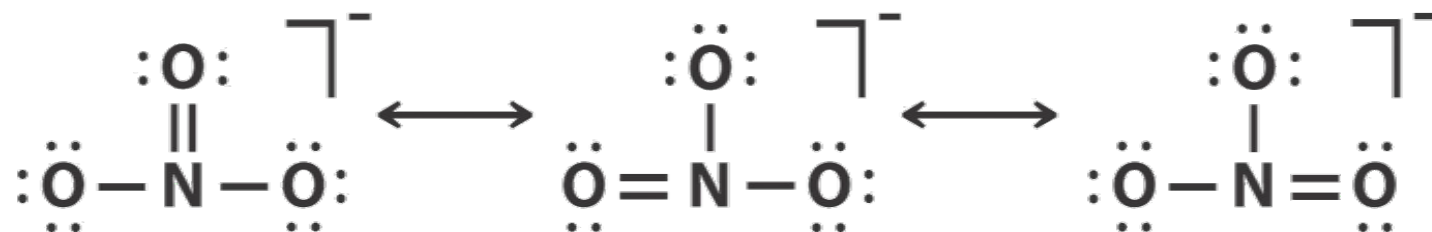
Blending of identical structures is called **resonance**

A blended structure is called a **resonance hybrid**

# Resonance

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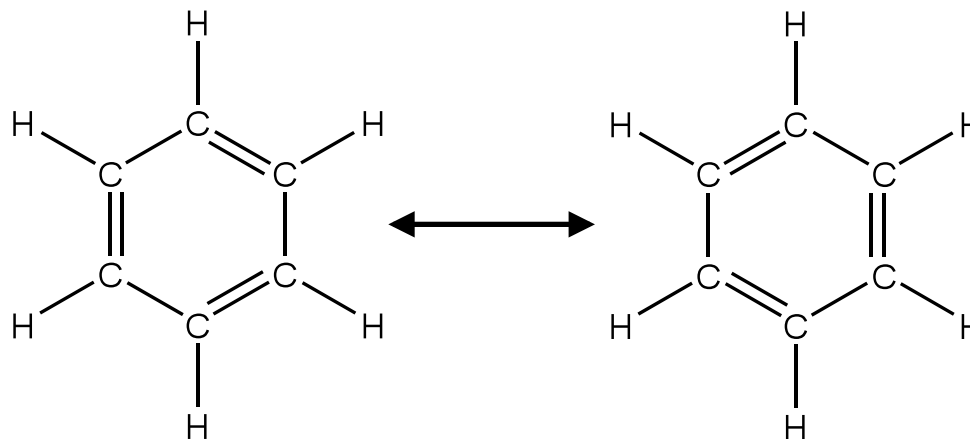
Arrows in between structures indicate resonance



Electrons which can be in different places in a resonance structure are **delocalized**

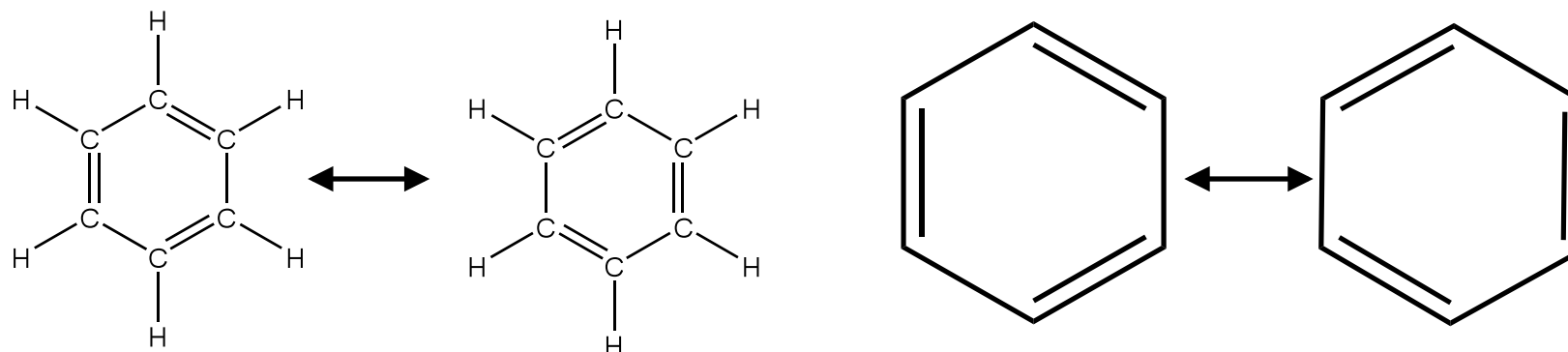
A shared electron pair which is distributed over several pairs of atoms and is not identified with just 1 pair

Benzene,  $\text{C}_6\text{H}_6$



# Benzene, cont.

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**Kekulé structure** – a line structure where each vertex is a C atom, and the H atoms are assumed by the # of bonds on each C

Benzene:

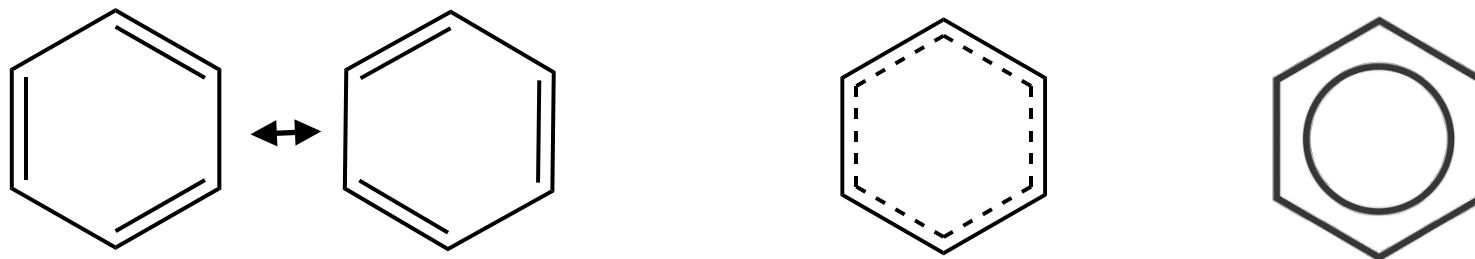
1. Does not undergo reaction typical of chemical bonds
2. All carbon-carbon bonds are the same length (double bonds are shorter than single bonds)
3. Structural evidence of substituted benzenes

All evidence suggests 1 structure of benzene...



# Benzene and Resonance

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Benzene:

Electrons are delocalized over the whole molecule

Each C-C bond is an intermediate between a single and double bond

Resonance stabilizes a molecule by lowering its total energy

Resonance only occurs between structures with the same arrangement of atoms

In general, a molecule is a blend of all reasonable Lewis structures, including those with different energies

The Lowest energy structures contribute the most to the overall structure

# Formal Charge

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2 Questions:

1. If there are several possible Lewis structures, how do we know which is the best?
2. How do we know which resonance hybrid contributes most to the overall structure?

Can compare the distribution of electrons in the structure to the valence of each atom.

The closer they are, the better

**Formal Charge** – the charge on an atom in a Lewis structure if the bonding was perfectly covalent

$$\text{Formal Charge} = V - (L + \frac{1}{2} B)$$

V = Valence e<sup>-</sup>s

L = Lone Pair e<sup>-</sup>s

B = Bonded e<sup>-</sup>s

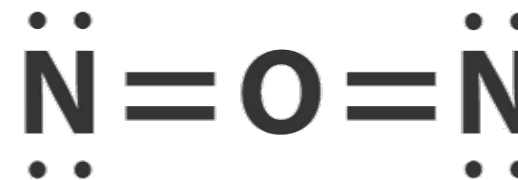
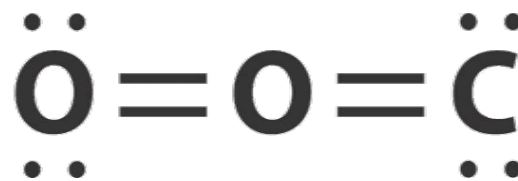
# Formal Charge

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Formal Charge – the charge on an atom in a Lewis structure if the bonding was perfectly covalent

$$\text{Formal Charge} = V - (L + \frac{1}{2} B)$$

Lowest energy structure will have Formal Charges closest to 0



# Exceptions to the Octet Rule

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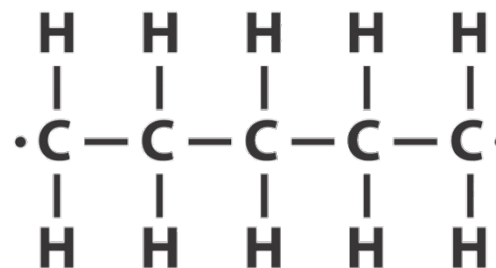
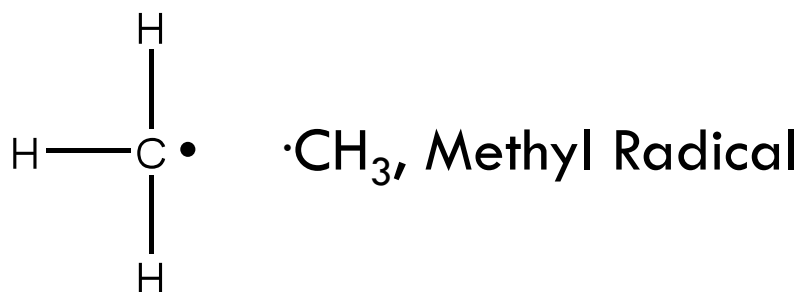
- Radicals and Biradicals
- Expanded Valence Shells
- Unusual Structures of Group III Compounds

# Radicals and Biradicals

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Some compounds have an odd # of valence electrons

When an atom in a compound has an unpaired electron, the compound is called a **radical**



- ▣ Biradical – a molecule with 2 unpaired electrons
- ▣ Radicals are extremely reactive
- ▣ Play an important role in ozone (O<sub>3</sub>) reactions
- ▣ Radicals often play a destructive role in everyday life
- ▣ Anti-oxidants slow down damage

# Expanded Valence Shells

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**Expanded valence shell** – When a central atom in a molecule has empty d-orbitals, it can accommodate more than 8 electrons

Additional electrons must be placed in valence orbitals, so only non-metals in Periods 3 and below can expand their valence shells

The size of the atom also plays a role. Larger atoms can fit more atoms around them



Expandable elements often show variable covalence – they can form different numbers of covalent bonds

# Expanded Valence Shells

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What is the Lewis structure of  $\text{AsF}_6^-$ ?

What about  $\text{XeF}_2$ ?

# Group III Compounds

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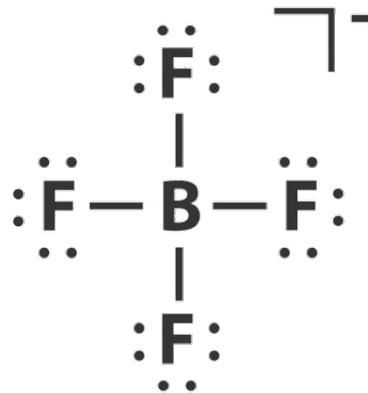
Compounds of Aluminum and Boron may have unusual Lewis structures:



**Incomplete octet** – can have a valence shell of only 6 electrons

Some evidence suggests  $\text{BF}_3$  exists as a resonance hybrid, with single bonded structure as major contributor

Can form coordinate covalent bonds – both electrons in bond come from same atom:

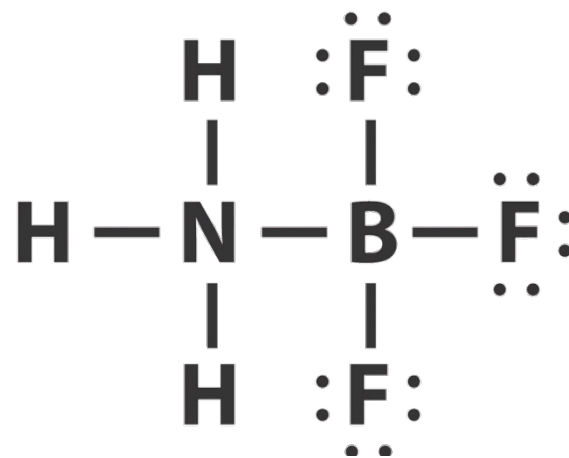
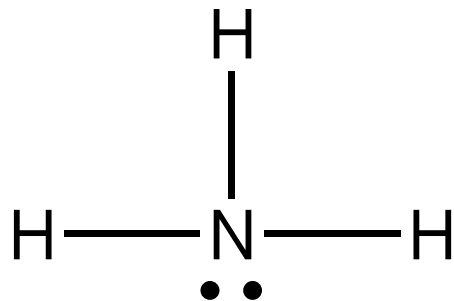
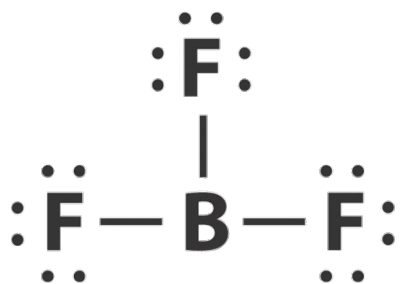
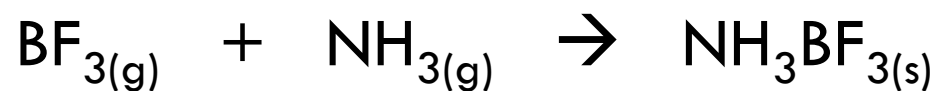




# Group III Compounds

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Coordinate covalent bonds – both electrons in bond come from same atom:

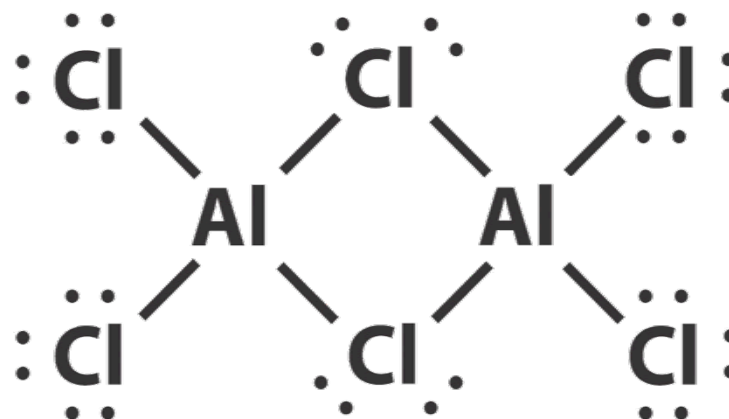
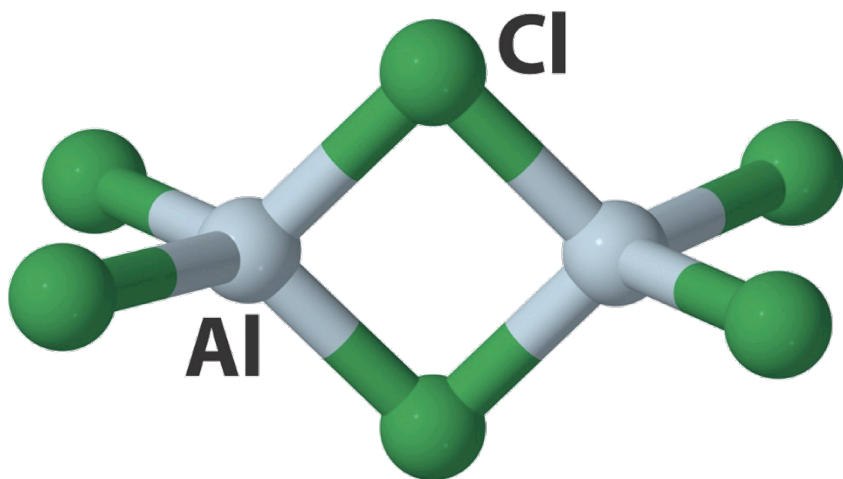


# Group III Dimer Compounds

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**Dimer** – linked pair of molecules

At 180 °C,  $\text{AlCl}_{3(s)}$  sublimates to form a gas of the  $\text{Al}_2\text{Cl}_6$  dimer



At 200 °C, the dimer splits into  $\text{AlCl}_3$  molecules

# Ionic vs Covalent Bonds

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- Electronegativity
- Polarizability

# Correcting the Covalent Model

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All bonds are resonance hybrids of ionic and covalent structures:

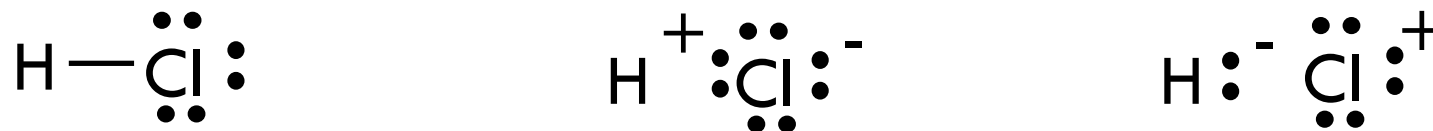


Cl<sub>2</sub>: the ionic structure contributes very little to overall structure

We think of the bond as purely covalent

Both ionic Cl<sub>2</sub> structures have the same energy and the average charge on Cl is 0

What about bonds between different elements? HCl, for example



The resonance structures have unequal energy. Cl has a greater attraction for electrons!

# Correcting the Covalent Model

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In HCl: small net (–) charge on Cl and small net (+) charge on H



The charges on H and Cl are partial charges ( $\delta^+$  and  $\delta^-$ )

A covalent bond with some ionic character (partial charges) is a **polar covalent bond**

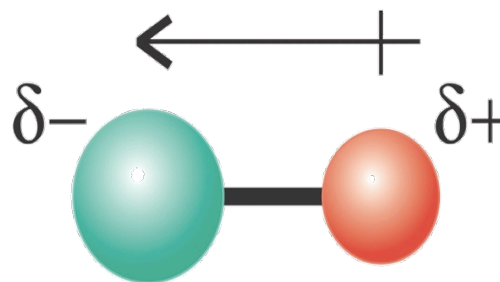
Any bond between atoms of different elements is somewhat polar

**Electric dipole** – a (+) charge next to an equal, but opposite (-) charge

Magnitude of dipole is the

**dipole moment,  $\mu$**

Unit is debye (D)



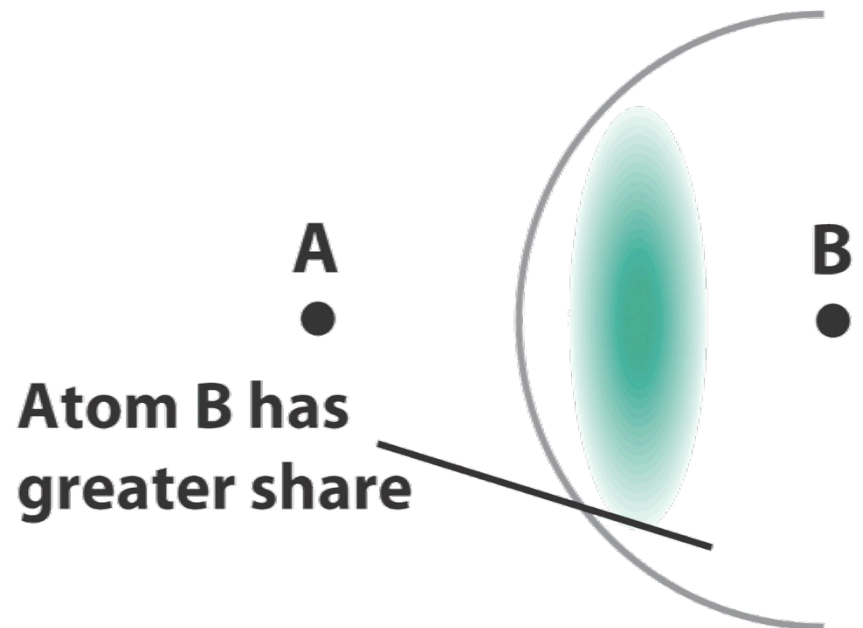
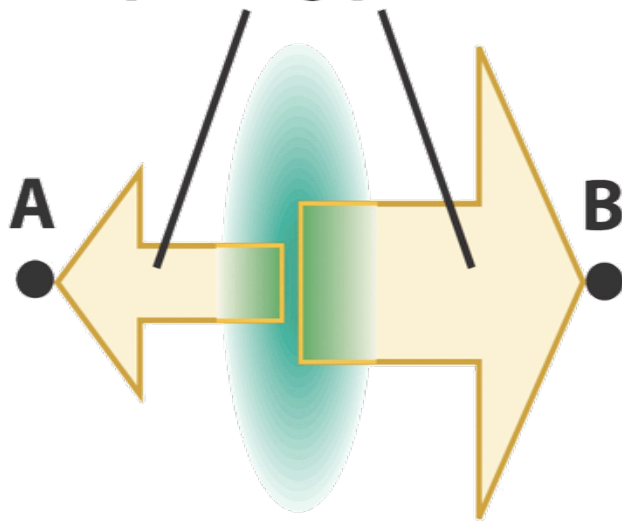
# Electronegativity

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Polar covalent bond: one atom has a greater attraction for electrons

Electron pair more likely to be found closer to the  $\delta^-$  atom

**Relative pulling power of atom**



# Electronegativity

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1932: Linus Pauling – quantitative measure of electron distribution in covalent bonds...

Electronegativity ( $c$ ) – electron-pulling power of an atom in a bond

Scale is based on dissociation energies of the A–A, B–B, and A–B bonds... there is a complicated equation for it.

Mulliken: a simpler way to determine  $c$ :

$$c = \frac{1}{2}(I + E_a)$$

An atom with a high  $I$  and a high  $E_a$  has a high  $c$

- doesn't want to give up electrons
- likes to get extra electrons

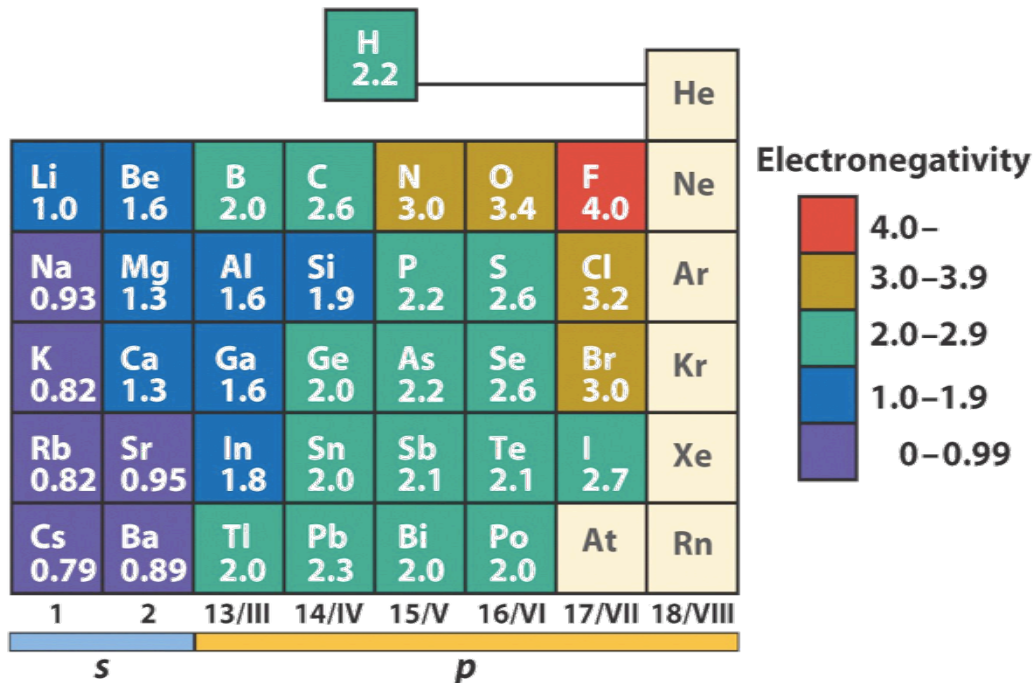
# Electronegativity

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Electronegativity values tend to be highest at the upper right

Ionic Bonding	Polar Covalent Bonding	Covalent Bonding
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Determine what 'type' of bond using difference in  $c$  of the 2 atoms

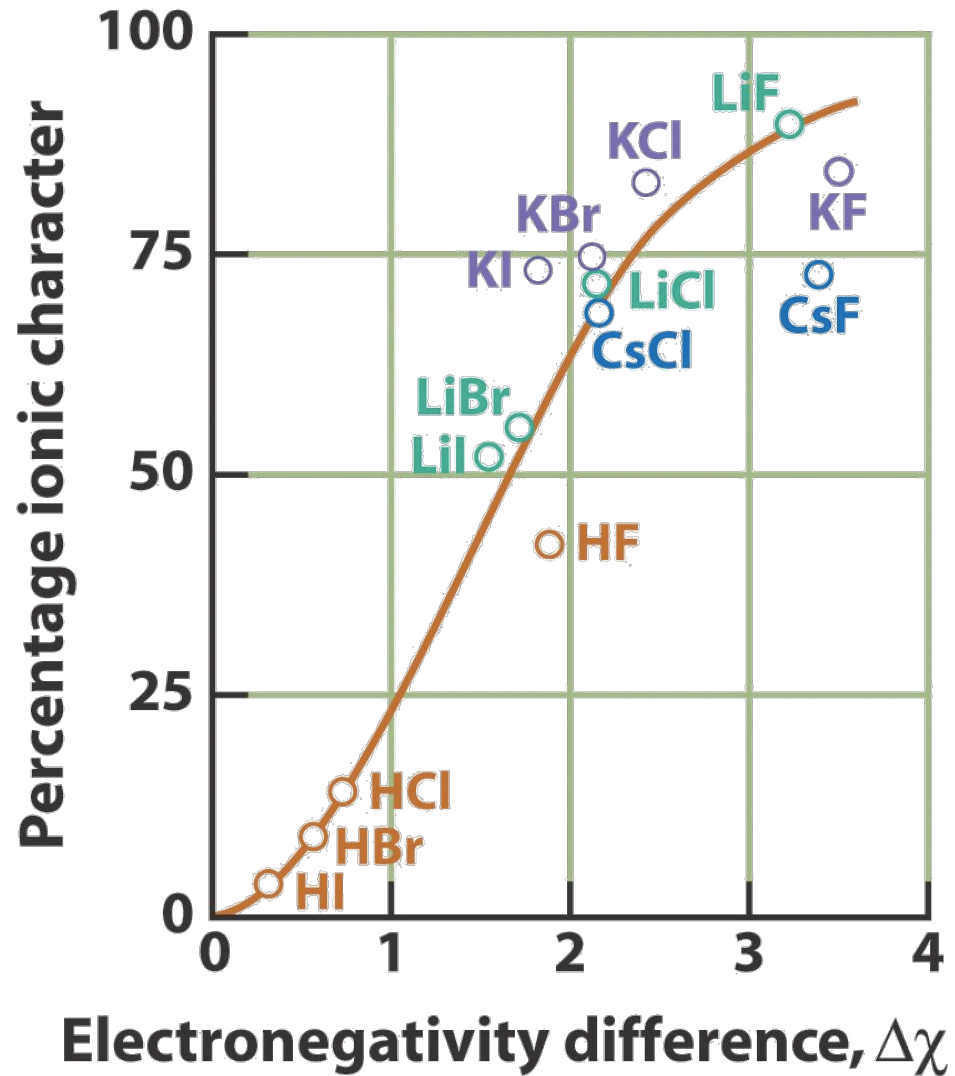


Rule of Thumb	
$\Delta c > 2$	Ionic
$2 > \Delta c > 0.5$	Polar
$\Delta c < 0.5$	Covalent



# Ionic Character

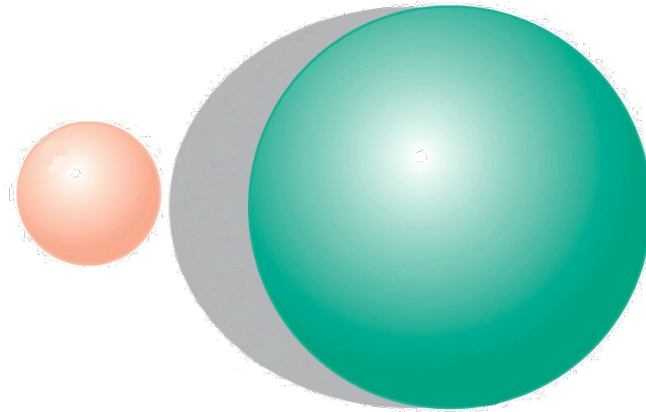
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# Polarizability

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All Ionic Bonds have some polar character. Consider NaCl:



(+) charge of  $\text{Na}^+$  pulls on electrons of  $\text{Cl}^-$ , distorts its electron cloud

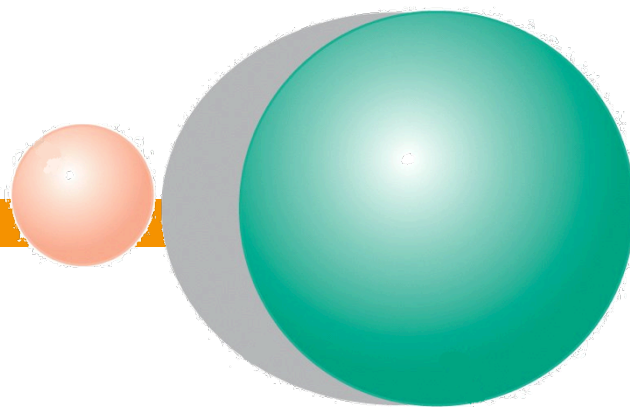
Electron pair pulled between the 2 atoms  $\rightarrow$  covalent character

Atoms and ions that undergo a large distortion are **polarizable**

Atoms and ions that cause large distortions have high **polarizing power**

# Polarizability

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Larger anions are more **polarizable**:

Outermost electrons are farther away from the nucleus

They are less tightly bound to the nucleus

Cations have more **polarizing power** if small and highly charged

Small radius means center of (+) charge can get very close to anion

Compounds with small, highly charged cations, and large, polarizable anions have more covalent character

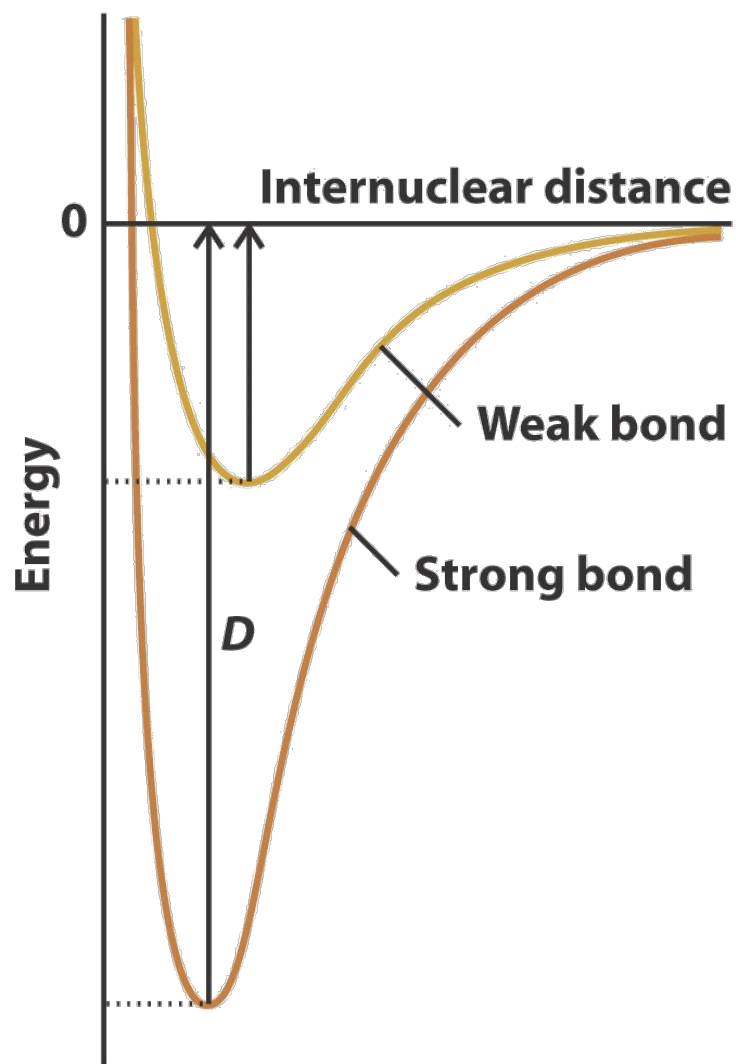
# Bond Length and Strength

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- Bond Strengths
- Variation in Bond Strength
- Bond Lengths

# Bond Strengths

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Strength of a bond is measured by its

**Dissociation energy (D)** – the energy required to separate bonded atoms

**Homolytic** bond breakage – each atom retains one of the electrons



High  $D$  indicates a strong bond

# Bond Strengths

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**TABLE 2.3** Average Bond Dissociation Energies ( $\text{kJ}\cdot\text{mol}^{-1}$ )

Bond	Average bond dissociation energy	Bond	Average bond dissociation energy
C—H	412	C—I	238
C—C	348	N—H	388
C=C	612	N—N	163
C <sup>*</sup> —C <sup>*</sup>	518	N=N	409
C≡C	837	N—O	210
C—O	360	N=O	630
C=O	743	N—F	195
C—N	305	N—Cl	381
C—F	484	O—H	463
C—Cl	338	O—O	157
C—Br	276		

\*In benzene.

- Table lists the average strength of a bond – measured from different molecules
- Values are typical, but not necessarily accurate

# Bond Strengths

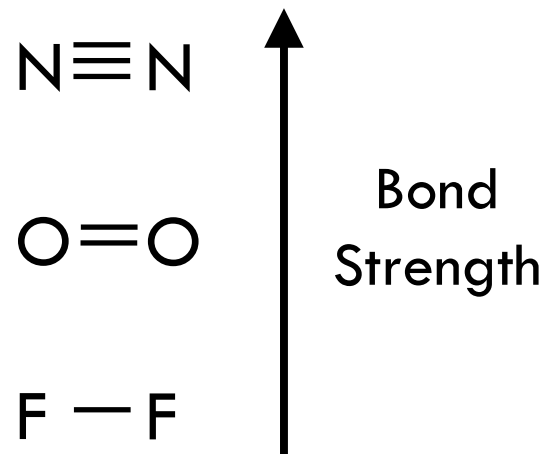
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**TABLE 2.2** Bond Dissociation Energies of Diatomic Molecules ( $\text{kJ}\cdot\text{mol}^{-1}$ )

Molecule	Bond dissociation energy
$\text{H}_2$	424
$\text{N}_2$	932
$\text{O}_2$	484
$\text{CO}$	1062
$\text{F}_2$	146
$\text{Cl}_2$	230
$\text{Br}_2$	181
$\text{I}_2$	139
$\text{HF}$	543
$\text{HCl}$	419
$\text{HBr}$	354
$\text{HI}$	287

## □ Diatomic Molecules

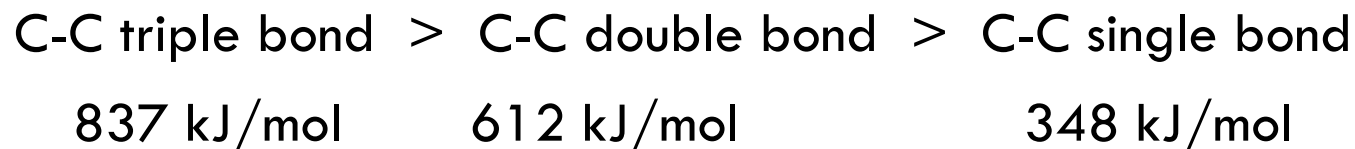
- Trends can be explained from Lewis structures
- Higher bond orders are stronger
- A Triple bond tends to be stronger than a single bond



# Bond Order vs Bond Strength

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Bonds between the same 2 atoms – bond strength increases with bond order

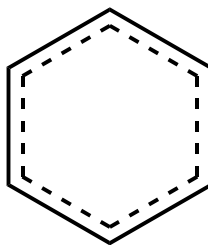


Notice, a double bond is not twice as strong as a single bond

Increased # electrons in a multiple bond has some e-e repulsion

As we will learn in Ch.3 double and triple bonds not the same as single bonds – known as  $\pi$  bonds....

Remember Benzene?



518 kJ/mol



# Lone Pairs, Size and Bond Strength

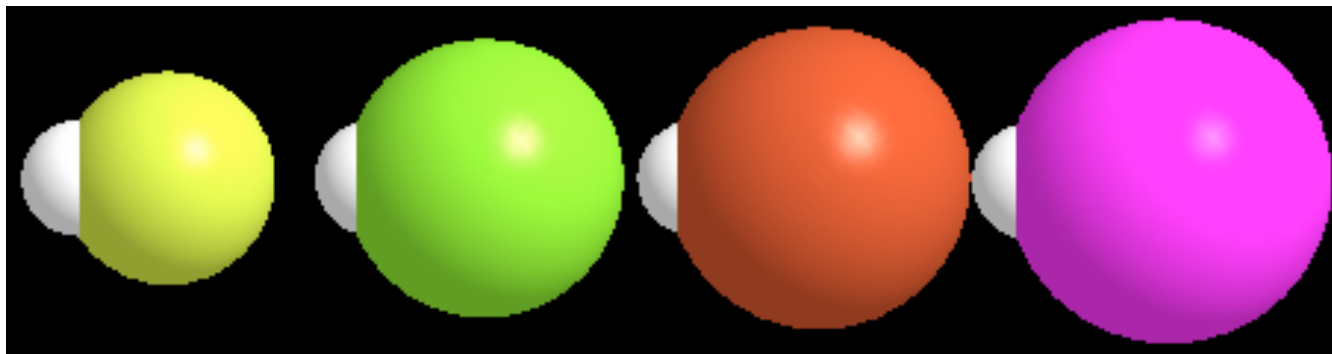
49

Lone pairs and Size of atoms also influence bond strengths

Lone pairs on neighboring atoms repel each other,  
decreasing bond strength



The larger the atoms are, the weaker the bonds. Nuclei can't get that close together....



	16/VI	17/VII	18/VIII
		HF 543	
		HCl 419	
		HBr 354	
		HI 287	

# Bond Length

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**Bond length:** distance between centers of two covalently bonded atoms

Determined experimentally through spectroscopy and x-ray diffraction

Consider the same factors as for Bond strength:

- ▣ Higher bond order = Shorter bond
- ▣ Larger atoms involved = Longer bond

