Reactivity/ Reactions

Thermodynamics of a chemical reaction:

T= Temperature in °K
(°K = °C + 273)

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

ΔH =Change in enthalpy = bond energy (large)

ΔS =Change in entropy = measure of disorder in system

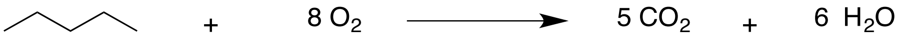
$\Delta G = -RT \ln K_{eq}$
R = Gas constant = 0.082 $\frac{L \cdot atm}{mol \cdot K}$
T = Temperature in °K
ΔG = Change in energy of system (determines equilibrium)
E_a = Activation energy → determines rate of reaction
K_{eq} = equilibrium constant = $\frac{[C][D]}{[A][B]}$ [C] = concentration of compound C

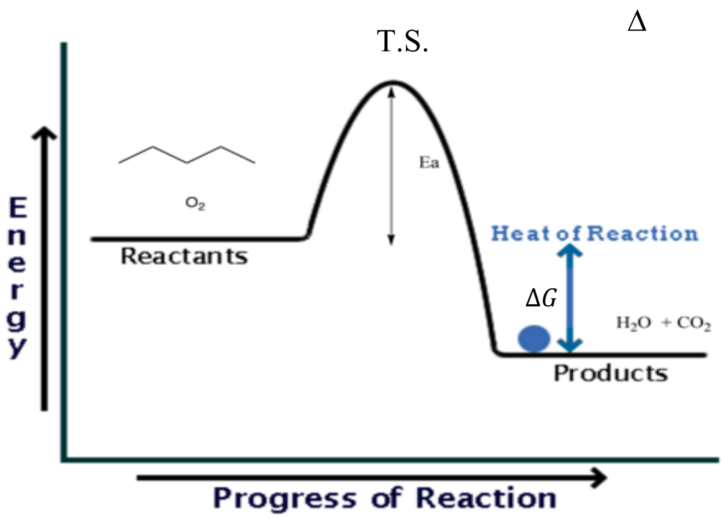
$$A + B \rightleftarrows C + D$$

ΔG determines product concentrations at equilibrium
E_a determines rate of reaction

Exothermic Reaction: Negative ΔG

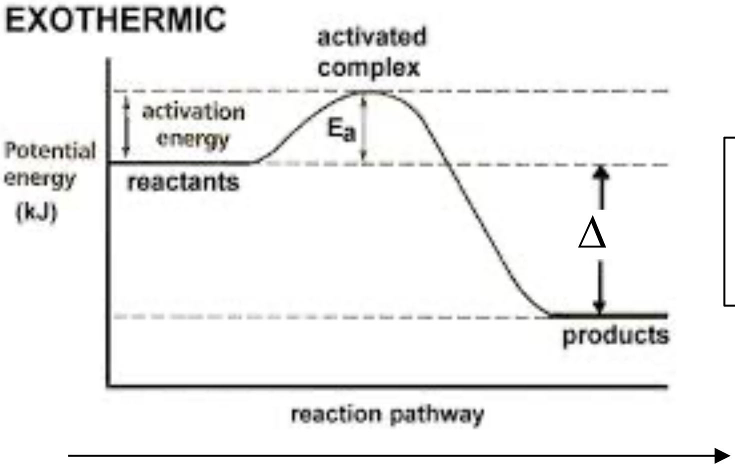
Example: Combustion of Pentane





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:



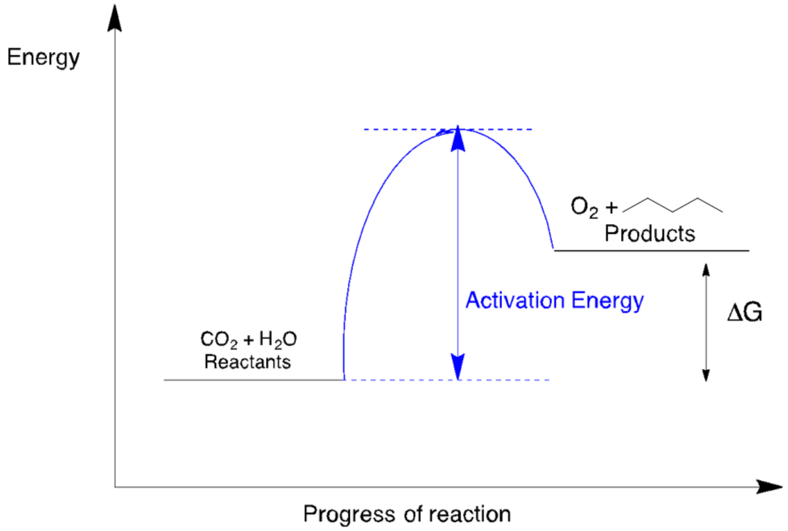
ΔE = ΔG: Gibbs free energy (total) change for the reaction

Reaction coordinate => progress of reaction

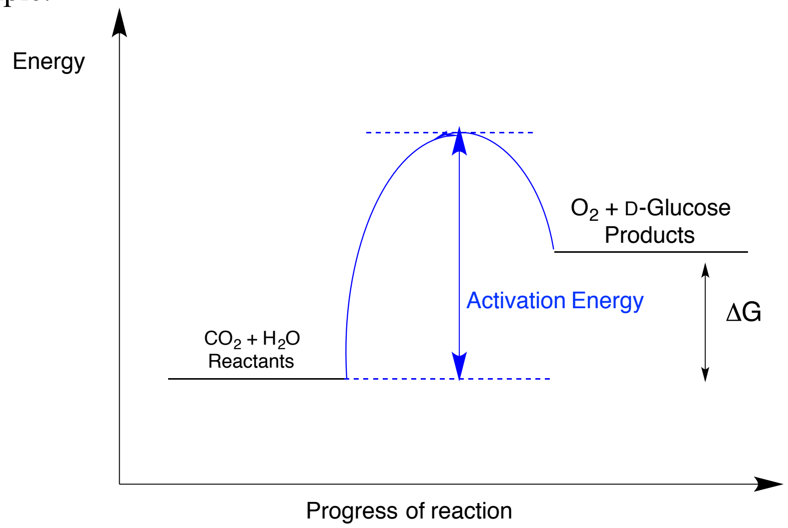
- The above reaction is an exothermic reaction, heat is released during reaction
- ΔG will be negative (ΔG <0) for an exothermic (heat releasing) reaction but will be positive (ΔG >0) for endothermic reaction.
- E_A= Activation energy: minimum amount of energy required to activate molecules or atoms 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 Energy

Example: Radicals

Change in enthalpy
= bond energy

$$H-CH_3 \rightleftharpoons H\bullet + \bullet CH_3$$

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

e.g.) Methane (CH_4)

$CH_4 + 2\ O_2 \xrightarrow{\Delta} CO_2 + 2\ H_2O$ – Exothermic reaction (releases Energy (E))

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

For CH_4:
4 x C-H bonds = 4 x 99 = 396 kcal/mol
2 x O=O = 2 x 119 = <u>238 kcal/mol</u>
ΔE_{SM} = 634 kcal/mol

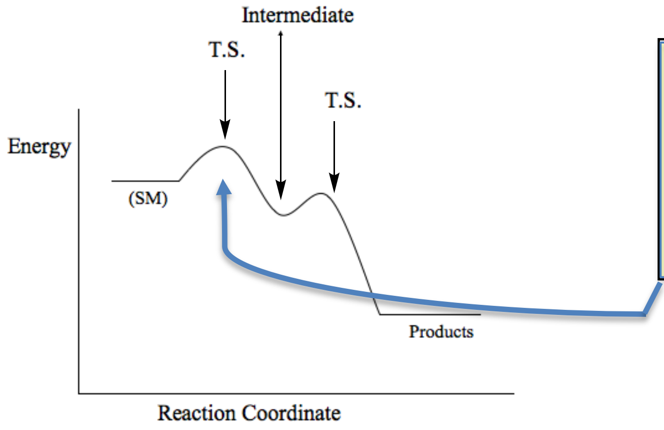
ΔE_{SM} = sum of bonds broken (enthalpy)

For products:
2 C=O = 2 x 179 = 358 kcal/mol
4 H-O = 4 x 111 = <u>444 kcal/mol</u>
ΔE_{pdt} = 802 kcal/mol

ΔE_{pdt} = sum of bonds formed

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

Reaction proceeding through an intermediate



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.

Exothermic reaction,
ΔG= negative

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

Change in Entropy

$$\Delta G = \Delta H - T\overset{\downarrow}{\Delta} S \text{ (2nd law of thermodynamics)}$$

$\downarrow$

Exothermic reactions have ΔG = Negative

Endothermic reactions have ΔG = 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) $HCl + H_2O \quad H_3O^+ + Cl^-$
- 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).

$$\mathrm{HCl} \longrightarrow \mathrm{H}^{+} + \mathrm{Cl}^{-}$$

$$\mathrm{NaOH} \longrightarrow \mathrm{Na}^{+} + \mathrm{OH}^{-}$$

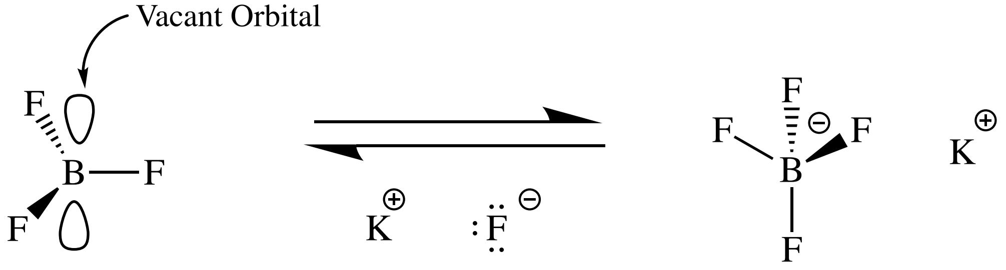
$$\mathrm{HCl} + \mathrm{NaOH} \longrightarrow \mathrm{NaCl} + \mathrm{H\text{-}OH}$$

Lewis Acid/Base:

- An **acid accepts a pair of electrons**
- A **base donates a pair of electrons**

e.g) BF_3

- Lewis Acid



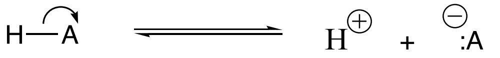
Boron trifluoride	Boron tetrafluoride
-sp^2	-sp^3
-Trigonal planar	-Tetrahedral
-120° bond angle	-109° bond angle

BF_3 can react with potassium fluoride (KF) to obtain an inert gas configuration. However, BF_4^- is unhappy with a formal negative charge, so the reaction is reversible.

- Every Bronsted-Lowry acid/base is also a Lewis acid/ base. The converse statement is not true; not all Lewis acids/bases can be classified as a Bronsted-Lowry acids/bases. BF_3 is not a Bronsted-Lowry acid as it has no hydrogen atoms to donate.

A general acid/base reaction:

$$\mathrm{HA} + \mathrm{B}^{\ominus} \rightleftharpoons \mathrm{A}^{\ominus} + \mathrm{HB}$$



$$K_{eq} = K_a = \frac{[H^+][A^-]}{[HA]}$$

K_a = acidity constant

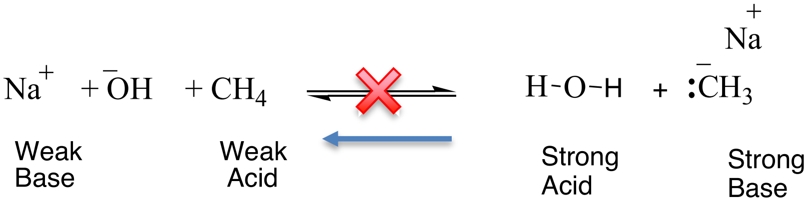
$pK_a = -\log K_a$

C-H > N-H > OH > F-H

Not acidic. Very acidic

Ex #1) Methane:

$$\text{H-CH}_3 \rightleftharpoons \text{H}^+ + \text{CH}_3^- \qquad K_a = \frac{[\text{H}^+][\text{CH}_3^-]}{[\text{HCH}_3]} = 10^{-46} \qquad pK_a = -\log K_a = 46$$



pK_a CH_4 = 46
pK_a H_2O = 15.7

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

Ex #2) Ionization of HF

$$\text{HF} \longrightarrow \text{H}^{\oplus} + \text{F}^{\ominus}$$

$pK_a = -10$
$K_a = 10^{10}$

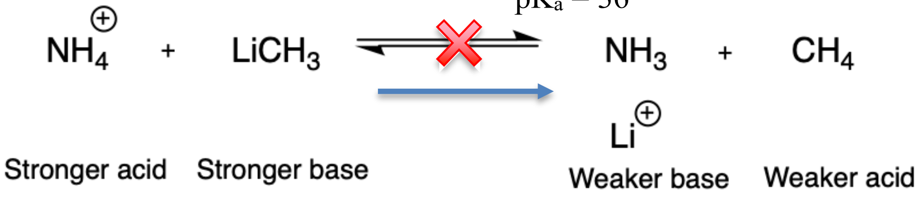
HF when solvated has a pKa of 3.5

Ex # 3) Ammonia Gas:

$$\text{H-NH}_2 \rightleftharpoons \text{H}^{\oplus} + {}^{\ominus}\ddot{\text{N}}\text{H}_2 \qquad K_a = \frac{[\text{H}^+][^-\text{NH}_2]}{[\text{NH}_3]} = 10^{-36}$$

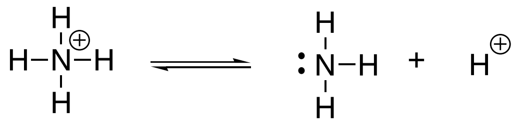
Biology of ammonium ion

$pK_a = 36$



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.

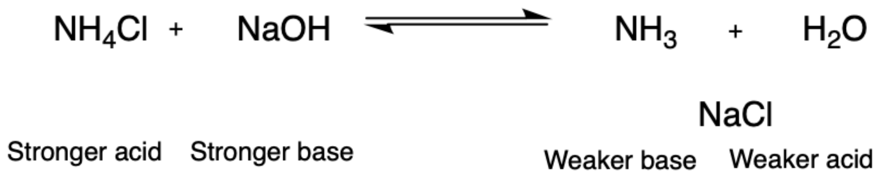
NB: The lower the pK_a the more acidic pK$_a$ of “Ammonia” in biological system



Ammonium Cation

pK$_a$ = 9.3

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.



$$NH_4Cl + NaOH \rightleftharpoons NH_3 + H_2O + NaCl$$

pK$_a$ H_2O = 15.7 (weaker acid)
pK$_a$ NH_4 = 9.3 (stronger acid)

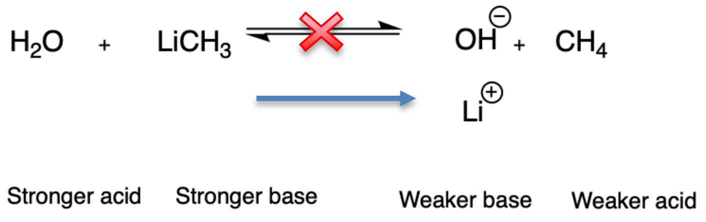
Ex #4) Water:

$$H{-}O{-}H \rightleftharpoons H^{+} + {:}\ddot{O}H^{-}$$

$$K_a = \frac{[H^+][^-OH]}{[HOH]} = 10^{-15.7}$$

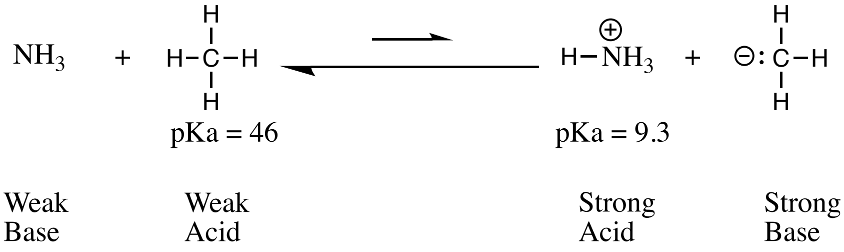
$$pK_a = -\log K_a = 15.7$$

Ex #5) Methyl Lithium



$$H_2O + LiCH_3 \rightarrow OH^{-} + CH_4 + Li^{+}$$

Ex #6) Strong acid/base



Another example:

$$LiNH_2 \quad + \quad H_2O \quad \rightarrow \quad LiOH \quad + \quad NH_3$$

pKa=15.7 stronger acid

pKa=36 Weaker acid

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:

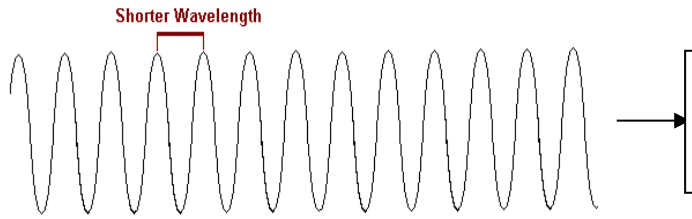
1) Electronegativity – the more electronegative the atom, the better it can hold a negative charge
2) Solvation – the larger the ion, the better solvated it can be and so the more acidic its conjugate acid will be

Electromagnetic Radiation:

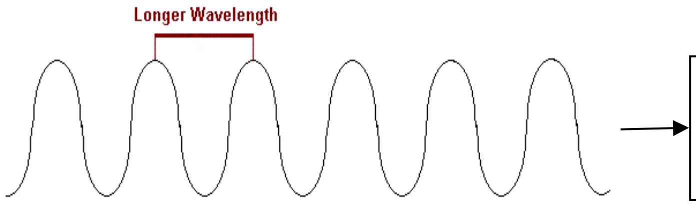
Infrared (IR) Spectroscopy – Background only:

$E = hc/\lambda = h\nu$, energy is quantized

E = Energy
h = Planck’s Constant= 6.6×10^{-34} joules/sec
ν = Frequency
λ = Wavelength
c = Speed of light = 3.0×10^{10} cm/sec



- ➢ Shorter Wavelength
- ➢ Higher Energy
- ➢ Higher Frequency

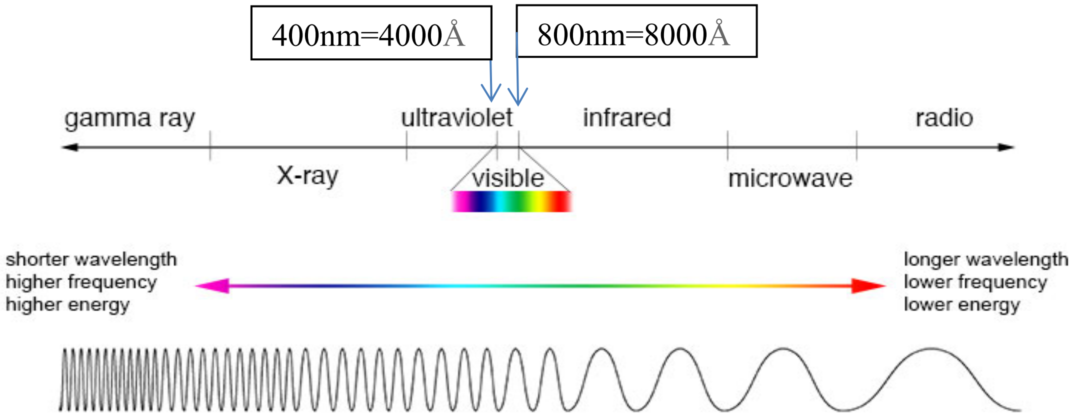


- ➢ Longer Wavelength
- ➢ Low Energy
- ➢ Low Frequency

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

Electromagnetic Spectrum:

NB: 1nm = 10 angstrom



UV and visible light: conjugated double bond systems

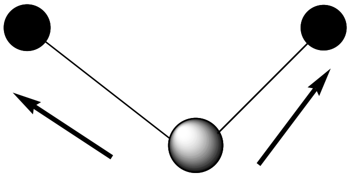
e.g. C=C bonds absorb UV light and some visible light

Infrared Radiation: bond stretching and bending modes

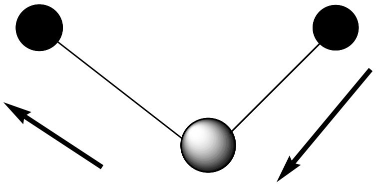
-Measured in wavenumbers (cm^{-1})

- Defined as cycles/second

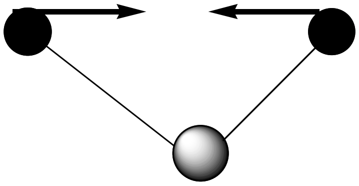
e.g. O-H bond can be seen around ~3400cm^{-1} in an IR spectrum



SYMMETRIC STRETCHING

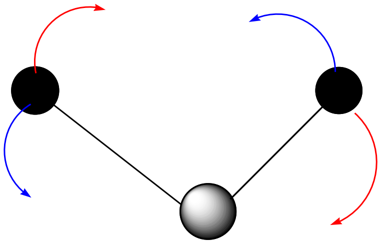


ASYMMETRIC STRETCHING



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

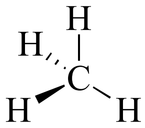
Hydrocarbons – Compounds that contain only C and H

- 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≡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) CH_4, methane

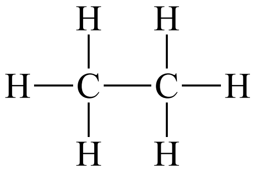


Bp = -161°C
(London
Forces)

BP = -164 °C

CH_4 H_4C CH_3-H

Ex #2) C_2H_6, ethane

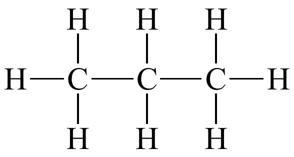


Bp = -88°C

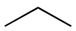
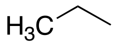
BP = -88 °C

C_2H_6 CH_3-CH_3 H_3C-CH_3

Ex #3) C_3H_8, propane

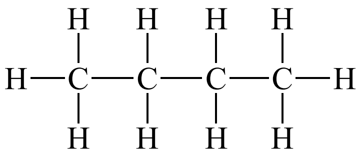


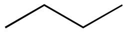
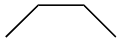
Bp = -42°C

C_3H_8 $CH_3CH_2CH_3$  

BP = -42 °C

Ex #4) C_4H_{10}, butane



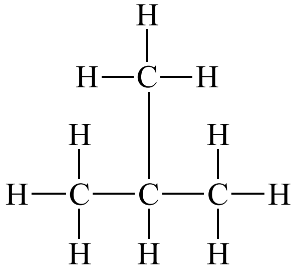
 

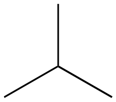
C_4H_{10}, $CH_3CH_2CH_2CH_3$

n-Butane: normal straight chain butane

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

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





structural isomer = constitutional isomer

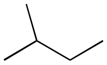
- Isomers are different compounds that have the same molecular formula and different structure. They have different physical properties (e.g. mp, bp, odour, biological effects)

\- iso - meros
same - parts

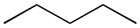
one type: structural (same as constitutional)

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

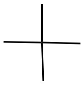
Ex #6) Pentane C_5H_{12}



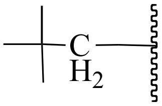
(isopentane or 2-methylbutane)



n - pentane



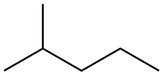
Neopentane



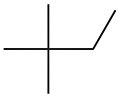
Neo Group

Ex #7) Hexane C_6H_{14}

n-hexane



Isohexane

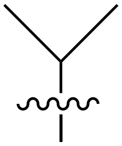


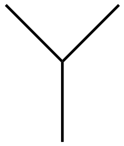
neohexane

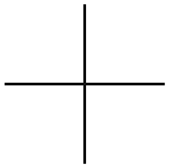
Systematic (IUPAC) Nomenclature

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	isobutane	neopentane
Systematic name:		2-methylpropane	2,2-dimethylpropane

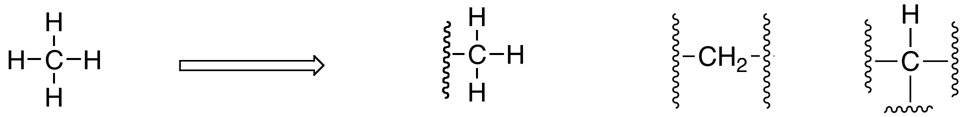
Note: iso = second-to-last carbon of the chain is disubstituted (2 methyl groups)
neo = second-to-last carbon of the chain is trisubstituted (3 methyl groups)

Prefixes for naming:
Di (2), Tri (3), Tetra (4), Penta (5), Hexa (6) etc.

Groups (part of an alkane structure)

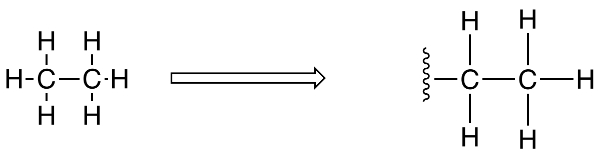
- In naming the particular group, drop the "ane" part and add "yl" to the name
- For example, methane → methyl

(i) Methyl group – CH_3



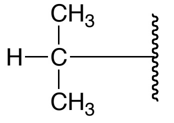
methane methyl group methylene methine

(ii) Ethyl group – CH_2CH_3

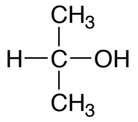


ethane ethyl

(iii) Isopropyl group

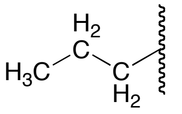


iso-propyl group

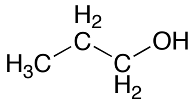


iso-propyl alcohol

(iv) *n*-Propyl group

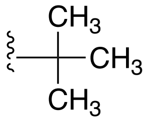


n-propyl chain

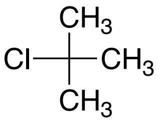


n-propyl alcohol

(v) *tert*-Butyl group (t-butyl)

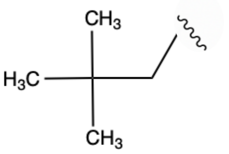


tert-Butyl chain

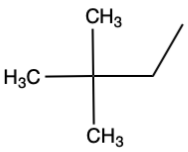


tert-Butyl chloride

(vi) neo group



neo chain



2,2-dimethylbutane