AS A REMINDER:

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 $\frac{1}{2}$ of the number of shared outer shell electrons

Examples:

1. Nitrite anion



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

Overall charge on the nitrite anion is = -1

2. Methyl anion



Overall charge on the methyl anion is = -1

3. Methyl radical

Overall charge on the methyl anion is = 0

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**

4. Methyl cation

- (sp² hybridized carbon, planer shape)
- can be reactive intermediate in principle

Overall charge on the methyl anion is = +1



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

DRAWING CHEMICAL STRUCTURES





 γ -Hydroxybutyric acid

Open chain form

Bond line form

 $MF = C_4H_8O_3$





Example:



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
- Good resonance structures:
 - 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
- Fish Hook and double headed arrows are used to show electron movement



Examples

1. Hydrogen gas, H₂



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

2. Sodium Nitrite Anion, NaNO₂



3. Sodium Nitrate, NaNO₃



NB: No inert gas configuration disrupted No extra charge created

4. CH₄ Methane – below are POOR resonance structures – additional charges or unshared electrons (not inert gas configuration)

Н

• CH₃

•ČH₃

but methyl radical – can be reactive intermediate in principle



but methyl anion – can be a reactive intermediate in principle

⊕ CH₃

but methyl cation – can be a reactive intermediate in principle



5. 1,2-Dichlorobenzene





⊕ H



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
 - 0
 - 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 <u>donors</u>
- Very electronegative atom needs a lone pair of electrons (N, O, F, Cl, Br, I)
 - Known as acceptors



Hydrogen bond





- 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

Dipole-Dipole Interactions:

Dipole drawing convention:

 δ^+ δ^-

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

- Oxygen is electronegative and it is sp³ 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, H₂O and NH₃ 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



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)

1. Methane; CH₄



- 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; CH₃Cl



- 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; CH₂Cl₂



- Liquid at room temperature BP 40 °C MP 95 °C
- More polar than chloromethane
- Not miscible with water

4. Trichloromethane, chloroform; CHCl₃



- More polar than methylene chloride BP 61 °C MP – 64 °C

5. Tetrachloromethane, carbon tetrachloride; CCl₄ (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

RECALL:

There are three attractive intermolecular forces

iv) Hydrogen bonding

- Donors: H on O, N, or Halogen
- Acceptors: Lone pair on O, N, or halogen
- v) Dipole-dipole interaction

$$\delta^+$$
 δ^-

vi) London forces (temporary dipole; hydrophobic bonding)

London Forces:

- Also known as dispersion forces
- Weakest attractive force
- Distortion of filled outer shell electrons
- Principal effect in hydrophobic interactions





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

This is the reason why CH4 associates with CH4, due to London forces

C₅H₁₂ hydrophobic bonding:

 $H_3C-CH_2-CH_2-CH_2-CH_3$ 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.

Reactivity/ Reactions

Exothermic Reaction: Negative ΔG

Example: Combustion of Pentane



Progress of reaction is also called Reaction Coordinate S.M. = starting material or reactants (e.g. pentane, oxygen)

Energy diagram for the reaction:



NB: $\Delta E = \Delta G$: Gibbs free
energy (total) change for
the reaction

Reaction coordinate => progress of reaction

- The above reaction is an exothermic reaction, heat is released during reaction

- ΔG will be negative ($\Delta G < 0$) for an exothermic (heat releasing) reaction, but will be positive ($\Delta G > 0$) for endothermic reaction.

- E_A = Activation energy: minimum amount of energy required to activate molecules or atoms to be able to undergo a chemical reaction.

- Activated complex **or transition state (T.S):** Highest energy point in a reaction pathway in which bonds are being formed and broken simultaneously. A T.S. cannot be observed or isolated. Should not be confused with and an intermediate.

Thermodynamic of a chemical reaction:



 $\Delta G = -RT \ln K_{eq}$ $R = Gas \text{ constant} = 0.082 \underline{L \cdot atm} \text{ mol} \cdot K$ $T = Temperature \text{ in } ^{\circ}K$ $\Delta G = Change \text{ in energy of system (determines equilibrium)}$ $E_a = Activation \text{ energy } \rightarrow \text{ determines rate of reaction}$

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

 ΔG determines product concentrations at equilibrium Ea determines rate of reaction

Reaction proceeding through an intermediate



NB: The Rate Determining Step is the TS with the larger E_A , which will be the slowest step; that is for the diagram to the left, the first step is the rate determining step.

Endothermic Reaction: Positive ΔG



Progress of reaction

Summary:

 $\Delta E = \Delta G$: Gibbs free energy (total) change for the reaction

Exothermic reactions have $\Delta G = Negative$

Endothermic reactions have $\Delta G = Positive$

TS = Transition State: Point where bonds are partially broken and partially formed

Intermediate: Short lived species

Review Calculation below

Bond Energy

Example:

Radicals

 $H-CH_3 \longrightarrow H \bullet + \bullet CH_3$

Bond	Bond Energy (kcal/mol)
H-C	99
H-O	111
C-C	83
C=O	179
0=0	119

e.g.)
$$CH_4 + 2 O_2 \xrightarrow{\Delta} CO_2 + 2 H_2O - Exothermic reaction (releases Energy (E))$$

 $\Delta E_{reaction} = \Delta E_{SM}$ - ΔE_{pdt}

For CH ₄ :	$4 \times C-H \text{ bonds} = 4 \times 99$		= 396 kcal/mol	$\Delta E_{SM} = sum of bonds$
	2 x O=O	= 2 x 119	= <u>238 kcal/mol</u>	broken (enthalpy)
	ΔE_{SM}		= 634 kcal/mol	· · · · · · · · · · · · · · · · · · ·

For products:	2 C = 0 = 2	x 179 = 358 kcal/mol	$\Delta E_{pdt} = sum of bonds formed$
	4 H-O = 4	x 111 = 444 kcal/mol	
	ΔE_{pdt}	= 802 kcal/mol	

 $\Delta E_{reaction} = 634 \text{ kcal/mol} - 802 \text{ kcal/mol} = -168 \text{ kcal/mol}$ (exothermic reaction, energy released)