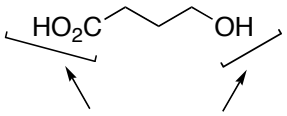
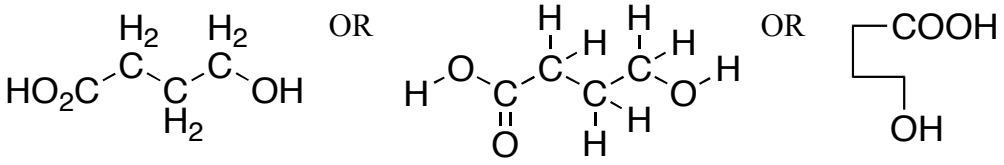
Review:

There are many ways to draw the same molecule -



Functional Groups

Could also be drawn -



Learn all Functional Groups on Handout !

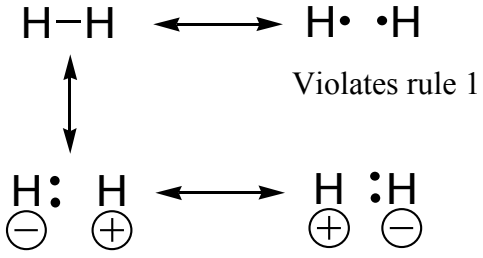
Resonance Structures:

- Give different pictures of the same molecule, they are made by moving electrons and keeping the position of the atoms same.
- Resonance structures are not all equal

Rules for good resonance structures

1) maintain inert gas configuration around each atom
2) avoid multiple charges
3) avoid like-charges on adjacent atoms

Eg. Hydrogen gas, H_2:



Violates rule 1

Violates rule 2 Violates rule 2

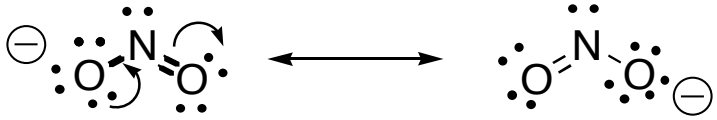
- they are all resonance forms but not necessarily good ones (accurate)
- H-H is the best resonance form

- Double headed arrow (⟷) is used to indicate resonance forms

* this is called "arrow pushing" → bookkeeping of electrons

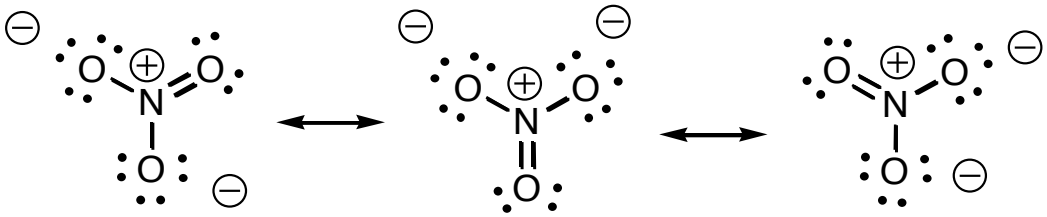
Resonance structure:

1. nitrite anion (NO_2^-)



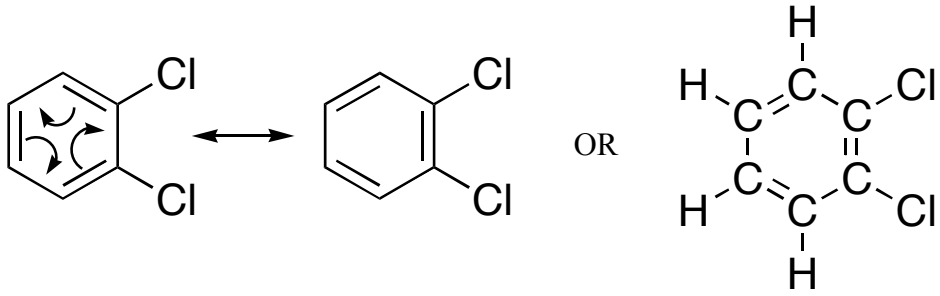
The two resonance structures shown above are equally valid.

2. nitrate anion (NO_3^-)



The structures above are all equally valid, only one needs to be drawn.

3. $C_6H_4Cl_2$



Intermolecular forces: (forces present between molecules)

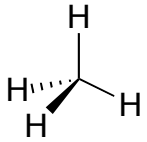
- Attractive intermolecular forces:
  - i) Hydrogen bonding – strongest on per atom basis (eg. base recognition in forming DNA helix)
  - ii) Dipole-dipole interaction
  - iii) London forces (temporary dipole) – weakest on per atom basis

Electronegativity:

- An atom's desire for electrons (negative charge).
- in Periodic table, electronegativity increases as you go from left to right (up to inert gases which are not electronegative) and as you go upwards
- Eg. Fluorine is the most electronegative atom (wants to gain the inert gas configuration of Ne)

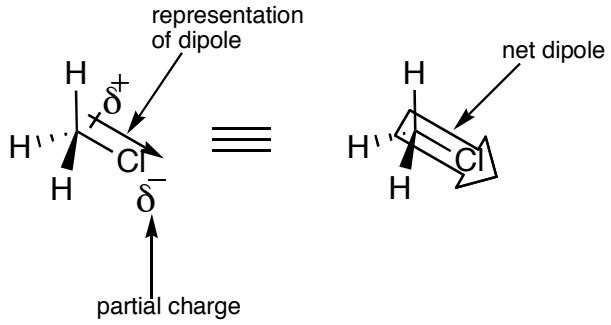
Dipole moment:

Eg.
1. Methane CH_4



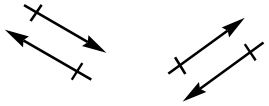
- Non-polar (net-zero dipole)
- Gaseous
- Low BP -164 ^oC
- Low MP -182 ^oC
-

2. Methyl chloride, CH_3Cl, $ClCH_3$

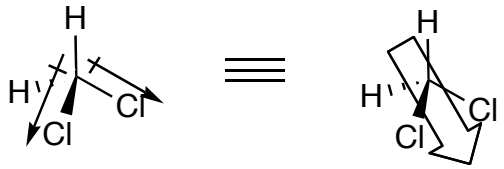


- H and C have similar electronegativity values (non-polar bond)
- Cl is very electronegative – due to the fact that it only needs one electron to get inert gas configuration. (C-Cl and C-F are polar bonds)
- Electron density is pulled towards chlorine atom – so a net dipole toward chlorine atom – net dipole is the vector sum of individual bond dipoles

* dipoles in different molecules tend to line-up temporarily with each other (partial positive / negative charge on the molecule) – causes molecules to "stick" to each other

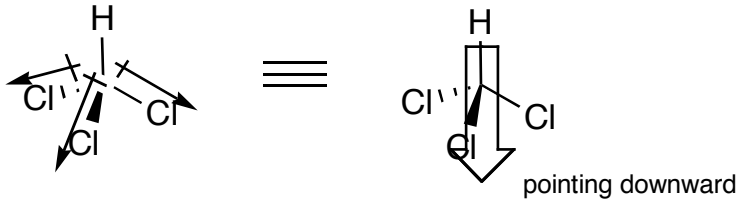


3. Dichloromethane, methylene chloride, CH_2Cl_2



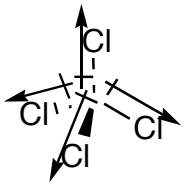
- Liquid at room temperature BP 40 ^{o}C MP – 95 ^{O}C
- More polar than methyl chloride

4. trichloromethane, chloroform, $CHCl_3$



- More polar than methylene chloride BP 61 ^{o}C MP – 64 ^{o}C

5. tetrachloromethane, carbon tetrachloride, CCl_4 (TOXIC)



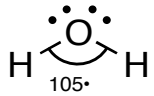
- net-zero dipole

- Non-polar molecule
- Has temporary dipoles and as chlorine is polarizable (see below), high BP

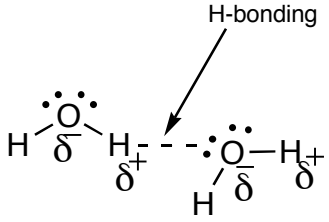
Hydrogen bonding:

- need a lone pair of electrons
- need hydrogen directly attached to a very electronegative atom (F, O, N) for Hydrogen bonding between molecules of same type
- strongest intermolecular attractive force on a per atom basis

eg. H-O-H (water)



- oxygen is electronegative and it is sp^3 hybridized

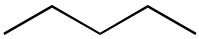


- leads to high boiling point and high melting point by self association
-

London Forces (temporary dipole):

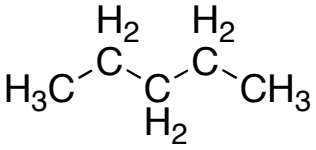
- also know as dispersion forces
- Principal effect in hydrophobic interaction

Pentane C_5H_{12}



Non-polar molecule

Liquid compared with Methane CH_4 which is a gas

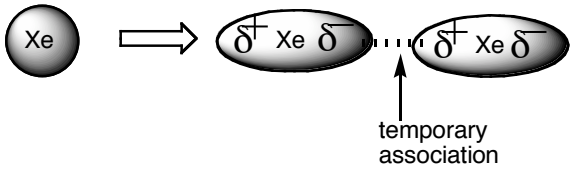


Atoms	boiling point
He	-269 °C
Ne	-246 °C
Ar	-186 °C
Kr	-153 °C
Xe	-108 °C

Small atom/ Low polarizability

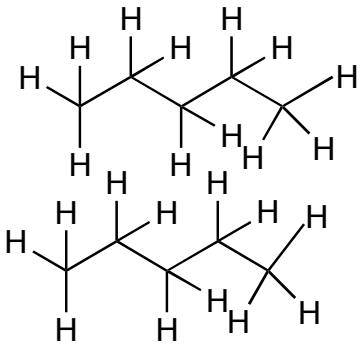
↓

Large atom/ High polarizability



- the larger the atom (expanded electron density), the easier the formation of temporary dipoles

Hydrophobic interaction: - pentane can develop a similar dipole to that seen for Xe



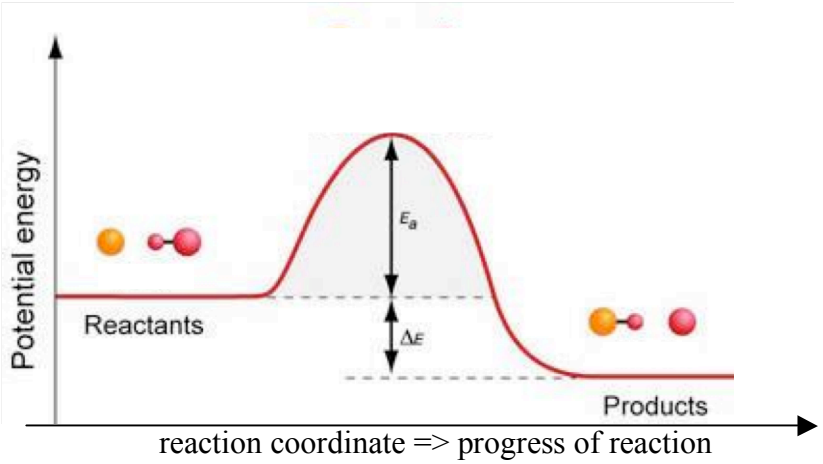
- two pentane molecules have a small attraction to one another at room temperature (hydrophobic interaction)
-

This can become a very strong effect with multiple interactions of this type

Reactivity:

C_5H_{12} (pentane) + O_2 (excess) $\xrightarrow{\text{heat}}$ 5 CO_2 + 6 H_2O

Energy diagram for reaction



Reactants (starting material): C_5H_{12} and O_2
Products: CO_2 and H_2O

E_a: activation energy
$\Delta E = \Delta G$: Gibbs free energy (enthalpy) change for the reaction
* this reaction is an exothermic reaction, heat is released during reaction

- ΔG = change in energy of system or change in Gibbs free energy.

Temperature in ^oK
($^oK = {}^oC + 273$)

$\Delta G = \Delta H - T\Delta S$ (2nd law of thermodynamics)

Change in enthalpy = bond energy

Change in entropy = measure of disorder in system

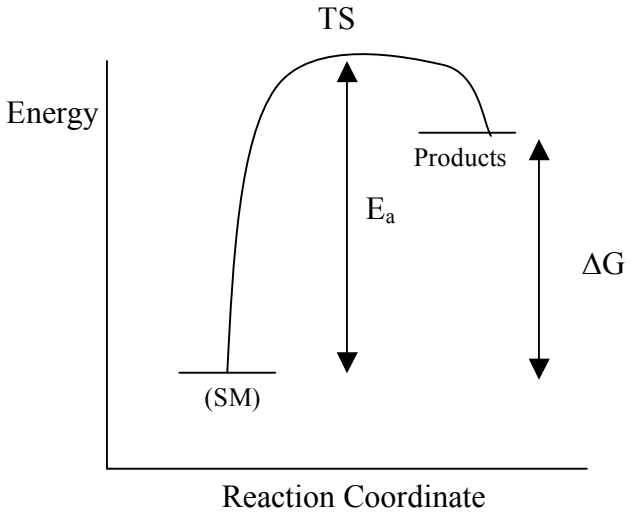
$\Delta G = -RT\ln K_{eq}$
R = gas constant = 0.082 $\frac{L \cdot atm}{mol \cdot K}$
T = temperature in ^oK
ΔG = change in energy of system (determines equilibrium)
E_a = activation energy → determines rate of reaction

$$A + B \rightleftharpoons C + D$$

K_{eq} = equilibrium constant = $\frac{[C][D]}{[A][B]}$ [C] = concentration of compound C

Endothermic Reaction

Transition state (TS) = bonds partially made/broken



The transition state is the point of highest energy on the diagram.

The transition state is not an intermediate.

Reaction proceeding through an intermediate