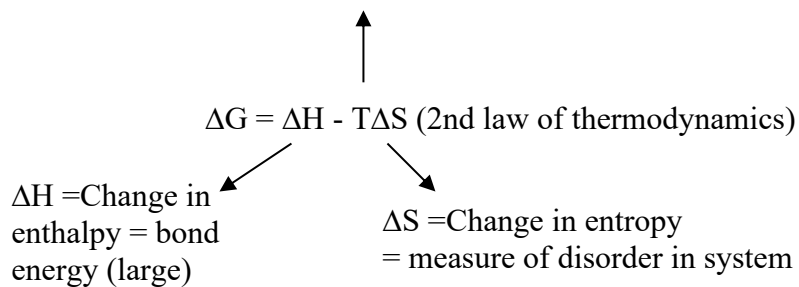


Reactivity/ Reactions**Thermodynamics of a chemical reaction:**

T = Temperature in °K
 (°K = °C + 273)



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

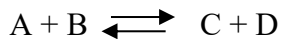
$$R = \text{Gas constant} = 0.082 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

T = Temperature in °K

ΔG = Change in energy of system (determines equilibrium)

E_a = Activation energy → determines rate of reaction

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

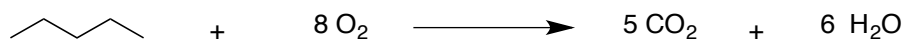


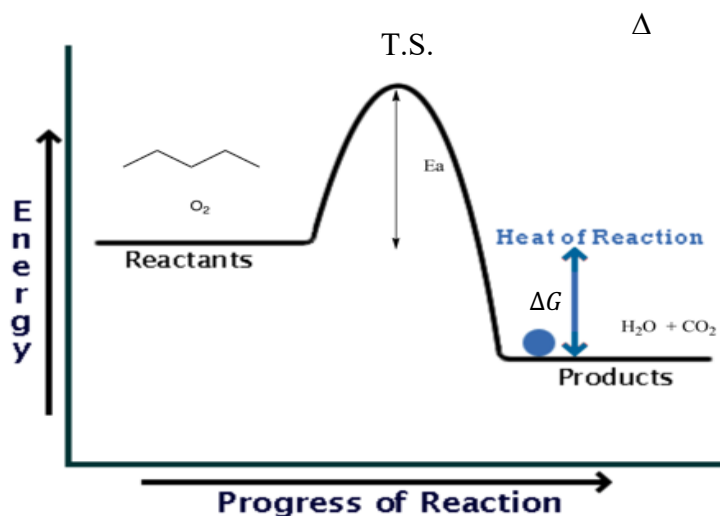
ΔG determines product concentrations at equilibrium

E_a determines rate of reaction

Exothermic Reaction: Negative ΔG

Example: Combustion of Pentane





Progress of reaction is also called Reaction Coordinate

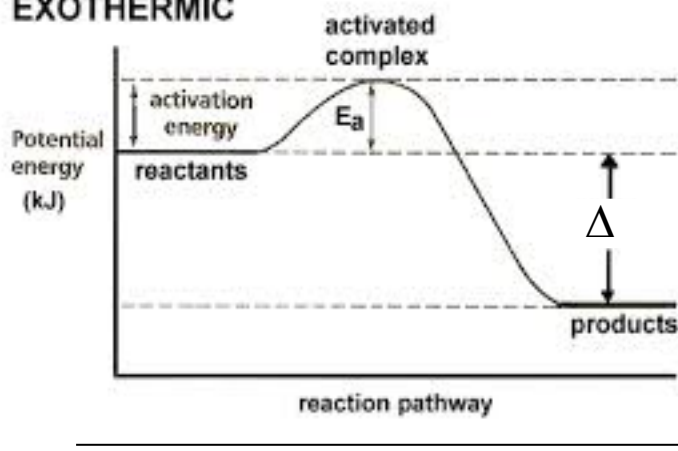
S.M. = starting material or reactants (e.g. pentane, oxygen)

P = product (carbon dioxide, water)

T.S = transition state (bonds are partially made and broken, not an intermediate)

Energy diagram for the reaction:

EXOTHERMIC



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

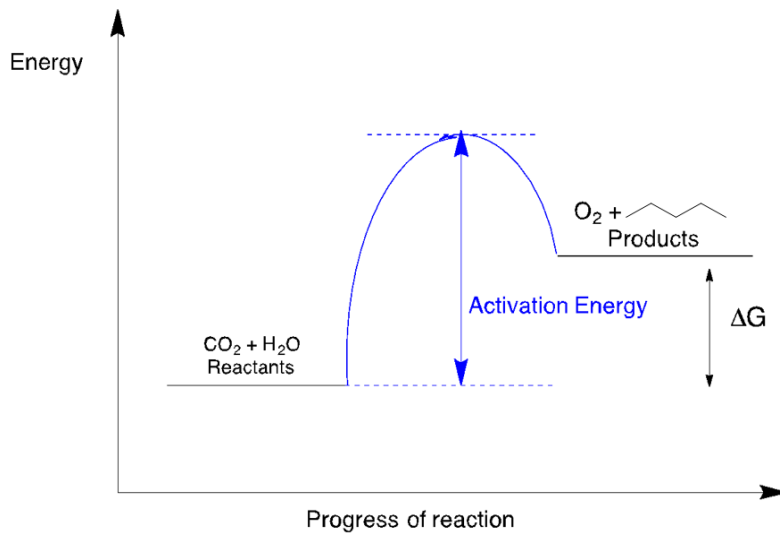
Reaction coordinate => progress of reaction

- 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. Controls the rate of the reaction.

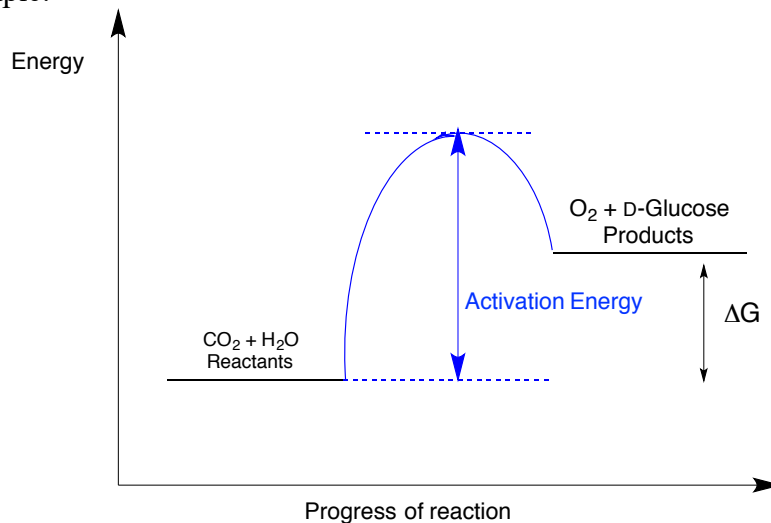
- Activated complex or **transition state (T.S)**: Highest energy point in a reaction pathway in which bonds are being formed and broken simultaneously. A T.S. cannot be observed or isolated. Should not be confused with and an intermediate.

Endothermic Reaction: Positive ΔG

If the reverse of the combustion of pentane were to happen:

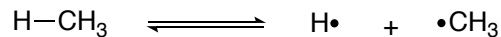


Another example:

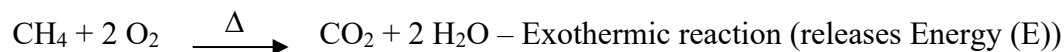


Bond EnergyExample: **Background Only**

Radicals

Change in enthalpy
= bond energy

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

e.g.) Methane (CH₄)

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

For CH₄:

$$\begin{aligned} 4 \times \text{C-H bonds} &= 4 \times 99 &= 396 \text{ kcal/mol} \\ 2 \times \text{O=O} &= 2 \times 119 &= \underline{238 \text{ kcal/mol}} \\ \Delta E_{\text{SM}} &&= 634 \text{ kcal/mol} \end{aligned}$$

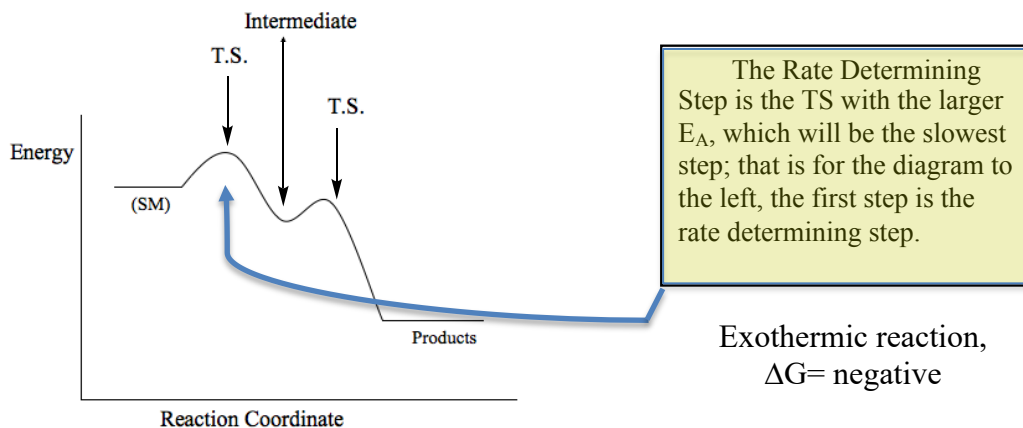
ΔE_{SM} = sum of bonds
broken (enthalpy)

For products:

$$\begin{aligned} 2 \text{ C=O} &= 2 \times 179 = 358 \text{ kcal/mol} \\ 4 \text{ H-O} &= 4 \times 111 = \underline{444 \text{ kcal/mol}} \\ \Delta E_{\text{pdt}} &= 802 \text{ kcal/mol} \end{aligned}$$

ΔE_{pdt} = sum of bonds formed

$\Delta E_{\text{reaction}} = 634 \text{ kcal/mol} - 802 \text{ kcal/mol} = -168 \text{ kcal/mol}$ (a negative energy result means it is an exothermic reaction, energy released). This is the enthalpy ΔH .

Reaction proceeding through an intermediate - Know this**Summary:**

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

$$\begin{array}{c} \text{Change in Entropy} \\ \downarrow \\ \Delta G = \Delta H - T\Delta S \text{ (2nd law of thermodynamics)} \\ \downarrow \end{array}$$

Exothermic reactions have $\Delta G = \text{Negative}$

Endothermic reactions have $\Delta G = \text{Positive}$

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

Intermediate: Short lived species

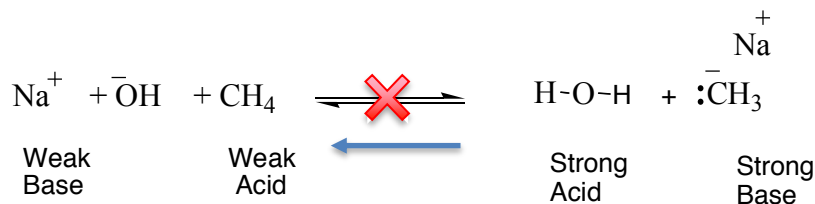
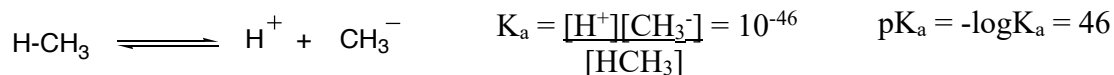
Acids and Bases**Bronsted – Lowry :**

- An acid **donates proton (H^+)**
- A base **accepts a proton (H^+)**

Ex) $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

- Very fast reaction as HCl is a strong acid and NaOH is a strong base. NaCl is a weak base (weak conjugate base) and H_2O is a weak acid (weak conjugate acid).

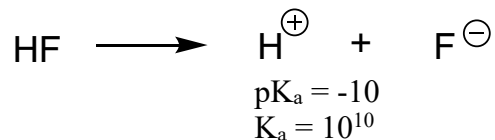
Ex #1) Methane:



$$\begin{aligned} \text{p}K_a \text{ CH}_4 &= 46 \\ \text{p}K_a \text{ H}_2\text{O} &= 15.7 \end{aligned}$$

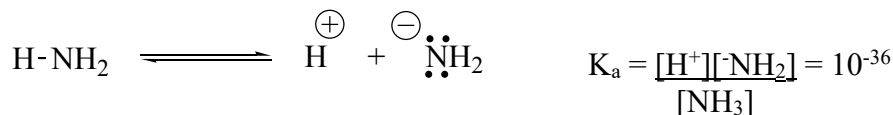
The equilibrium above lies far (exclusively) to the left. Hydroxide will NOT deprotonate methane.

Ex #2) Ionization of HF

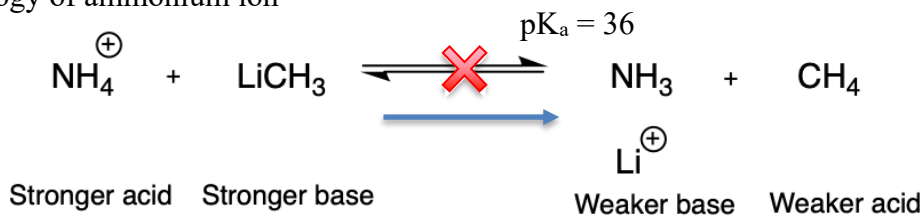


HF when solvated has a pKa of 3.5

Ex #3) Ammonia Gas:



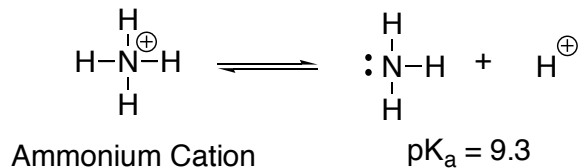
Biology of ammonium ion



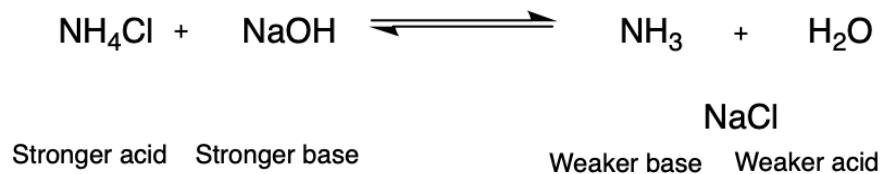
Ammonia gas is a better acid compared to methane (bigger K_a), because nitrogen is more electronegative than carbon. It can hold a negative charge easier than carbon.

NB: The lower the $\text{p}K_a$ the more acidic

pK_a of "Ammonia" in biological system



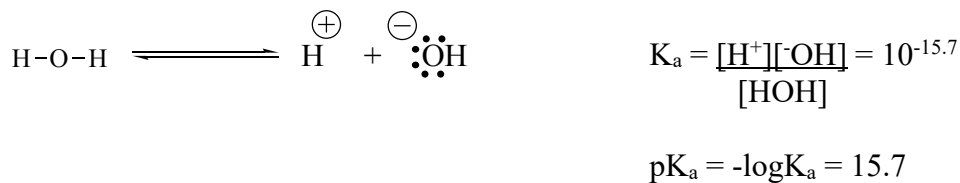
NB: Oxygen is more electronegative than nitrogen, which makes water more acidic than ammonia. Nitrogen more electronegative than carbon and that makes ammonia more acidic than methane.



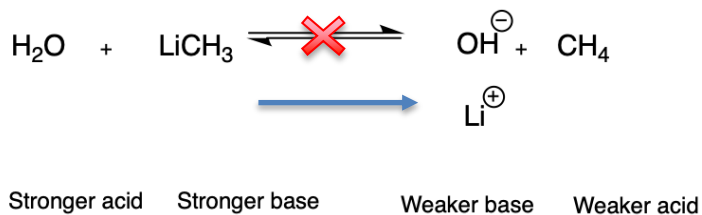
pK_a H₂O = 15.7 (weaker acid)

pK_a NH₄ = 9.3 (stronger acid)

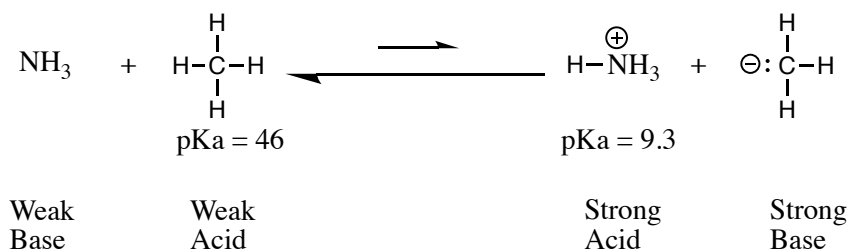
Ex #4) Water:



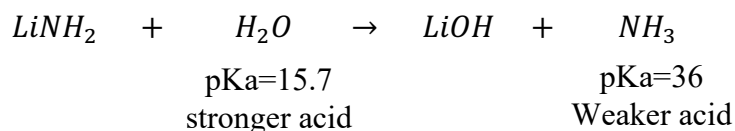
Ex #5) Methyl Lithium



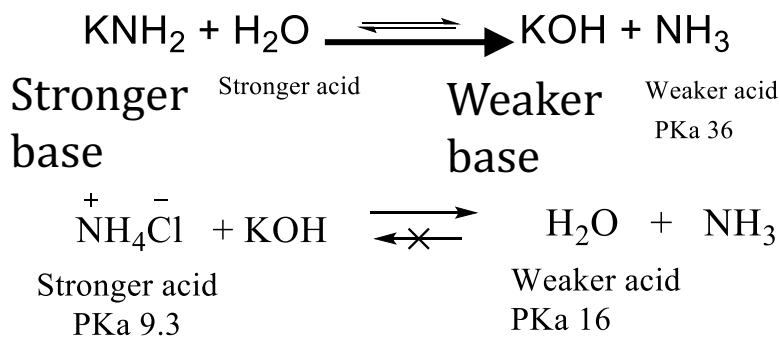
Ex #6) Strong acid/base



Another example:



Another example:



The reaction lies far (exclusively) to the left since ammonia is not a strong enough base to deprotonate methane

The lower the pK_a the more acidic the compound

Examples of strong acids:

Acid	pK_a
HI	-10
HBr	-9
HCl	-7
HF	-10
H_3O^+	-1.75

Can go up to +3.17 in a diluted solution (in water)

Two factors that affect acidity of the above acids:

- 1) Electronegativity – the more electronegative the atom, the better it can hold a negative charge
- 2) Solvation – the larger the ion, the better solvated it can be and so the more acidic its conjugate acid will be

Electromagnetic Radiation:

Infrared (IR) Spectroscopy – Background only:

$E = hc/\lambda = hv$, energy is quantized

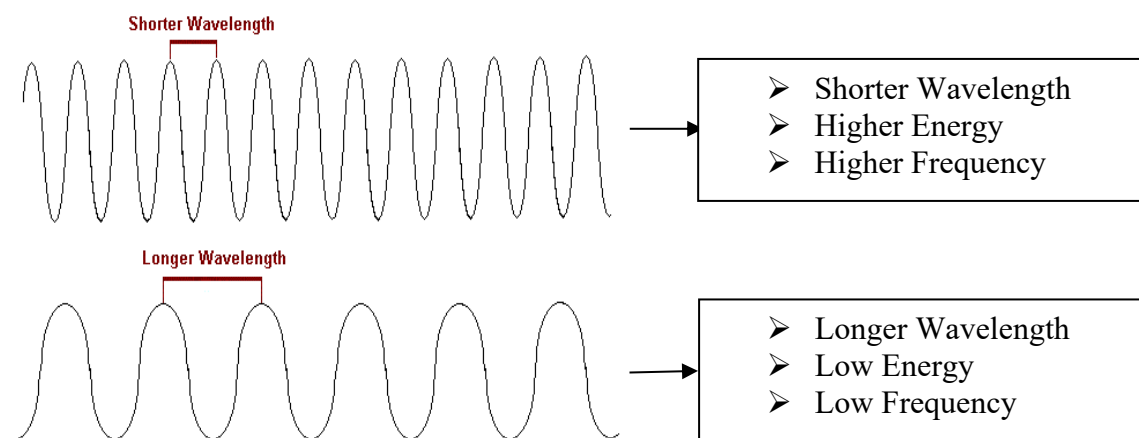
E = Energy

h = Planck's Constant = 6.6×10^{-34} joules/sec

v = Frequency

λ = Wavelength

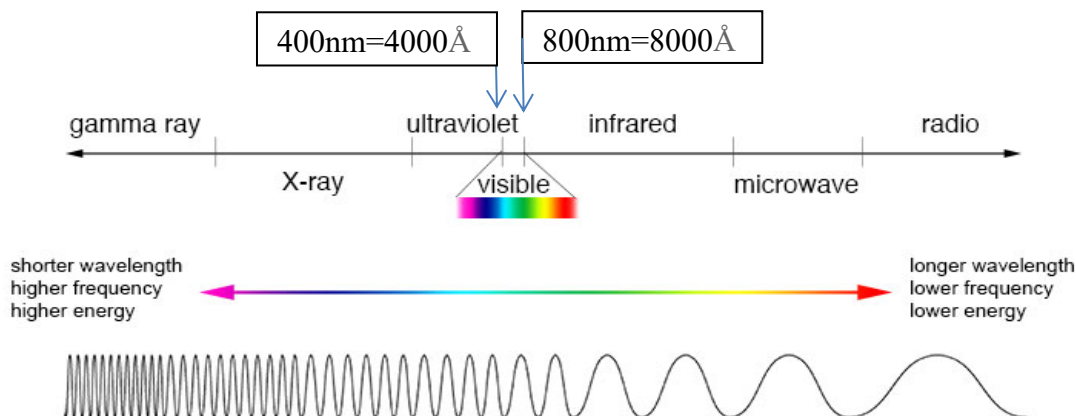
c = Speed of light = 3.0×10^{10} cm/sec



NB: There is an inverse relationship between wavelength and frequency.

Electromagnetic Spectrum:

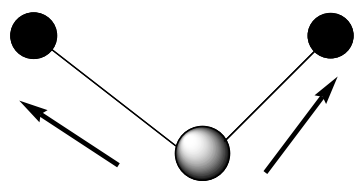
NB: 1nm = 10 angstrom



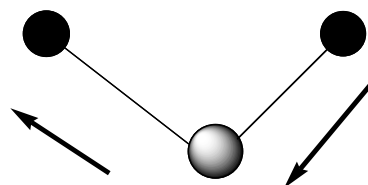
UV and visible light: conjugated double bond systems
 e.g. C=C bonds absorb UV light and some visible light

Infrared Radiation: bond stretching and bending modes-Measured in wavenumbers (cm^{-1})

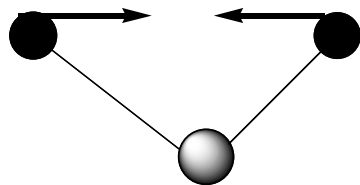
- Defined as cycles/second

e.g. O-H bond can be seen around $\sim 3400\text{cm}^{-1}$ in an IR spectrum

SYMMETRIC STRETCHING

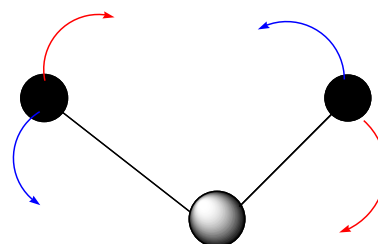


ASYMMETRIC STRETCHING



IN PLANE BENDING

(SCISSORING)



OUT OF PLANE BENDING

(TWISTING)

IR is Background Only - NOT on Midterm for Lecture Part

NEXT SECTION: Lecture Outline 2: ALKANES - Next Lecture on January 22

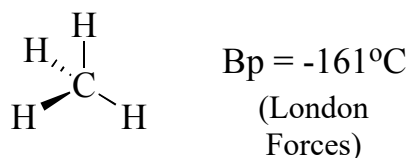
Hydrocarbons – Compounds that contain only C and H

- Alkanes contain only single bonds (C-H, C-C), sp^3
- Alkenes = contains C=C and has sp^2 hybridization (e.g. olefins)
- Alkynes = contains C \equiv C and has sp hybridization (acetylenes)

Alkanes

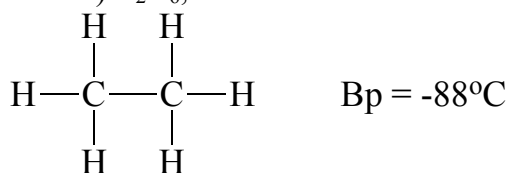
- All carbons are sp^3 hybridized (optimal bond angle of 109°)
- Single bonds (σ bonds).
- Tetrahedral geometry at every carbon
- Held together by London (dispersion) forces

Ex #1) CH₄, methane



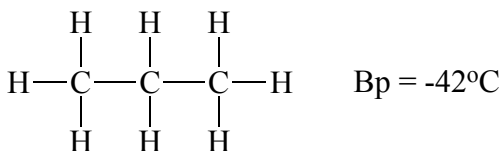
BP = -164°C
CH₄ H₄C CH₃-H

Ex #2) C₂H₆, ethane



C₂H₆ CH₃-CH₃ H₃C-CH₃ BP = -88°C

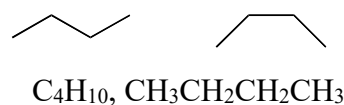
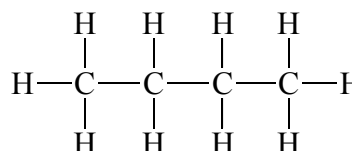
Ex #3) C₃H₈, propane



C₃H₈ CH₃CH₂CH₃  H₃C-

BP = -42°C

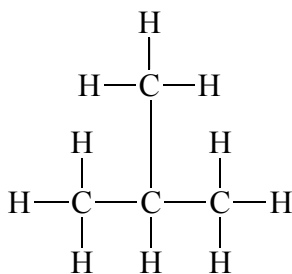
Ex #4) C₄H₁₀, butane



n-Butane: normal straight chain butane

NOTE: Propane has a boiling point of -42°C , which is higher than methane because its chain-like structure allows for more surface area for London dispersion forces to take effect.

Ex #5) C_4H_{10} , isobutane or i-Butane

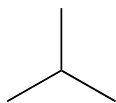


- Isomers are different compounds that have the same molecular formula and different structure. They have different physical properties (e.g. mp, bp, odour, biological effects)

- iso - meros
same - parts

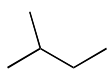
one type: structural (same as constitutional)

second type: stereoisomers (diastereomers and enantiomers) – will talk about more

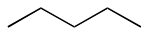


structural isomer = constitutional isomer

Ex #6) Pentane C_5H_{12}



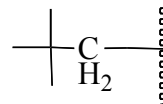
(isopentane or 2-methylbutane)



n - pentane



Neopentane

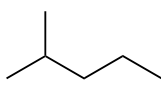


Neo Group

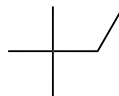
Ex #7) Hexane C_6H_{14}



n-hexane



Isohexane

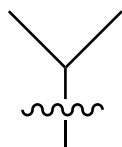


neohexane

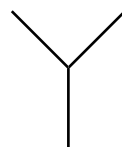
Systematic (IUPAC) Nomenclature

RULES:

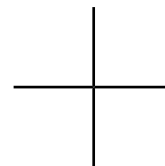
1. Find the longest straight chain
2. Number from end of the chain, so that the 1st branch point has the lowest number
3. Name the chain, then add prefixes (for the groups attached) with number and name the groups attached
4. Separate numbers and names by dash



Common name: isopropyl
 Systematic name:



isobutane
 2-methylpropane



neopentane
 2,2-dimethylpropane

Note: iso = second-to-last carbon of the chain is disubstituted (2 methyl groups)
 neo = second-to-last carbon of the chain is trisubstituted (3 methyl groups)

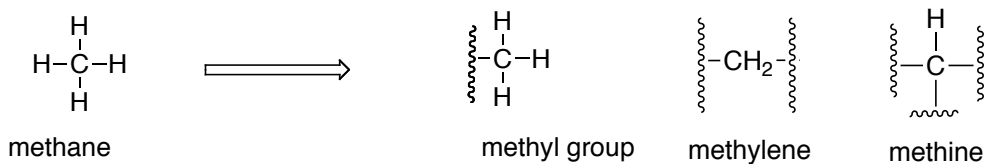
Prefixes for naming:

Di (2), Tri (3), Tetra (4), Penta (5), Hexa (6) etc.

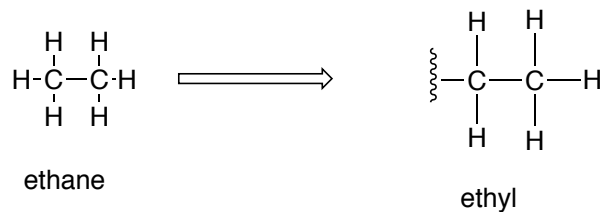
Groups (part of an alkane structure)

- In naming the particular group, drop the “ane” part and add “yl” to the name
- For example, methane → methyl

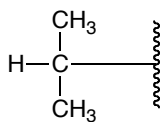
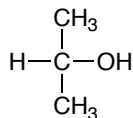
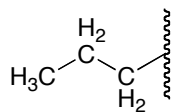
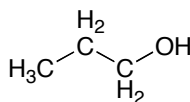
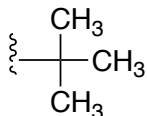
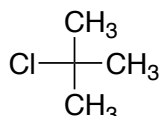
(i) Methyl group – CH₃



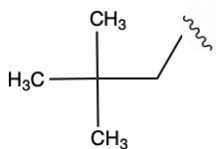
(ii) Ethyl group – CH₂CH₃



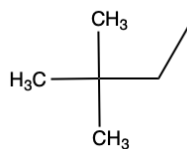
(iii) Isopropyl group

iso-propyl
groupiso-propyl
alcohol(iv) *n*-Propyl group*n*-propyl chain*n*-propyl alcohol(v) *tert*-Butyl group (t-butyl)*tert*-Butyl chain*tert*-Butyl chloride

(vi) neo group



neo chain



2,2-dimethylbutane