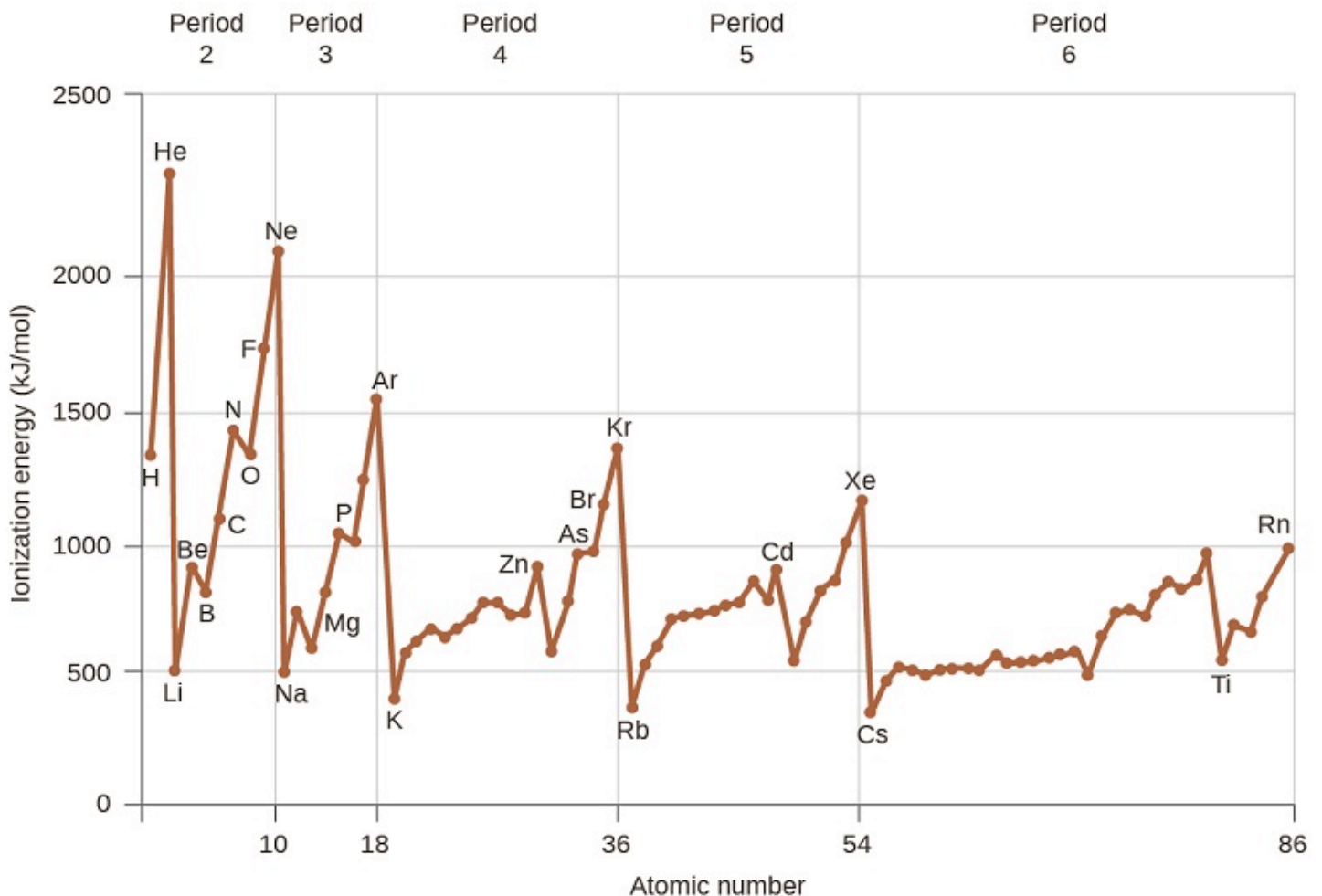


# First ionization Energy plot

## (Energy versus atomic number)

The **first ionization energy** is the **energy** required to remove one mole of the most loosely held electrons from one mole of gaseous atoms to produce 1 mole of gaseous ions each with a charge of 1+. This is more easily seen in symbol terms. It is the **energy** needed to carry out this change per mole of X



The first ionization energy of the elements in the first five periods are plotted against their atomic number

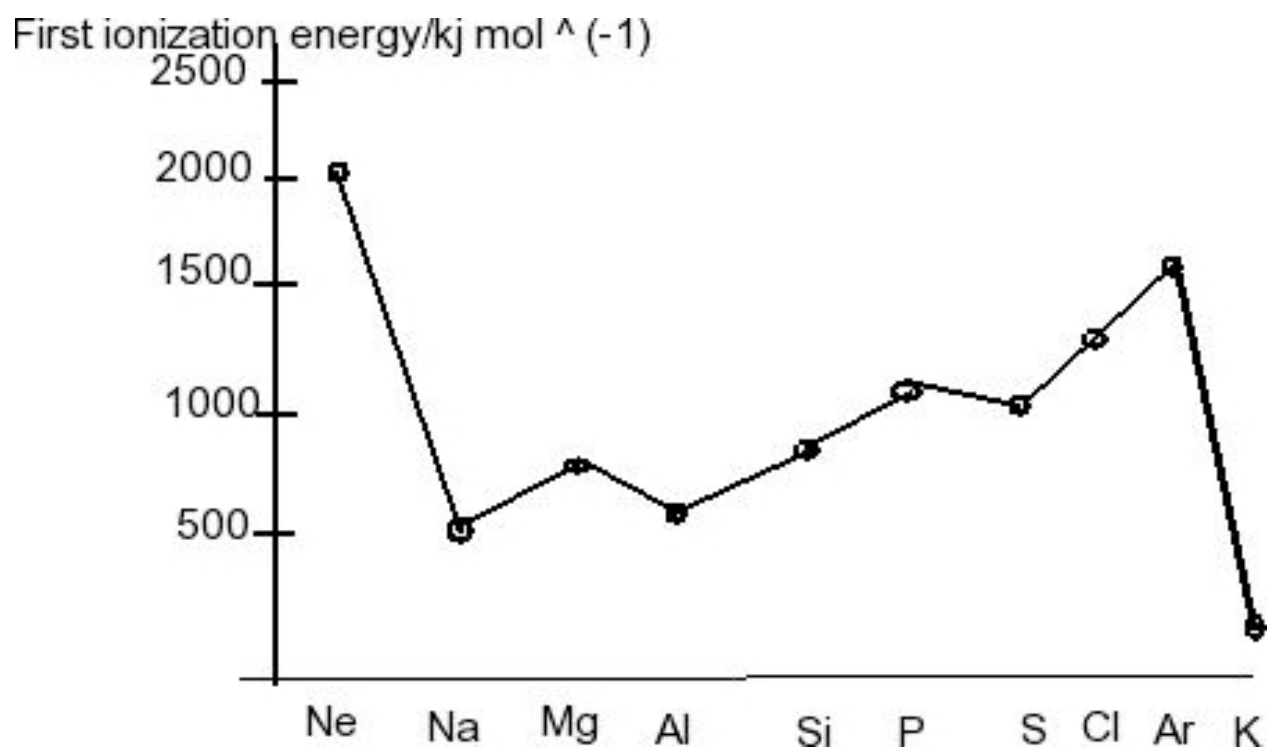
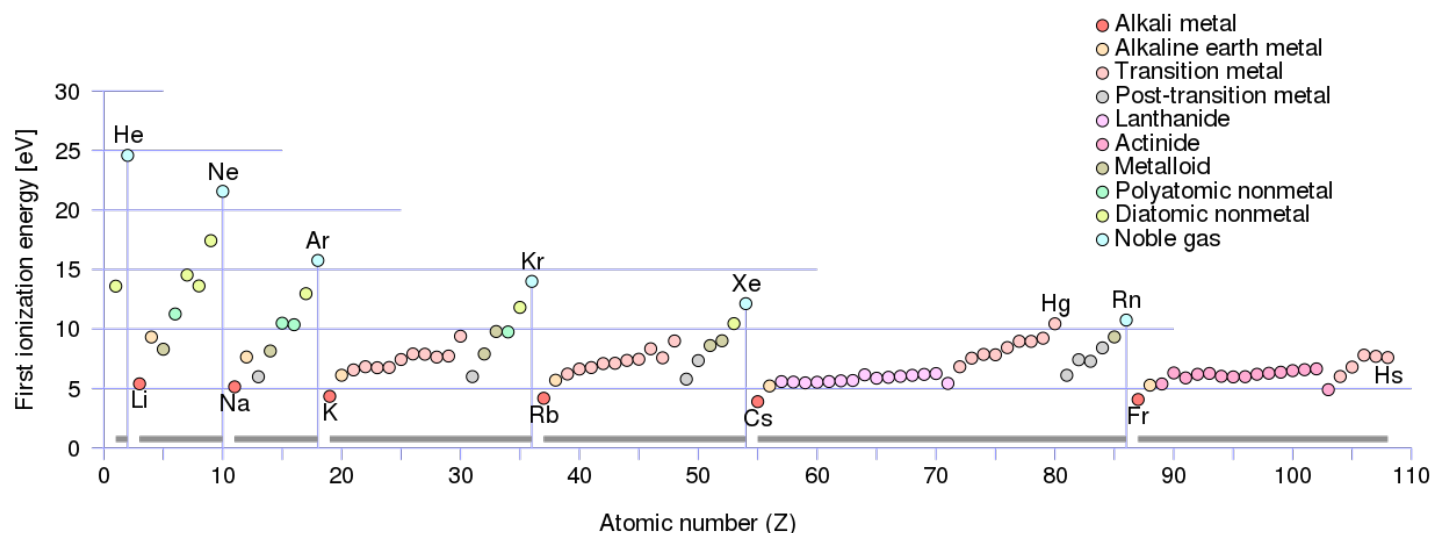


TABLE 3.1

Successive Ionization Energies of the Elements Hydrogen through Argon (in eV Atom<sup>-1</sup>)

Z	Element	IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	IE <sub>5</sub>	IE <sub>6</sub>	IE <sub>7</sub>	IE <sub>8</sub>	IE <sub>9</sub>	IE <sub>10</sub>
1	H	13.60									
2	He	24.59	54.42								
3	Li	5.39	75.64	122.45							
4	Be	9.32	18.21	153.89	217.71						
5	B	8.30	25.15	37.93	259.37	340.22					
6	C	11.26	24.38	47.89	64.49	392.08	489.99				
7	N	14.53	29.60	47.45	77.47	97.89	552.06	667.03			
8	O	13.62	35.12	54.93	77.41	113.90	138.12	739.32	871.39		
9	F	17.42	34.97	62.71	87.14	114.24	157.16	185.18	953.89	1103.08	
10	Ne	21.56	40.96	63.45	97.11	126.21	157.93	207.27	239.09	1195.79	1362.16
11	Na	5.14	47.29	71.64	98.91	138.39	172.15	208.47	264.18	299.87	1465.10
12	Mg	7.65	15.04	80.14	109.24	141.26	186.50	224.94	265.90	327.94	367.53
13	Al	5.99	18.83	28.45	119.99	153.71	190.47	241.43	284.59	330.21	398.57
14	Si	8.15	16.35	33.49	45.14	166.77	205.05	246.52	303.17	351.10	401.43
15	P	10.49	19.73	30.18	51.37	65.02	220.43	263.22	309.41	371.73	424.50
16	S	10.36	23.33	34.83	47.30	72.68	88.05	280.93	328.23	379.10	447.10
17	Cl	12.97	23.81	39.61	53.46	67.8	97.03	114.19	348.28	400.03	455.62
18	Ar	15.76	27.63	40.74	59.81	75.02	91.01	124.32	143.46	422.43	478.68
19	K	4.34	31.63	45.72	60.91	82.66	100.0	117.56	154.86	175.82	503.44
20	Ca	6.11	11.87	50.91	67.10	84.41	108.78	127.7	147.24	188.54	211.27
21	Sc	6.54	12.80	24.76	73.47	91.66	111.1	138.0	158.7	180.02	225.32

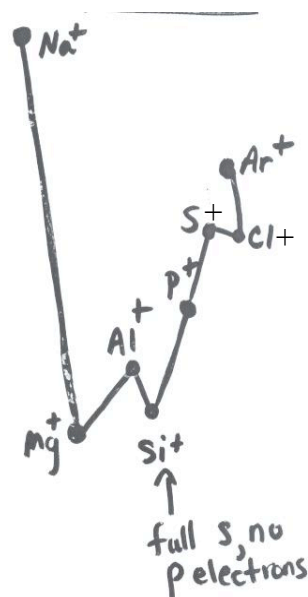
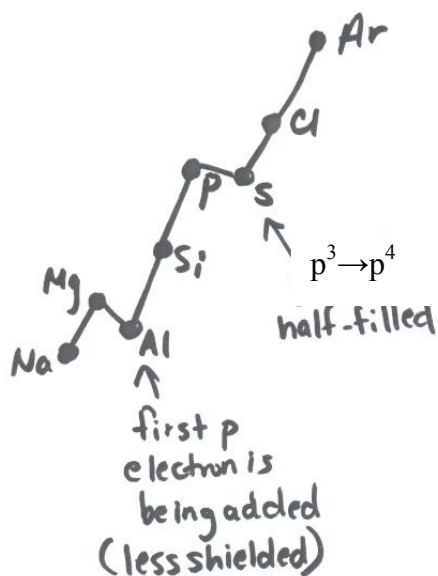
Note that 1 eV/atom = 96.521 kJ/mol



# Ionization Energies

1<sup>st</sup> I.E.

2<sup>nd</sup> I.E.



The **second ionization energy** is almost ten times that of the first because the number of electrons causing repulsions is reduced. It doesn't take **much energy** to remove one electron from a **sodium** atom to form an **Na<sup>+</sup>** ion with a filled-shell electron configuration. ... The **second ionization energy** is **larger than the first** because it always takes more **energy** to remove an electron from a positively charged ion **than** from a neutral atom.

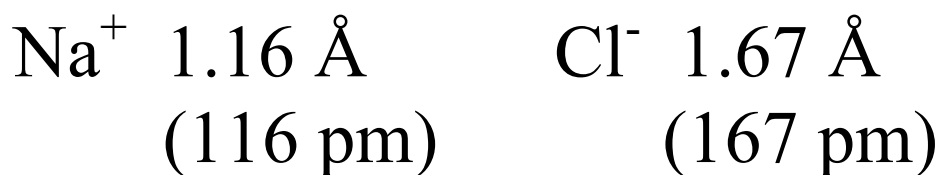


Overall trend of increasing I.E. from left to right is evident, but major exceptions in the second I.E.

## Atomic Radii

1. Single – bond covalent radius ( $r_{\text{cov}}$ )  
of an element. Used in bond length determination.
2. van der waals radius ( $r_{\text{vdw}}$ )  
non-bonded distance of two atoms that are touching one another.
3. ionic radius ( $r_{\text{ion}}$ )  
Radius used in ionic compounds  
these have been tabulated and are additive.

Page 61, Table 2-15



Therefore NaCl internuclear separation is 2.83 Å

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1																	He 2
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La 57	Hf 58	Ta 59	W 60	Re 61	Os 62	Ir 63	Pt 64	Au 65	Hg 66	Tl 67	Pb 68	Bi 69	Po 70	At 71	Rn 72

● Metals  
● Semimetals  
● Nonmetals

	DECREASING ATOMIC RADIUS →							
	I	II	III	IV	V	VI	VII	VIII
	H							He
	Li	Be	B	C	N	O	F	Ne
	Na	Mg	Al	Si	P	S	Cl	Ar
	K	Ca	Ga	Ge	As	Se	Br	Kr
	Rb	Sr	In	Sn	Sb	Te	I	Xe
	Cs	Ba	Tl	Pb	Bi	Po	At	Rn

↑ INCREASING ATOMIC RADIUS













































## Atomic Radii & van der Waals radii

1. Alkali metals are largest
2. Halogens (noble gases) are smallest  
Why?

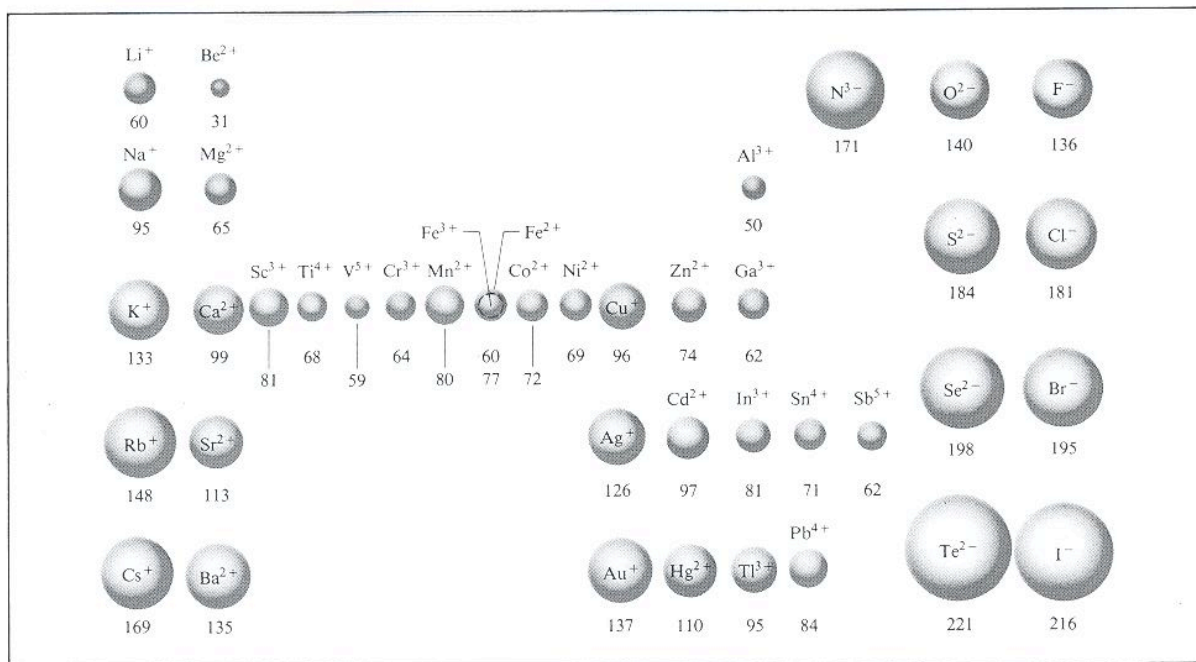
(page 62. Effective nuclear charge increases but electrons in the orbitals are added to the same level,  $n$ , and are progressively less shielded from the increasing positive charge of the nucleus from each added proton)

## Ionic Radii

1. Alkali metals become positively charged (lose  $e^-$ 's) so they are smallest.
2. Halogens become negatively charged (gain  $e^-$ 's) so they are largest.

← Increasing atomic radius							
1A	2A	3A	4A	5A	6A	7A	8A
H  32							He  50
Li  152	Be  112	B  98	C  91	N  92	O  73	F  72	Ne  70
Na  186	Mg  160	Al  143	Si  132	P  128	S  127	Cl  99	Ar  98
K  227	Ca  197	Ga  135	Ge  137	As  139	Se  140	Br  114	Kr  112
Rb  248	Sr  215	In  166	Sn  162	Sb  159	Te  160	I  133	Xe  131
Cs  265	Ba  222	Tl  171	Pb  175	Bi  170	Po  164	At  142	Rn  140

Increasing atomic radius



## Electron Affinities (Electron Attachment Enthalpies)

$$\Delta H_{ea}$$

Tendency of an atom to form an anion

$$-\Delta H_{ea}$$

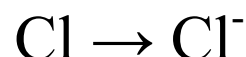
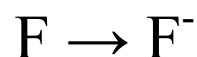
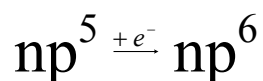
Means exothermic so the more negative the number, the more favorable

1. Alkali metals have mostly positive (endothermic)  $\Delta H_{ea}$ , but most positive are Be, Mg, Ca (alkaline earths)

Going from  $ns^2$  to  $ns^2np^1$  or  $ns^2(n-1)d^1$   
is not favorable!

Closed shell is favorable.

2. The most negative  $\Delta H_{\text{ea}}$  values are for the halogens which have a great tendency to achieve the noble gas configuration



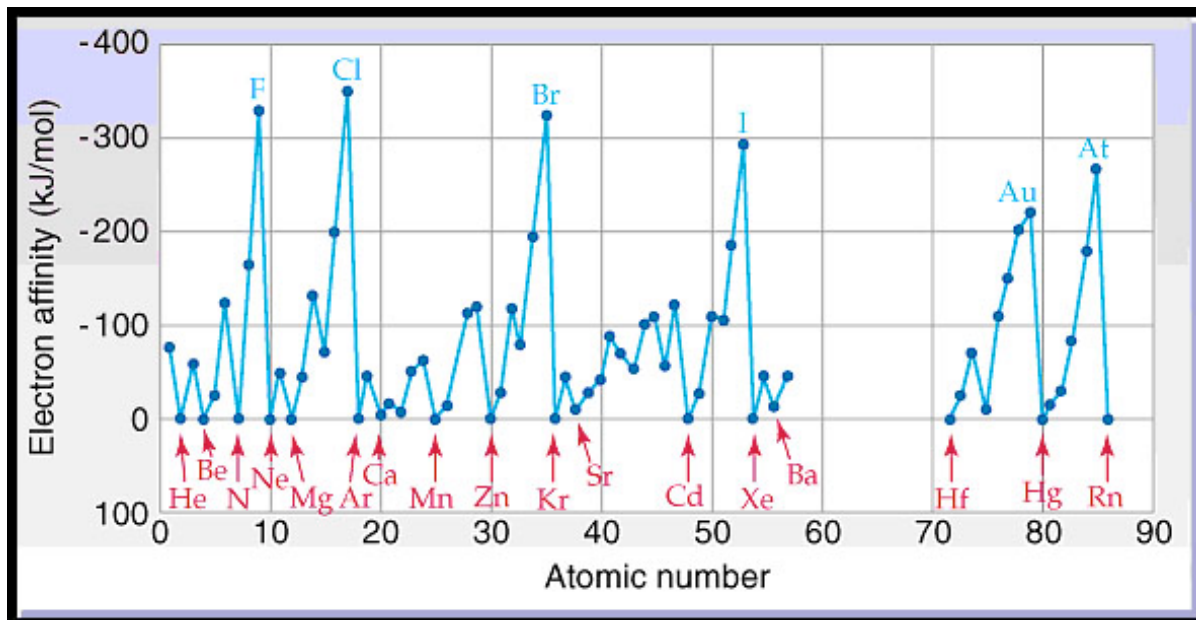
### Electronegativities

*Empirical measure* of the tendency of an atom in a molecule to attract the electrons in a bond.

Called  $\chi$  (chi).

It is not the same as  $\Delta H_{\text{ea}}$ , although they are related





### Electron Affinity Plot

Note that the noble gases, alkali metals and alkali earth metals have E.A. close to zero - indicating that these groups of elements do not particularly like to become anions. However, the nonmetals and especially the halogens are highly negative and thus readily become anions. A periodic trend is evident, as was the case for the ionization energy. This periodic trend can be understood as a reflection of the underlying periodicity in the electronic configuration of the elements.

**Q:** How would you explain why the electron affinity of nitrogen is lower (less negative) than those of both carbon and oxygen?

A few important aspects about the **sign** used to express electron affinities are:

Electron affinity is directly related to *change in energy* by the equation  $EA = -\Delta E$

This means that if energy is **released** when an electron is added to the atom, i.e.  $\Delta E$  is **negative**, the electron affinity will be **positive**.

Likewise, if energy is **required** to add an electron to an atom, i.e.  $\Delta E$  is **positive**, then electron affinity will be **negative**.

-----  
The key to why the electron affinity of nitrogen is *actually negative* lies with two factors

- *effective nuclear charge*
- *electron configuration*

**electron affinity** tells you how much energy is *released* (hence the negative sign) when **one mole** of electrons is added to **one mole** of atoms in the gaseous state.



Now, for elements in the same period, atomic size **decreases** as you move from left to right. This happens because *effective nuclear charge*, which is a measure of the net positive charge felt by the electrons, **increases**. This implies that the atomic size of carbon will be a little bigger than that of nitrogen, which in turn will be a little bigger than that of oxygen.

In essence, electron affinity tells you how "badly" an atom wants an incoming electron.

It goes without saying that the *higher* the effective nuclear charge, the more attracted to the nucleus an incoming electron will be, and the *more negative* the electron affinity of the atom will be.

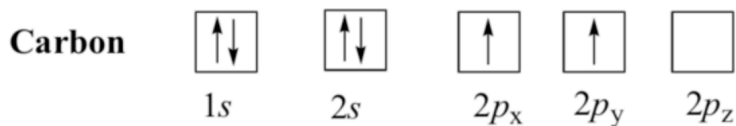
**Q:** Now, what happens when you **require energy** to add

an electron to an atom?

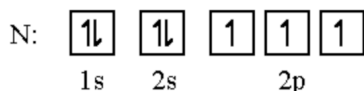


In this case, electron affinity will be **positive**, but the value listed will be *negative*.

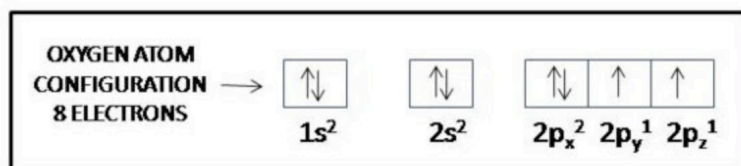
electron configurations of carbon, nitrogen, and oxygen



[chemwiki.ucdavis.edu/Organic\\_Chemistry/Organic\\_Chemistry\\_With\\_a\\_Biological\\_Emphasis](http://chemwiki.ucdavis.edu/Organic_Chemistry/Organic_Chemistry_With_a_Biological_Emphasis)



<http://www.chem.wisc.edu/deptfiles/genchem/ssstutorial/Text5/Tx54/tx54.html>



**Point 1:** In the case of carbon, an incoming electron would be added to the empty 2p<sub>z</sub> orbital. This means that it will encounter **no repulsion** from other electrons, since the orbital is *empty*.

**Point 2:** For nitrogen, an incoming electron will be added to a *p* orbital that **already contains an electron**. This means that the incoming electron will experience significant repulsion compared with when it's added to an empty orbital. As a result, you **need energy** to add an electron to nitrogen.

**Point 3:** So why isn't this the case for oxygen, since an incoming electron also would be added to an orbital that already contains an electron?

Because the *effective nuclear charge* **overpowers this repulsion**, and energy is being **released** when an electron is being added to oxygen, hence the electron affinity will be *positive*.

## Chapter 3 Structure and Bonding in Molecules

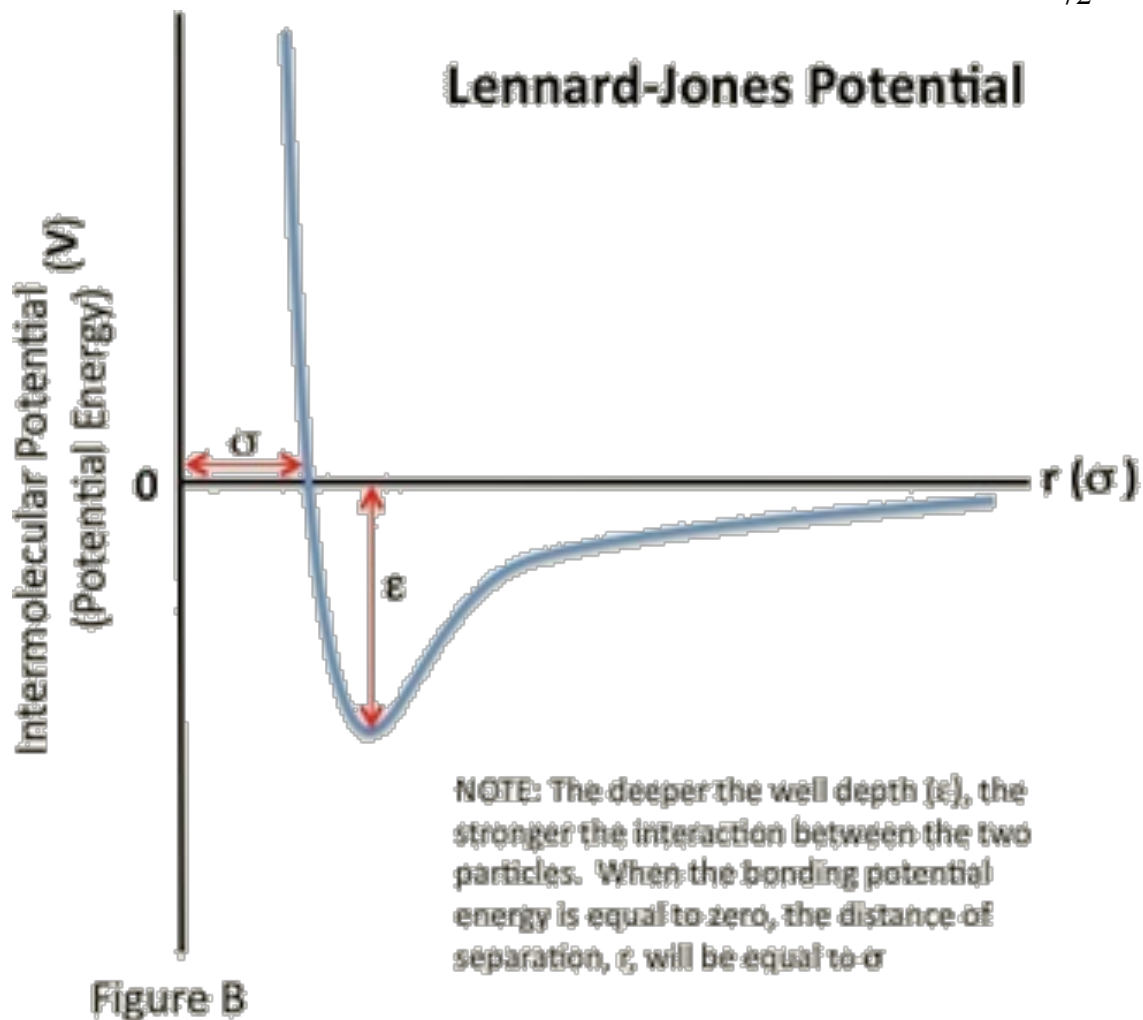
- Our current understanding of bonding is quite high due to the use of X-ray crystallography and spectroscopy. We can make detailed predictions and comparisons based on a large database of experimental evidence.
- In the absence of detailed data

→ Models

Many different levels of Bonding Theories exist

Imagine two rubber balls separated by a large distance. Both objects are far enough apart that they are not interacting. The two balls can be brought closer together with minimal energy, allowing interaction. The balls can continuously be brought closer together until they are touching. At this point, it becomes difficult to further decrease the distance between the two balls. In order to bring the balls any closer together, increasing amounts of energy must be added. This is because eventually, as the balls begin to invade each other's space, they repel each other; the force of repulsion is far greater than the force of attraction.

This scenario is similar to that which takes place in neutral atoms and molecules and is often described by the **Lennard-Jones potential**.



Proposed by Sir John Edward Lennard-Jones, the Lennard-Jones potential describes the potential energy of interaction between two non-bonding atoms or molecules based on their distance of separation. The potential equation accounts for the difference between attractive forces ([dipole-dipole](#), dipole-induced dipole, and [London interactions](#)) and repulsive forces.

The Lennard-Jones model consists of two 'parts'; a steep repulsive term, and smoother attractive term, representing the London dispersion forces. Apart from being an important model in itself, the Lennard-Jones potential frequently forms one of 'building blocks' of many force fields.

## Two Main Types:

- Localized bonding Theories
- Delocalized Bonding Theories

Chapter 2 – Electronic Structure – and orbitals are very important to bear in mind for the models.

Electrons  $\rightarrow$  orbitals  $\rightarrow$  bonds

## Three types of Bonding:

1. Covalent (two-center) bonding between pairs of electrons (localized)
2. Delocalized covalent bonding (multicenter bonding)
3. Ionic Bonding

In this section, localized and delocalized covalent bonding will be discussed. Ionic Bonding is really a separate subject, as it treats the bond as a purely electrostatic attraction.

**Important Point while you are studying the subject of covalent bonding:**

There are three theories that are presented together as inter-related topics

1. Lewis Dot structures (electron –pairs)
2. VSEPR Theory: valence shell electron pair repulsion theory
3. Hybridization

## 1. Lewis Concept - Localized Electron Pairs

G. N. Lewis described Bonding as a sharing of electrons

### **Bonding Pairs**



Pairs of electrons between two atoms lead to a covalent bond

→ localized between two atoms

### **Lone Pairs**



A lone pair is localized on one atom here

Electronic Structure based on this model is the sum of all the bonding pairs and lone pairs.

We use a Lewis Diagram to represent this

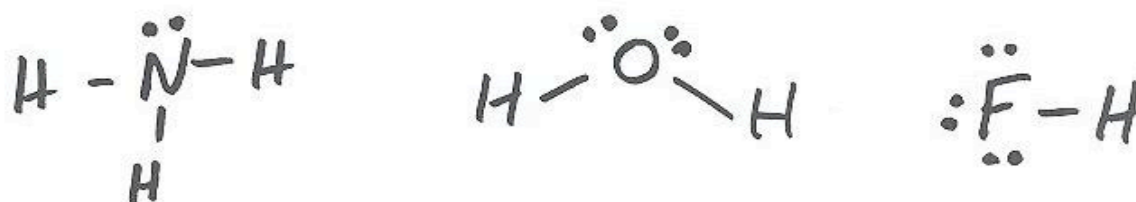
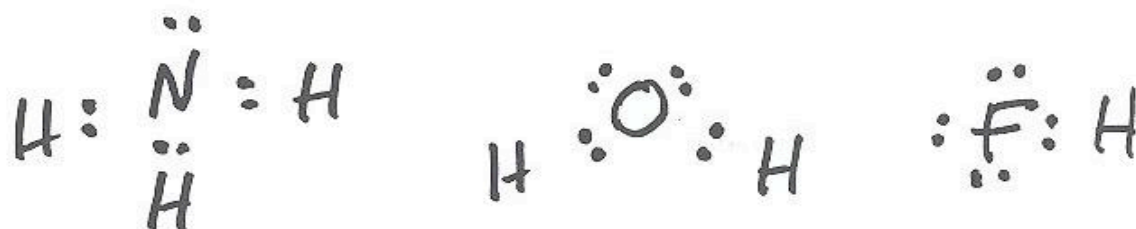
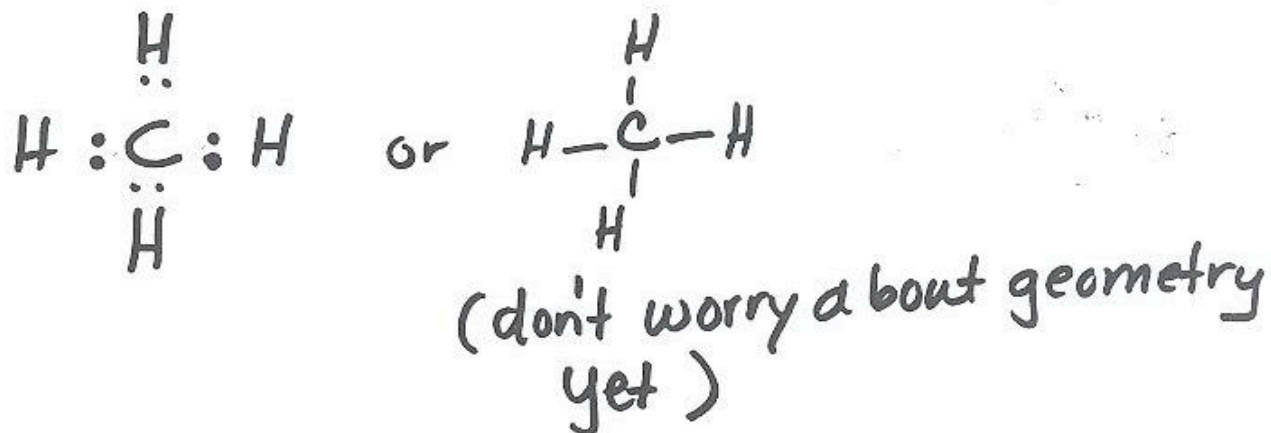


## Lewis Diagrams

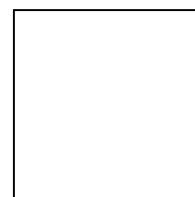
- Use only valence electrons
- Electrons are either involved in a two electron bond or they are localized as a lone pair (or lone electrons)
- Bear in mind that the simplest, most symmetrical structure is typically correct
- The central atom is typically:
  - A metal or least electronegative
  - Odd atom in the formula
  - Never hydrogen
- Atoms usually need to achieve a full octet if they are in the 1<sup>st</sup> and 2<sup>nd</sup> periods (exceptions are B, Be, Al)
- Atoms beyond 2<sup>nd</sup> row, atom can acquire more than an octet.
  - valence shell expansion

# A. Octet Systems

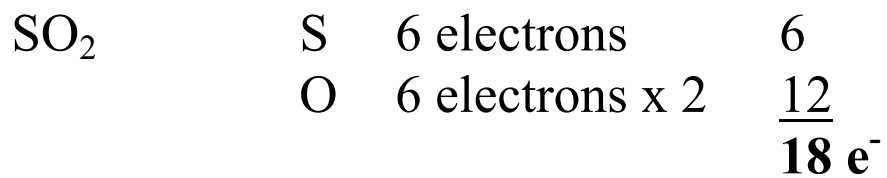
## 1. Saturated Systems – Single bonds only



<b>C</b>	<b>4e<sup>-</sup></b>	<b>O</b>	<b>6e<sup>-</sup></b>	<b>Valence electron counts</b>
<b>N</b>	<b>5e<sup>-</sup></b>	<b>F</b>	<b>7e<sup>-</sup></b>	
<b>H</b>	<b>1e<sup>-</sup></b>			





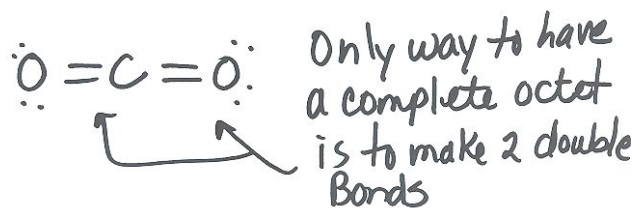


Better structure is this one

Q. What about CO<sub>2</sub>?

C	4 electrons	4
O	6 electrons x 2	<u>12</u>
		<b>16 e<sup>-</sup></b>

A.



## B. Electron Deficient (less than an octet)

e.g.  $\text{BeH}_2$

$\text{H-Be-H}$



Be does not need an octet

Total of 4 valence electrons

Not the same as unsaturated systems that achieve the  $8e^-$  (octet) through the formation of multiple bonds.

## C. Electron Rich (greater than an octet)

Valence shell expansion occurs with elements beyond the 2<sup>nd</sup> row

s, p, d levels are all available



$2e^- \quad 6e^- \quad 10e^- \rightarrow$  total of  $18e^-$  possible

e.g., transition metals have expanded electron counts, typically  $18e^-$

referred to as valence shell expansion

$\text{PCl}_5$

P  $5e^-$

$5e^-$

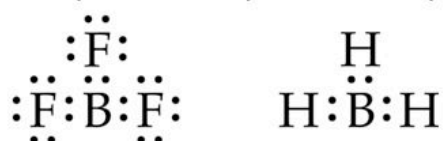
Cl  $7e^- \times 5 =$

$35e^-$

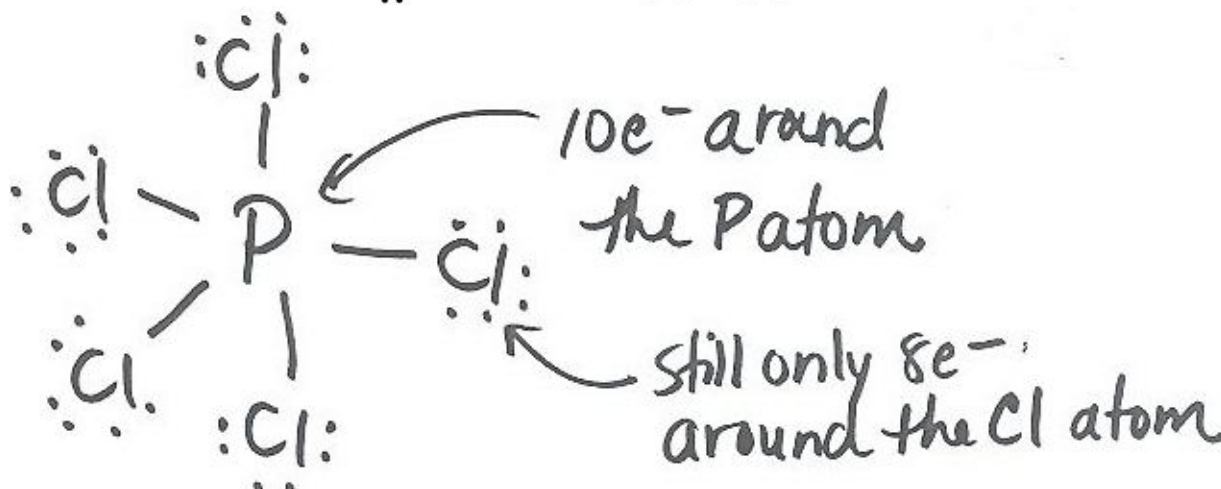
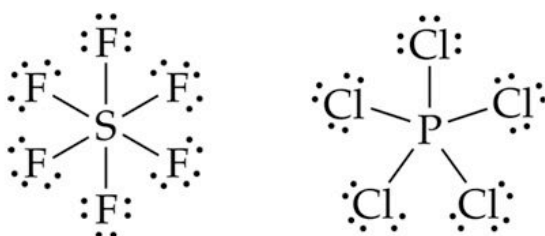
$40e^-$

# Exceptions to the Octet Rule

- There are two elements which don't want an octet of electrons and those are **Be (wants 4)** and **B (wants 6)**.



- Third-row and heavier** elements often satisfy the octet rule but **can exceed the octet rule** using their empty valence d orbitals, especially when surrounded by highly electronegative atoms such as chlorine, bromine, and oxygen.



Q. What about transition metals?

A. They tend to exhibit  $18e^-$  valence shells (full s, p, d levels). They form bonds to lone pairs of molecules (called ligands) until they reach the  $18e^-$  configuration.

Ex.  $Ni^{2+}$  compounds

Ni has 10 valence electrons - it needs 4 bonds to reach 18 valence electrons.

-  $Ni(CO)_4$  is a compound that illustrates this point.

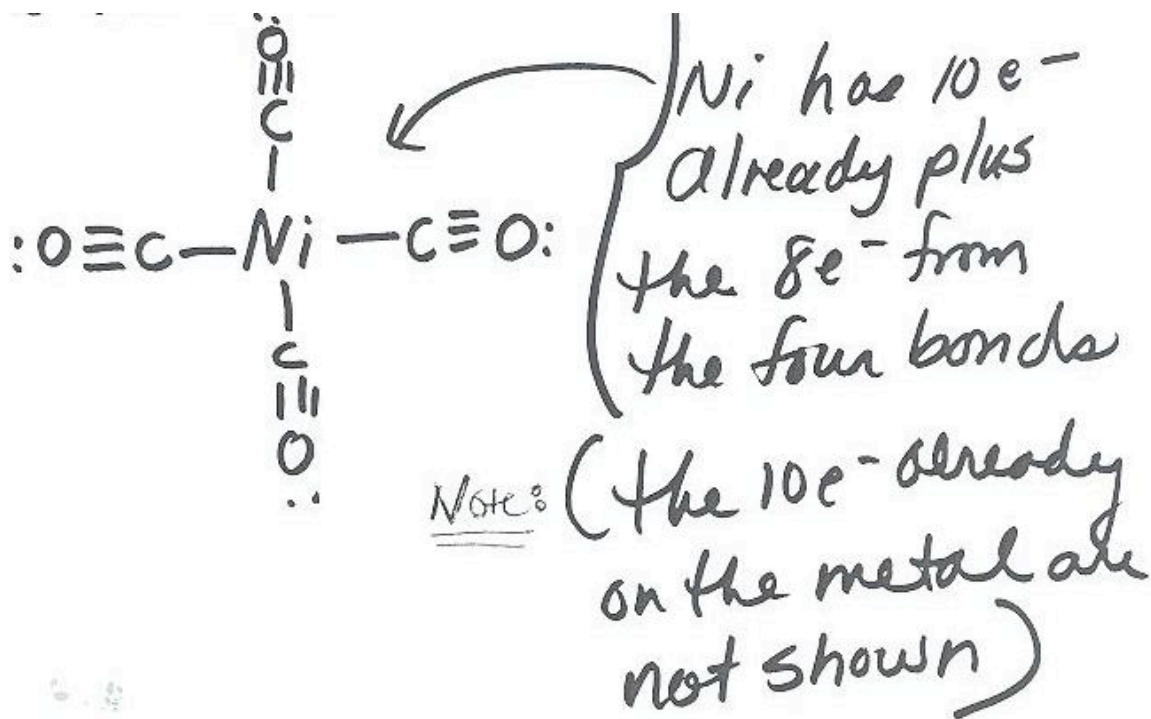
CO valence electrons       $4+6 = 10e^-$

$:C \equiv O:$   
(unsaturated)

Lewis structure is this one  
to allow for an octet

CO can then act as a ligand with the lone pair of C bonding to the Ni atom.\*





\*  $\text{:C} \equiv \text{O:}$

The C lone pair is more basic (donating) than the O lone pair

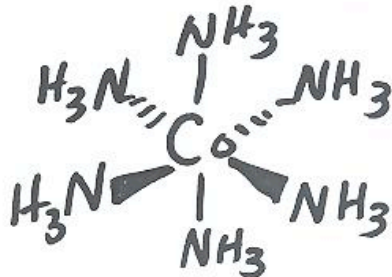
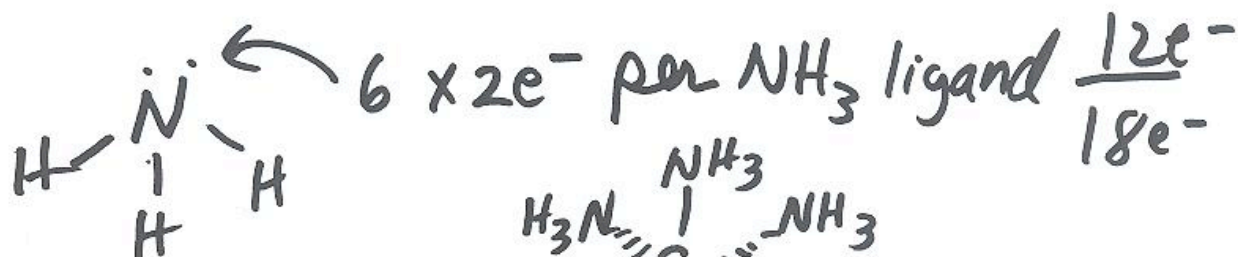
The ligand,  $\text{:C} \equiv \text{O:}$ , is considered to be a Lewis base (electron – pair donor) and the metal, Ni, is the Lewis acid (electron – pair acceptor).

The bonds formed in this way are coordinate covalent bonds.

→ **The ligand supplies both electrons of the metal – ligand bond.**

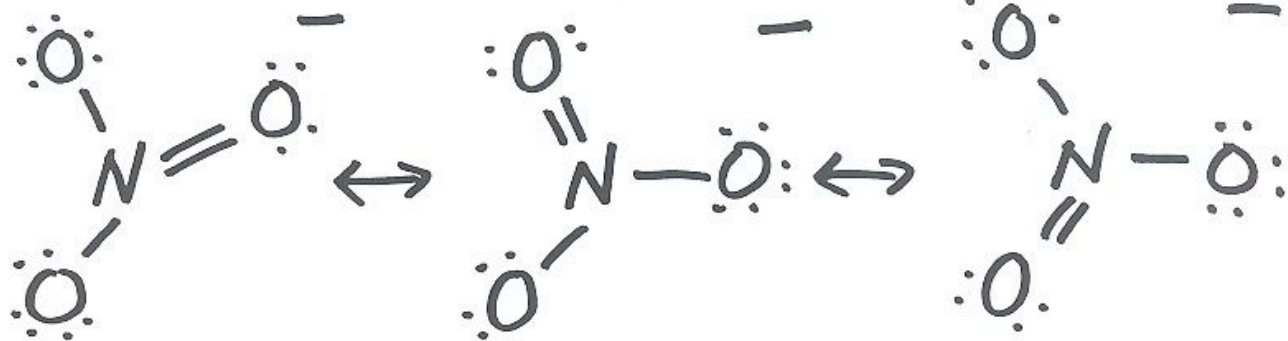


$\text{Co}^{3+}$  6 valence electrons  $6e^-$



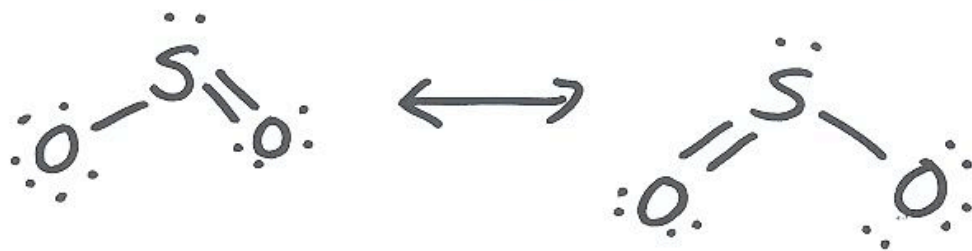
Resonance

Recall  $\text{NO}_3^-$ :



the real structure is a "resonance hybrid"

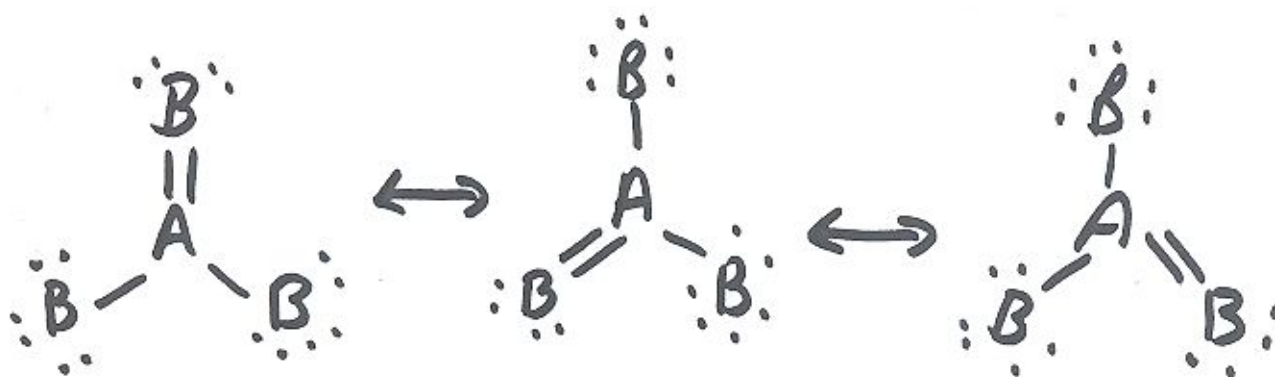
$\text{SO}_2$



Q. How did we justify the concept of resonance?

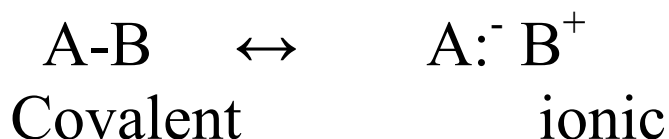
A. Experimental evidence says that all the bonds are the same length in these molecules.  
→ more of a delocalization model.

Summary of Resonance Hybrids



- 
- (a.) None of these “canonical forms” is an actual representation of the real structure. These structures don’t really exist, but their average corresponds to the real structure.
  - (b.) Experiment shows that all bonds A-B are equal in length so theory and experiment correlate.
  - (c.) The average “hybrid” structure has a lower energy than any of the contributing structures.

**A special case of resonance**  
**is covalent  $\leftrightarrow$  ionic resonance**



- A is more electronegative than B
- A-B bond enthalpy is a combination of the two contributing structures.

Consequently

A-B  $\Delta H_{\text{A-B}}$  (bond energy) is greater than the average of  $\Delta H_{\text{A-A}}$  &  $\Delta H_{\text{B-B}}$  due to the ionic contribution.

**In the end, however, Lewis structures are not enough to describe localized bonding in molecules.**

**Q.** Besides Lewis structures, what other localized bond theories do we need?

**A.** VSEPR and Hybridization

**Q.** Why do we need to go further than the concept of Lewis?

**A.** Because there are numerous issues that Lewis structures do not address such as:

(a). How is the electron – pair bond shared?

(b). Which orbitals are involved in the bonding?

(c). **What geometry should one assign to the molecule? (bonds, angles?)**

(d). Why does sharing electrons lead to stability for a molecule?

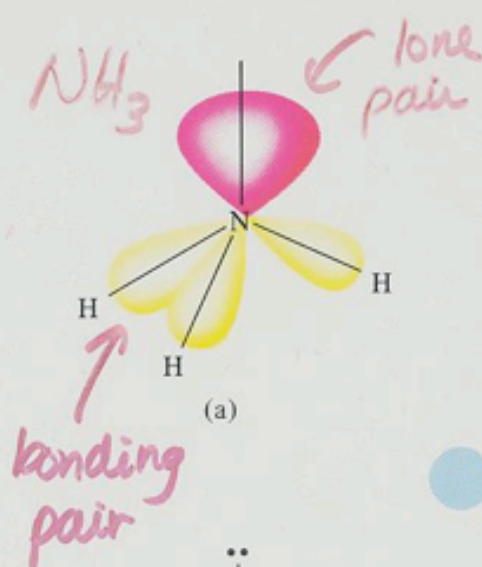
**IN LOCALIZED BONDING THEORY, WE USE EITHER VSEPR OR HYBRIDIZATION TO ANSWER THESE QUESTIONS.**

We need to be able to explain these structures

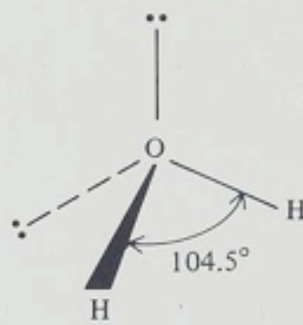
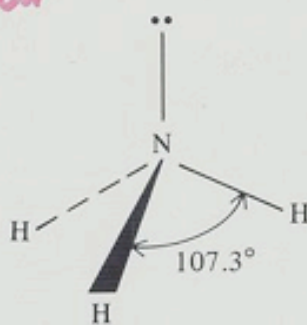
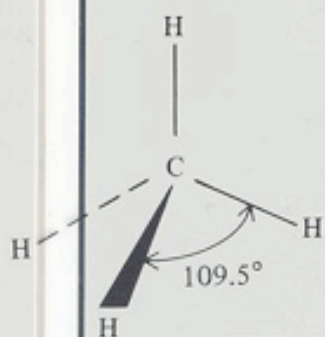
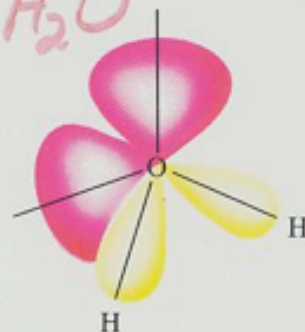
CH<sub>4</sub>



NH<sub>3</sub>



H<sub>2</sub>O



## 2. Hybridization Theory or Model

For this, we need the concept of valence state

Ex:      H-Be-H

X – Be – X

X = halogen

How does one explain the linear shape?

(a.) Be  $1s^2 2s^2$

- $2s^2$  is the valence shell

If we promote an  $e^-$  to the 2p level it is now possible to pair the two unpaired electrons with those of incoming group H or X (halide)

- $2s^1 2p^1$  valence state requires 323 kJ/mol  
(this doesn't explain the shape, only how it happens)

(b.) Hybridization occurs between the s and p orbitals

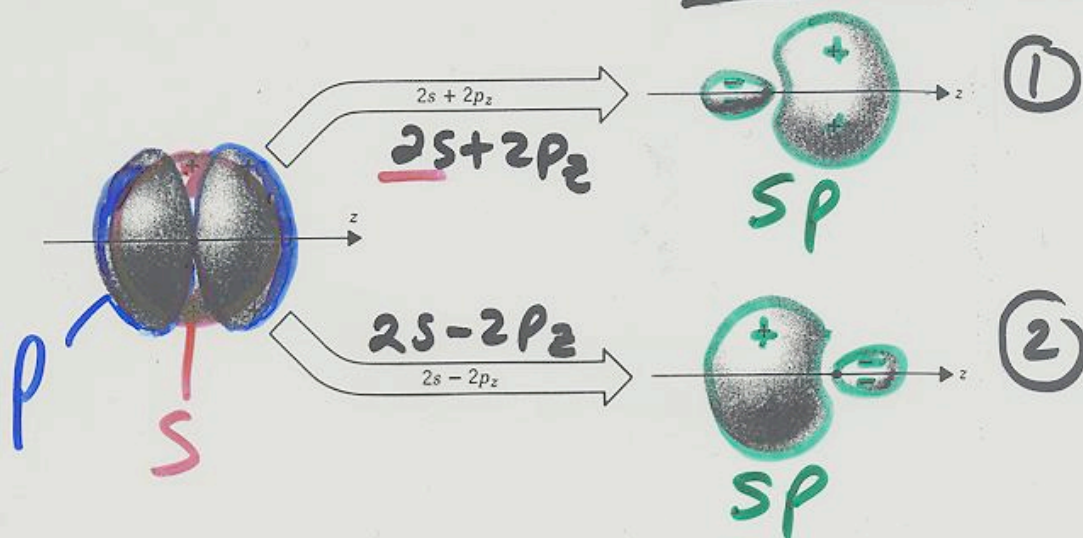
$2s+2p_z$

$2s-2p_z$

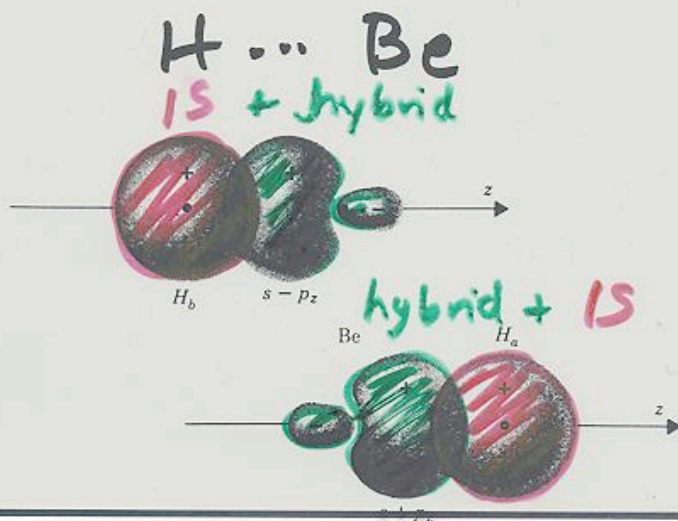




Two HYBRIDS

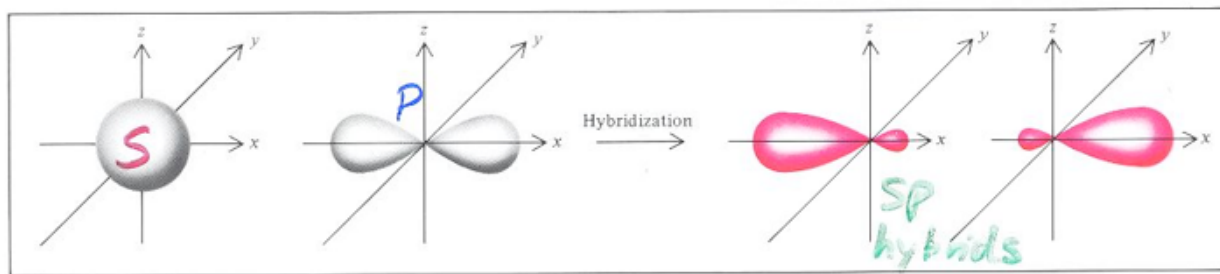


OVERLAP of HYBRIDS WITH H atoms

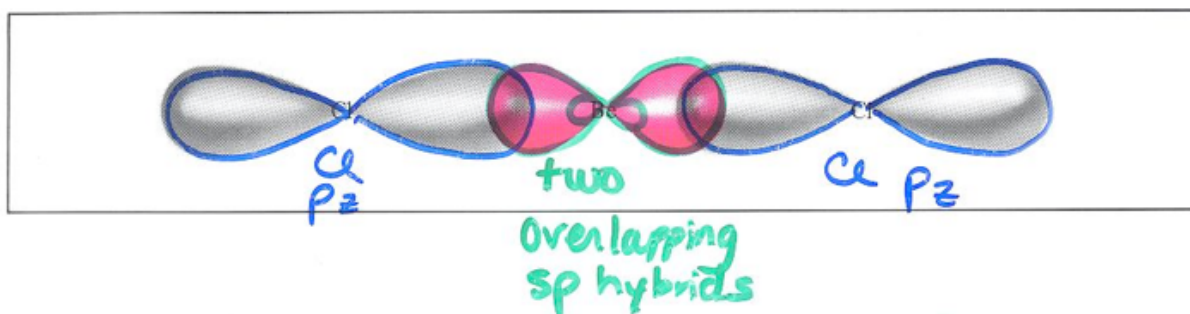


So, the linear shape of the  $\text{H} - \text{Be} - \text{H}$  molecule is due to best overlap with H  $1s$  orbitals and  $sp$  hybrids



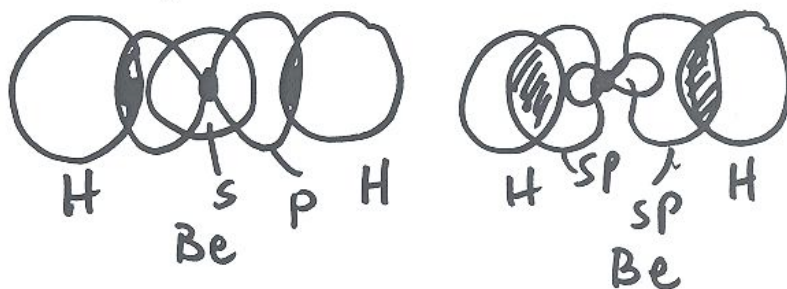


*BeCl<sub>2</sub> molecule*

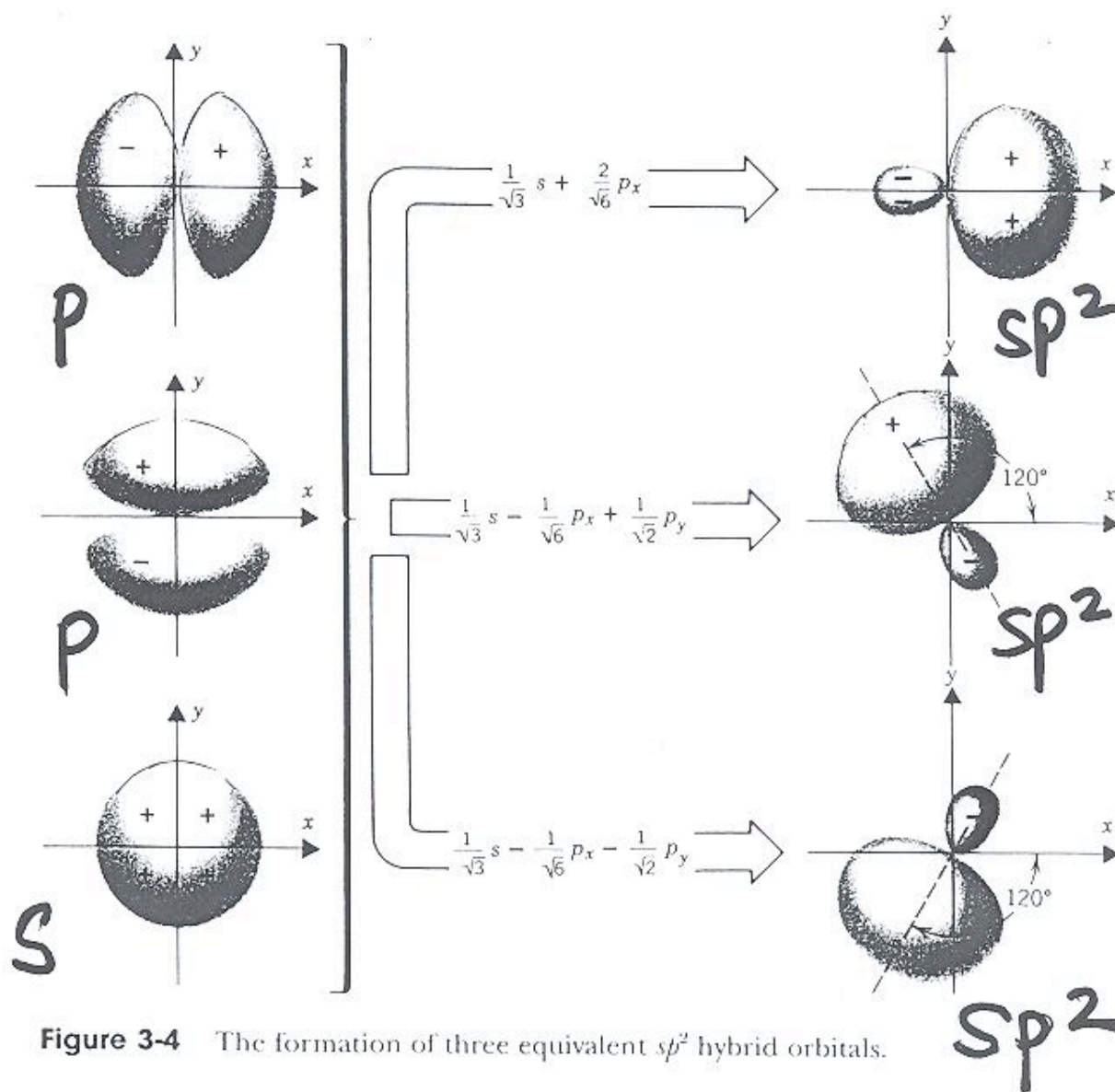


## Main Point about Hybrid Orbitals

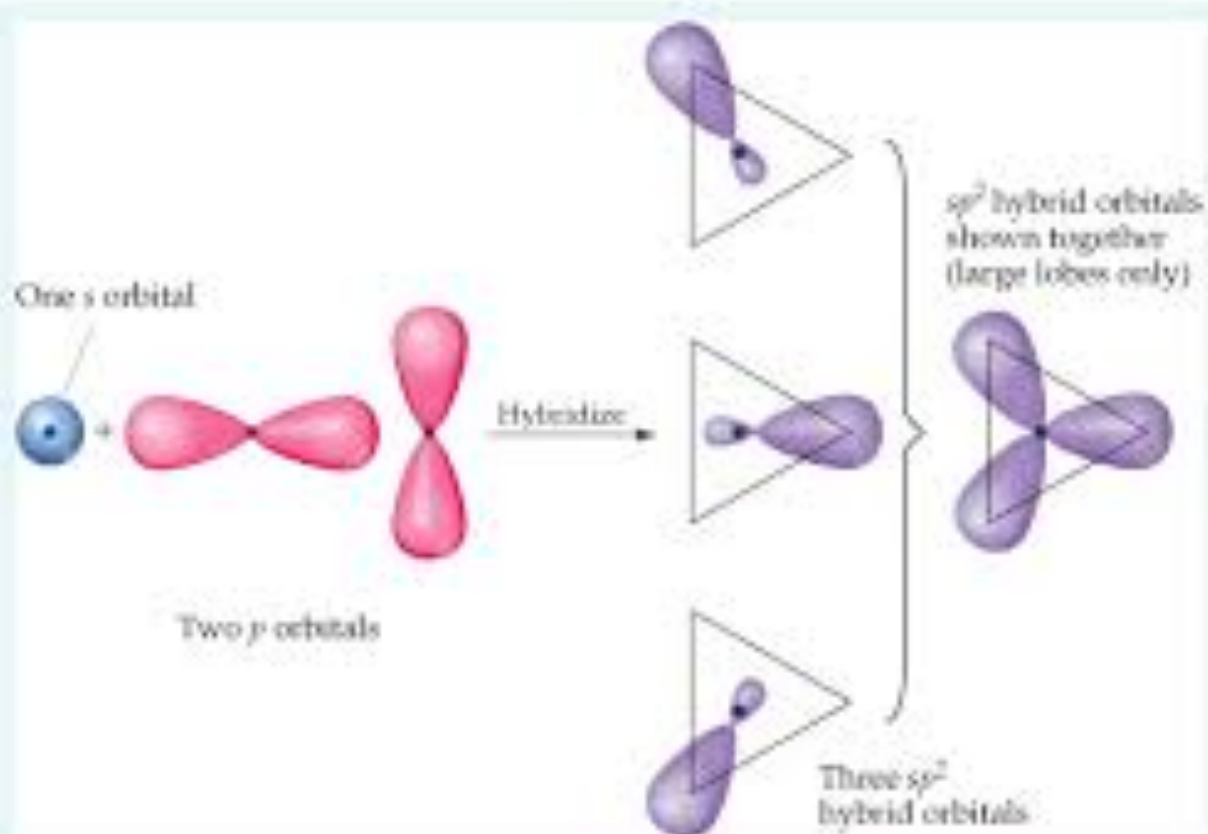
- They have a huge lobe pointed in a particular direction that can overlap strongly with an atom along that direction.
- Calculations show that the extent of overlap obtained of the hybrid orbitals of H-Be-H (sp) is much greater than it would be with pure s and p orbitals on Be



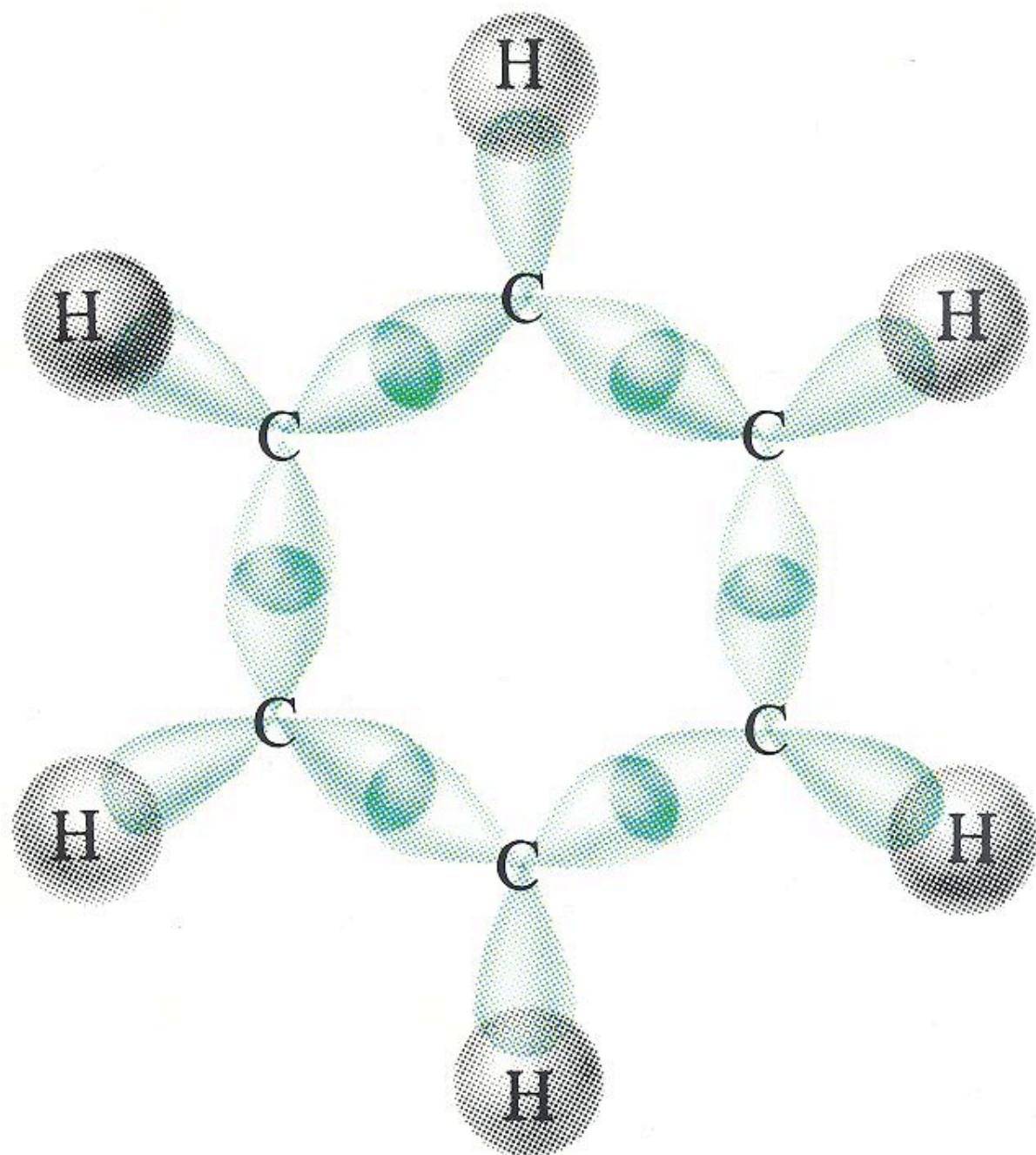
## sp<sup>2</sup> Hybridization

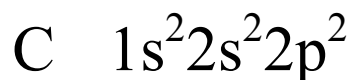


B  $1s^2 2s^2 2p^1$  is the starting, standard electron config.  
 B tends to form  $BX_3$  if the bonding configuration is  $1s^2 2s^1 2p^2$ , this allows for three decoupled spins,  $2s^1 2p^2$ , to form three bonds with  $H\cdot$ ,  $X\cdot$ .

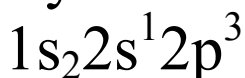


Sigma bond framework  
in benzene based on  $sp^2$  hybrids





For hybridization:



4 uncoupled spins

now we can hybridize these orbitals

$sp^3$  hybridization

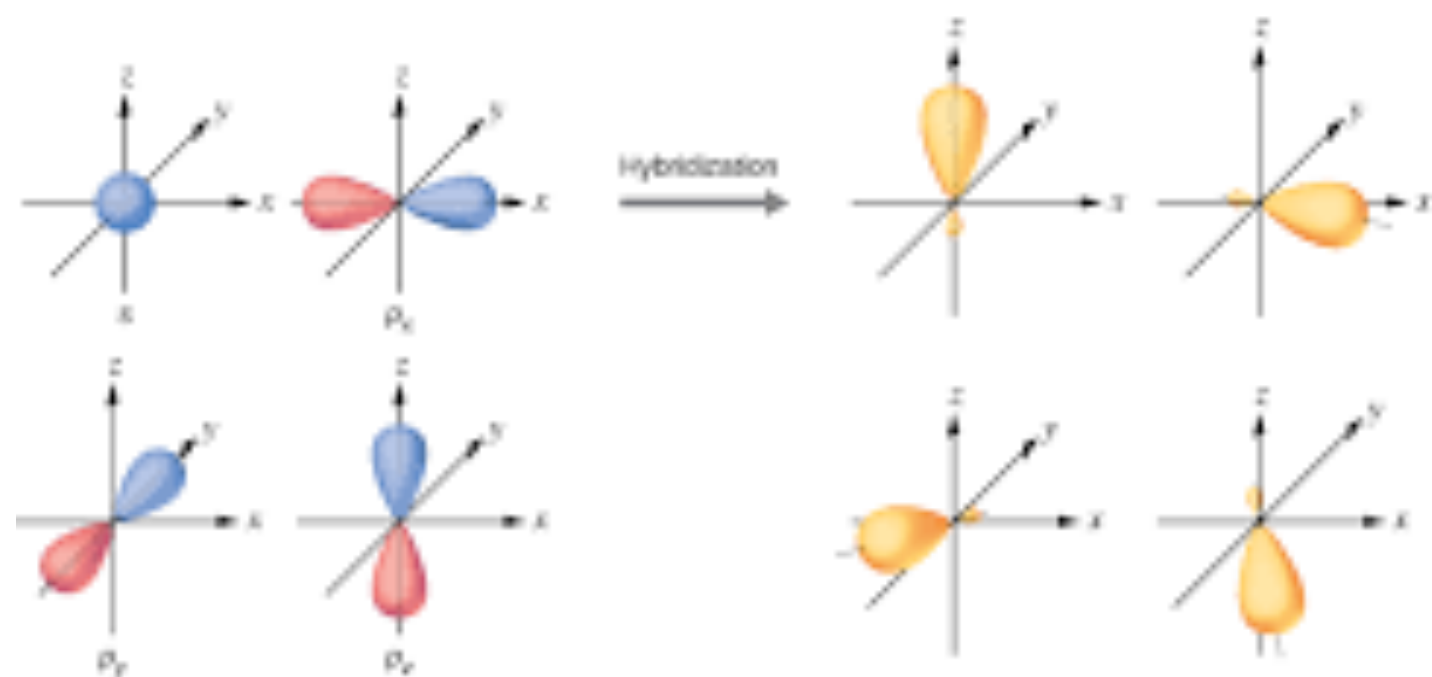
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### Summary s, p Hybridization

---

$sp$	linear molecule
$sp^2$	planar triangular molecule
$sp^3$	tetrahedral molecule

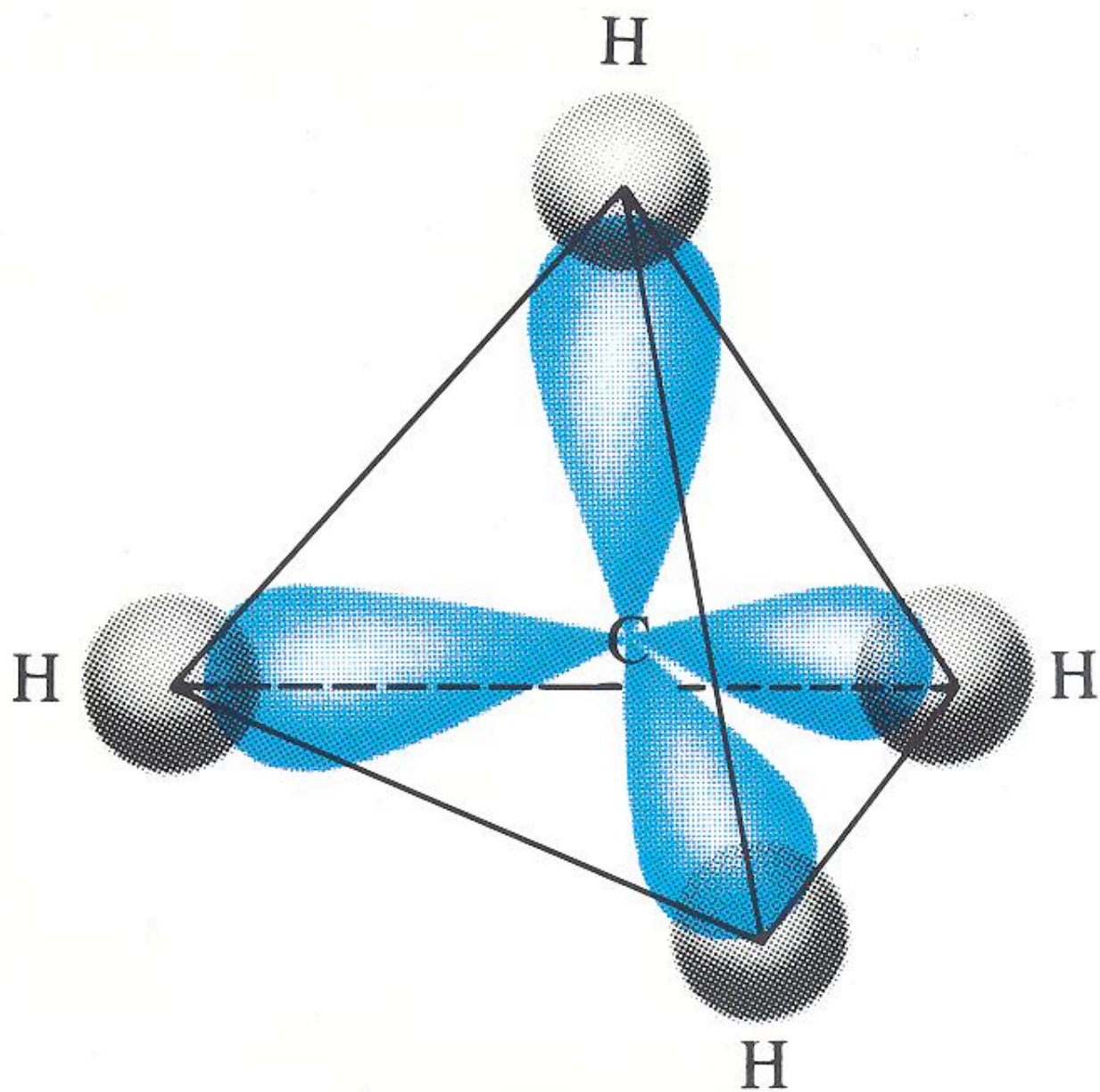
The geometries arise from maximum overlap along these directions ( $sp$ ,  $sp^2$ ) and from the algebra of the hybridization for  $sp^3$   
(it also happens to be the maximum distance from each other in each case)



↓ Gives a tetrahedral arrangement



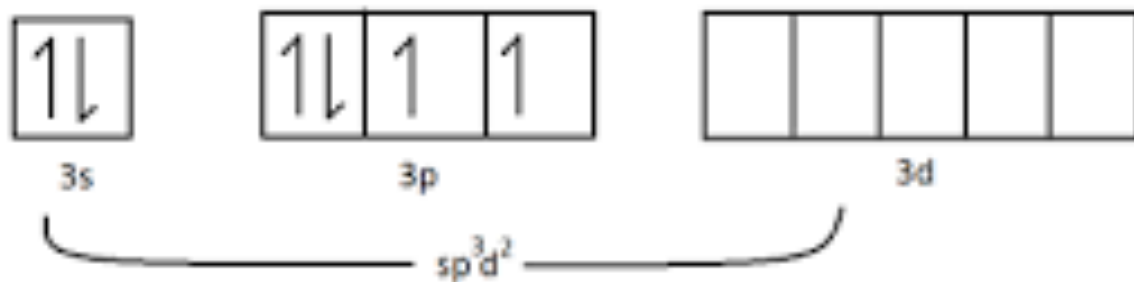




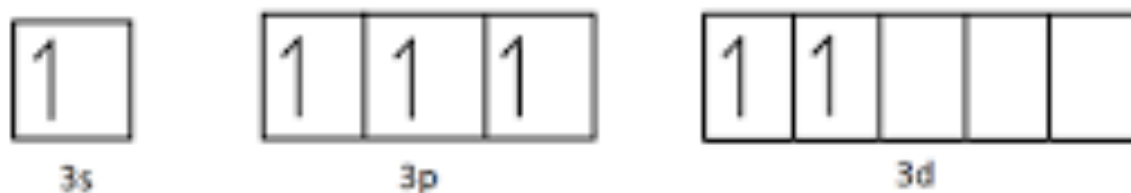
# Hybridization with s,p,d orbitals: d orbitals become available after the second row

For example

Before hybridization:



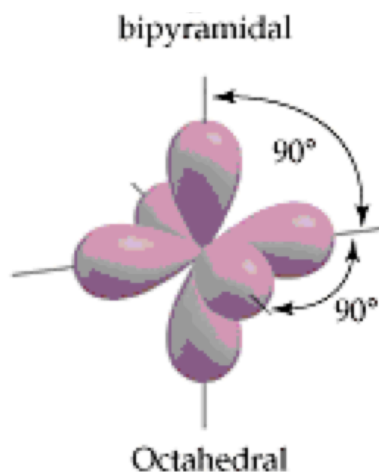
After hybridization:



Difference Between

$s, p, p, p, d, d$

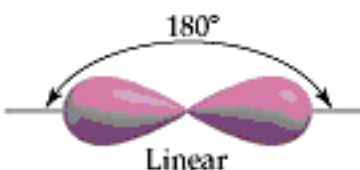
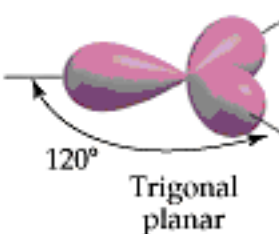
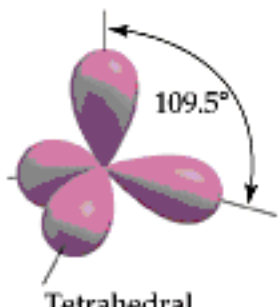
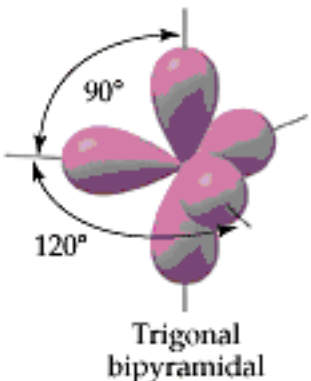
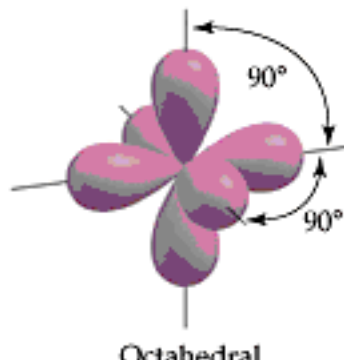
Six  $sp^3d^2$



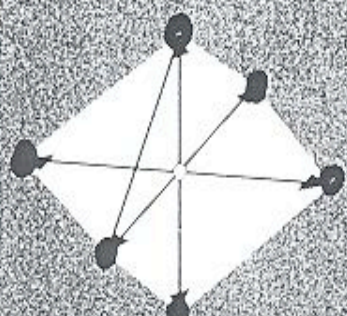
$SF_6$ ,  $ClF_5$ ,  $XeF_4$ ,  $PF_6^-$



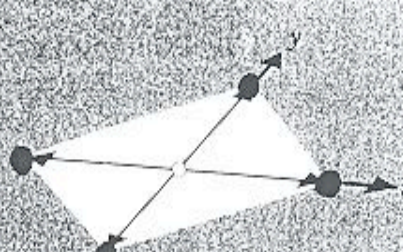
**TABLE 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets**

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
$s, p$	Two $sp$	 <p>Linear</p>	$\text{BeF}_2, \text{HgCl}_2$
$s, p, p$	Three $sp^2$	 <p>Trigonal planar</p>	$\text{BF}_3, \text{SO}_3$
$s, p, p, p$	Four $sp^3$	 <p>Tetrahedral</p>	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$
$s, p, p, p, d$	Five $sp^3d$	 <p>Trigonal bipyramidal</p>	$\text{PF}_5, \text{SF}_4, \text{BrF}_3$
$s, p, p, p, d, d$	Six $sp^3d^2$	 <p>Octahedral</p>	$\text{SF}_6, \text{ClF}_5, \text{XeF}_4, \text{PF}_6^-$

$d^2sp^3$   
Octahedron



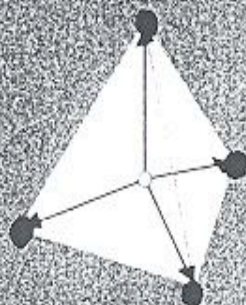
$d^2sp^3$ , Octahedral  
( $s, p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$ )



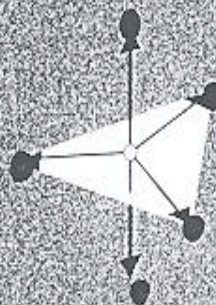
$dsp^2$ , Square planar  
( $s, p_x, p_y, d_{x^2-y^2}$ )

$dsp^2$   
Square  
Planar

$sd^3$   
Tetrahedral

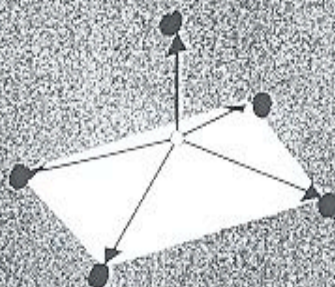


$sd^3$ , Tetrahedral  
( $s, d_{xy}, d_{yz}, d_{zx}$ )



$dsp^3$ , Trigonal bipyramid  
( $s, p_x, p_y, p_z, d_{z^2}$ )

$dsp^3$   
Trigonal  
Bipyramidal



$dsp^3$ , Square pyramidal  
( $s, p_x, p_y, p_z, d_{z^2}$ )

$dsp^3$   
Square  
Pyramidal

What about trigonal bipyramidal versus square pyramidal. To be a little more specific, the d orbital which contributes to this hybrid determines the geometry. The  $d_{z^2}$  orbital is concentrated in a single axial direction, so it will combine with the  $sp^3$  geometry to push out on that axis in both directions, and the remaining 3 lobes are evenly distributed on the plane perpendicular to that axis. The  $d_{x^2-y^2}$  orbital is concentrated in a plane, with lobes pointing directly in the x and y directions. When combined with the  $sp^3$  geometry, a single lobe from the tetrahedral  $sp^3$  hybrid is pointed up in the z direction, while the other 4 are localized in the same fashion as the  $d_{x^2-y^2}$  orbital, along the perpendicular x and y directions. Which geometry is adopted depends upon a combination of steric and electronic factors, and isn't necessarily trivial to predict, though MO theory and crystal field theory can help understand which might be more favorable.

## Five Main Types

Geometries are:

Six coordinate (octahedron)

Five coordinate (trigonal bipyramidal tbp and square pyramid)

Four coordinate (tetrahedral, square planar)

(Note that the  $dx^2-y^2$  and  $dz^2$  are chosen in particular cases because of standard coordinate labels – we assign the x and y axis to coincide with the ligands)

1.  $d^2sp^3$       octahedral hybridization  
 $dx^2-y^2, dz^2, p_x, p_y, p_z$
2.  $dsp^2$       square planar hybridization  
 $dx^2-y^2, s, p_x, p_y$
3.  $sd^3$       tetrahedral hybridization  
 $dxy, dxz, dyz, s$
4.  $dsp^3$       trigonal bipyramidal hybridization  
 $dz^2, s, p_x, p_y, p_z$
5.  $dsp^3$       square pyramidal hybridization

**$dx^2-y^2$ , s,  $p_x$ ,  $p_y$ ,  $p_z$**

These hybridization schemes help to explain bonding and to correlate structures, albeit in a qualitative sense. (molecular orbital theory is used more commonly now, as it is possible to be quantitative)

### 3. VSEPR Model

#### Valence Shell Electron Pair Repulsion Theory

Electron pairs will tend to stay as far apart as possible to minimize repulsions

- 1.) Bonding Pairs B
- 2.) Lone Pairs E
- 3.) Central Atom A

For  $A B_x E_y$  which is the general notation

$X = \# \text{ of B pairs}$        $y = \# \text{ of Lone Pairs}$

4. Occupancy factor =  $x + y$   
Total number of electron pairs

Repulsions increase in the order:

Bonding Pair – Bonding Pair

Bonding Pair – Lone Pair

Lone Pair – Lone Pair



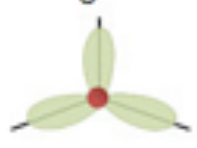



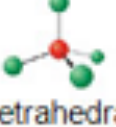
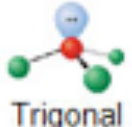




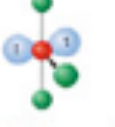
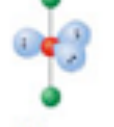



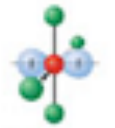

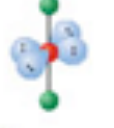
Q. Why?

A. Bonding Pair electrons are diffused through orbitals of A-B

$AB_xE_y$  :

<u>x+y</u>	<u>Basic Geometry</u>	<u>Hybridization</u>
2	Linear	$sp$
3	Triangular	$sp^2$
4	Tetrahedral	$sp^3, sd^3$
	Square planar	$dsp^2$
5	Square pyramidal	$dsp^3$
	Trigonal bipyramidal	$dsp^3$
6	octahedral	$d^2sp^3$



Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2 	Linear	 Linear				
3 	Trigonal planar	 Trigonal planar	 Bent			
4 	Tetrahedral	 Tetrahedral	 Trigonal pyramidal	 Bent		
5 	Trigonal bipyramidal	 Trigonal bipyramidal	 Sawhorse	 T-shaped	 Linear	
6 	Octahedral	 Octahedral	 Square pyramidal	 Square planar	 T-shaped	 Linear



# Prototype Shapes for $AB_xE_y$

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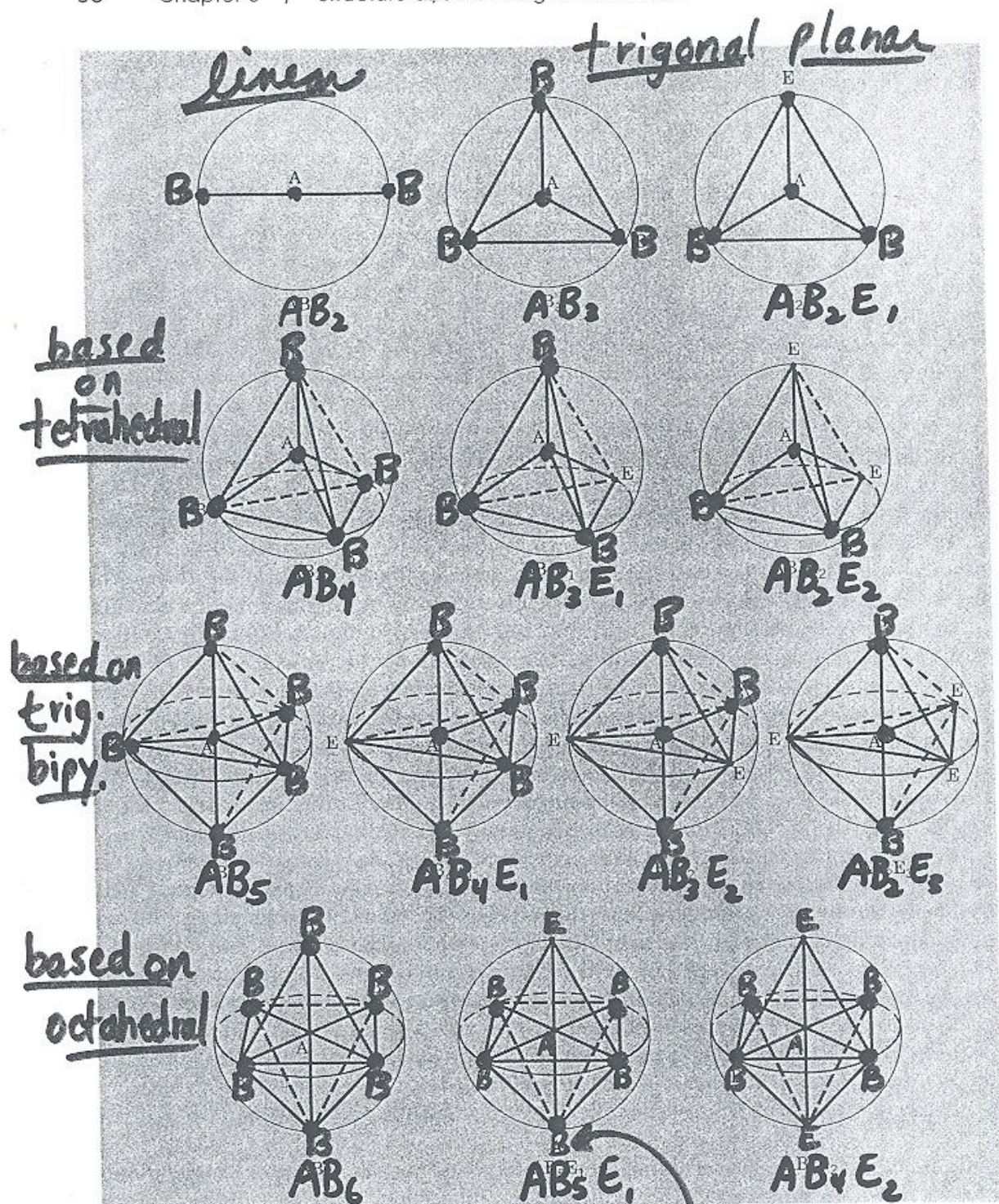


Figure 3-7 Idealized geometries for structures having the formula  $AB_xE_y$ , where A is a central atom, B are peripheral atoms, and E are lone pairs residing on A.

scription of the multiple bonds, and VSEPR adjustments of the prototype geometries.

mistake in the book  
it says "A"



For every basic geometry type, there are different ways to achieve the same occupancy factor  $x + y$  in the  $AB_xE_y$  formulae

---

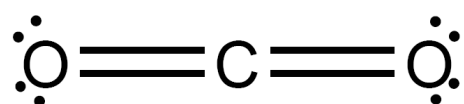
## occupancy of 2:

**$AB_2$**

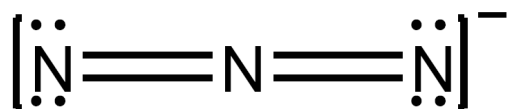
$x = 2$

$y = 0$

linear



sp hybridized C  
 $\angle O-C-O = 180^\circ$



sp hybridized N  
 $\angle N-N-N = 180^\circ$

**$ABE$**

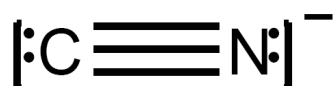
$x = 1$

$y = 1$

linear

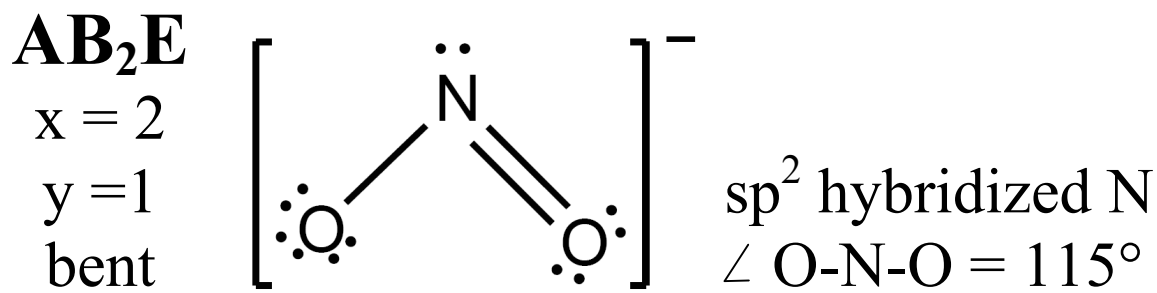
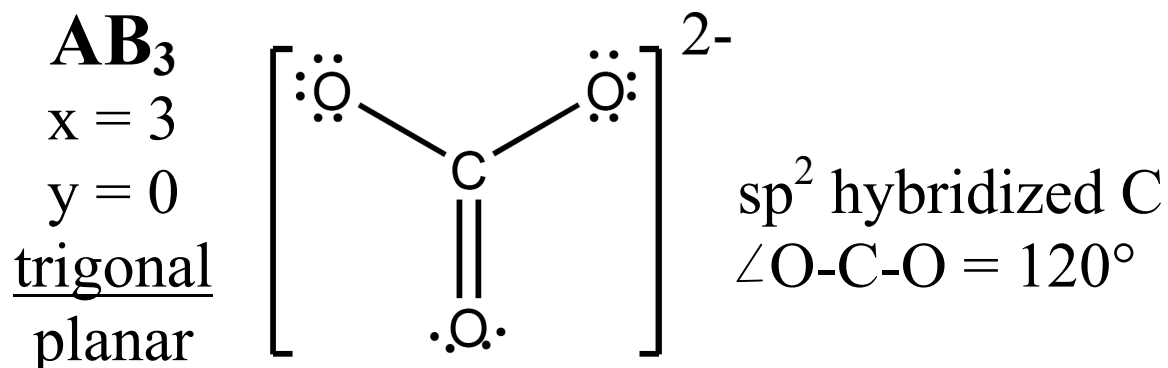


sp C, O

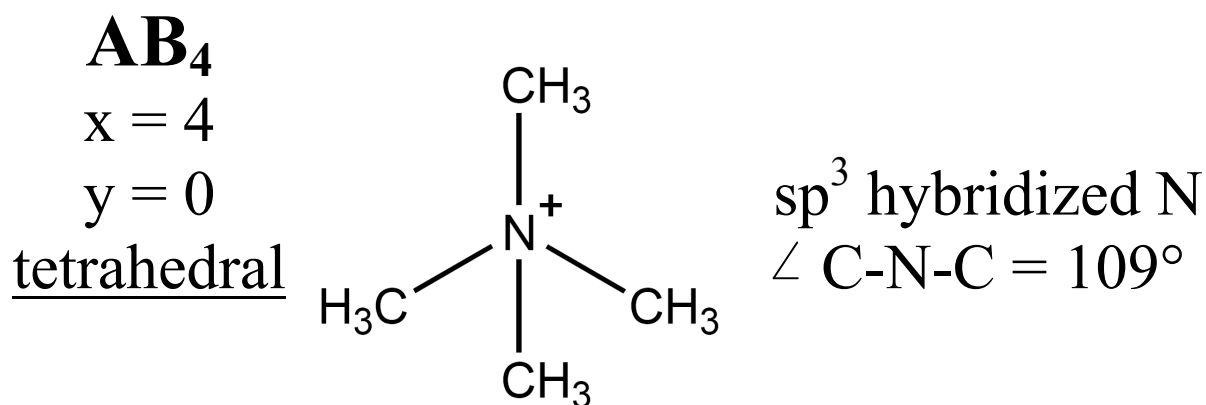


sp C, N

## occupancy of 3:



## occupancy of 4:

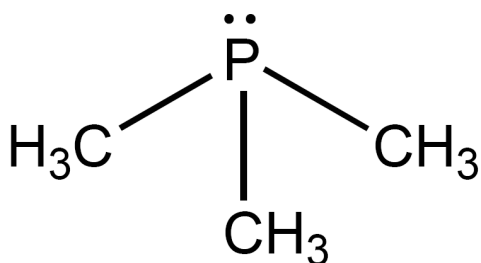


**AB<sub>3</sub>E**

$$x = 3$$

$$y = 1$$

trigonal  
pyramid



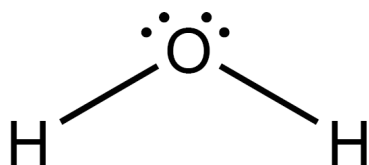
$sp^3$  hybridized P  
 $\angle \text{C-P-C} = 99^\circ$

**AB<sub>2</sub>E<sub>2</sub>**

$$x = 2$$

$$y = 2$$

bent



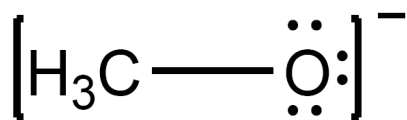
$sp^3$  hybridized O  
 $\angle \text{H-O-H} = 104^\circ$

**ABE<sub>3</sub>**

$$x = 1$$

$$y = 3$$

linear



presumably,  $sp^3$   
hybridized O,  
although with lone pairs it  
is hard to know where  
they really are in space!

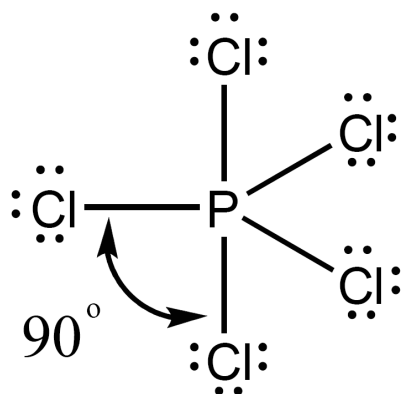
## occupancy of 5:

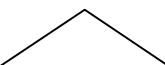


$$x = 5$$

$$y = 0$$

trigonal  
bipyramid  
(tbp)\*



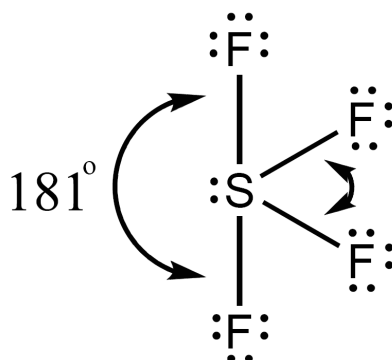
$\text{dsp}^3$  hybridized P  
 $\angle \text{Cl-P-Cl} = 120^\circ$   
in  plane



$$x = 4$$

$$y = 1$$

saw-horse



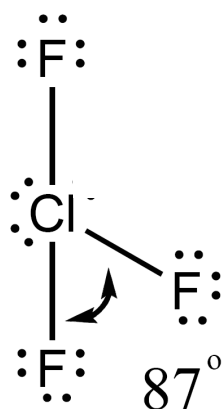
$\text{dsp}^3$  hybridized S  
 $\angle \text{F-S-F} = 103^\circ$



$$x = 3$$

$$y = 2$$

T-shaped

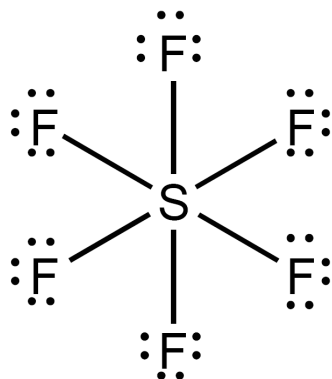


$\text{dsp}^3$  hybridized Cl

\*note that tbp is the most common  $\text{AB}_5$  basic geometry

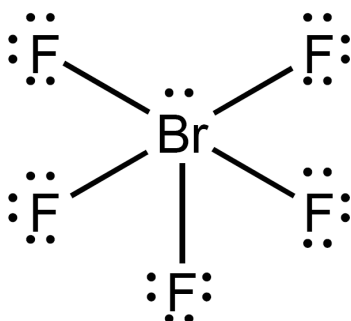
## occupancy of 6:

**AB<sub>6</sub>**  
 x = 6  
 y = 0  
octahedron



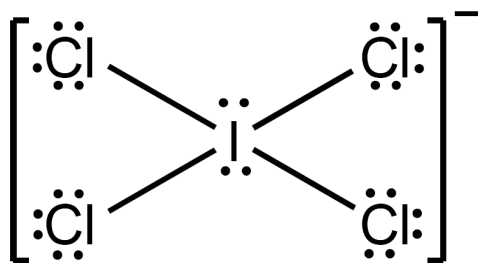
$d^2sp^3$  hybridized S

**AB<sub>5</sub>E**  
 x = 5  
 y = 1  
square  
pyramid



$d^2sp^3$   
 hybridized Br

**AB<sub>4</sub>E<sub>2</sub>**  
 x = 4  
 y = 2  
square  
planar



$d^2sp^3$  hybridized I

Summary of main types of Hybridization & shapes of orbitals

Occupancy is  
how many  
orbitals you  
are using

- 1)  $sp$  – linear
- 2)  $sp^2$  – trigonal planar
- 3)  $sp^3$  \ tetrahedral
- 4)  $sd^3$
- 5)  $dsp^2$
- 6)  $dsp^3$ 
  - a)  $dz^2sp^3 \rightarrow$  trigonal bipyramidal
  - b)  $dx^2-y^2sp^3 \rightarrow$  square pyramid
- 7)  $d^2sp^3$  octahedral

Occupancies for:

$sp = 2$	$dsp^2 = 4$
$sp^2 = 3$	$dsp^3 = 5$
$sp^3 = 4$	$d^2sp^3 = 6$
$sd^3 = 4$	

## **Main Point:**

Armed With:

- 1) An understanding of how to draw Lewis structures
- 2) How to determine occupancies of a molecule (bonding + lone pairs)

We can use (1) and (2) to predict structures by both the Hybridization and the VSEPR methods & correlate them

## **Process of applying Lewis structures**

### **VSEPR and Hybridization:**

- (1) Determine the Lewis Structure Diagram
- (2) Determine occupancy factor  $x+y$
- (3) Determine how many hybrid orbitals you will need (same as  $x+y$ ) and choose type of hybridization.
  - a) use only s, p orbitals for elements in rows 1,2 (elements below Ne which is #10)
  - b) s,p and d orbitals are all available after row 2
  - c) note that multiple bonds can be made from unhybridized orbitals
- (4) from the occupancy factor ( $x+y$ ) determine a basic geometry type. After arranging the Bonding Pairs and Lone Pairs, determine the actual geometry of the molecule.



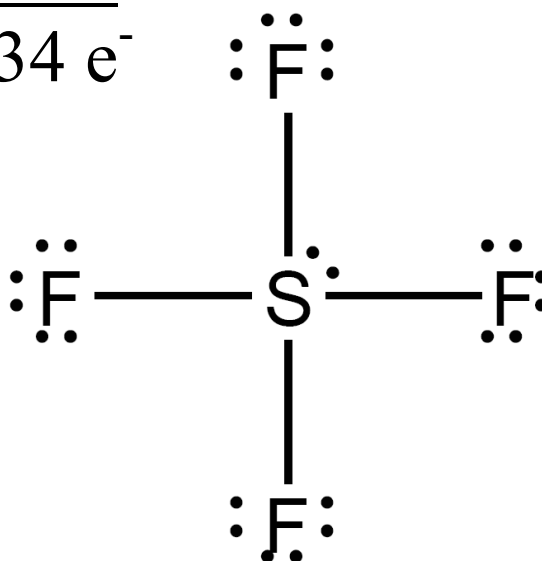
## Example 1:



### (1) Lewis Structure

A: S      6 e<sup>-</sup>                  6 e<sup>-</sup>

B: F      7 e<sup>-</sup> x 4 = 28 e<sup>-</sup>  
34 e<sup>-</sup>



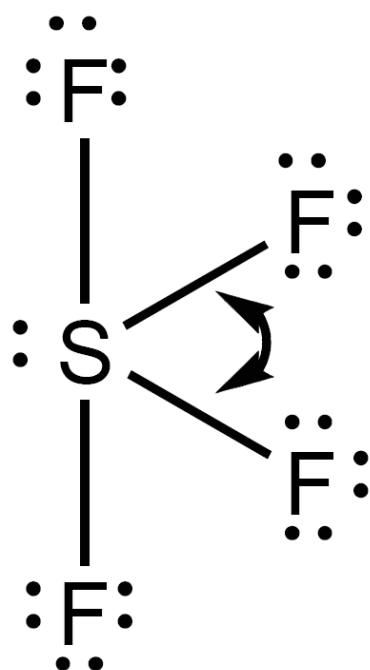
### (2) AB<sub>4</sub>E

occupancy = 5

(3) for an occupancy of 5, with d orbitals available we have dsp<sup>3</sup> hybridization.

(5) for an occupancy of 5,  $AB_4E$ , one can either a trigonal bipyramid or square pyramidal Tbp is, by far, the most common.

so tbp is the Basic Geometry, but saw-horse is actual structure with the atoms



angle is  $< 120^\circ$   
because of l.p.-b.p.  
repulsion being  
greater than b.p.-b.p.