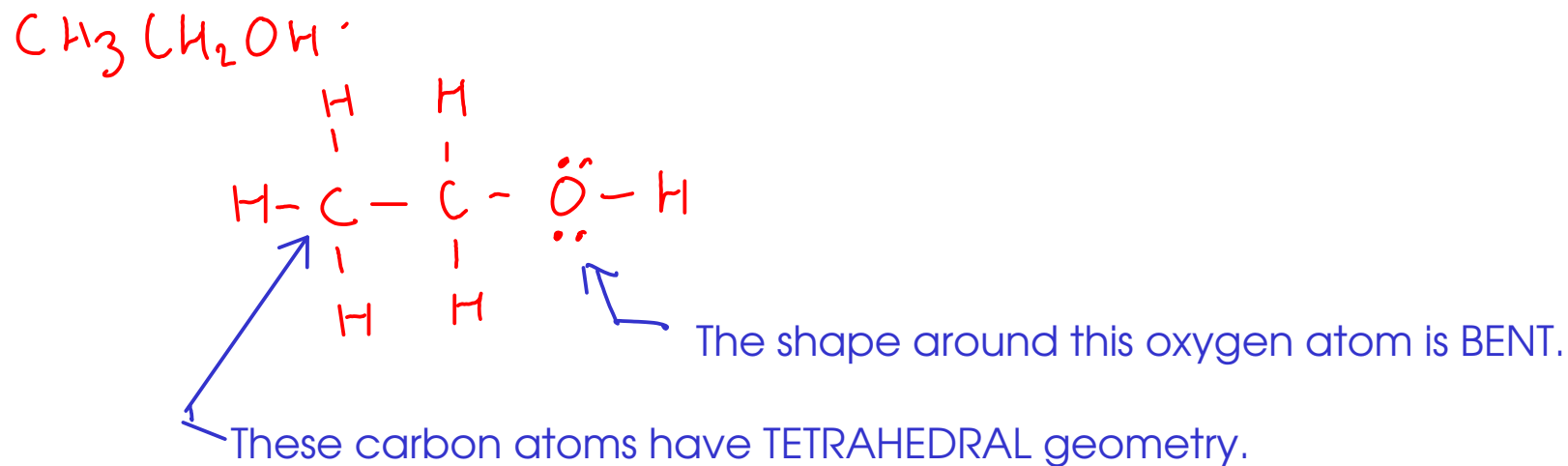
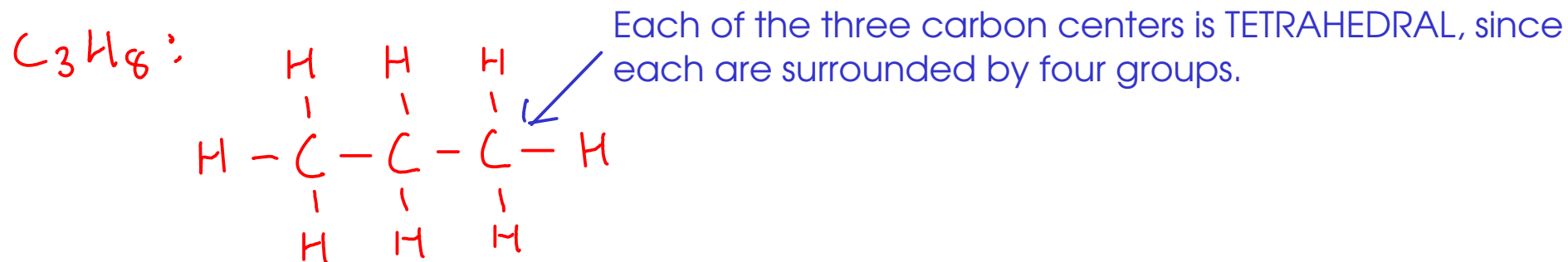
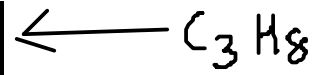
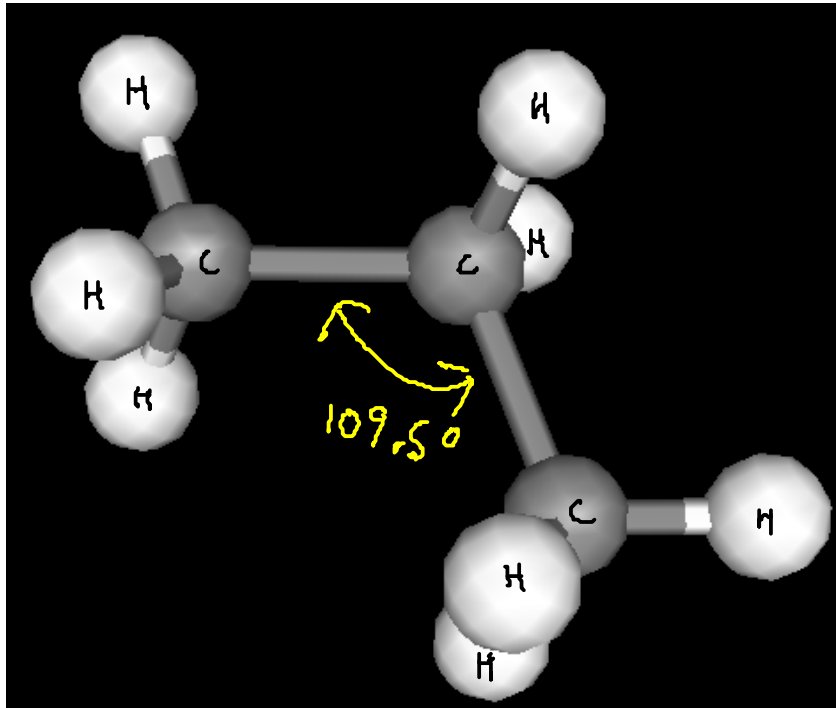


12
VSEPR and large molecules

- Large molecules have more than one "center" atom
- Describe the molecule by describing the shape around each "center".

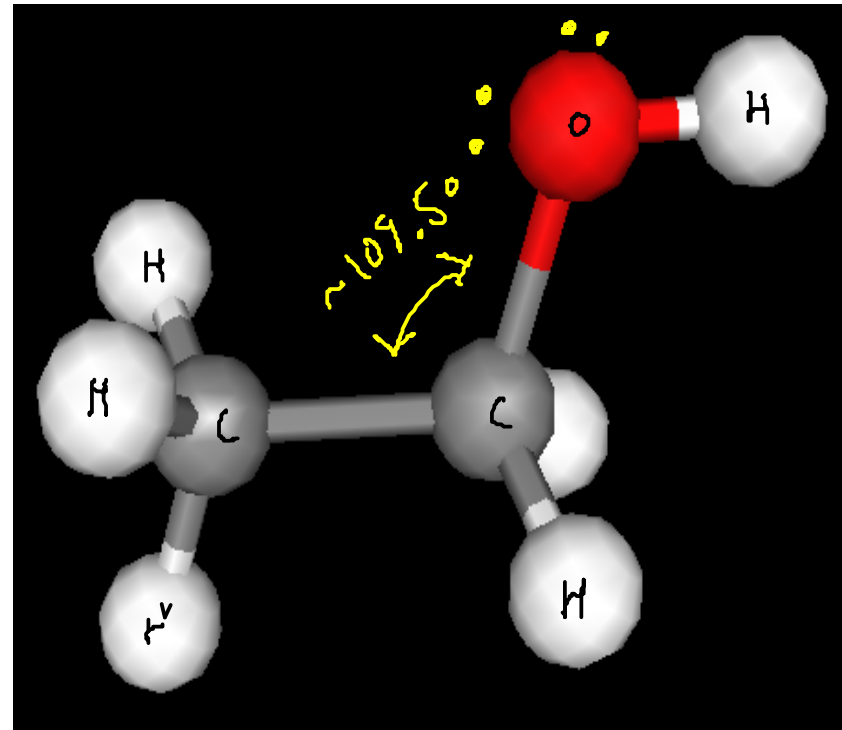




All bond angles in the propane molecule are 109.5 degrees



Like propane, the bond angles in ethanol are also close to 109.5 degrees.



14 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 dissolve 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! { chart, p 352 }

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

ELECTRONEGATIVITY TRENDS

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

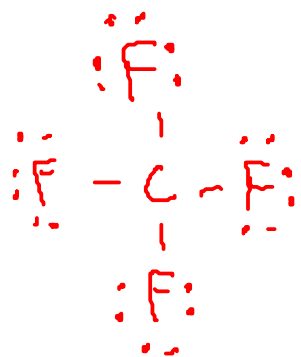
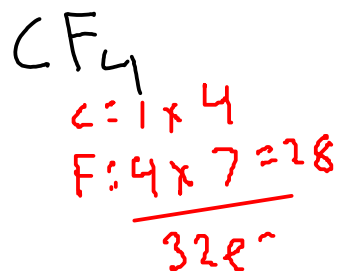
INCREASING
ELECTRO-
NEGATIVITY

	IA	IIA											IIIA	IVA	VA	VIA	VIIA
2	Li	Be											B	C	N	O	F
3	Na	Mg	IIIB	IVB	VB	VIB	VII B	VIII B	IB	IIB			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 electronegative 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

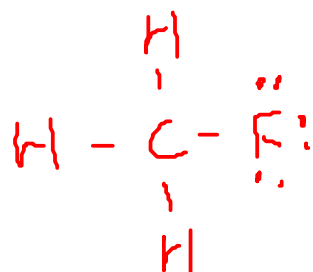
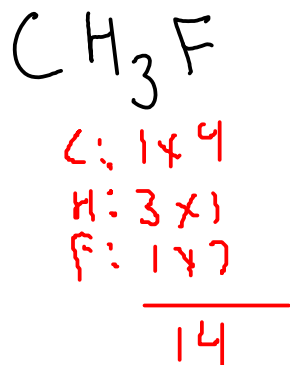
Examples:



Polar molecule?

POLAR BONDS? YES - C-F bonds should be polar due to the electronegativity difference between C and F.

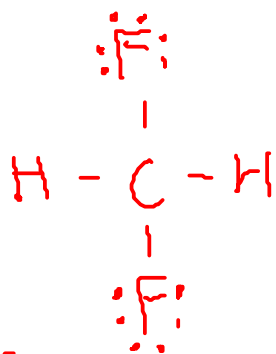
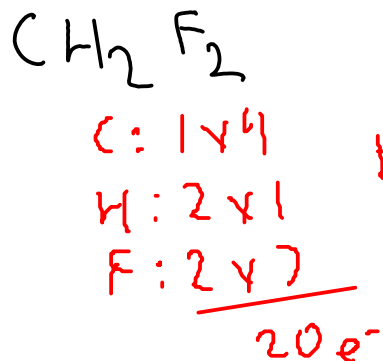
GEOMETRY? TETRAHEDRAL. The molecule is symmetric - there's no positive side and no negative side, so the molecule is NONPOLAR.



Polar molecule?

POLAR BONDS? YES - C-F bonds should be polar due to the electronegativity difference between C and F. But C-H bonds are NONPOLAR..

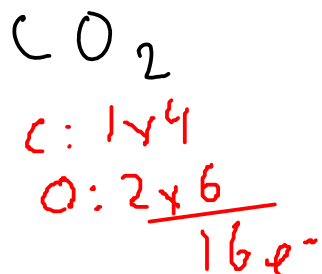
GEOMETRY? TETRAHEDRAL. Fluorine will pull electrons to its side of the molecule, making the molecule polar.



Polar molecule?

POLAR BONDS? YES - C-F bonds should be polar due to the electronegativity difference between C and F. But C-H bonds are NONPOLAR..

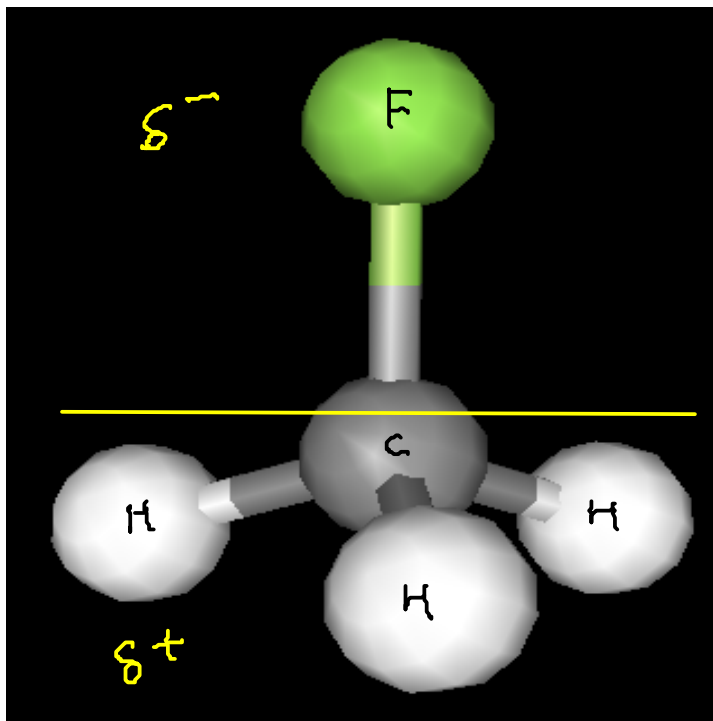
GEOMETRY? TETRAHEDRAL. In three dimensions, this molecule has a hydrogen side and a fluorine side, and will be polar.



Polar molecule?

POLAR BONDS? YES C=O bonds should be polar.

GEOMETRY? LINEAR. This molecule is NONPOLAR because the oxygen atoms directly oppose each other. (In the previous example, the fluorines don't really oppose each other!)

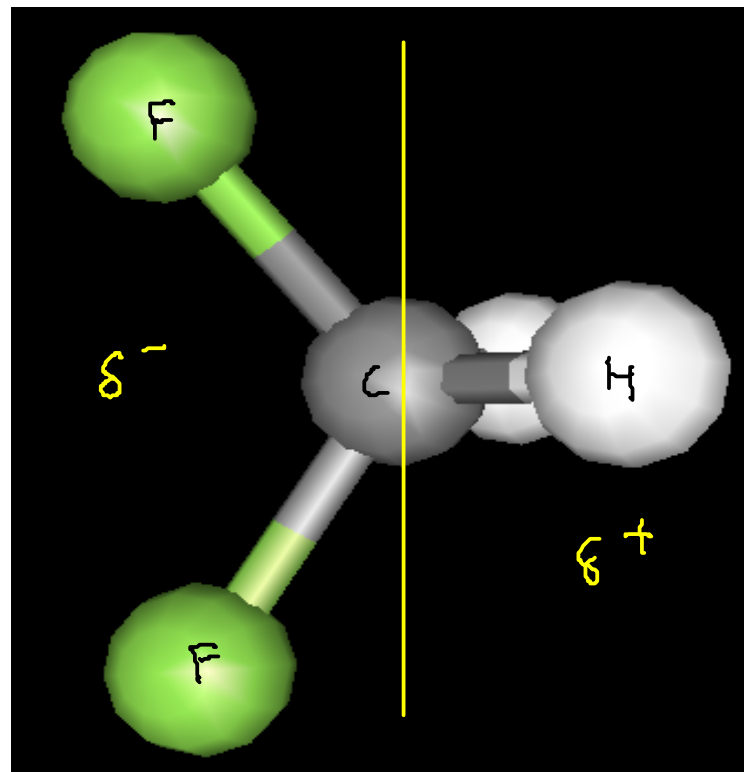
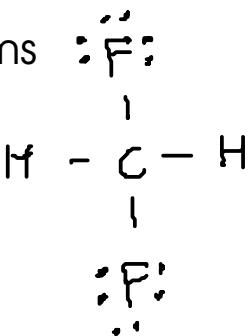


← CH_3F "fluoromethane"

Fluorine is able to pull electron density through the molecule, as it is being opposed by much less electronegative hydrogen atoms.

"difluoromethane" CH_2F_2 →

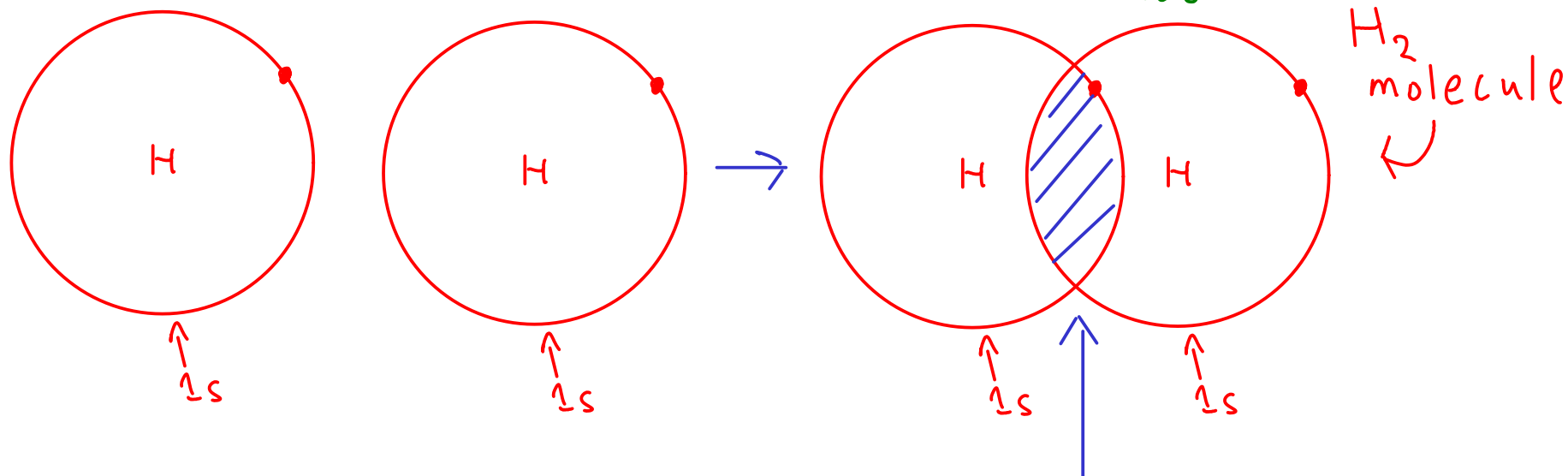
In 2D, the fluorine atoms appear to be on the opposite sides of the molecule, but in 3D they are on the same side.



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.

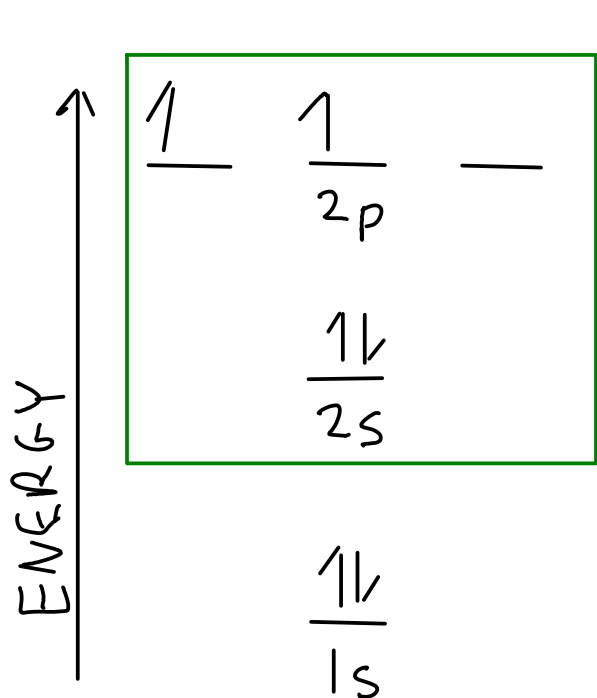
- 1 Bonds are formed when two atoms are close enough together so that their ORBITALS OVERLAP (share the same space).
- 2 Each SET of overlapping orbitals can contain at most a total of TWO electrons. So, two orbitals with one electron each may bond. An orbital with two electrons can only bond with an EMPTY orbital (This is called a COORDINATE COVALENT BOND.) **Ag⁺ with :NH₃... the cleanup in the AgCl lab*



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

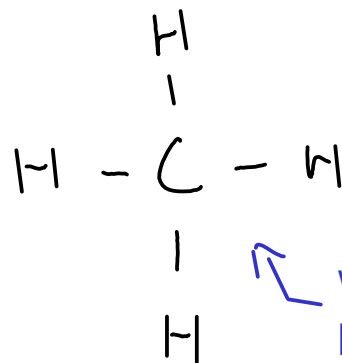
Hybridization

- Look at carbon's electron configuration:



valence

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?

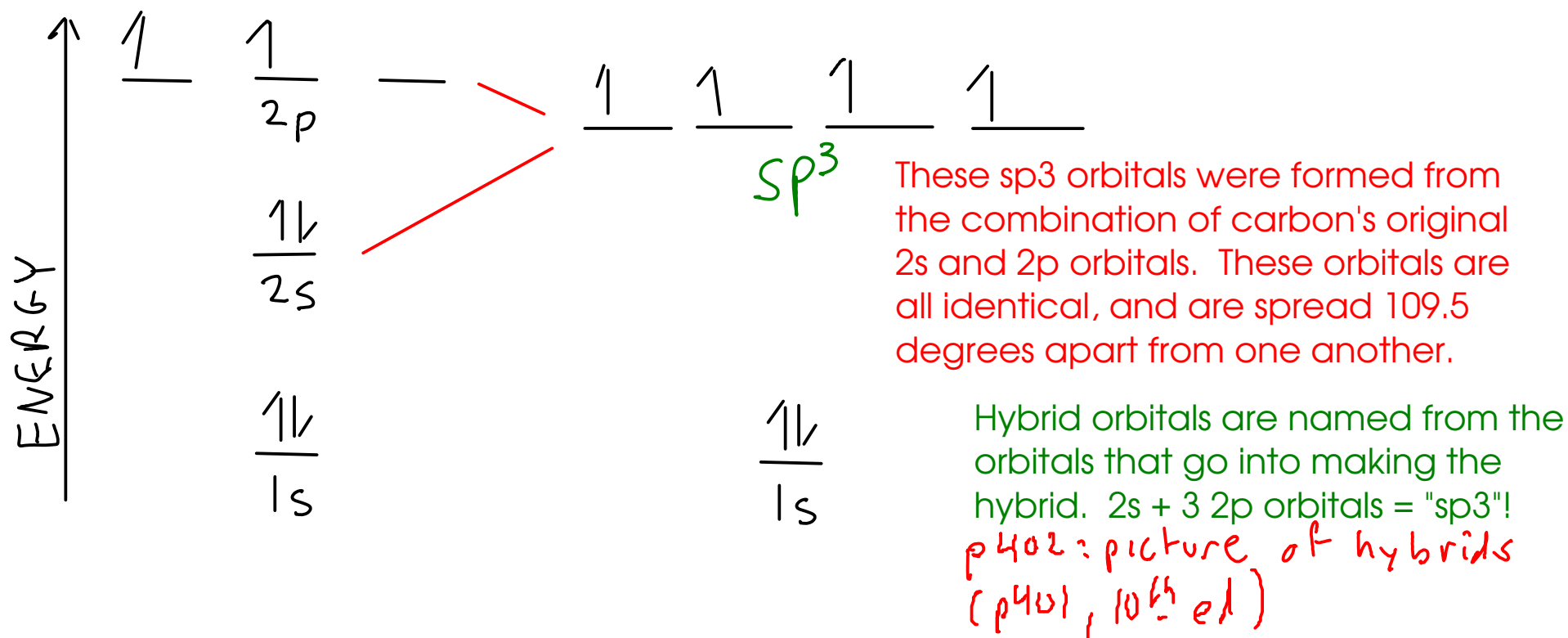


↙ We observe that these bonds are IDENTICAL! Same bond energy, distance, and angle.

- 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.



Types of hybrid orbitals:

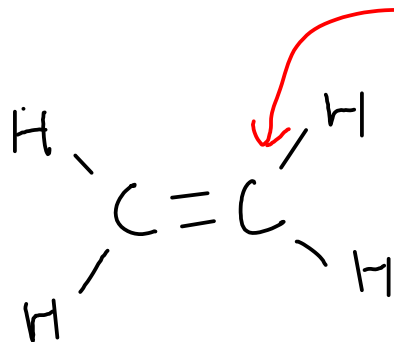
Hybrid type	Number of orbitals	Molecular shape
sp	2	linear
sp ²	3	trigonal planar
sp ³	4	tetrahedral (or derivatives)
sp ³ d	5	trigonal bipyramidal (or derivatives)
sp ³ d ²	6	octahedral (or derivatives)

p402 : picture of hybrids
(p401, 104b)

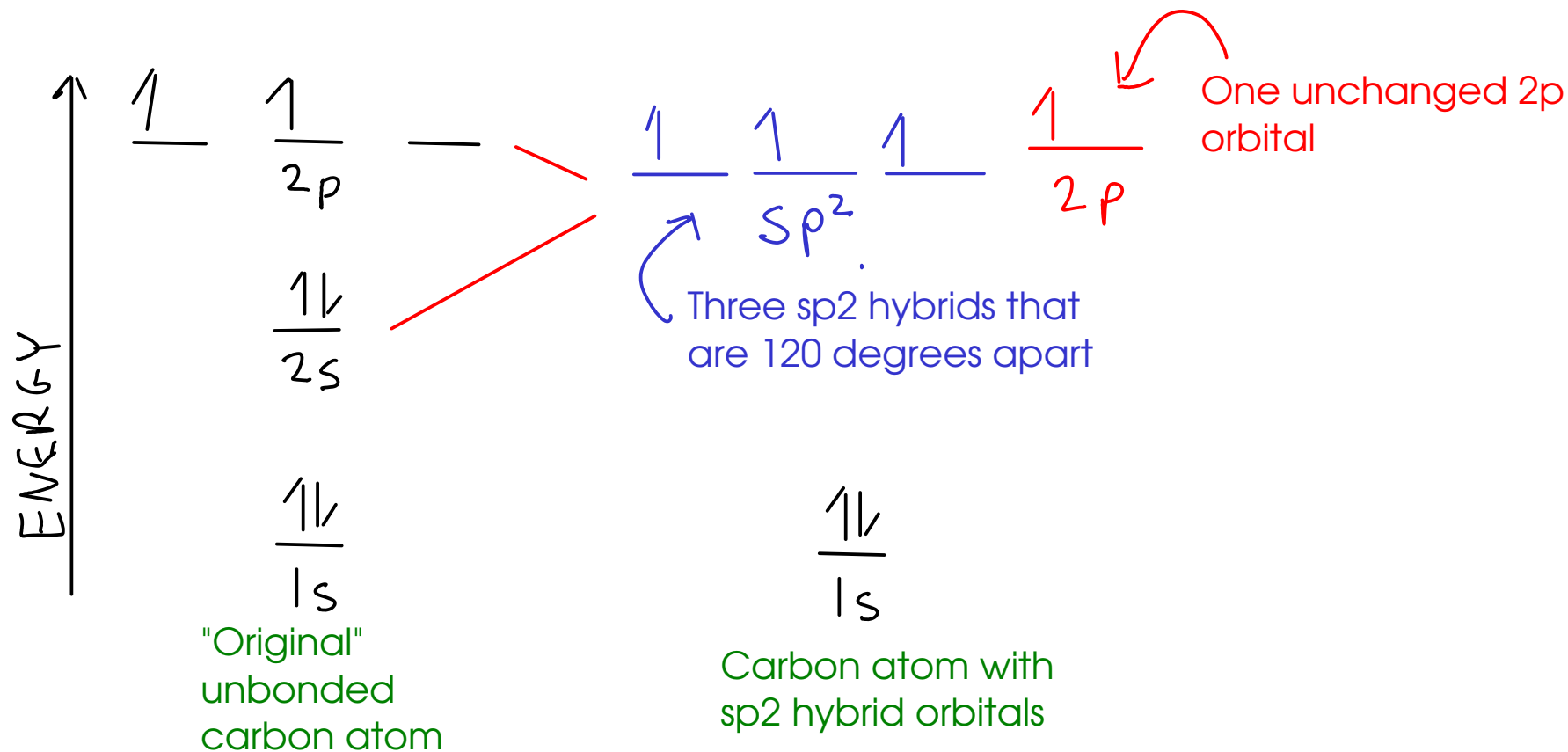
MULTIPLE BONDS and VALENCE BOND THEORY

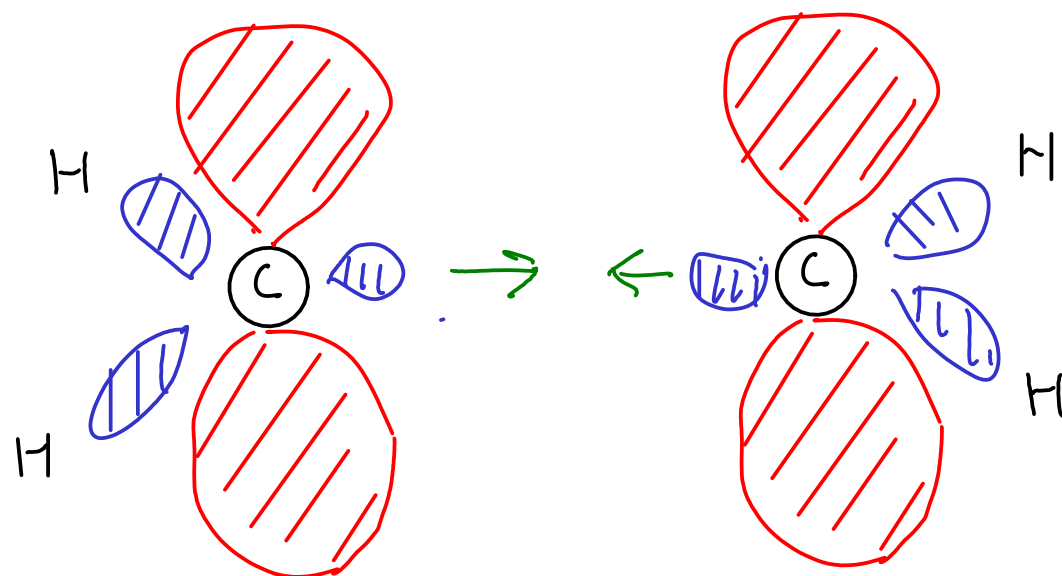
- Valence bond theory provides an explanation of multiple (double and triple) bonding that explains some interesting observations about these kinds of bonds.

C_2H_4 :
ethylene



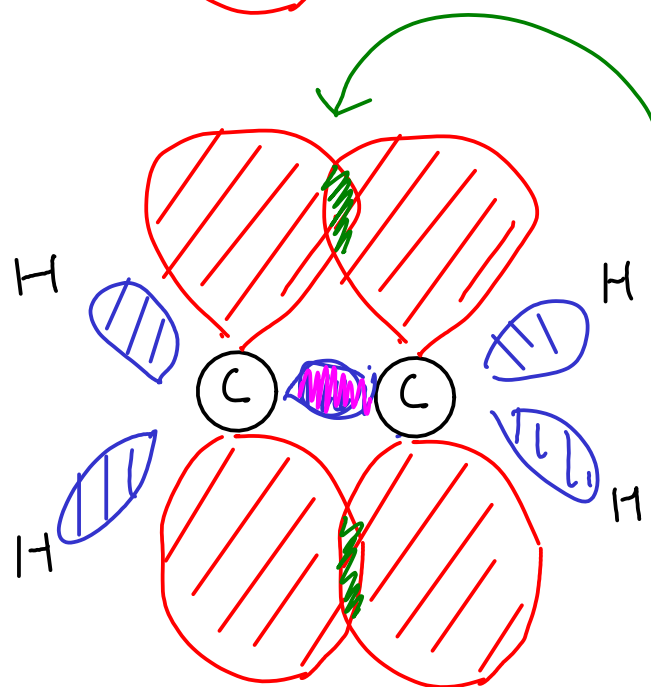
Each carbon has a TRIGONAL PLANAR geometry. This suggests that the carbons are "sp² hybridized".





sp^2 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 sp^2 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.

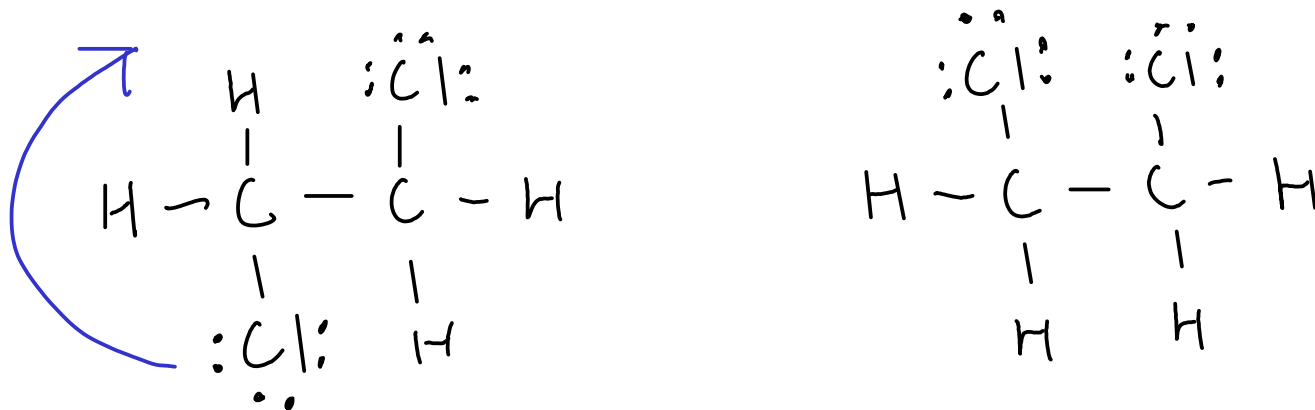
② PI bonds are formed when off-axis orbitals (usually p orbitals) overlap. Since the overlapping orbitals do not face each other as in the sigma bond, the overlap in pi bonds tends to be poorer than in sigma bonds. As a result, pi bonds tend to be weaker than sigma bonds. Double bonds contain a single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

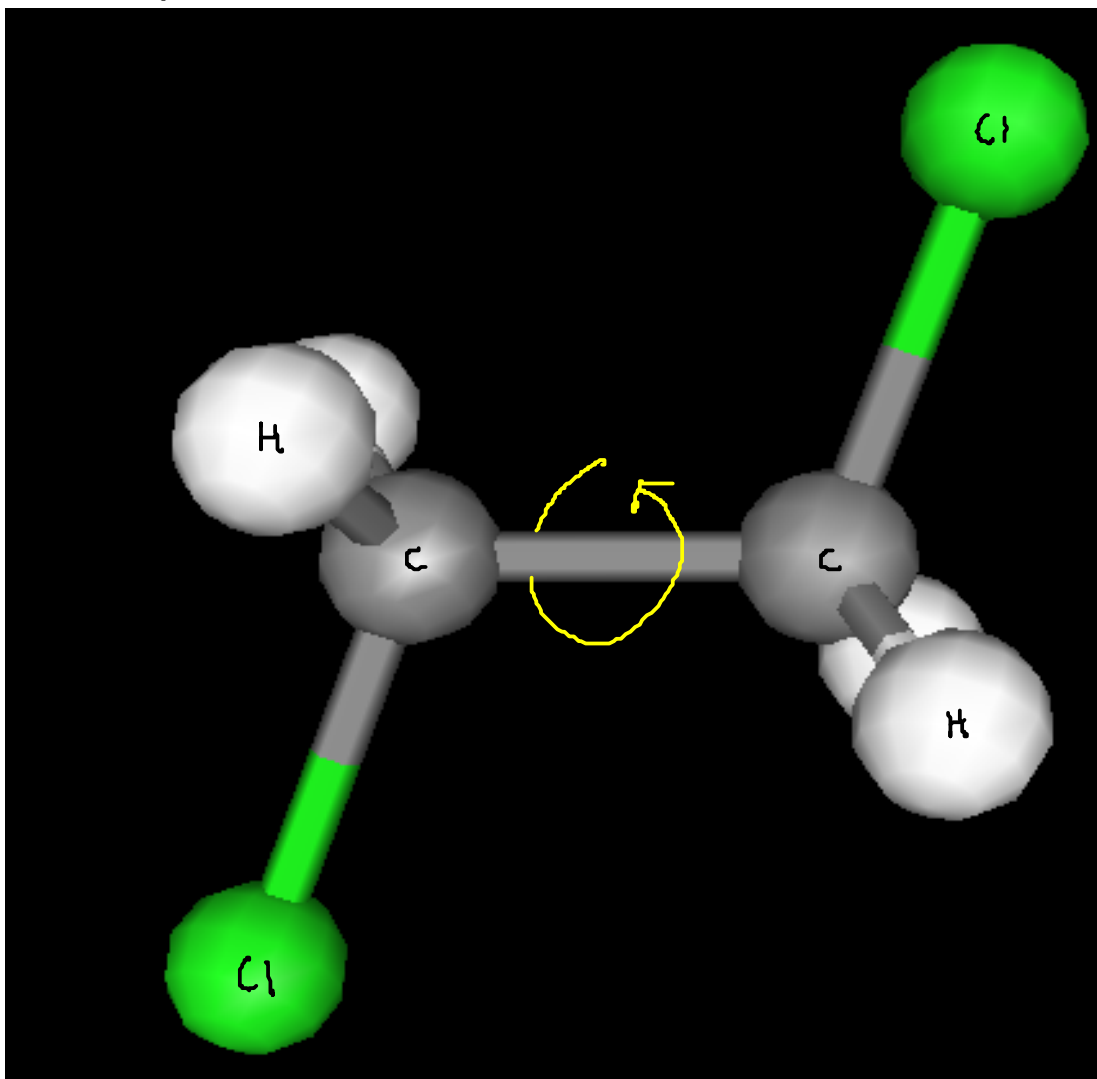
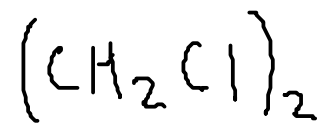
ROTATION, ISOMERS, and VALENCE BOND THEORY

- Consider this molecule: $(\text{CH}_2\text{Cl})_2$
 "1,2-dichloroethane"



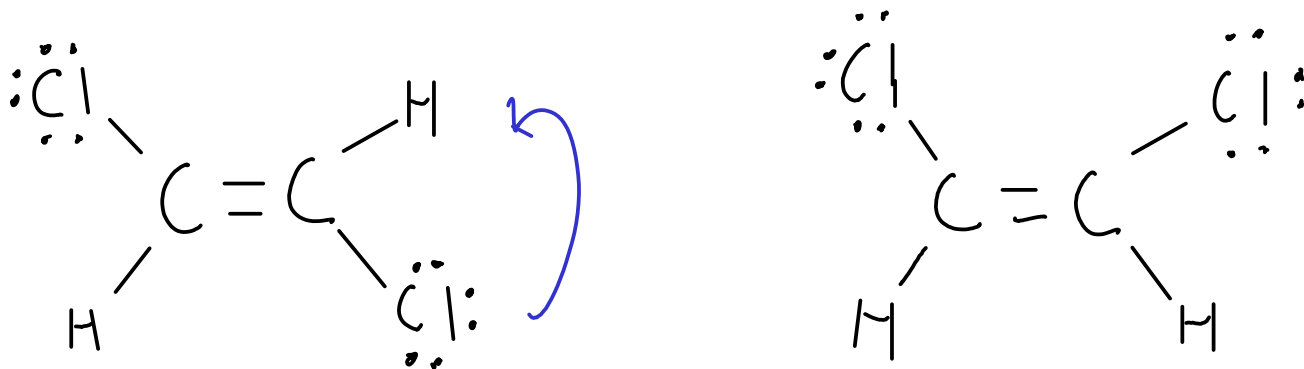
... are these two structures different?

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.



The molecule is free to rotate about the carbon-carbon bond!

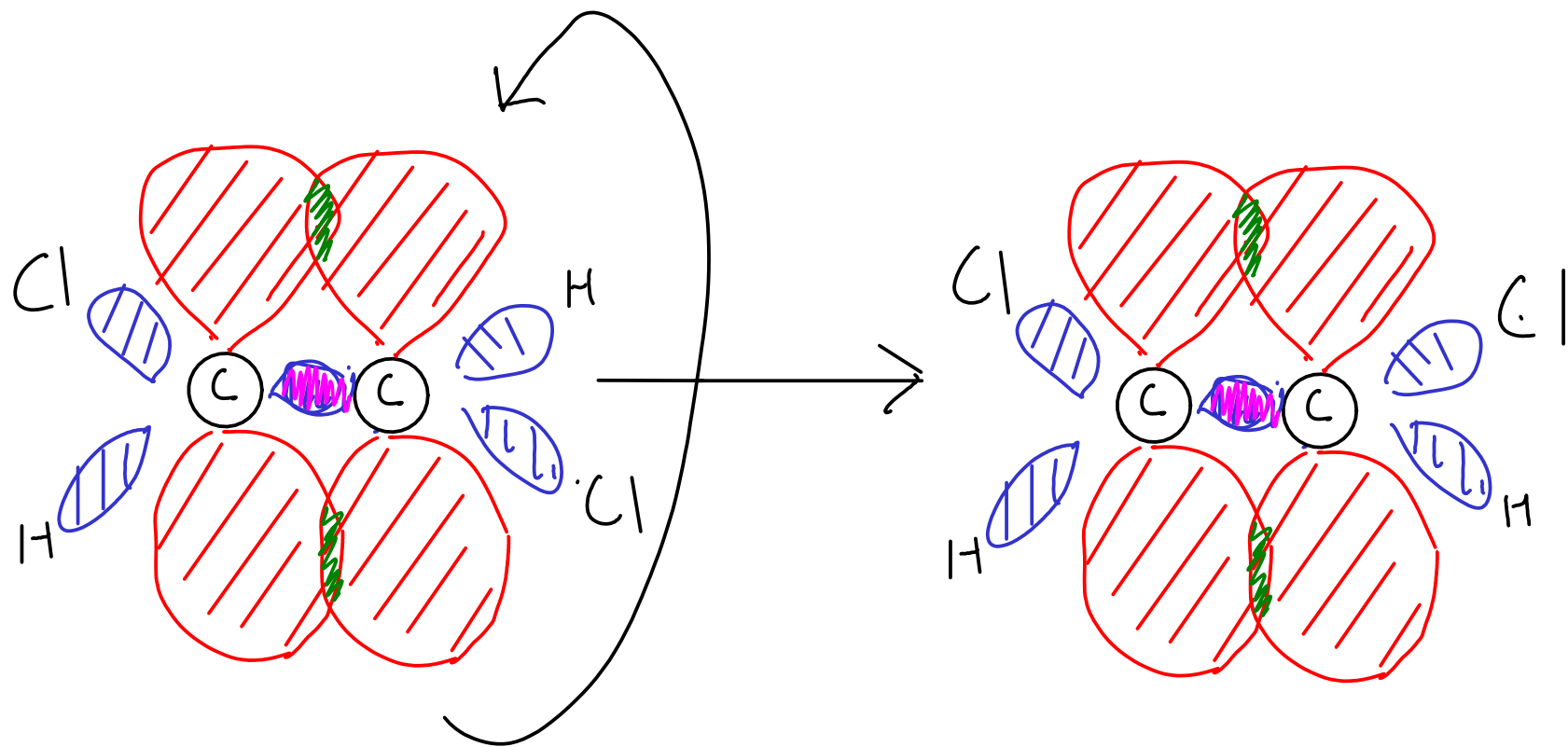
... now consider "1,2-dichloroethene": $(\text{CHCl})_2$



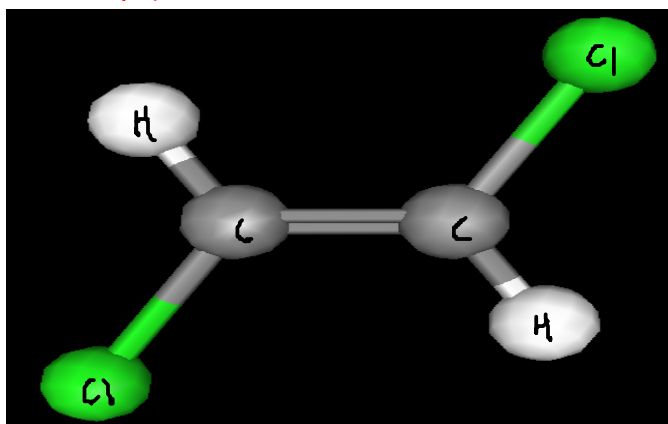
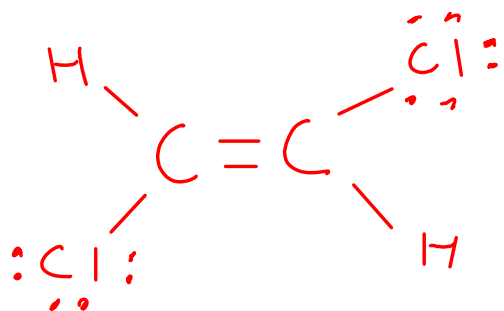
... are these two structures different?

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!

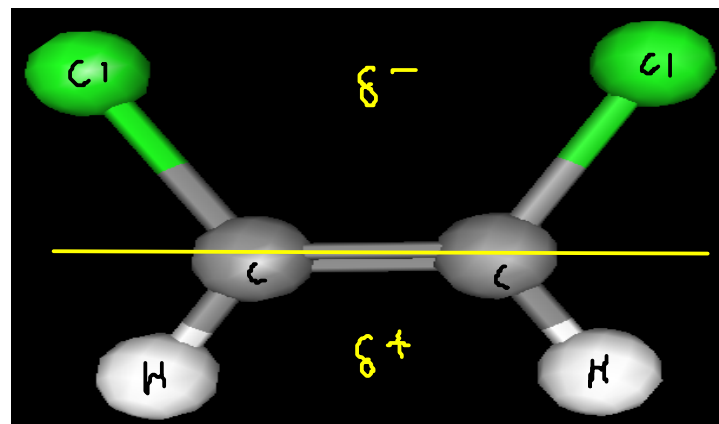
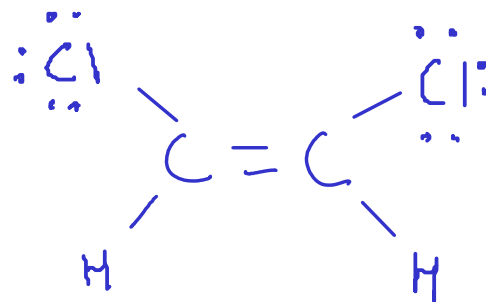


trans 1,2-dichloroethene

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

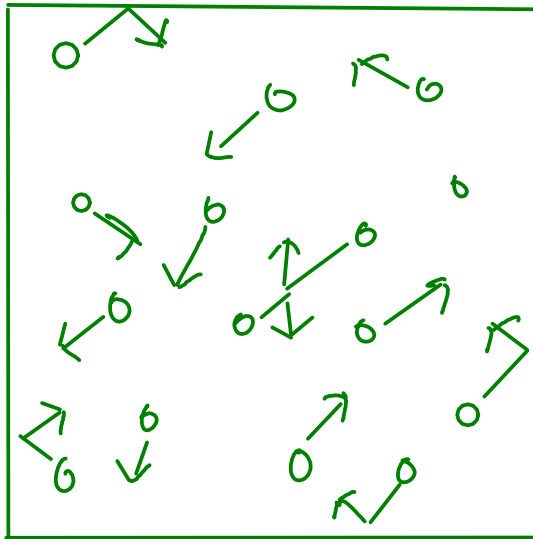
* As you can see, some of the properties of these two molecules are very different! The presence of the pi bond (part of the double bond) in each of these molecules means conversion from one form to the other requires a chemical reaction instead of a simple rotation.

* 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 of 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.

... kinetic energy depends on velocity of gas molecules!

$$E_k = \frac{1}{2}mv^2$$

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

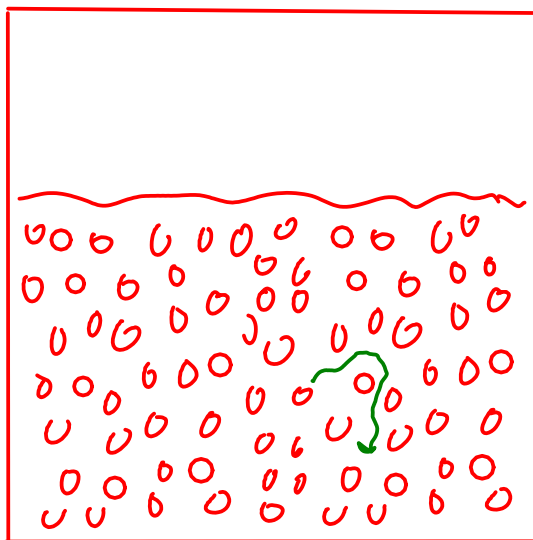


variable volume!

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

$$PV = nRT$$

LIQUIDS



- * Molecules are much closer together than in the gas phase.
- * Molecules are free to move 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

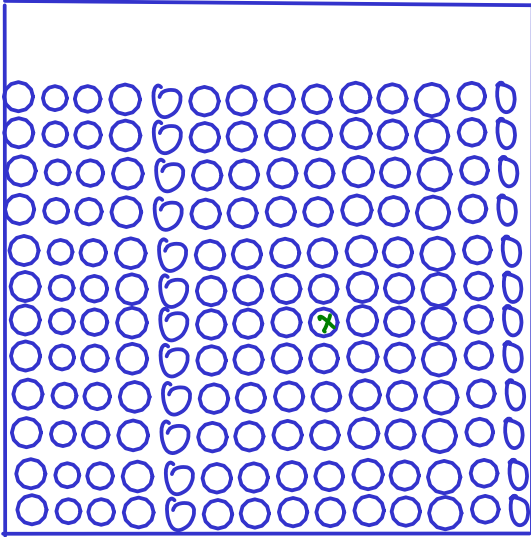
Liquids are FLUID, DENSE, and INCOMPRESSIBLE!

↑
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!

no simple " $PV = nRT$ " for liquids.!

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!

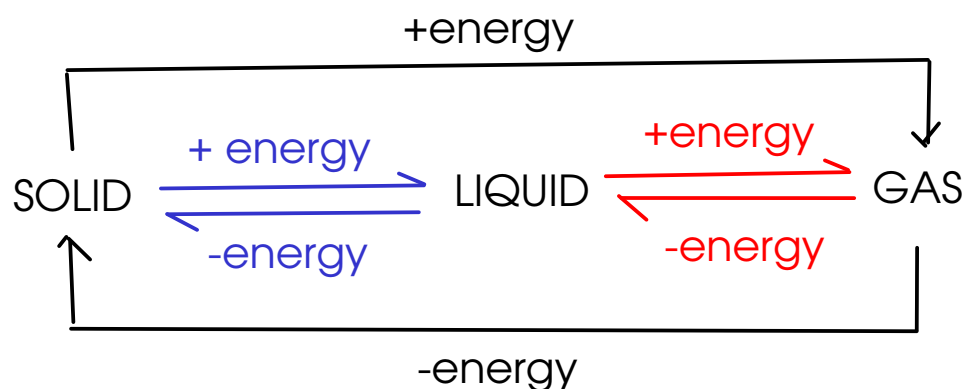
- As for the liquids, the properties of different solids often differ considerably. Compare a sample of candle wax to a sample of quartz.

PHASE CHANGES

- To understand solids and liquids at the molecular level, it will help to examine PHASE CHANGES in a little more detail.

A quick review of the phase changes...

Phase change	Description	Energy change
Melting	Solid to liquid	Endothermic
Sublimation	Solid to gas	Endothermic
Vaporization	Liquid to gas	Endothermic
Deposition	Gas to solid	Exothermic
Freezing	Liquid to solid	Exothermic
Condensation	Gas to liquid	Exothermic

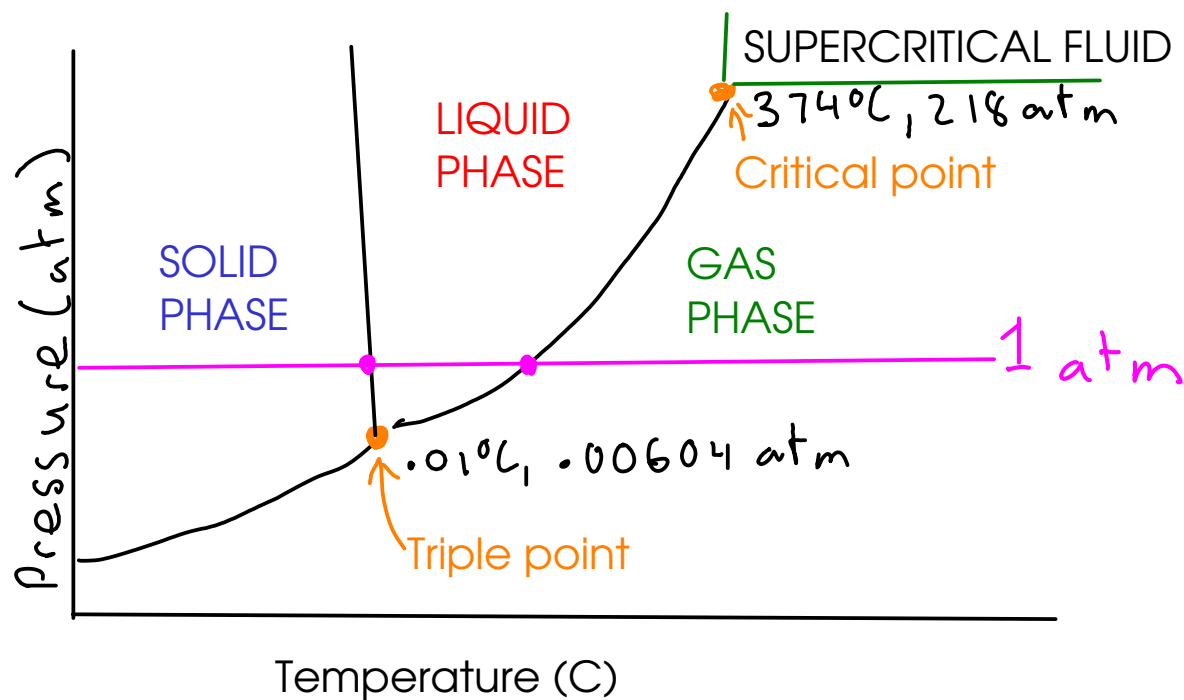


ΔH_{fus} : enthalpy change to melt 1 mol of solid

ΔH_{vap} : enthalpy change to vaporize 1 mol of liquid

34 PHASE DIAGRAMS

- are a convenient way to show experimental data on when bulk phase changes occur.



SAMPLE PHASE
DIAGRAM FOR
WATER

See p 439-440
for more!

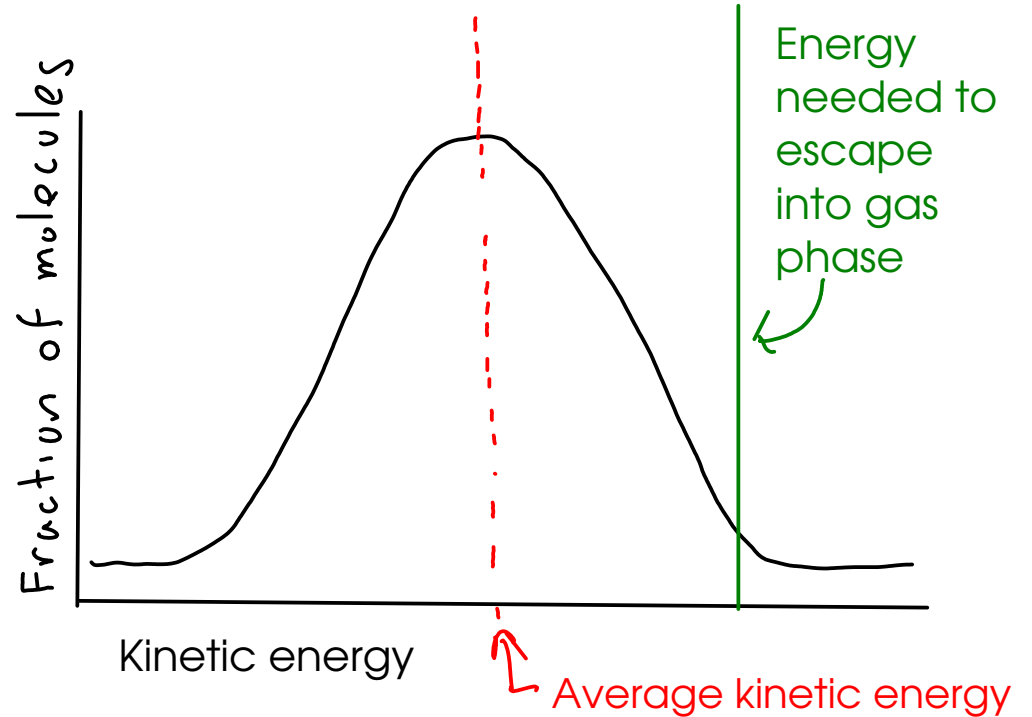
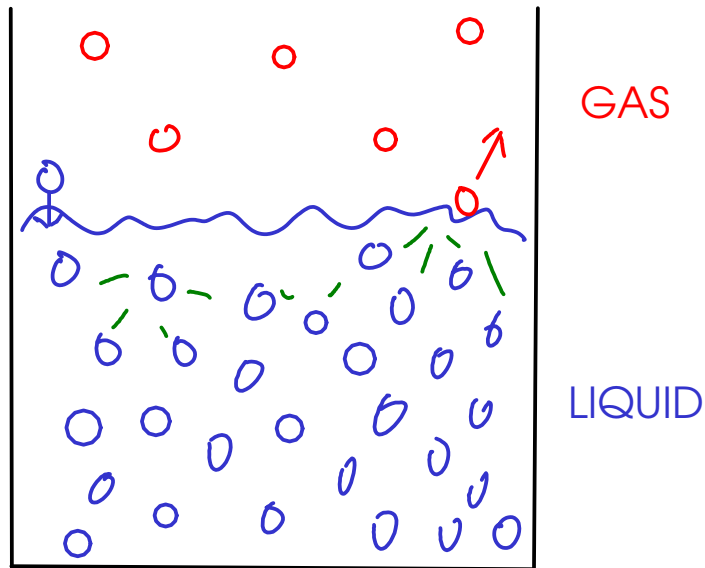
- The curves on the phase diagram represent bulk phase changes.

- The TRIPLE POINT is a set of conditions where all six phase changes occur at the same time; in other words all three phases coexist

- The CRITICAL POINT occurs where there stops being a distinction between the gas and liquid states. This occurs at high pressure and high temperature, where the substance has the density of a liquid but the fluidity of a gas. This is called a SUPERCRITICAL FLUID. Supercritical fluids - like supercritical carbon dioxide - are often used as environmentally friendly SOLVENTS.

- The normal boiling point and freezing points are on the curves. The normal melting point is the point on the solid/liquid curve at 1 atm , while the normal boiling point is on the liquid/gas curve at 1 atm !

35 VAPORIZATION IN MORE DETAIL



- For a molecule to move from the liquid phase to the gas phase, it must acquire enough KINETIC ENERGY (which depends on molecular SPEED) to break away from the INTERMOLECULAR FORCES holding the molecule in the liquid.

- The AVERAGE KINETIC ENERGY of molecules is proportional to the TEMPERATURE. On average, molecules in both the liquid and the solid state move faster at higher temperatures.

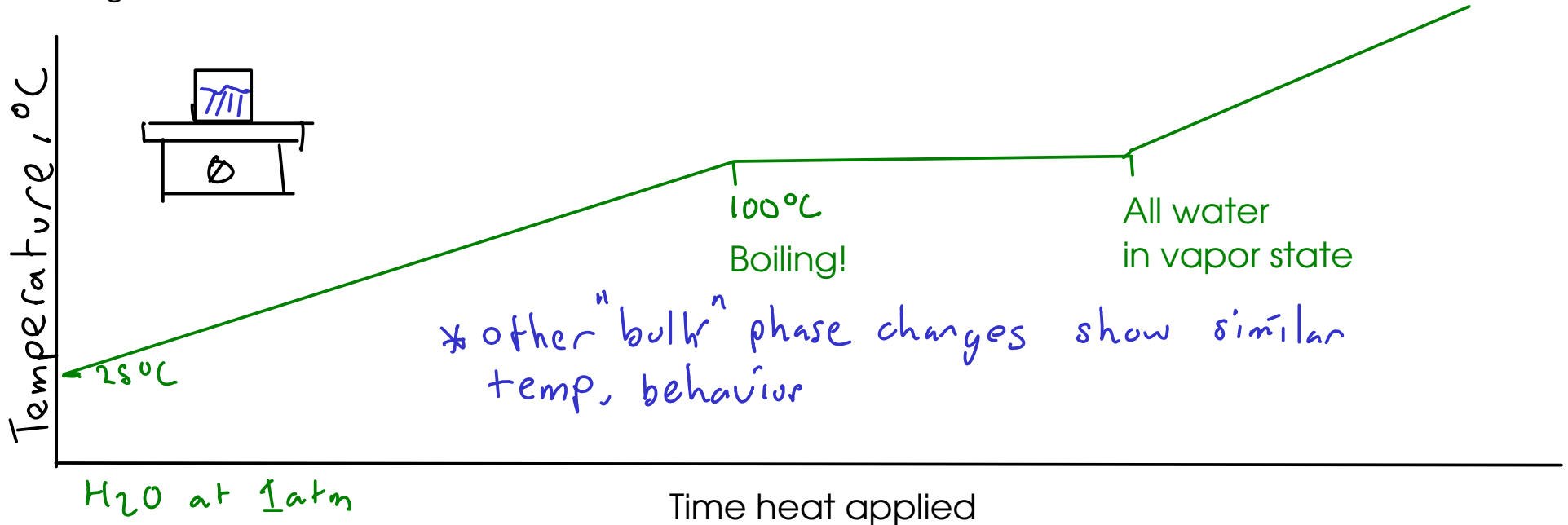
- Even at room temperature, some of the molecules have enough kinetic energy to escape into the gas phase. This accounts for the tendency of volatile liquids to evaporate from open containers even well away from the boiling point.

- As we increase temperature, the gaussian curve above shifts to the right, and a higher fraction of molecules have enough energy to vaporize.

36 TEMPERATURE PROFILE OF VAPORIZATION

- To increase the rate of vaporization, we can increase the temperature. At the BOILING POINT, the pressure of the vaporizing water is enough to push back against the liquid water and bubbles of vapor form in the liquid: BOILING

- If we look at the temperature changes up to and through the boiling point, we see something interesting...



DURING THE BOILING PROCESS, as long as you have some liquid water remaining, the temperature will remain constant - EVEN AS YOU CONTINUE TO APPLY HEAT!

How do we explain this behavior?



- The VAPORIZATION itself requires an energy input. What's that energy doing? Breaking water molecules away from one another (breaking apart the water's intermolecular forces).

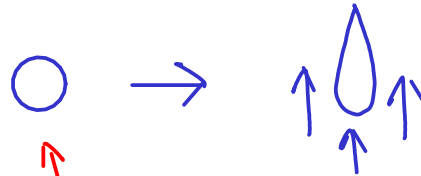
LIQUIDS

- FLUID, DENSE, INCOMPRESSIBLE
- Possess a few unique properties

① SURFACE TENSION

- a measure of the tendency of a liquid to minimize its surface area, or the resistance to the breaking of a liquid surface.

Liquid droplets tend to be spherical...



... but friction causes falling droplets to take on the traditional "drop" shape.

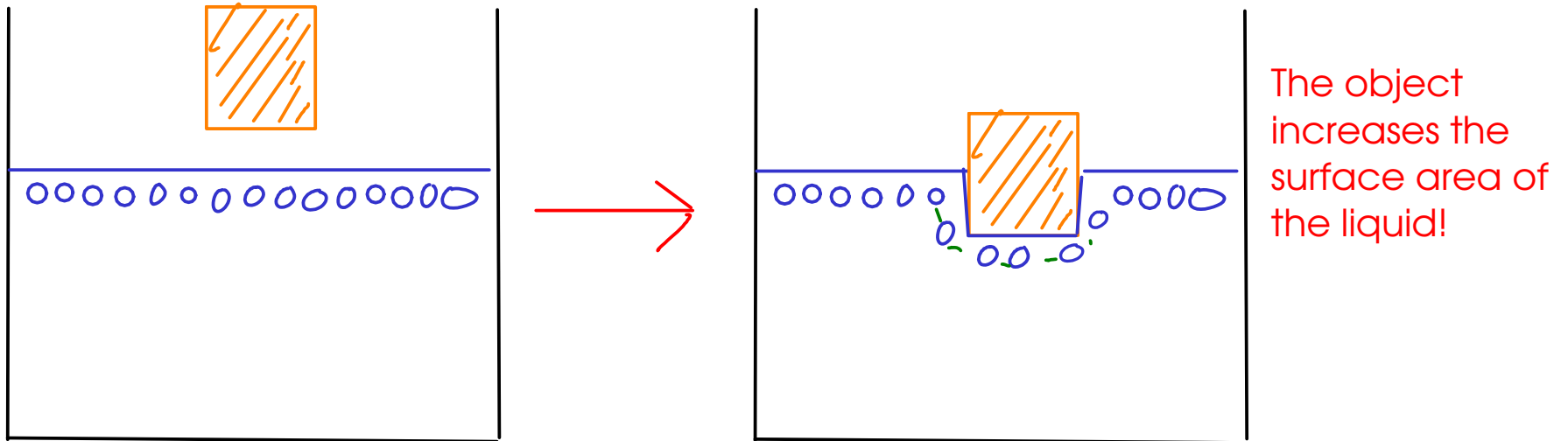
A sphere has the smallest surface area for a given volume.

② VISCOSITY (also for gases)

- a measure of a liquid's resistance to flow, or "thickness"

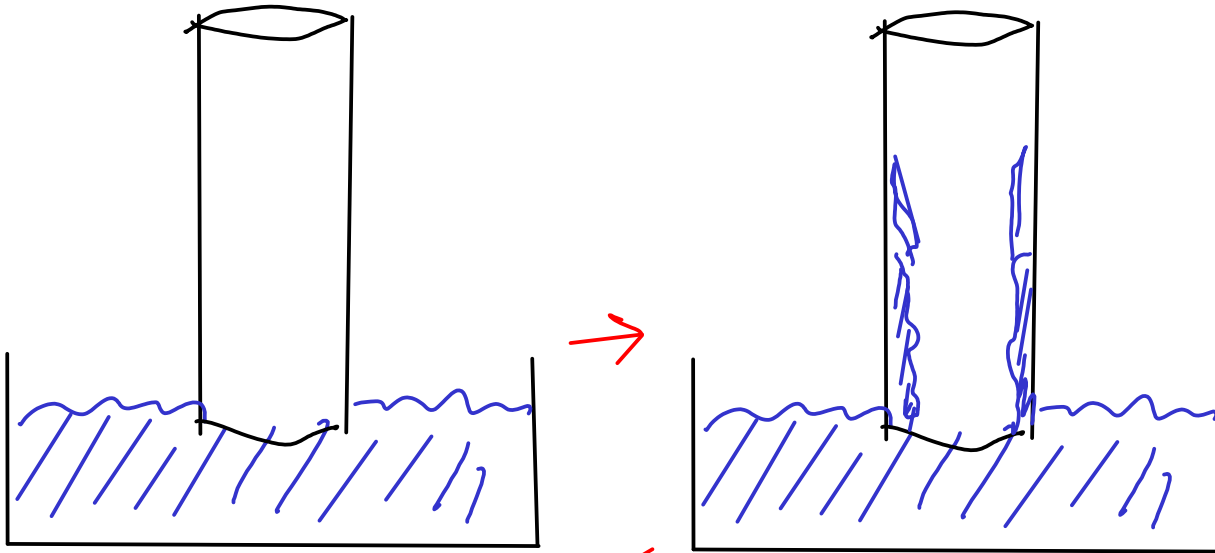
SURFACE TENSION

- Surface tension can be explained by looking at liquid molecules as being attracted to each other by INTERMOLECULAR FORCES.

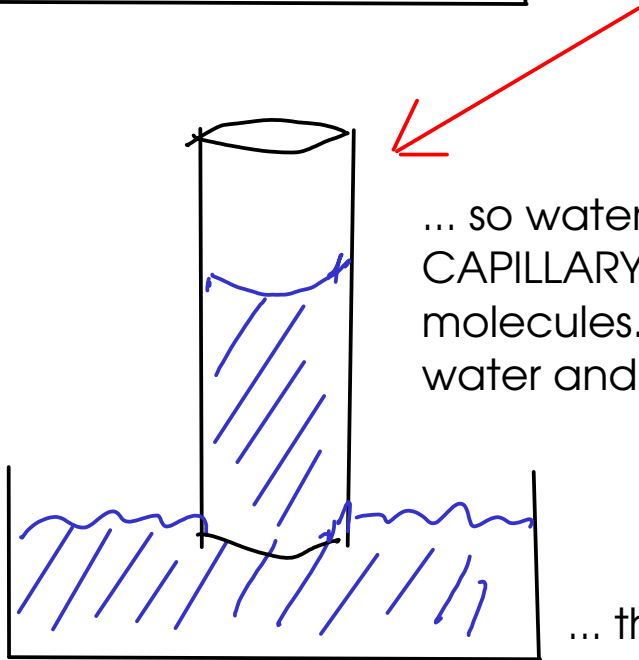


For the object to penetrate the liquid surface, it must push water molecules at the surface apart. Since these water molecules ARE ATTRACTED TO ONE ANOTHER, the liquid will resist!

³⁹ - Surface tension also explains CAPILLARY ACTION, the drawing up of WATER into a glass tube. Water is attracted to glass, and will climb up the surface of a glass tube.



... but this greatly increases the SURFACE AREA of the water, and pulls the water molecules farther from each other.

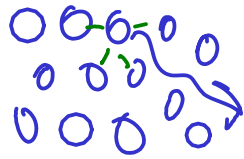


... so water is PULLED UP THE MIDDLE OF THE CAPILLARY by the attractive force between water molecules. This minimizes the surface area of the water and gets water molecules closer to one another.

... the water is pulled up AGAINST GRAVITY!

⁴⁰ VISCOSITY

- viscosity can also be explained (at least partially) by looking at INTERMOLECULAR FORCES!
- For a liquid to FLOW, its molecules must move past one another. This means that some of the molecules must move farther away from other molecules. Since the molecules in the liquid state are ATTRACTED TO ONE ANOTHER, that means the flowing will be slowed.
- Viscosity is also determined by STRUCTURE. Liquids with large chains (like oils) which can rotate and tangle in one another will also be viscous.



Molecules have to move past one another to flow, and stronger attractions between molecules make that more difficult!