( 4 ) **Today**

Section 1.4
Introduction to Chemical Bonding Theories
octet rule etc

Sections 1.5-1.10
Valence Bond Theory

**Next Class** ( 5 )

Sections 1.5-1.10
Valence Bond Theory

Sections 1.12
Drawing Chemical Structures

( 6 ) **Second Class from Today**

Sections 2.1 - 2.4
Polar Covalent Bonds, Formal Charges,
Resonance/Electron Delocalization

Sections 2.4 – 2.6
Resonance/Electron Delocalization

Bring Modeling Kits to Class

**Third Class from Today** ( 7 )

Sections 2.7 – 2.11
Acids and Bases

**Bring Modeling Kits to Lab this Week**

Introduce Valence Bond Theory

Determine the hybridization of the atoms involved in a bond

Introduce the concepts of $\sigma$ (sigma) and π (pi) bonds

Use Valence Bond Theory (hybridization) to explain the shape of molecules

Use Valence Bond Theory to explain the ability or the lack of the ability of atoms to rotate about a bond

Use Valence Bond Theory to explain the strength of different kinds of single bonds bond $2e^-$ shared between 2 atoms

# The Periodic Table Is Your Friend and Basic Bonding Theory



room for $2e^-$ (→ O)

room for $1e^-$ (→ F)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 H | | | | | | | | | 2 He |
| 3 Li | 4 Be | | | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne |
| 11 Na | 12 Mg | | | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar |
| 19 K | 20 Ca | 2 S | n | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 37 Rb | 38 Sr | 3 | d | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| 55 Cs | 56 Ba | 5 L | g | 81 Tl | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| 87 Fr | 88 Ra | 8 A | 2 n | 113 Nh | 114 Fl | 115 Mc | 116 Lv | 117 Ts | 118 Og |

| | | | | |
|---|---|---|---|---|
| 58 Ce | 68 Er | 69 Tm | 70 Yb | 71 Lu |
| 90 Th | 100 Fm | 101 Md | 102 No | 103 Lr |

$[He]\ 2s^2 2p^5$ ← room for $1e^-$

$F + e^- \rightarrow F^-$

$2s^2 2p^5 \rightarrow 2s^2 2p^6$

$O + 2e^- \rightarrow O^{2-}$

$2s^2 2p^4 \qquad 2s^2 2p^6$

these 2 additional $e^-$'s get to experience the "same" nuclear charge as the original 6

F will only make 1 bond

O will tend to make 2 bonds
can make 1 bond but will be ⊖
can make 3 bonds but will be ⊕

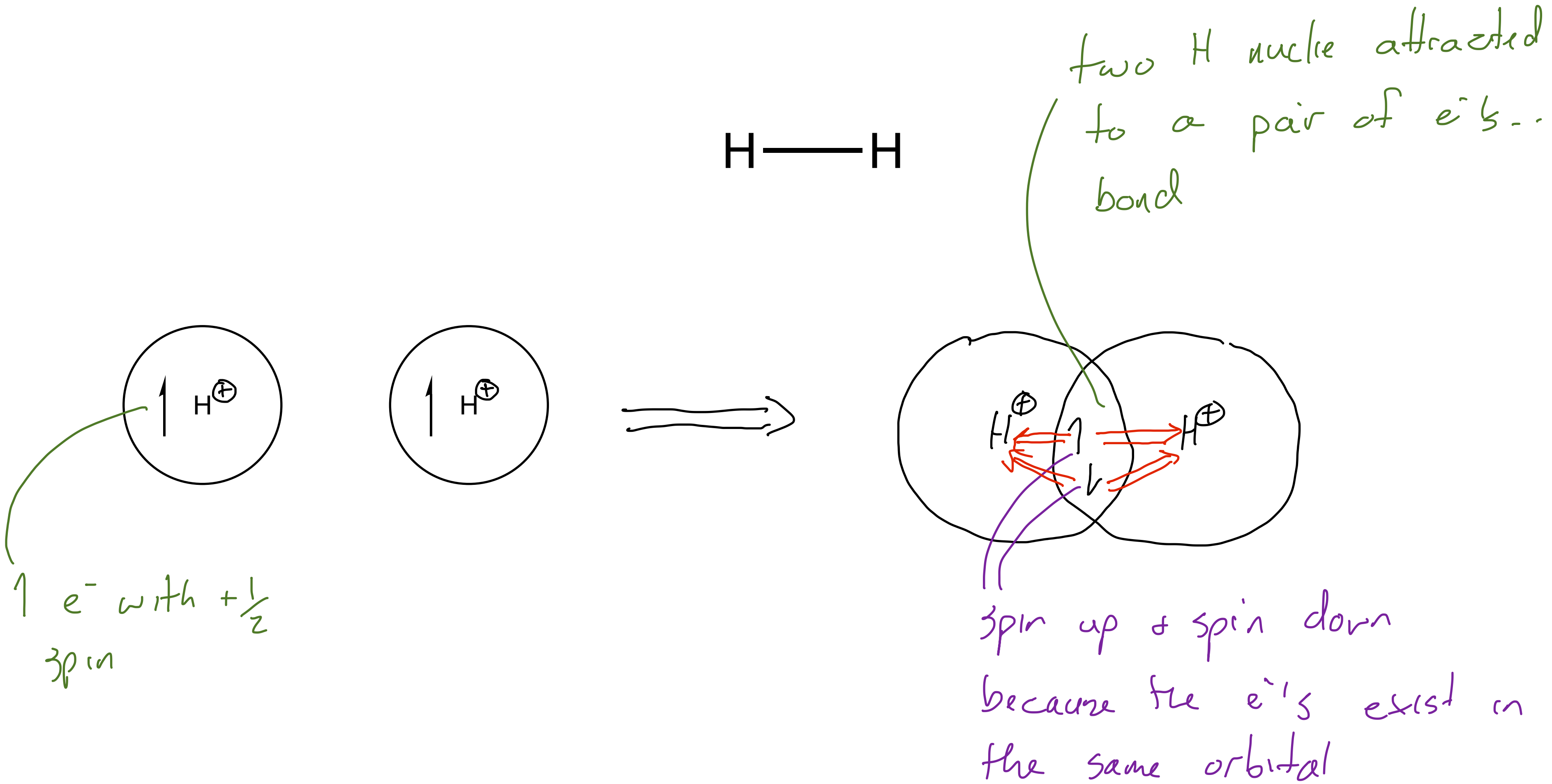
N will tend to make 3 bonds
can make 2 bonds but will be ⊖
can make 4 bonds but will be ⊕

C makes 4 bonds

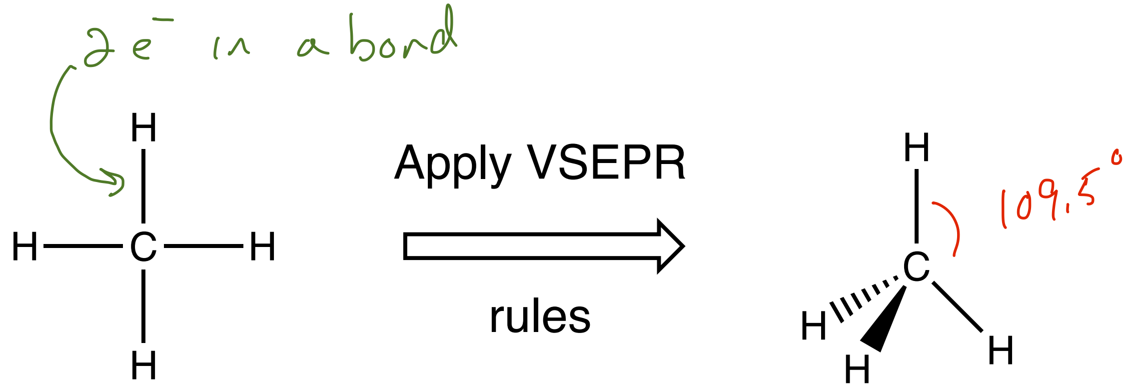
$C{\equiv}N^{\ominus}$ $\qquad C{\equiv}O$

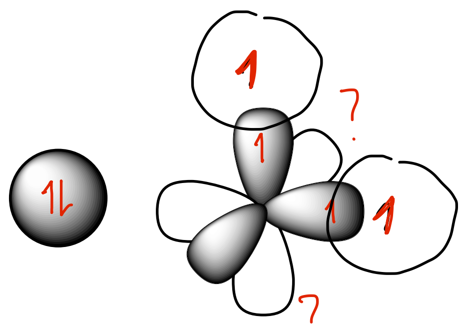
Predict the number of electrons or bonds needed for an element to form a stable compound

$H{-}\ddot{O}{-}H + H^{\oplus} \longrightarrow H_3O^{\oplus}$ $\qquad {}^{\ominus}O{-}H \qquad H{-}O{-}H$ (with H, ⊕)

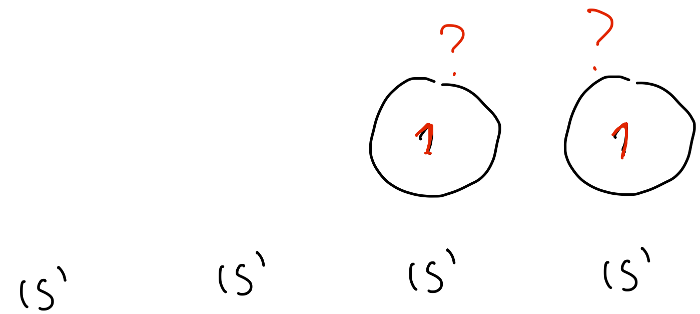


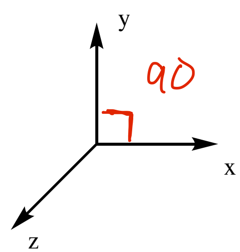

The mutual attraction of two nuclei for a pair of electrons



2s 2px, 2py, 2pz



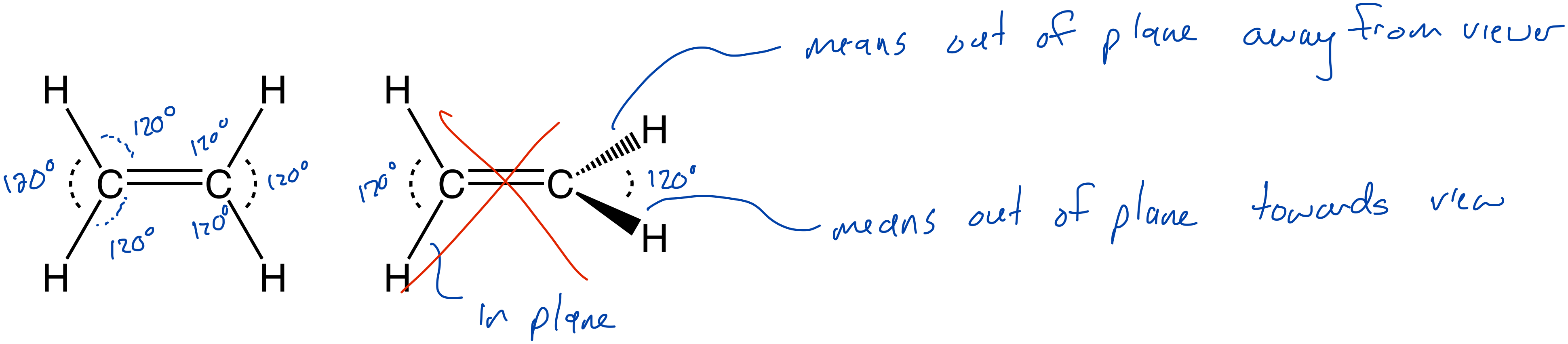




1st problem 2s is full. How do I bond with it?
Do 2 H's bond with empty p?

To get orbitals with the properties we need we are going to mix or hybridize the atomic orbitals to make hybrid orbitals

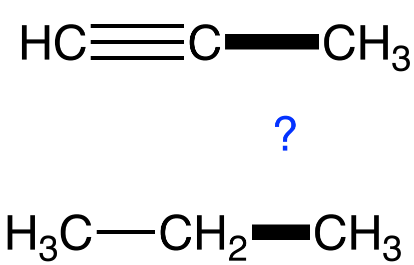
and problem... orbitals are the wrong shape

Wait, what can we use Valance Bond Theory for?

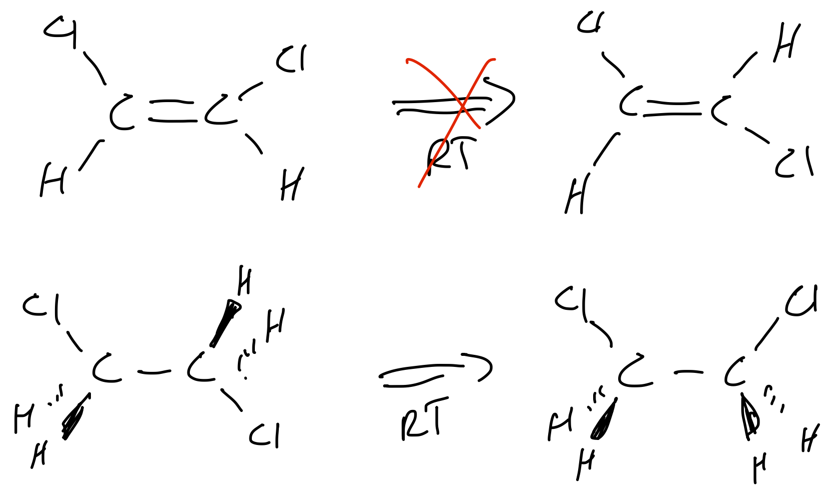



Which one? Both C atoms are trigonal planar

Which bond is stronger?



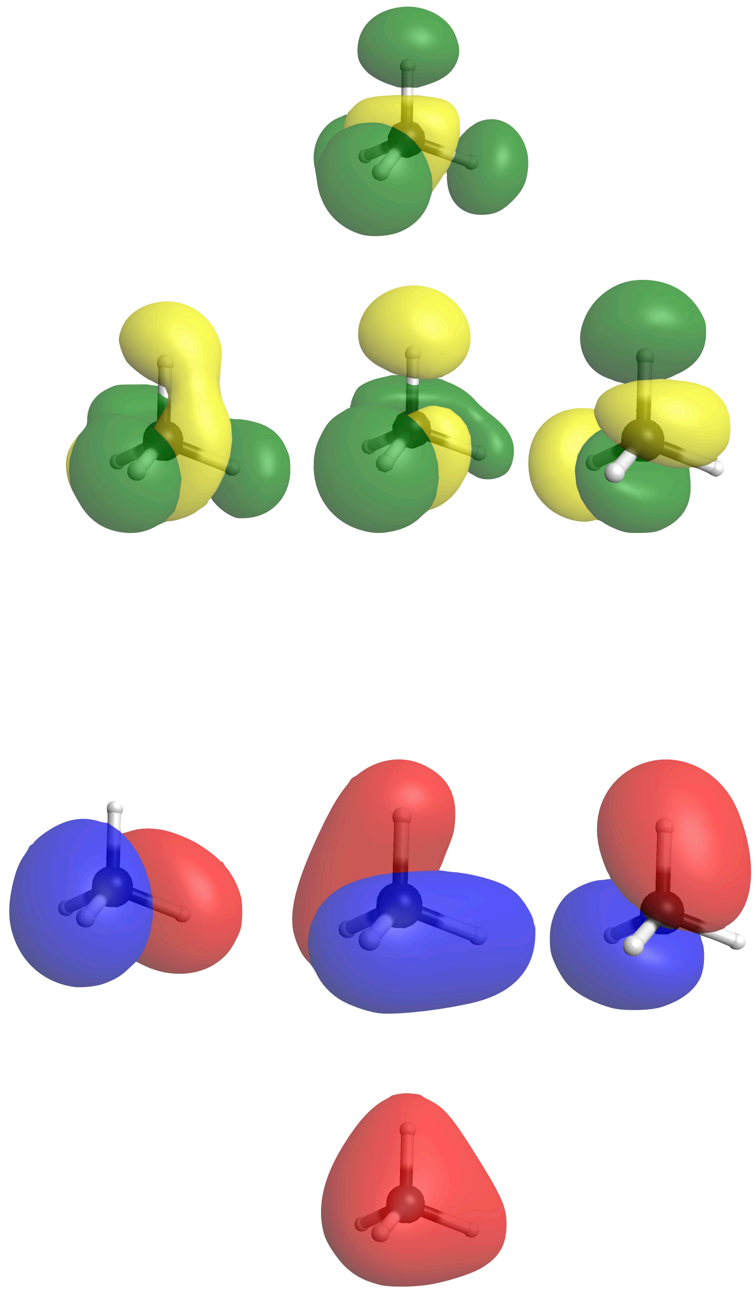

Why is there free rotation around C to C single bonds but not C to C double bonds?




Explain observations and make predictions based on Valence Bond Theory

Just a Reminder that what I just said about orbitals being the "wrong" shape isn't a problem in MO theory





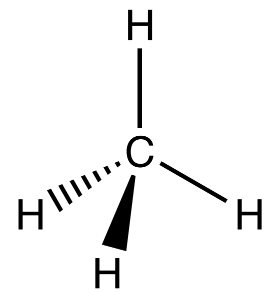
one 2s orbital
and
three 2p orbitals
from
one C atom

four 1s orbitals
from
four H atoms

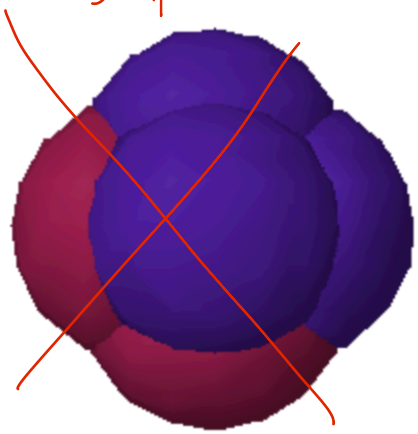
https://www.westfield.ma.edu/cmasi/organic/hybrid/hybrid.html

Identify atoms that use $sp^3$ hybrid orbitals to form bonds and hold lone-pair electrons

$2s + 2p_x + 2p_y + 2p_z \xrightarrow{\text{hybridize}} sp^3, sp^3, sp^3, sp^3$




p orbitals don't have the correct shape . . .



hybrid orbitals do

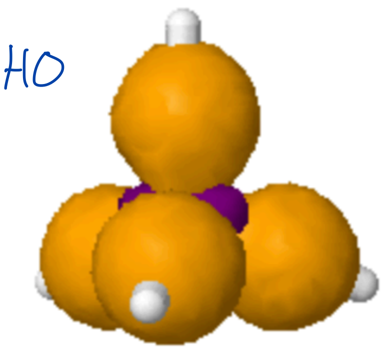
VSEPR says 4 directions

mix 4 AO's to make 4 HO

$2s + 2p + 2p + 2p$

name based on

parts s + parts p

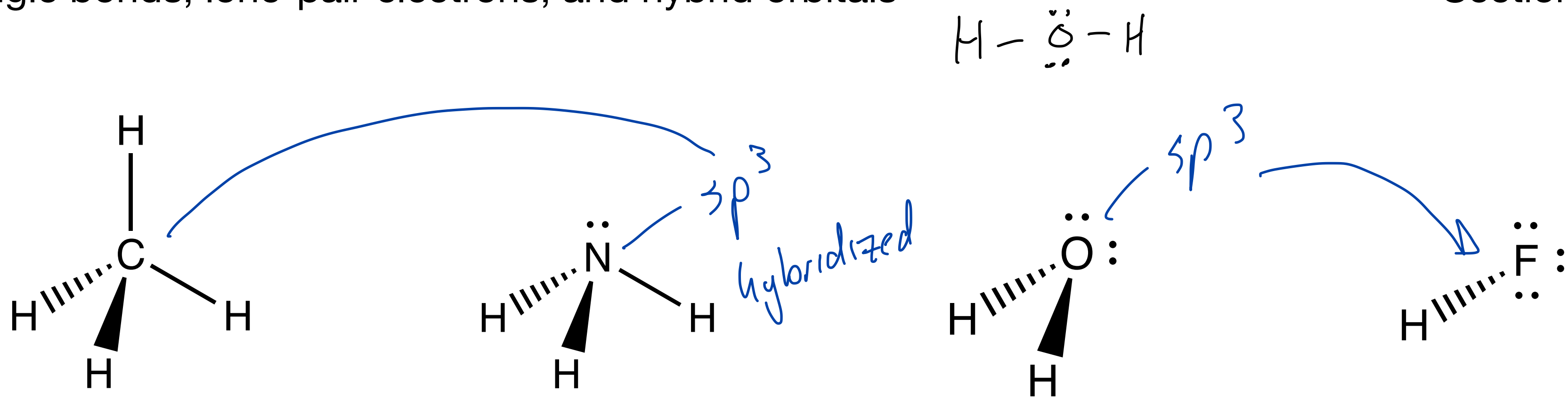


2p ↿ ↿ —

2s ⥮ $\xrightarrow{\text{hybridize}}$ $sp^3$ ↿ ↿ ↿ ↿

https://www.westfield.ma.edu/PersonalPages/cmasi/organic/hybrid/hybrid.html

Identify atoms that use $sp^3$ hybrid orbitals to form bonds and hold lone-pair electrons




| | | | |
|---|---|---|---|
| 4 directions | 4 directions | 4 directions | 4 directions |
| need 4 HO's | need 4 HO's | need 4 HO's | need 4 HO's |
| mix 4 AO | mix 4 AO | mix 4 AO | mix 4 AO |
| starting with | starting with | starting with | starting with |
| s×p×p×p | s×p×p×p | s×p×p×p | s×p×p×p |
| $sp^3$ | $sp^3$ | $sp^3$ | $sp^3$ |

single bonds + lp $e^-$'s go in hybrid orbitals

σ bonds

Identify atoms that use $sp^3$ hybrid orbitals to form bonds and hold lone-pair electrons

hybrid orbitals are used to form σ bonds and to hold lone-pair electrons

in the valence bond model, single bonds are always σ bonds

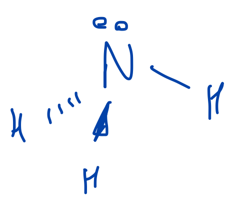
double and triple bonds are formed from σ bonds plus π bonds

3 1 4

# of σ bonds + pairs of lone-pair electrons = # of hybrid orbitals needed

count out the # of atomic orbitals need to make the hybrid orbitals starting with the 2s orbital (or 3s if appropriate)

name the hybrid orbitals $sp^n$ where n is the number of p orbitals used

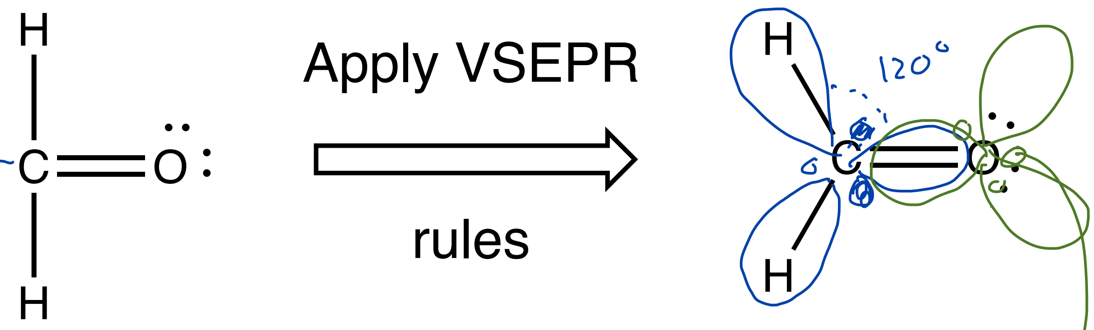



4 AO's needed

mix 4 AO's

$2s + 2p_x + 2p_y + 2p_z$

name 1 parts s 3 parts p => $sp^3$




3 different directions (or 3 σ bonds)

3 HO's needed

2s + 2px + 2py

⇓ hybridize

sp², sp², sp²

2pz not hybridized

3 different directions (or 1 σ bond + 2 sets lp e⁻'s)

3 HO's needed

2s + 2px + 2py

⇓ hybridize

sp², sp², sp²

2pz not hybridized

https://www.westfield.ma.edu/cmasi/organic/hybrid/hybrid2.html

Identify atoms that use hybrid orbitals to form bonds and hold lone-pair electrons

## Triple bonds and sp$^?$ hybridization

Sections 1.5 - 1.10


https://www.westfield.ma.edu/PersonalPages/cmasi/organic/hybrid/hybrid2.html

Identify atoms that use hybrid orbitals to form bonds and hold lone-pair electrons

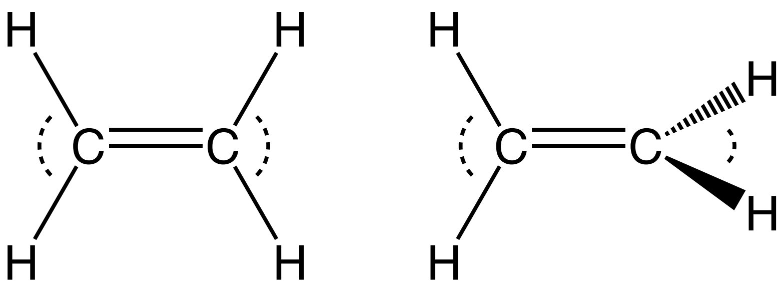
# The methyl cation, anion, and radical



$CH_3^+$ $CH_3^-$ $CH_3^\bullet$

Determine the hybridization of unusual molecular fragments

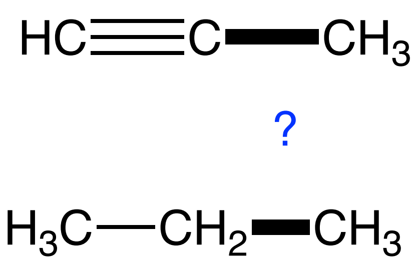
What can we use Valance Bond Theory for?



Which one? Both C atoms are trigonal planar

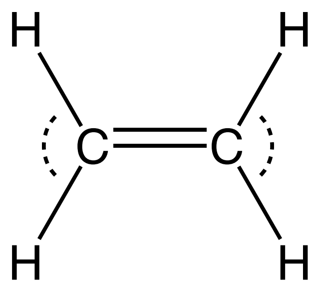
Why is there free rotation around C to C single bonds but not C to C double bonds?

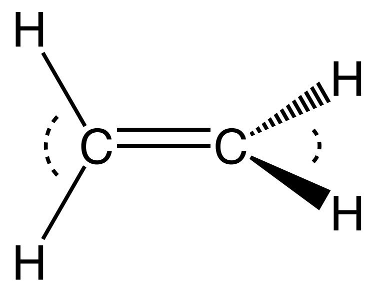
Which bond is stronger?




Explain observations and make predictions based on the hybridization of an atom

What can we use Valance Bond Theory for?




Which one? Both C atoms are trigonal planar

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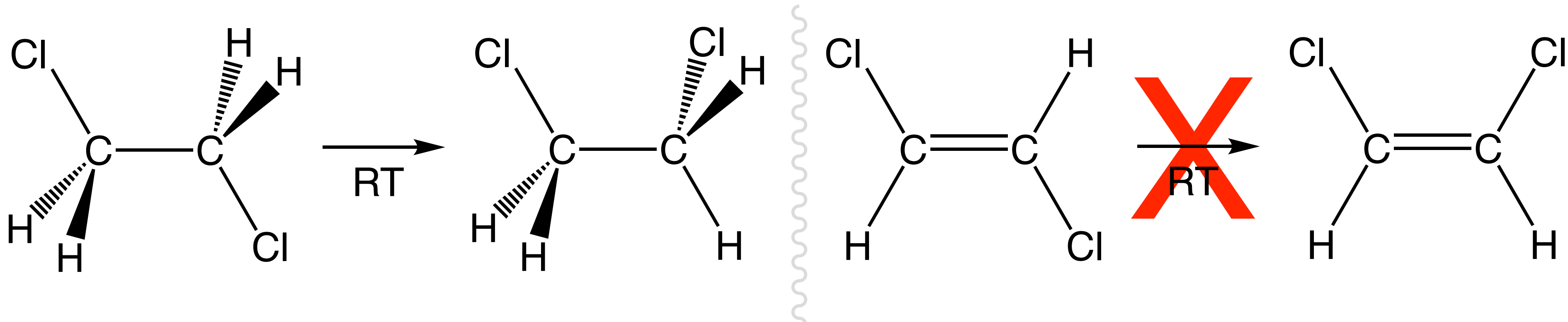
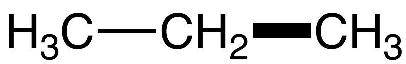



Explain observations and make predictions based on the hybridization of an atom

What can we use Valance Bond Theory for?

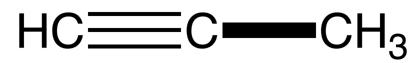
Which bond is strongest?

370 kJ/mol[2], 355±8 kJ/mol[3]



426 kJ/mol[1]

490 kJ/mol[4]

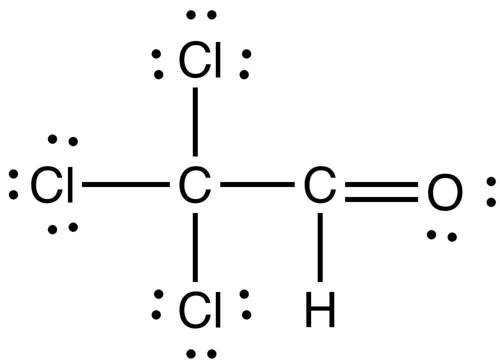


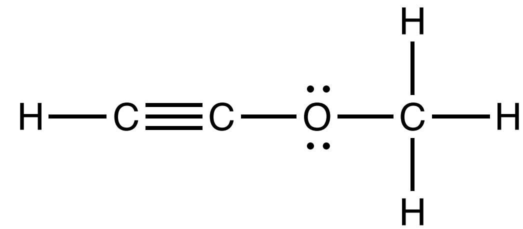
[2] Organic Chemistry, 10th ed. McMurry.

[3] Chem. Rev. **66**, 465 (1966).

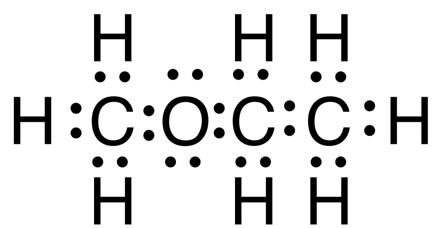
[4] J.Chem.Ed. **42**, 502 (1965)

# Practice





$$N \equiv C - CH_2 - NH_2$$



Chemists use different drawings to place emphasis on different aspects of a molecule.

Representations are used to solve typographical issues.

# Molecular Formulas as Compared to Condensed Structures/Structural Formulas



In organic, molecular formulas are written $C_xH_y$(and other elements listed alphabetically)

$C_3H_8O$

In organic, condensed structures typically start with a C, and everything immediately to the right of the C is connected to that first C. When the the first C is finally connected to the second C, now that atoms right of the second C are connected to second C. In acyclic unbranched molecules atoms to the right of the second C are not connected to the first C.

$C_3H_8O$ $CH_3CH_2OCH_3$ $CH_3CH_2CH_2OH$ $CH_3CHOHCH_3$

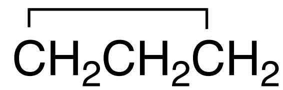
In organic, condensed structures typically start with a C, and everything immediately to the right of the C is connected to that first C. When the the first C is finally connected to the second C, now that atoms right of the second C are connected to second C. In acyclic unbranched molecules atoms to the right of the second C are not connected to the first C.

$CH_2CHCH_3$

Because bonds are not drawn, condensed structures require the reader to bring some chemical knowledge to their interpretation.

# Condensed Structures/Structural Formulas: Cyclic Molecules

Section 1.12



$CH_3CH(OH)CH_2CH_3$ $CH_3(CH_2)_3CH_3$ $CH_3CH_2CH(CH_3)_2$

Parentheses **( )** in structures are typically used to set off side chains, to indicate a repeating unit, or to indicate multiple groups of the same structure.

Often, chemists omit parentheses when they are not absolutely necessary,

$CH_3(CH_2)_3CH_3$

$CH_3CHOHCH_3$

$CH_3CH(OH)CH_3$

$CH_3COCH_2CH_3$

$CH_3C(O)CH_2CH_3$

and sometimes chemists do things for aesthetic reasons.

$C(CH_3)_3OH$ $CH_3C(CH_3)_2OH$ $(CH_3)_3COH$

# Convert Condensed Structures to Kekulé Structures



$CH_3CHOHCH_2CH_3$

$CH_3C(O)CH(CH_3)_2$

$CH_3CHO$

When a bond ends and the atom isn't labeled it is assumed to be C.

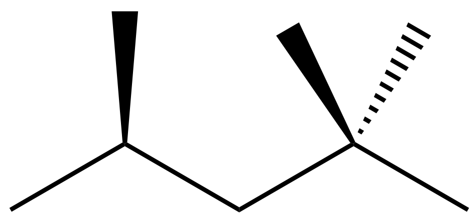
When there aren't enough bonds drawn to a C atom, the "missing" bonds are C atom to H atom bonds.

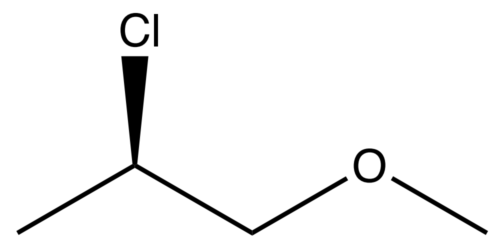
All other atoms are labeled.

Heptane

2-heptanol

Different structures serve different purposes, but they represent the same things






$CH_3CH(OH)CH_2CH(CH_3)CH_2CH_3$