# CHEM 261 AS A REMINDER:

# More examples for representation of molecules



Steroid (C<sub>17</sub>)

1. Estradiol



Female hormone All purple atoms are in the same plane

## **DRAWING CHEMICAL STRUCTURES**





 $\gamma$  -Hydroxybutyric acid

Open chain form

Bond line form

$$MF = C_4H_8O_3$$

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



Example:



Note: Single bonds, in general, have free rotation

### **Formal Charge**

- Convention to keep track of charges
- $\sum$  (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

: O - N = O  $\leftarrow$  Formal charge

Overall charge on the nitrite anion is = -1

Single bonded oxygen: +8 (number of protons) -2 (1s electrons) -6 (unshared electrons)  $\frac{1}{2} \ge 2 = -1$  (1/2 of shared electrons) -1 Central N: +7 (number of protons) -2 (1s e<sup>-</sup>) -2 (unshared e<sup>-</sup>) -3 (1/2 shared e<sup>-</sup>) = 0 2. Methyl anion



Overall charge on the methyl anion is = -1

3. Methyl radical

Overall charge on the methyl anion is = 0Very unstable since it doesn't have an inert gas configuration

### 4. Methyl cation

- (sp<sup>2</sup> hybridized carbon, planer shape)
- can be reactive intermediate in principle

Overall charge on the methyl anion is = +1



**Resonance Structures:** Different drawings (or pictures) of the same molecule made by moving electrons but not atoms

- Move the electrons, keeping the position of the atoms same
- Good resonance structures:
  - $\circ$   $\,$  Maintain inert gas configuration around each atom  $\,$
  - Avoid separation of charges
- Avoid like-charges on adjacent atoms
- Double headed arrow ( + ) is used indicate resonance forms

Formal Charge on Carbon+6 (number of protons)-2 (1s electrons)-2 (unshared electrons) $\frac{1}{2} \ge 6 = -3$  (1/2 of shared electrons)-1

Formal Charge on Carbon +6 (number of protons) -2 (1s electrons) 1 (unshared electrons)  $\frac{1}{2} \ge 6 = -3$  (1/2 of shared electrons) 0

Formal Charge on Carbon+6 (number of protons)-2 (1s electrons)0 (unshared electrons) $\frac{1}{2} \ge 6 = -3$  (1/2 of shared electrons)+1

- Fish Hook and double headed arrows are used to show electron movement



## Examples

1. Hydrogen gas, H<sub>2</sub>



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

2. Sodium Nitrite, NaNO<sub>2</sub>



Nitrite anion is reactive in both O atoms. Electrons are delocalized in more than one atom - both O atoms has -1/2 charge and contains partial double and single bond character.

3. Sodium Nitrate, NaNO<sub>3</sub>



## No inert gas configuration disrupted No extra charge created

- The O atoms contain partial single and double bond characteristics (each O has -2/3 charge)
- 4. Allyl Radical



The radical is relatively stable due to resonance.

5. Propyne cation



6. CH<sub>4</sub> Methane – below are POOR resonance structures – additional charges or unshared electrons (not inert gas configuration)

# • CH<sub>3</sub>

CH<sub>3</sub>

but methyl radical – can be reactive intermediate in principle





but methyl anion – can be a reactive intermediate in principle



### 7. 1,2-Dichlorobenzene





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### **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 electronegative
  - 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)



Hydrogen bond



- Oxygen is electronegative and it is sp<sup>3</sup> 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<sub>2</sub>O and NH<sub>3</sub> 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



- 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



Isobutyraldehyde

Can't form H-bonds with itself (not a H-bond donor) Lone pairs on O can form H-bonds with water (H-bond acceptor) Poorly soluble in water



- 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)



### Dimethylformamide

Can't form H-bonds with itself (not a H-bond donor) Lone pairs on O and N can form H-bonds with water (H-bond acceptor) Infinitely soluble (miscible) in water

Note: The more H-bonds it can form, the more soluble it is in water

### **Dipole-Dipole Interactions:**

Dipole drawing convention:

 $\delta^+$   $\delta^-$ 

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

1. Methane; CH<sub>4</sub>



- C and H have ~same electronegativity
- Non-polar (net-zero ~dipole); gas at room temperature
- Low BP -164 °C (this is relatively low compared to water at 100°C)
- Low MP -182 °C

2. Chloromethane, methyl chloride; CH<sub>3</sub>Cl



- 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.
- Has a higher MP and BP than methane

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<sub>2</sub>Cl<sub>2</sub>



- Liquid at room temperature BP 40 °C MP 95 °C
- More polar than chloromethane
- Not miscible with water
- 4. Trichloromethane, chloroform; CHCl<sub>3</sub>



- More polar than methylene chloride BP 61 °C MP 64 °C
- Higher than dichloromethane due to dipole dipole interaction

5. Tetrachloromethane, carbon tetrachloride; CCl<sub>4</sub> (toxic)



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

## **London Forces:**

- Also known as dispersion forces, temporary dipoles or Van der Waals forces (less good)
- Weakest attractive force
- Distortion of filled outer shell electrons
- Principal effect in hydrophobic interactions

Boiling Point	
-269 °C	Small atom/ Low polarizability
-246 °C	
-186 °C	
-153 °C	$\checkmark$
-108 °C	Large atom/ High polarizability
	<u>Boiling Point</u> -269 °C -246 °C -186 °C -153 °C -108 °C



Steric effect: interaction of a filled shell of electrons. Causes repulsion. temporary association • The larger the atom (expanded electron density), the easier the formation of temporary dipoles.

This is the reason why CH<sub>4</sub> associates with CH<sub>4</sub>, due to London forces

C<sub>5</sub>H<sub>12</sub> hydrophobic bonding:

 $H_3C - CH_2 - CH_2 - CH_3$  n-pentane n= Normal=straight



n-Pentane has a boiling point of 35 °C; therefore, it is a liquid at room temperature - why is it a liquid? Because its temporary dipoles – it is not miscible in water – water would rather hydrogen bond to itself – like dissolves like.

# **Example: DMF - dimethylformamide**



soluble in water