

## 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.\*

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\*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!

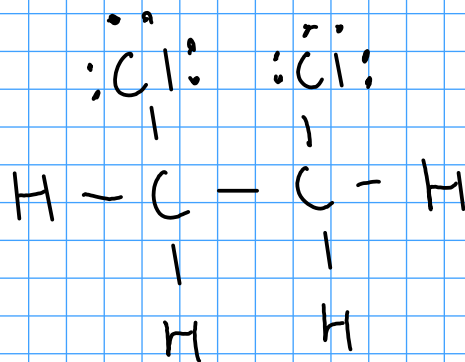
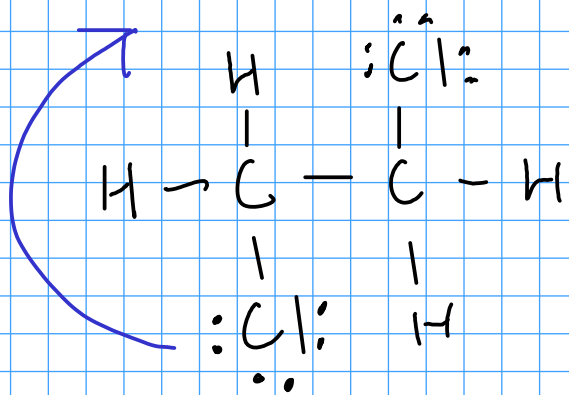
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3

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

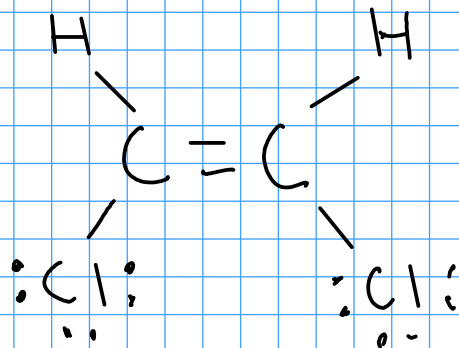
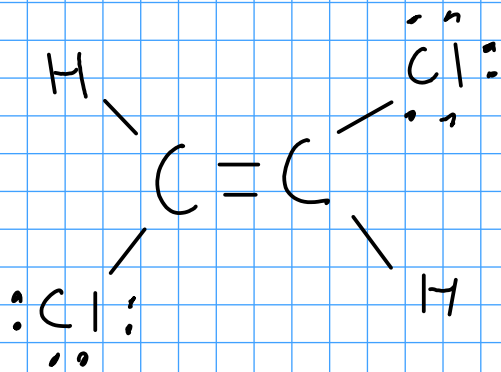
- Consider this molecule:  $(\text{CH}_2\text{Cl})_2$   
"1,2-dichloroethane"



... 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.

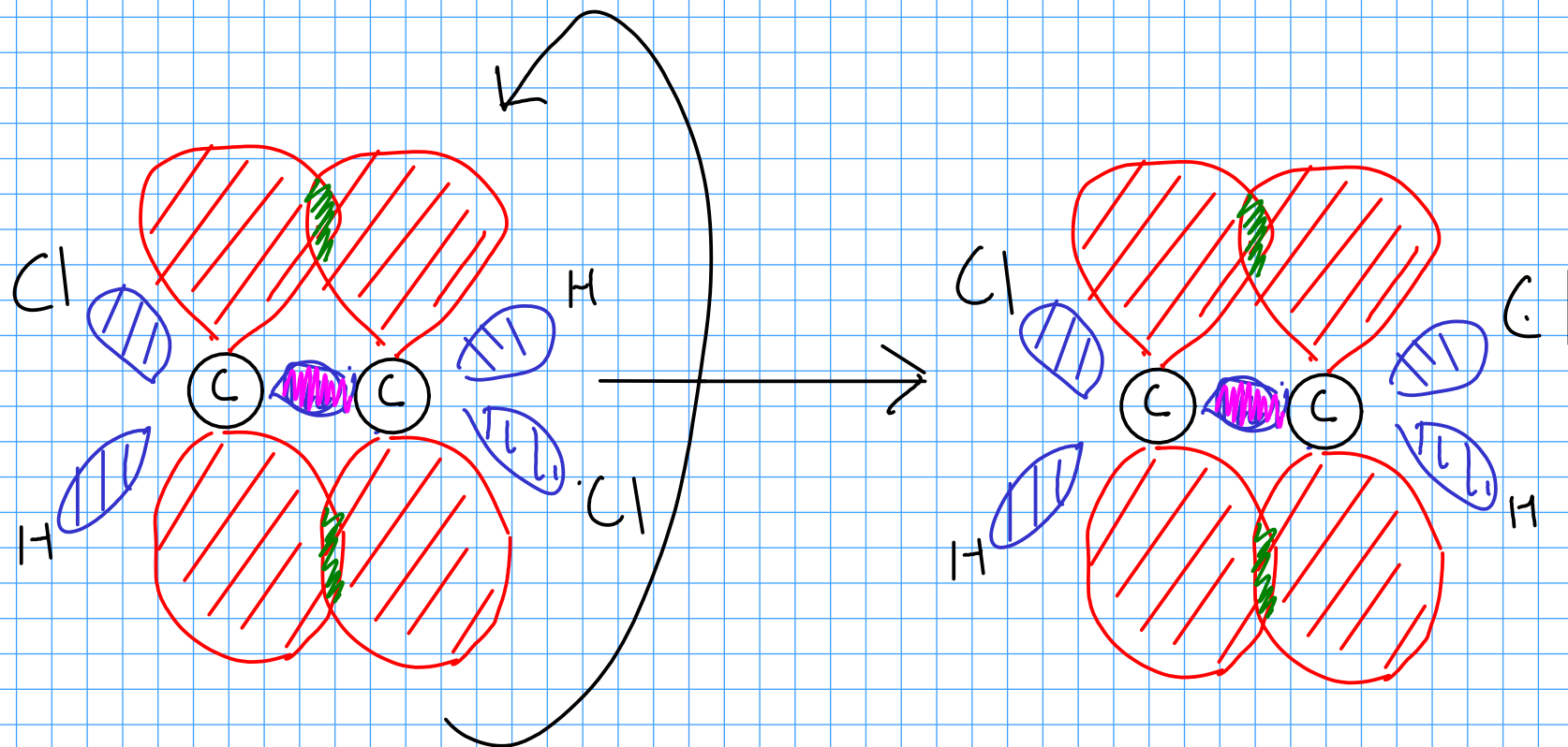
... now consider "1,2-dichloroethene":  $(\text{CHCl})_2$



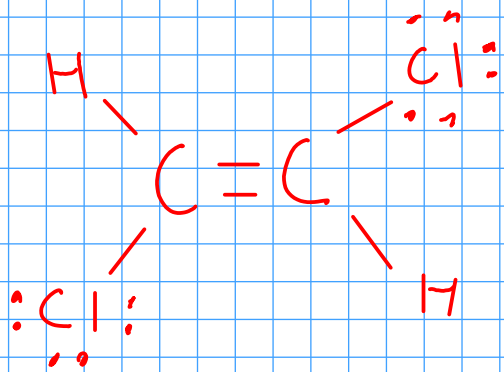
... are these two structures different?

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!

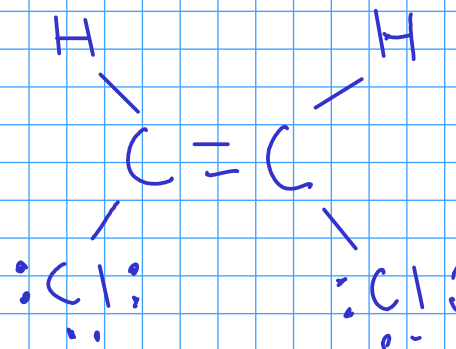


trans 1,2-dichloroethene

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 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.

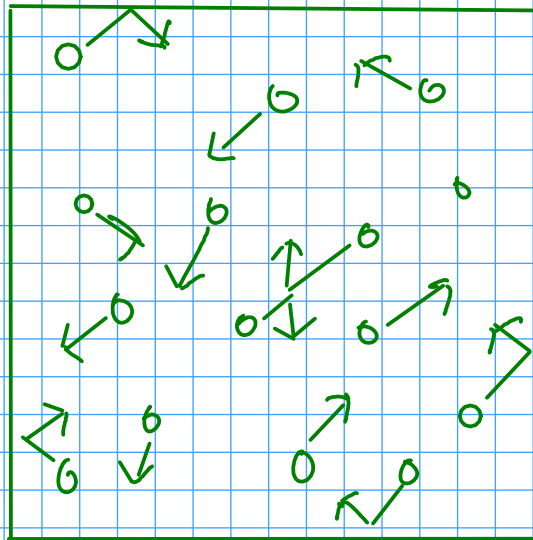
\* Double (and triple) bonds prevent rotation and "fix" the structure of a molecule. This is easily explained by valence bond theory!

# SOLIDS AND LIQUIDS

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

## Kinetic theory says...

### GASES



- \* 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)!

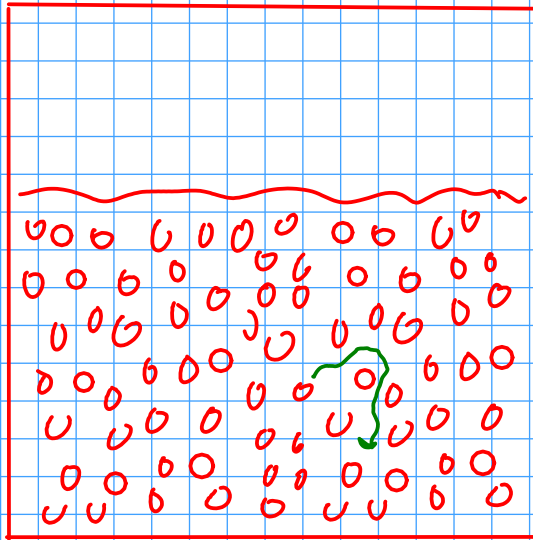
↑  
variable volume!

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

- 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

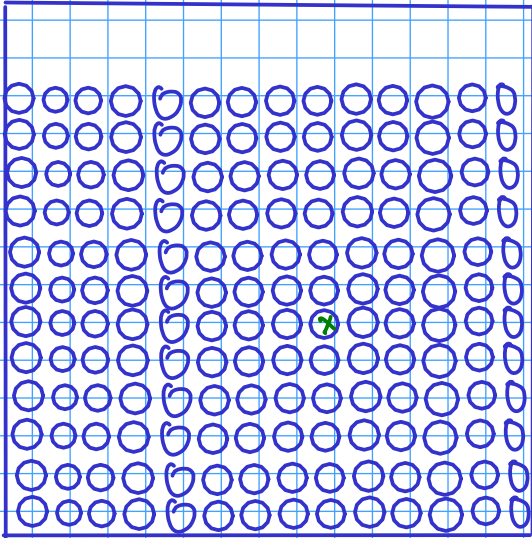
Liquids are FLUID, DENSE, and INCOMPRESSIBLE!

↑  
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

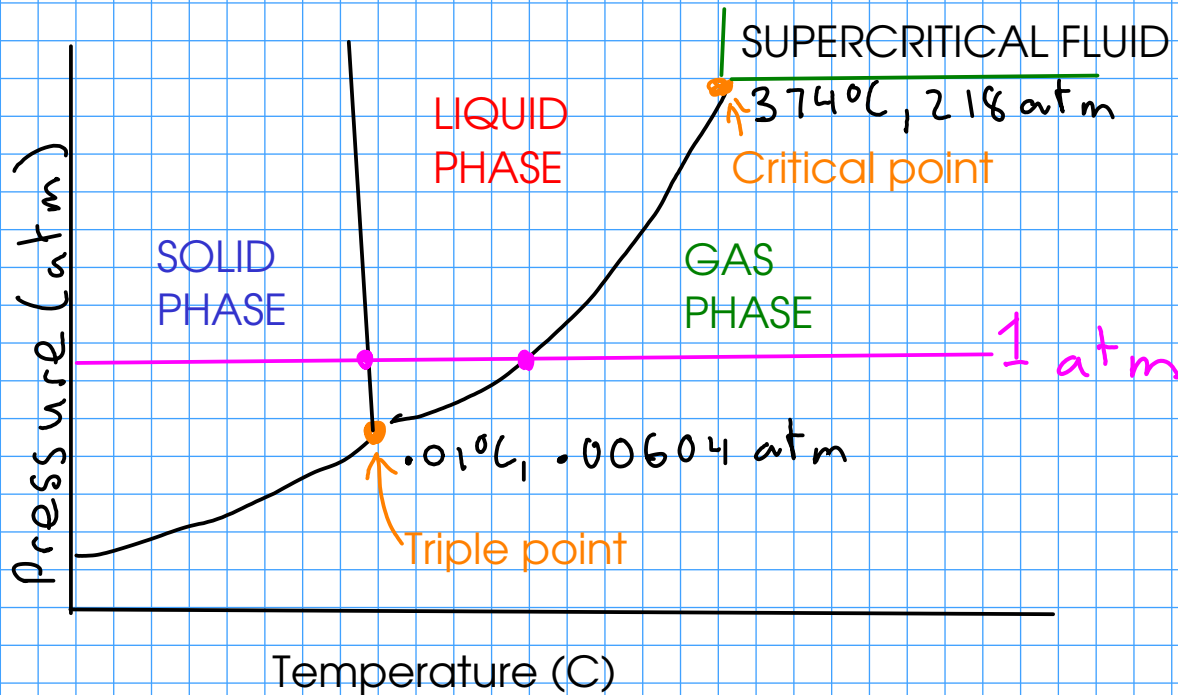
- To understand solids and liquids at the molecular level, it will help to examine PHASE CHANGES in a little more detail.

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

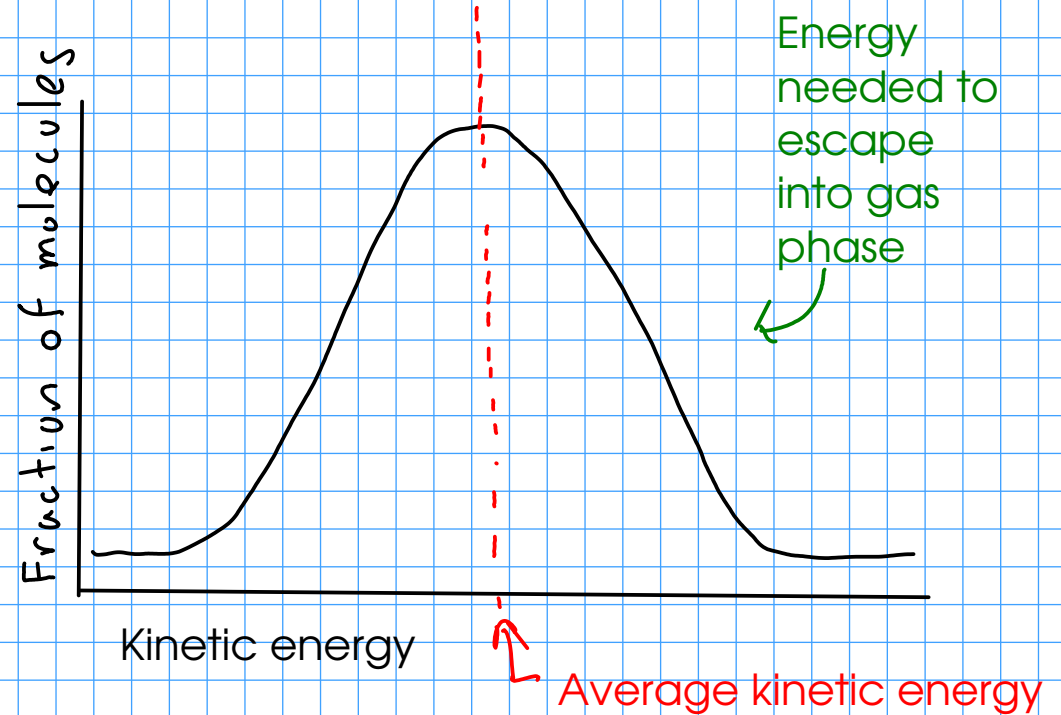
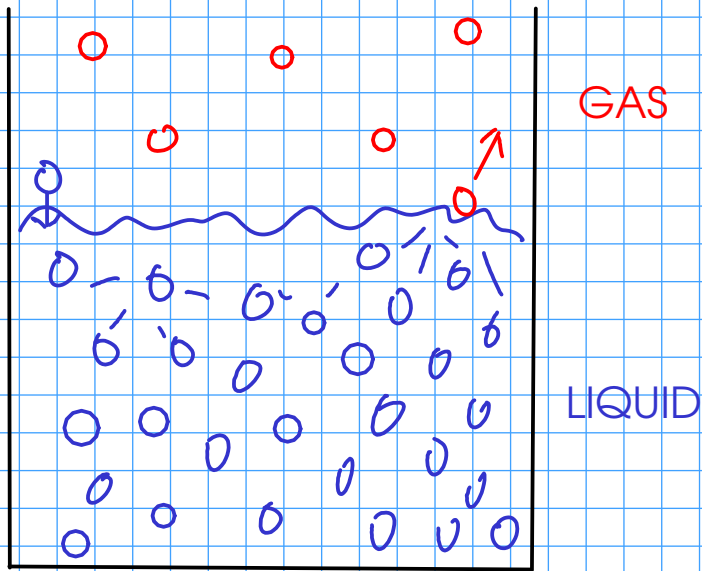
## PHASE DIAGRAMS

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



- 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!

## 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.