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 ½ of the number of shared outer shell electrons

1. Nitrite anion



Overall charge on the nitrite anion is = -1

Resonance Structures: Different drawings of the same molecule.

- 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 (+) is used indicate resonance forms
- 1. CH₄ Methane below are POOR resonance structures additional charges or unshared electrons (not inert gas configuration)

• CH₃

but methyl radical – can be reactive intermediate in principle





but methyl anion – can be a reactive intermediate in principle





Methyl cation can be a

- reactive intermediate in principle

⊕ CH₃

1. 1,2-Dichlorobenzene



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
 - 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.

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)
 - ii) Dipole-dipole interaction
 - iii) London forces (temporary dipole; hydrophobic bonding) weakest on per atom basis

Hydrogen Bonding:

- Donors: H attached to a very electronegative atom (N, O, F, Cl)
- Acceptors: A lone pair of electrons, usually on N or O or F
- Strongest intermolecular attractive force on a per atom basis

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



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

Dipole-Dipole Interactions:

Dipole drawing convention:

$$\delta^+$$
 δ^-

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

1. Methane; CH₄



- C and H have ~same electronegativity
- Non-polar (net-zero ~dipole)
- Gaseous
- Low BP -164 °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 $^{\circ}$ C MP – 64 $^{\circ}$ C

5. Tetrachloromethane, carbon tetrachloride; CCl₄ (toxic)



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

London Forces (Temporary Dipoles):

- Also know as London dispersion forces
- Distortion of filled outer shell electrons
- Principal effect in hydrophobic interactions

Atoms	Boiling Point	
Не	-269 °C	Small atom/ Low polarizability
Ne	-246 °C	
Ar	-186 °C	
Kr	-153 °C	\checkmark
Xe	-108 °C	Large atom/ High polarizability



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

 CH_4 associates with CH_4 due to London forces C_5H_{12} hydrophobic bonding



n-pentane is a liquid at 20° C - 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:

 CH_4

+ $2 O_2$ + $2 H_2O$

Energy diagram for the reaction:



Reaction coordinate => progress of reaction

Reactants or starting material (S.M.): CH_4 and O_2 Products: CO_2 and H_2O

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

- This reaction is an exothermic reaction, heat is released during reaction
- ΔG = negative for an exothermic (heat releasing) reaction, positive 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:

Temperature in °K
(°K = °C + 273)

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

$$\Delta G = \Delta H - T\Delta S (2nd law of thermodynamics)$$
Change in enthalpy
= bond energy Change in entropy
= bond energy = measure of disorder in system

$$\Delta G = -RT \ln K_{eq}$$

$$R = Gas constant = 0.082 L:atm
mol·K
T = Temperature in °K
$$\Delta G = Change in energy of system (determines equilibrium)$$

$$E_a = Activation energy \rightarrow determines rate of reaction$$

$$A + B \longrightarrow C + D$$

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

$$Keq = \frac{\left[CH_4 \right] \left[O_2 \right]^2}{\left[CO_2 \right] \left[H_2O \right]^2}$$
Hence ΔG determines product concentrations at equilibrium and the concentration of the concentratic the con$$$$

Hence ΔG determines product concentrations at equilibrium Ea determines rate of reaction

Endothermic Reaction: Positive ΔG .



Reaction Coordinate