AS A REMINDER:

Formal Charge

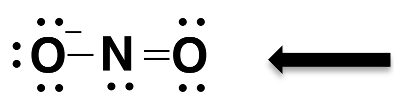
- Convention to keep track of charges
- ∑ (sum of) of formal charges on all atoms in a molecule = overall charge on molecule

Rules for calculating formal charge

- Add number of protons in nucleus
- Subtract number of inner shell electrons
- Subtract number of unshared electrons
- Subtract ½ of the number of shared outer shell electrons

Examples:

1. **Nitrite anion**



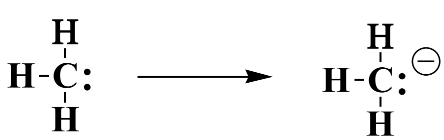
Formal charge

Single bonded oxygen:

+8 (number of protons)
-2 (1s electrons)
-6 (unshared electrons)
½ x 2 = -1 (1/2 of shared electrons)
-1

Overall charge on the nitrite anion is = **-1**

2. **Methyl anion**

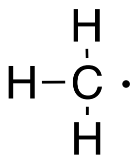


Formal Charge on Carbon

+6 (number of protons)
-2 (1s electrons)
-2 (unshared electrons)
½ x 6 = -3 (1/2 of shared electrons)
-1

Overall charge on the methyl anion is = **-1**

3. **Methyl radical**



Formal Charge on Carbon

+6 (number of protons)
-2 (1s electrons)
1 (unshared electrons)
½ x 6 = -3 (1/2 of shared electrons)
0

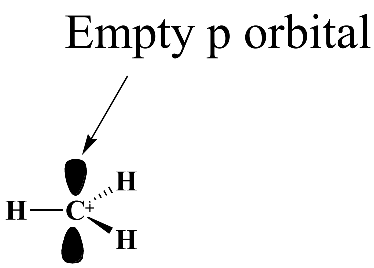
Overall charge on the methyl anion is = **0**

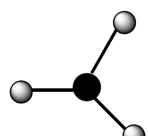
4. **Methyl cation**
   - (sp^2 hybridized carbon, planer shape**)**
   - can be reactive intermediate in principle

Formal Charge on Carbon

+6 (number of protons)
-2 (1s electrons)
0 (unshared electrons)
½ x 6 = -3 (1/2 of shared electrons)
+1

Overall charge on the methyl anion is = **+1**

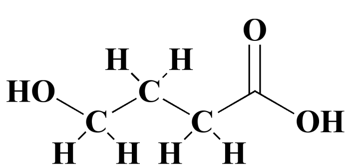




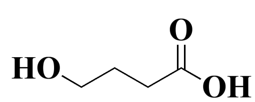
Top view

DRAWING CHEMICAL STRUCTURES

γ **-Hydroxybutyric acid**



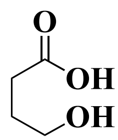
Open chain form

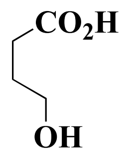


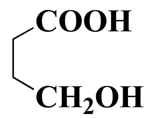
Bond line form

MF = $C_4H_8O_3$

NB:The above compound can also be represented in the following forms, resulting from the free rotation of single bonds (sigma).

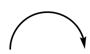






Resonance Structures: Different drawings of the same molecule made by moving electrons but not atoms

- Move the electrons, keeping the position of the atoms same
- Maintain inert gas configuration around each atom
- Avoid separation of charges
- Avoid like-charges on adjacent atoms
- Double headed arrow ($\longleftrightarrow$) is used indicate resonance forms
- Fish Hook and double headed arrows are used to show electron movement



Double Headed Arrow
Show movement of $2e^-$

Fish Hook Arrow
Show movement of $1e^-$

Examples

1. **Hydrogen gas, H_2**

Good representation: H:H Or H-**H**

Bad representations:

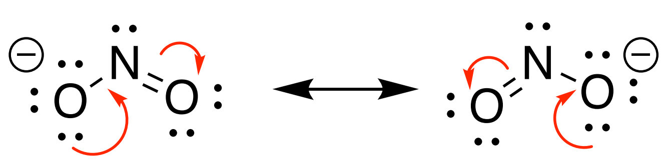
H-**H** $\longleftrightarrow$ $\cdot$H H$\cdot$

$\longleftrightarrow$:$H^{\ominus}$ $H^{\oplus}$

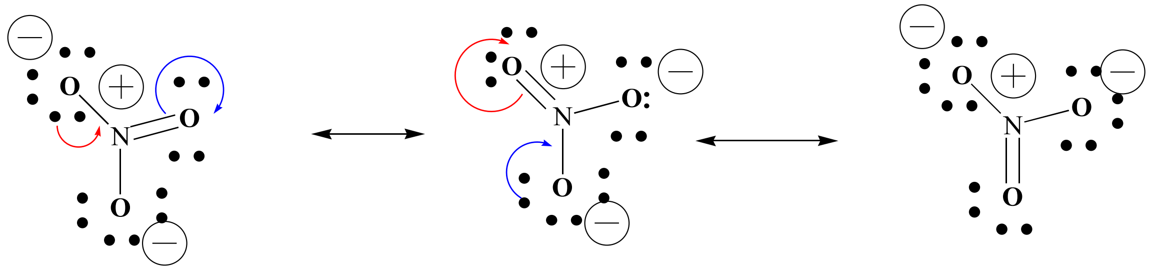
$\longleftrightarrow$ $H^{\oplus}$ $H:^{\ominus}$

NB: In the bad representations, non- inert gas configuration and extra charges have been created

2. **Sodium Nitrite Anion, $NaNO_2$**



3. Sodium Nitrate, $NaNO_3$

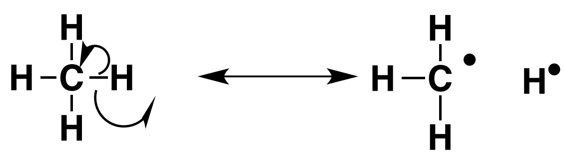


NB: No inert gas configuration disrupted
No extra charge created

5. CH_4 Methane – below are **POOR** resonance structures – additional charges or unshared electrons (not inert gas configuration)

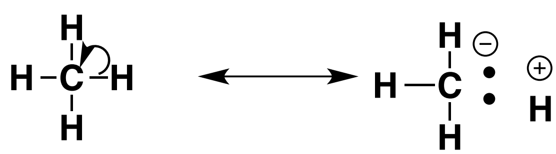
• CH_3

but methyl radical – can be reactive intermediate in principle



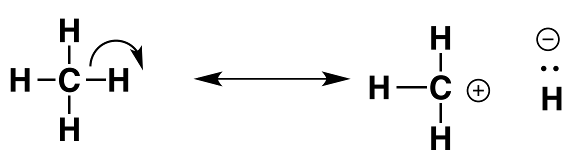
$:CH_3^{\ominus}$

but methyl anion – can be a reactive intermediate in principle

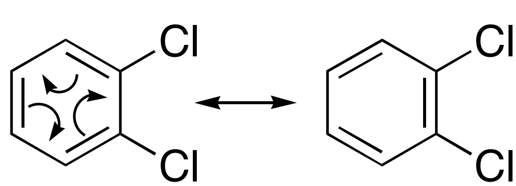


$CH_3^{\oplus}$

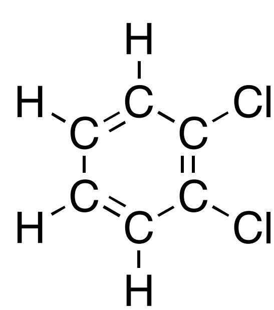
but methyl cation – can be a reactive intermediate in principle

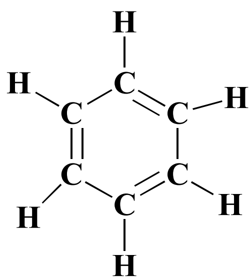


5. 1,2-Dichlorobenzene



OR





BENZENE

Intermolecular Forces: (forces present between molecules)

- Attractive intermolecular forces:
  - i) Hydrogen bonding – strongest on per atom basis (e.g. base recognition in forming DNA helix) (also in RNA)
  - ii) Dipole-dipole interaction (Intermediate strength)
  - iii) London forces (temporary dipole; hydrophobic bonding) – weakest on per atom basis – distortion of inner shells.

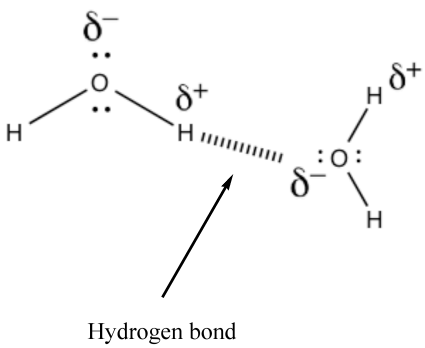
Electronegativity:

- An atom's desire for electrons (negative charge).
- On the periodic table, electronegativity increases as you go from left to right (up to inert gases, which are not electronegative) and as you go from down to up
- Halogens (F, Cl, Br, I) are highly electonegative
  -
  - i.e. Fluorine is the most electronegative atom (wants to gain the inert gas configuration of Ne) and is small (has few electrons)
- It influences acidity of H's attached, as well as the intermolecular forces between molecules.

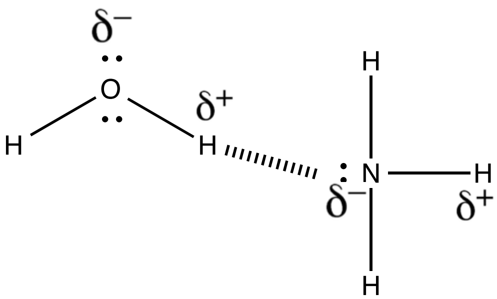
Hydrogen Bonding:

- Strongest intermolecular attractive force
- Need H directly attached to a very electronegative atom (N, O, F, Cl, Br, I)
  - Known as **donors**
- Very electronegative atom needs a lone pair of electrons (N, O, F, Cl, Br, I)
  - Known as **acceptors**

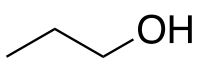
e.g. H-O-H (water)



- Oxygen is electronegative and it is sp^3 hybridized
- The partial positive charge on H and the partial negative charge on O lead to their attraction
- Results in high boiling point (100 C) and high melting point by self-association
- HF, H_2O and NH_3 form hydrogen bonds

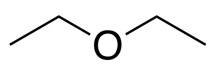


1. Water is a liquid at RT while ammonia is a gas
2. Oxygen is more e-neg than nitrogen, so the protons on water have a higher positive partial charge than the protons on ammonia
3. In an ammonia solution, water would be the hydrogen bond donor and ammonia would be the acceptor
4. Water dissolves ammonia very well – up to 18M



n-Propanol
(1-Propanol)

- Can hydrogen bond to itself
    - Has H directly attached to oxygen
- Has a high boiling points relative to its size due to hydrogen bonding
- Can dissolve in water very well

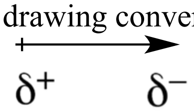


Diethyl Ether

- Cannot hydrogen bond to itself
    - Has no H directly attached to oxygen (No donor)
    - Can H-bond to water because it has an acceptor
- Has a low boiling point
- Will not dissolve in water very well (although a little bit will be dissolved)

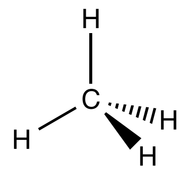
Dipole-Dipole Interactions:

Dipole drawing convention:



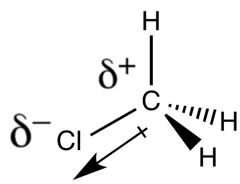
Partial positive charge is the “plus” end, partial negative charge is the arrow head

1. Methane; CH_4



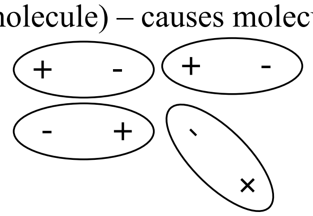
- C and H have ~same electronegativity
- Non-polar (net-zero ~dipole)
- Gaseous
- Low BP -164 ^{o}C (this is relatively low compared to water at 100^{o}C)
- Low MP -182 ^{o}C

2. Chloromethane, methyl chloride; CH_3Cl

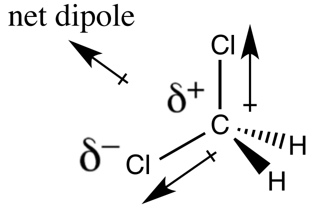


- H and C have similar electronegativity values (non-polar bond)
- Cl is very electronegative due to the fact that it only needs one electron to get inert gas configuration.
- Electron density is pulled toward the chlorine atom, creating a net dipole toward chlorine atom. A net dipole is the vector sum 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

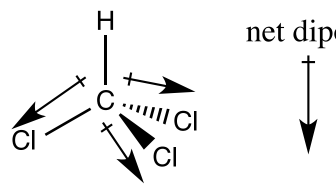


3. Dichloromethane, methylene chloride; CH_2Cl_2



- Liquid at room temperature BP 40 ^oC MP – 95 ^oC
- More polar than chloromethane
- Not miscible with water

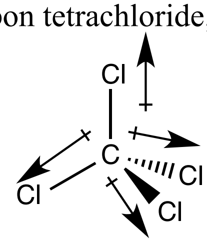
4. Trichloromethane, chloroform; $CHCl_3$



net dipole

- More polar than methylene chloride BP 61 ^oC MP – 64 ^oC

5. Tetrachloromethane, carbon tetrachloride; CCl_4 (toxic)



NO net dipole

- Non-polar molecule (net-zero dipole)
- Has temporary dipoles since chlorine is polarizable (see below), BP ~77
- Historically used as a dry cleaning fluid