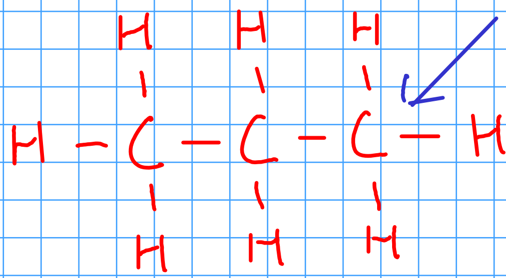
VSEPR and large molecules

- Large molecules have more than one "center" atom

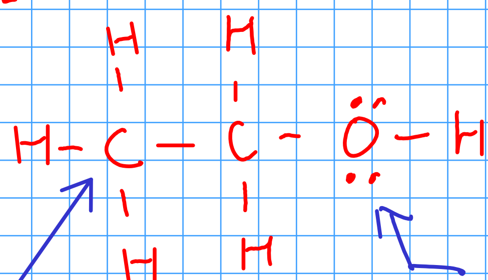
- Describe the molecule by describing the shape around each "center".

C_3H_8:



Each of the three carbon centers is TETRAHEDRAL, since each are surrounded by four groups.

CH_3CH_2OH:



The geometry around this oxygen atom is BENT.

These carbon atoms have TETRAHEDRAL geometry.

POLARITY and shape:

- A polar molecule has an uneven distribution of electron density, making it have ends (poles) that are slightly charged.

POLARITY influences several easily observable properties.

- Melting point. (Polar substances have higher melting points than nonpolar substances of similar molecular weight.)
- Boiling point. (Polar substances have higher boiling points than nonpolar substances of similar molecular weight.)
- Solubility. (Polar substances tend to dissolve in other polar substances, while being insoluble in nonpolar substances. Nonpolar substances dissove other nonpolar substances, and generally have poor solubility in polar solvents.)

- Polar molecules contain POLAR BONDS arranged in such a way that they do not cancel each other out.

... but how can we tell whether or not a bond will be POLAR? Use experimental data on ELECTRONEGATIVITY!

ELECTRONEGATIVITY:
-A measure of how closely to itself an atom will hold shared electrons

- A bond where there is a LARGE electronegativity difference between atoms will be either POLAR or (for very large differences) IONIC!

- A bond with little or no electronegativity difference between atoms will be NONPOLAR

ELECTRONEGATIVITY TRENDS (AGAIN!)

- You may look up elecronegativity data in tables, but it helps to know trends!

INCREASING ELECTRO-NEGATIVITY

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA
2	Li	Be											B	C	N	O	F
3	Na	Mg											Al	Si	P	S	Cl
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
6	Cs	Ba	* ~~La~~	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
7	Fr	Ra	* ~~Ac~~	Rf	Db	Sg	Bh	Hs	Mt								

*"inner" transition metals go here

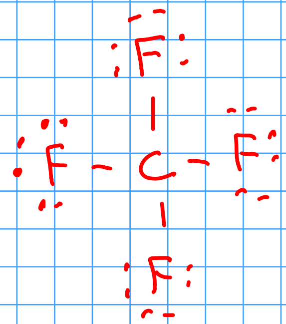
Notes:

1. - FLUORINE is the most elecronegative element, while FRANCIUM is the least!
2. - All the METALS have low electronegativity, and metal/nonmetal combinations form IONIC bonds
3. - HYDROGEN is similar in electronegativity to CARBON, so C-H bonds are considered NONPOLAR

Examples:

CF_4:

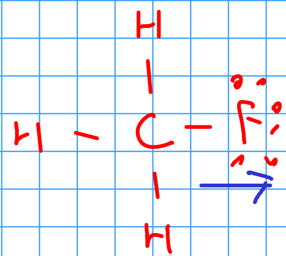
C : 4
F : 7 x4
32



Polar or nonpolar?
* Polar bonds? YES. C-F should be polar
* Geometry? C-F bonds are arranged symmetrically. They cancel each other, so the molecule is NONPOLAR!

CH_3F

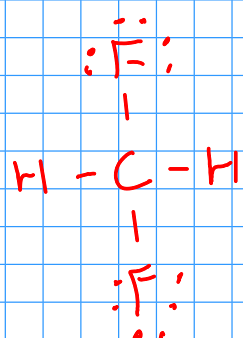
C : 4
H : 1 x3
F : 7
14



Polar or nonpolar?
* Polar bonds? YES. C-F should be polar, C-H is nonpolar.
* Geometry? Electrons are pulled towards FLUORINE, making this a POLAR molecule.

CH_2F_2.

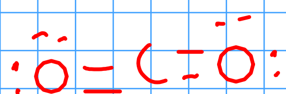
C 4
H 1 x2
F : 7 x2
20



Polar or nonpolar?
* Polar bonds? YES, C-F are polar, C-H are nonpolar.
* Geometry: In 3D, this molecule has a hydrogen side and a fluorine side. Electrons will be pulled towards FLUORINE, making the molecule polar.

CO_2

C : 4
O : 6 x2
16



Polar or nonpolar?
* Polar bonds? YES, C=O should be polar.
* Geometry? Linear - one C=O cancels the other, so NONPOLAR.

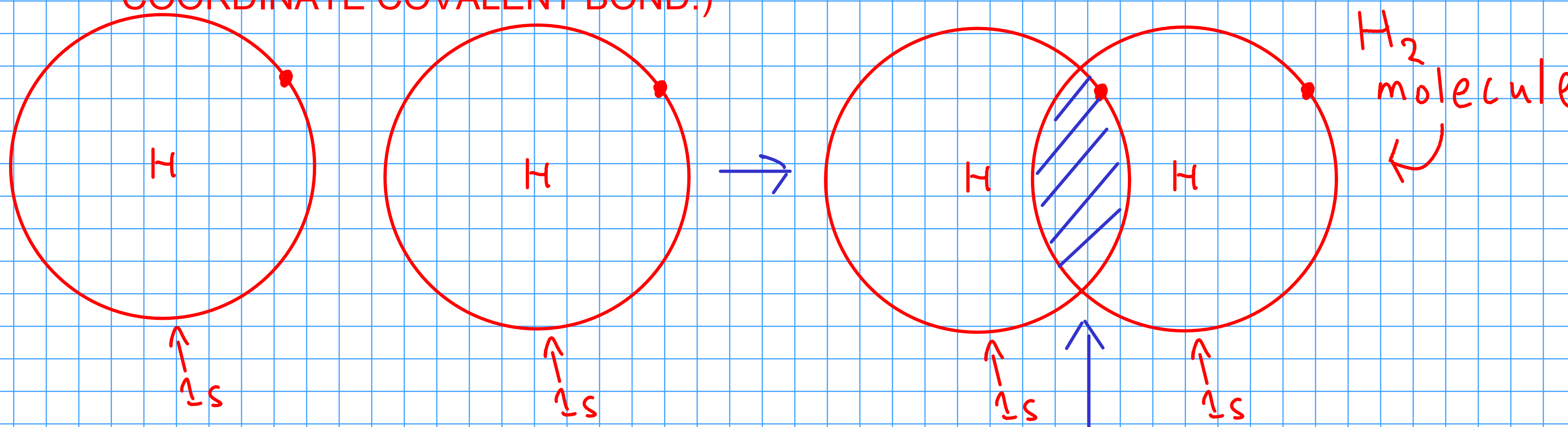
VALENCE BOND THEORY

- an attempt to explain why molecules behave in the way that the VSEPR model predicts.

- Describes the formation of bonds in terms of the OVERLAP of ORBITALS from the bonding atoms.

1. Bonds are formed when two atoms are close enough together so that their ORBITALS OVERLAP (share the same space).

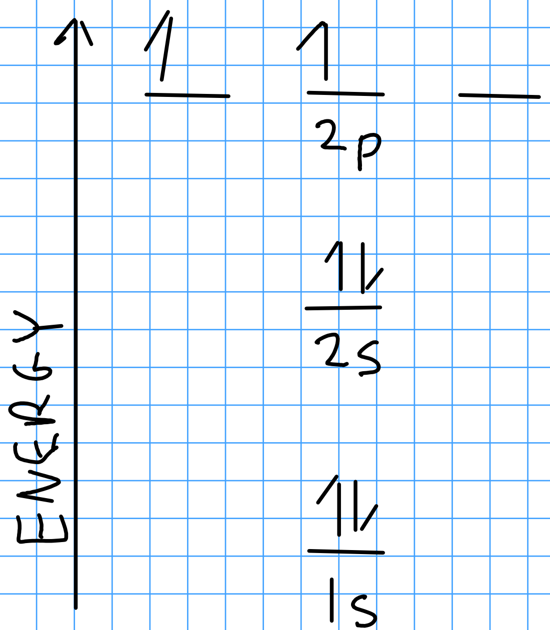
2. Each SET of overlapping orbitals can contain at most a total of TWO electrons. So, two orbitals with one electron each may bond. An orbital with two electrons can only bond with an EMPTY orbital (This is called a COORDINATE COVALENT BOND.)



These 1s orbitals overlap to form what we call a "sigma bond" with overlap BETWEEN the two atomic nuclei.

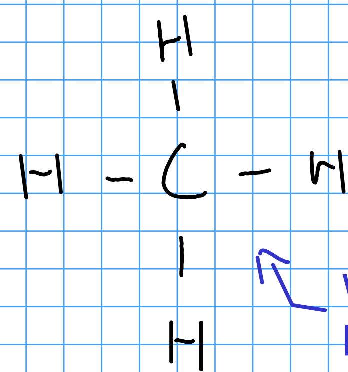
Hybridization

- Look at carbon's electron configuration:



You would expect that carbon would form several different kinds of bonds in a molecule like methane. But, methane's bonds are experimentally all identical. How does carbon form the four equivalent C-H bonds we see in methane?

CH_4 :

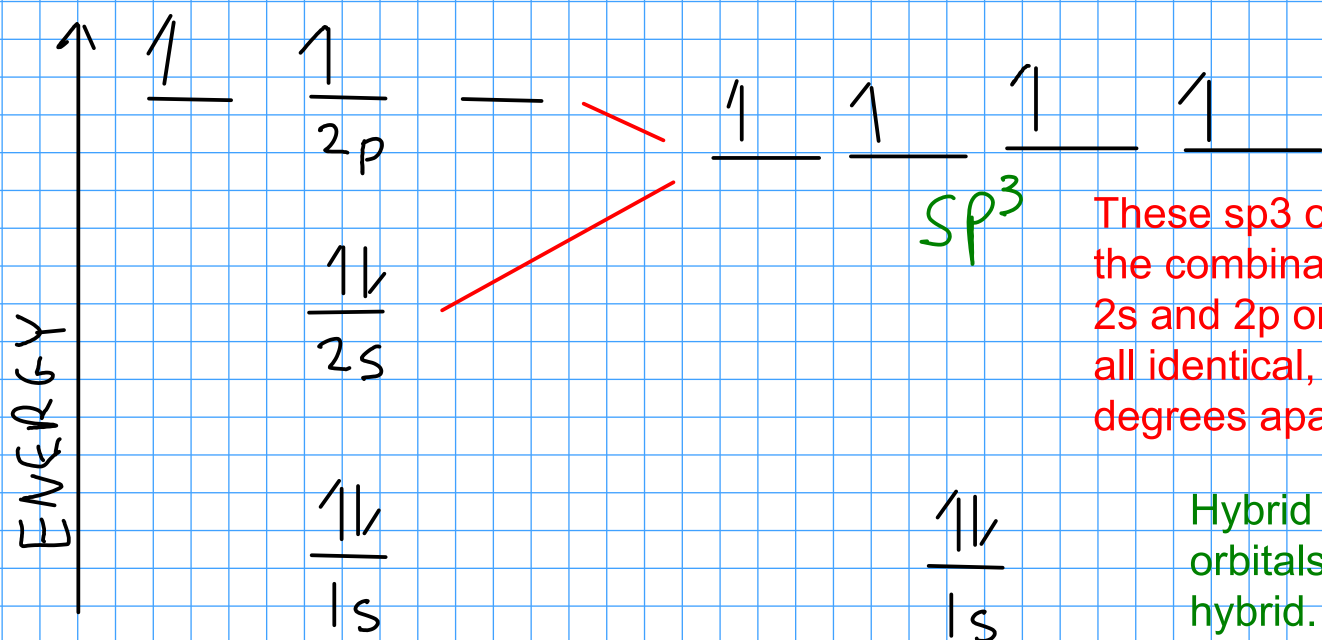


We observe that these bonds are IDENTICAL! Same bond energy, distance, and angle.

- In valence bond theory, atomic orbitals can COMBINE to make new orbitals that can then go on to bond with other molecules.

- When orbitals combine to make HYBRID ORBITALS, ...

1. The overall NUMBER OF ORBITALS does not change.
2. The overall NUMBER OF ELECTRONS around the atom does not change
3. The energy of the orbitals is between the energies of the orbitals that combine.



These sp3 orbitals were formed from the combination of carbon's original 2s and 2p orbitals. These orbitals are all identical, and are spread 109.5 degrees apart from one another.

Hybrid orbitals are named from the orbitals that go into making the hybrid. 2s + 3 2p orbitals = "sp3"!

Types of hybrid orbitals:

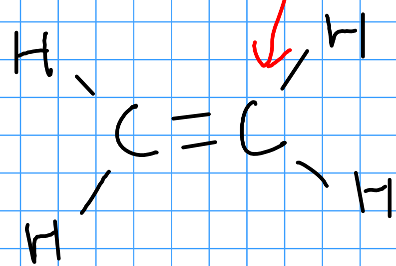
Hybrid type	Number of orbitals	Molecular shape
sp	2	linear
sp2	3	trigonal planar
sp3	4	tetrahedral (or derivatives)
sp3d	5	trigonal bipyramidal (or derivatives)
sp3d2	6	octahedral (or derivatives)

MULTIPLE BONDS and VALENCE BOND THEORY

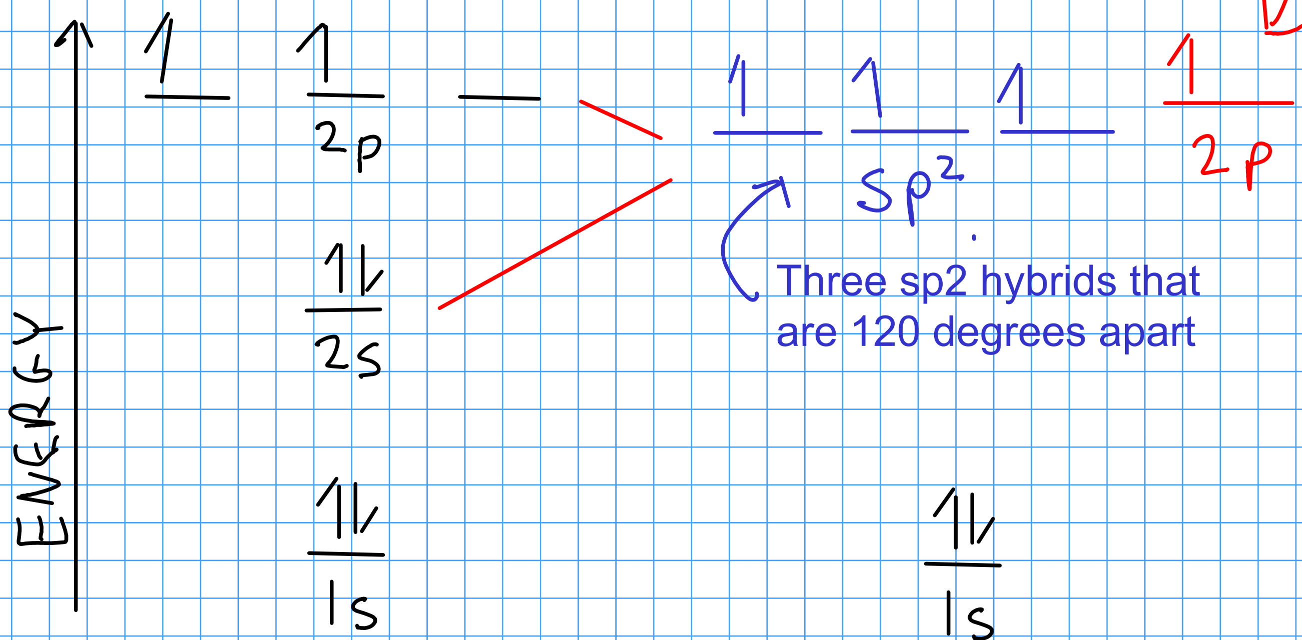
- Valence bond theory provides an explanation of multiple (double and triple) bonding that explains some interesting observations about these kinds of bonds.

C_2H_4:

ethylene

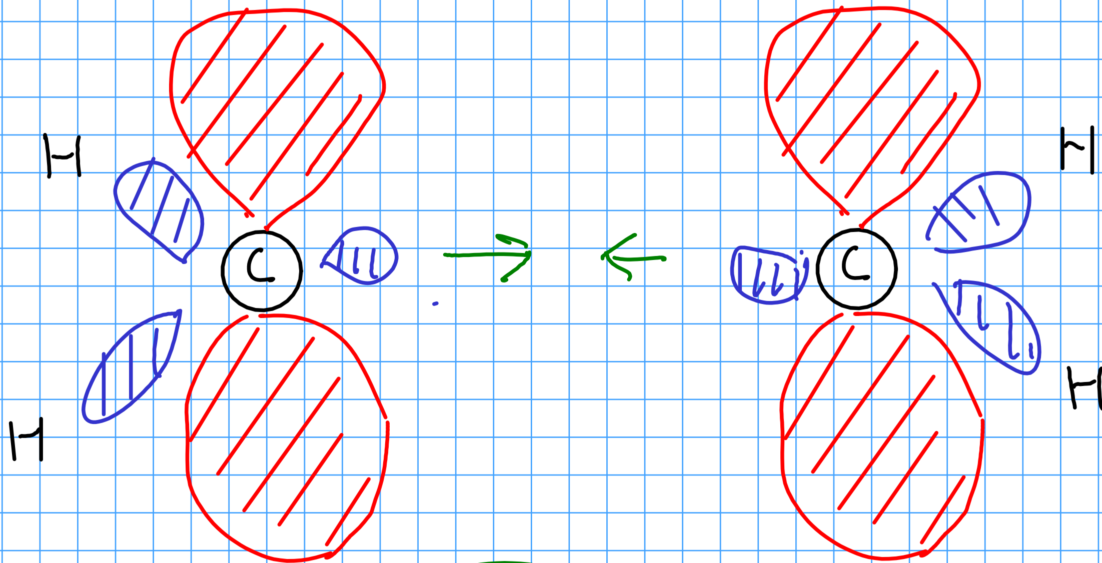


Each carbon has a TRIGONAL PLANAR geometry. This suggests that the carbons are "sp2 hybridized".



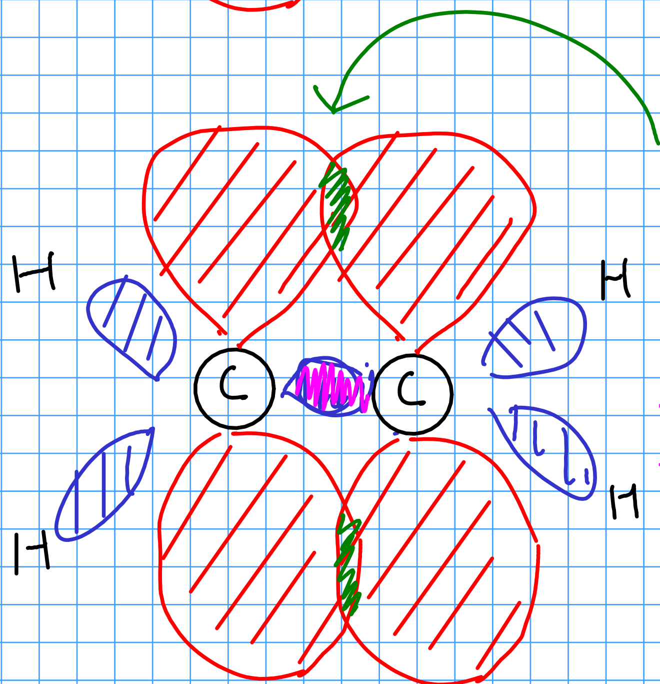
Three sp2 hybrids that are 120 degrees apart

One unchanged 2p orbital



sp2 hybrid orbitals in BLUE

2p orbital in RED



The 2p orbitals overlap above and below the axis between the two carbon atoms. This OFF-AXIS overlap is called a PI BOND.

The sp2 hybrid orbitals overlap ON THE AXIS between the two carbon atoms. This bond is called a SIGMA BOND.

As you can see, the carbon-carbon double bond in ethylene is made up of TWO DIFFERENT KINDS OF BONDS!

Some notes on sigma and pi bonds:

1. SIGMA bonds are formed when orbitals overlap along the axis between two atoms. These bonds have good overlap between the bonding orbitals, meaning that they are strong. Single bonds are always sigma bonds. Double and triple bonds contain one sigma bond each.

2. PI bonds are formed when off-axis orbitals (usually p orbitals) overlap. Since the overlapping orbitals do not face each other as in the sigma bond, the overlap in pi bonds tends to be poorer than in sigma bonds.* As a result, pi bonds tend to be weaker than sigma bonds. Double bonds contain a single pi bond, and triple bonds contain two pi bonds.

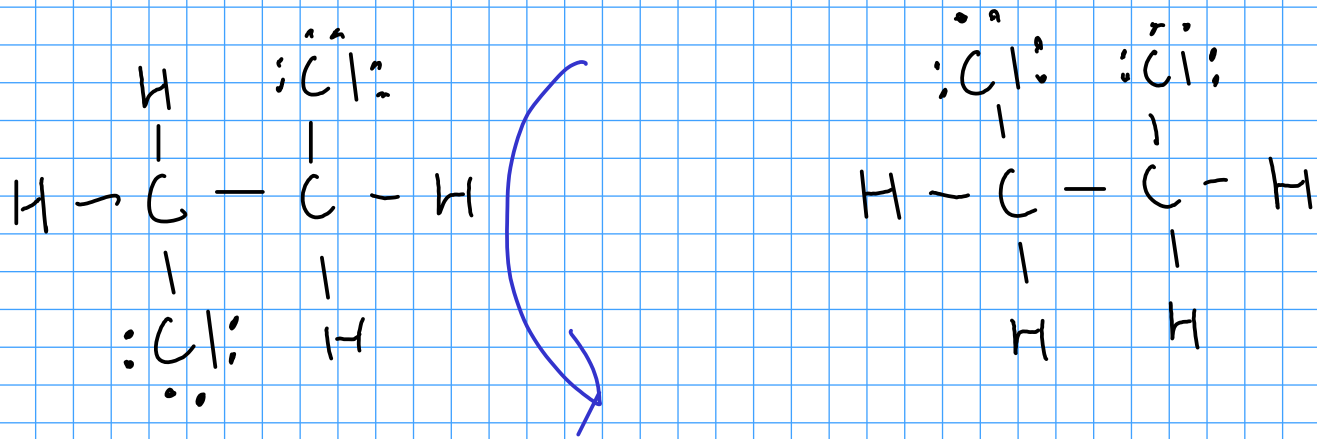
> *Experimentally, we observe that the bond energy of the C=C bond is less than the bond energy of two C-C bonds. This suggests that the second bond in a double bond is different from the first!

3. Molecules may rotate around SIGMA bonds, since rotation around the axis between two atoms will not affect the overlap and break the bond. Off-axis PI BONDS prevent rotation because rotation would break the pi bond.

ROTATION, ISOMERS, and VALENCE BOND THEORY

- Consider this molecule: $(CH_2Cl)_2$

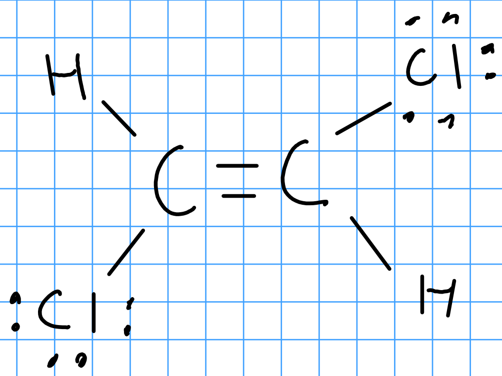
"1,2-dichloroethane"

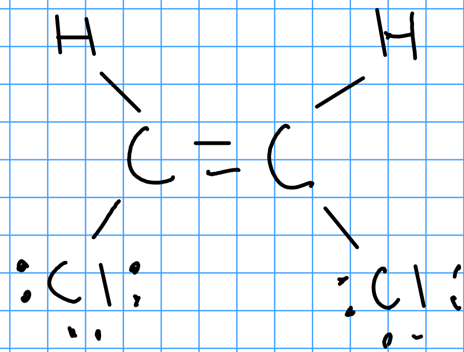


... are these two structures different?

No! The molecule is free to rotate around the C-C single (sigma) bond, and we do not observe two different versions of 1,2-dichloroethane. Both of the forms drawn above are equivalent.

... now consider "1,2-dichloroethene": $(CHCl)_2$

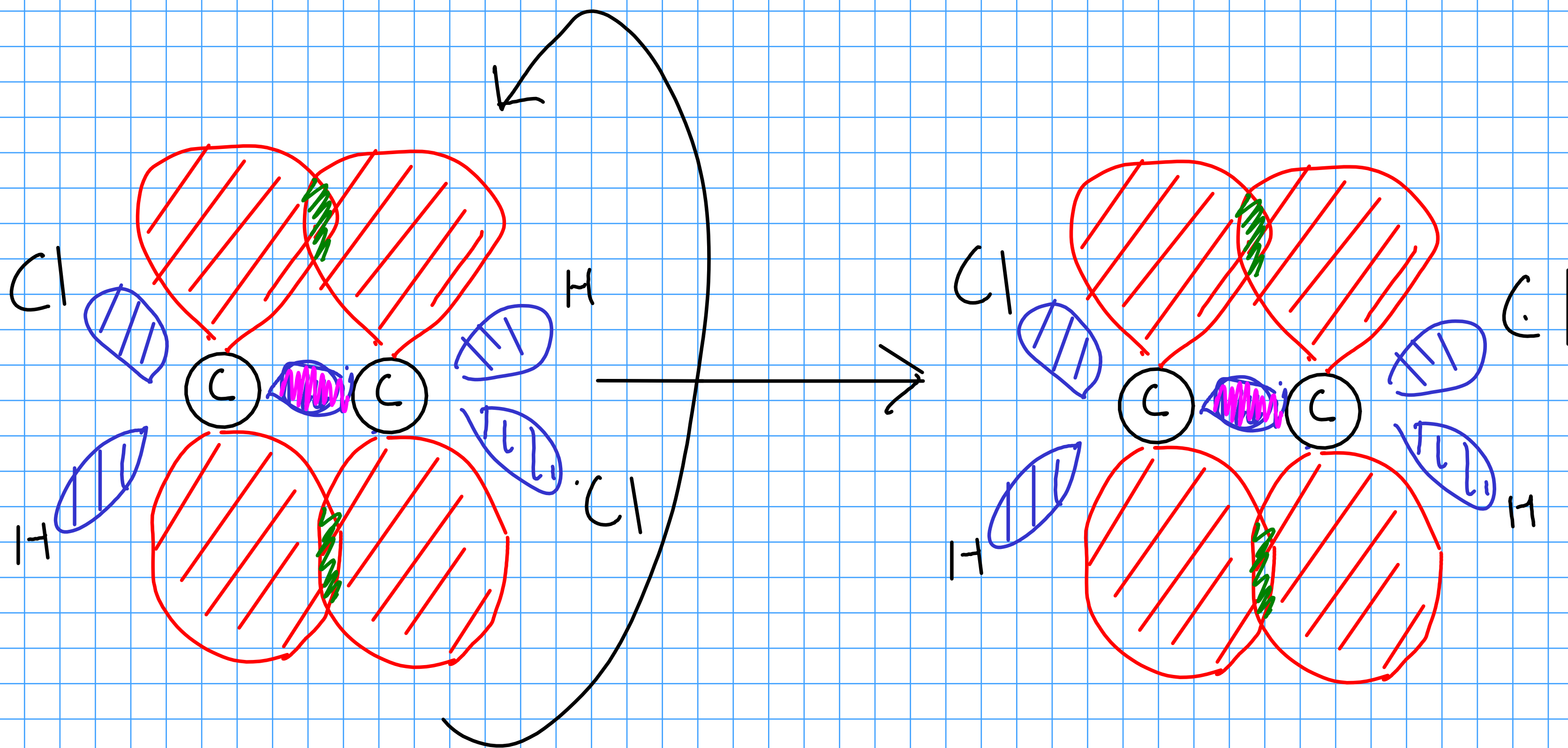




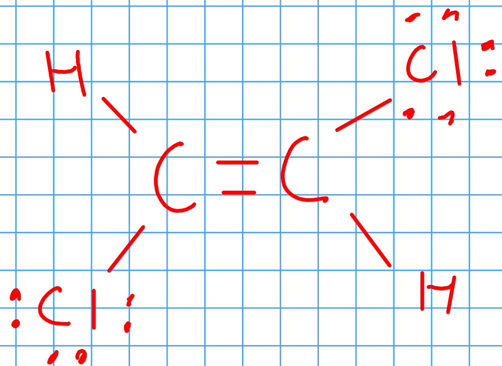
... are these two structures different?

YES! The two carbon atoms in these structures are held together by a DOUBLE BOND, which contains a pi bond. The molecule cannot rotate around the C=C double bond without breaking the pi bond, so the form with the two chlorine atoms on opposite sides cannot freely flip over to the form with the chlorine atoms on the same side.

These two Lewis structures actually represent DIFFERENT MOLECULES. They are called ISOMERS, since they have the same chemical formula but different arrangements of atoms.



For this rotation to take place, the PI BOND must break and then re-form!

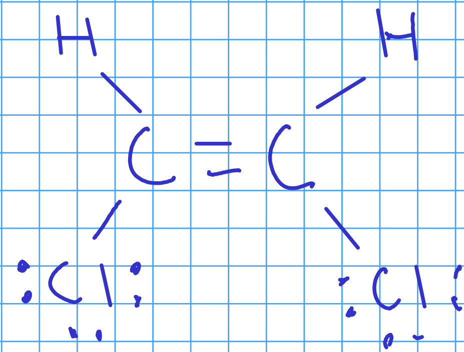


trans 1,2-dichloroethene

BOILING POINT: 47.5 C

POLARITY: NONPOLAR (0 D dipole moment)

DENSITY: 1.26 g/mL



cis 1,2-dichloroethene

BOILING POINT: 60.3 C

POLARITY: POLAR (1.9 D dipole moment)

DENSITY: 1.28 g/mL

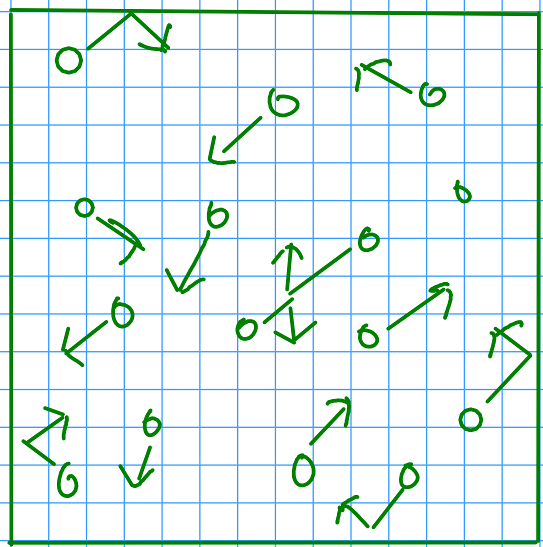
* As you can see, some of the properties of these two molecules are very different! The pi bond (part of the double bond) in each of these molecules makes conversion of one of the molecules to the other require a chemical reaction instead of a simple rotation.

* Double (and triple) bonds prevent rotation and "fix" the structure of a molecule. This is easily explained by valence bond theory!

SOLIDS AND LIQUIDS

- Here's a brief review of the atomic picture or gases, liquids, and solids

GASES



kinetic theory says...

* Gas molecules are small compared to the space between them.

* Gas molecules move in straight lines until they hit another gas molecule or the walls of the container.

* There are no attractive or repulsive forces between gas molecules except during a collision.

* When gas molecules collide, energy may be transferred, but no energy is lost as heat.

* The temperature of a gas is proportional to the average kinetic energy of the gas molecules.

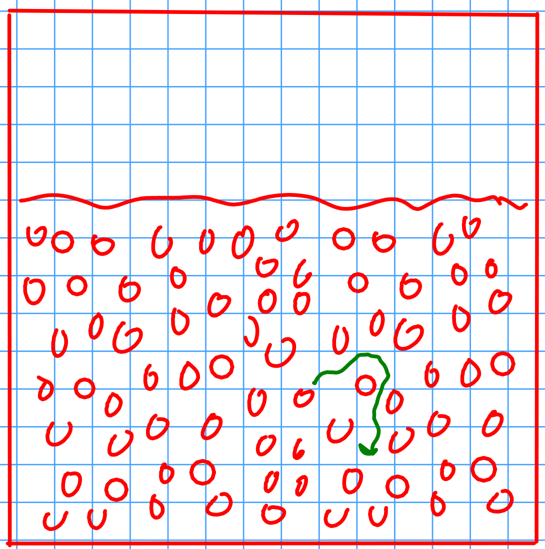
K.E. depends on speed.

Gases are FLUID, COMPRESSIBLE, and DIFFUSE (NOT DENSE)!

variable volume!

- The properties of different gases are very similar to one another. At moderate conditions, different gases obey the simple IDEAL GAS EQUATION.

LIQUIDS



* Molecules are much closer together than in the gas phase.

* Molecules are free t omove around each other, but there is much less freedom of motion than in the gas phase

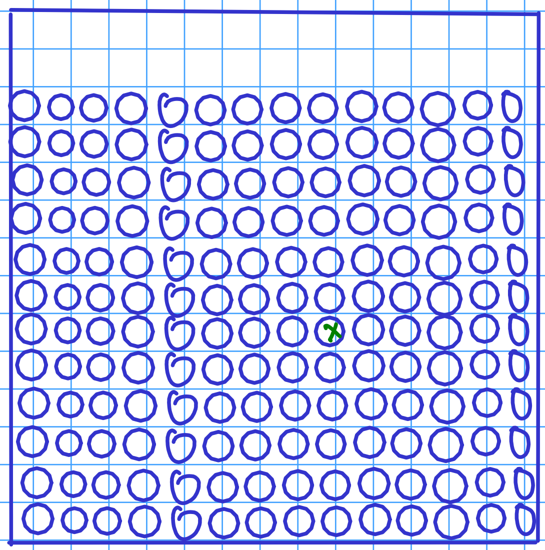
* Molecules in the liquid state are held together by attractive forces that we will call INTERMOLECULAR FORCES

Liquids are FLUID, DENSE, and INCOMPRESSIBLE!

fixed volume!

- The properties of different liquids are often very different from one another, Compare liquids like water and motor oil, which are different enough so that they won't readily mix with one another!

SOLIDS



* Molecules are usually packed closer together in the solid phase than in the gas or liquid phases.

* Molecules are not free to move around each other as in the liquid phase. Molecular/atomic motion in the solid phase is limited to vibration.

* Most solids have a regular structure - unlike liquids or gases. This structure is called a CRYSTAL LATTICE.

* Molecules are held together by INTERMOLECULAR FORCES. These are usually stronger than in the liquid phase.

Solids are RIGID, DENSE, and INCOMPRESSIBLE!

- As for the liquids, the properties of different solids often differ considerably. Compare a sample of candle wax to a sample of quartz.