

Thermochimistry

*net all anti by
of heat supplied*

$Q = \Delta U - w$ (first law of Thermodynamics)
 change in net energy can't be created or destroyed
 internal work it can only be transferred.
 done on the system

→ at Constant Volume

$$w = 0 = P\Delta V$$

$$P\Delta V = \text{work}$$

work done

by the system

$$\Delta U = \Delta E = q_V$$

→ at Constant pressure

$$Q = \Delta U + P\Delta V$$

$$\Delta H = \Delta U + P\Delta V$$

enthalpy

enthalpy of rxn. is heat

change at constant pressure

$$q_p = q_V + \Delta n gRT$$

at STP → 0°C, 273K
1 atm

R → 2 cal/or?/mole K

for systems we use

Kilocalorie

R → 8.314 Joules/Mole K

R → 0.082 atm/Mole K

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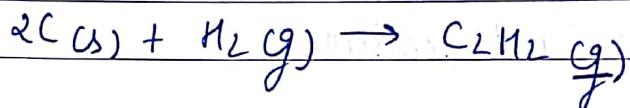
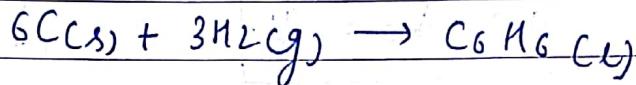
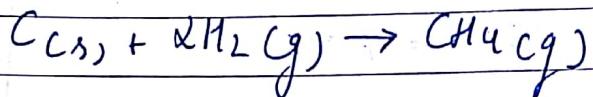
Enthalpy or heat of reaction: the amount of heat liberated or absorbed when the given quantity in a reaction is completely reacted.



Types of Enthalpy-

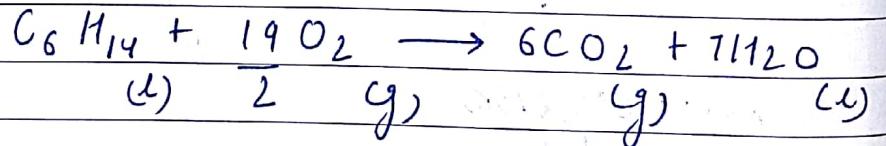
① Enthalpy of formation-

It is the heat change in formation of 1 mole of a compound from its constituents in their natural elemental form at a given temperature and pressure



② Enthalpy of Combustion-

The heat change in complete burning of 1 mole of a substance in presence of oxygen is known as enthalpy of combustion.



③ Enthalpy of Neutralisation-

The heat change when one gram equivalent of an acid completely neutralises one gram equivalent of a base. For a strong acid and strong base enthalpy of neutralisation is fixed i.e. -13.7 Kcal/g equiv

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January,
11

classmate

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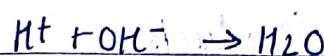
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T-2

$$\text{Eq. wt.} = \frac{\text{Mol. wt.}}{n}$$

$$\text{Moles} = \frac{\text{Mass}}{\text{Mol. wt.}}$$

$$\text{No. g. equiv.} = \frac{\text{Mass}}{\text{Eq. wt.}} = \frac{\text{Mass}}{\text{Mol. wt.}} \times n$$



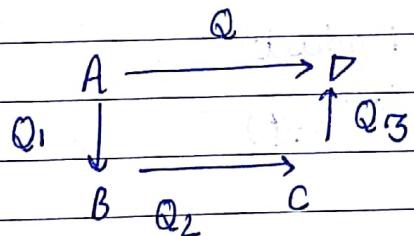
-13.7 Kcal / g. equiv.

(4) Bond Enthalpy-

The amount of energy required to break 1 mole of a substance into its constituent elements in their gaseous state.

Hess's Law -

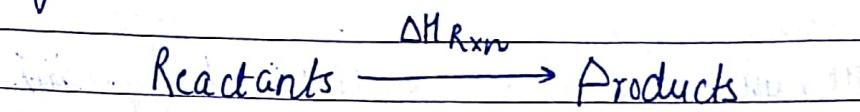
According to this law the heat change of a rxn. depends upon only initial and final states and is independent of path taken



$$Q = Q_1 + Q_2 + Q_3 \quad (\text{According to Hess's law})$$

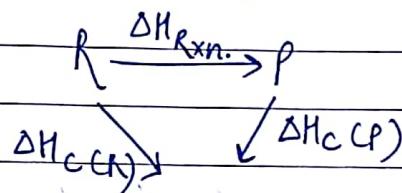
Applications-

- It is used to provide heat of rxn. if enthalpy of formations of Reactants and products are given.

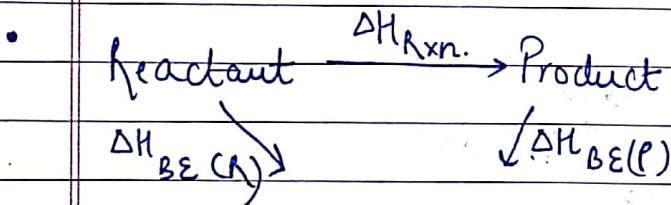


$$\Delta H_{Rxn.} = \sum H_f \text{Products} - \sum H_f \text{Reactants}$$

- We can determine heat of rxn. if enthalpy of Combustion is given.



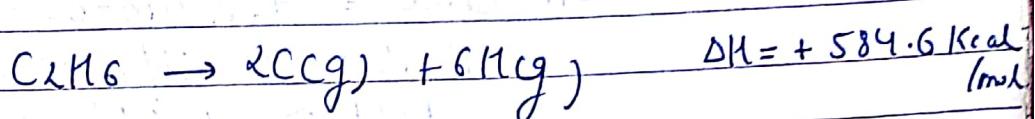
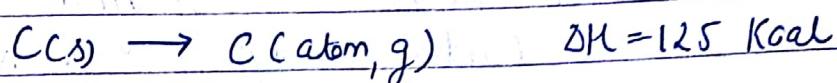
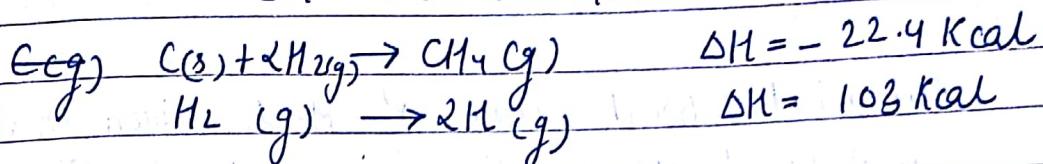
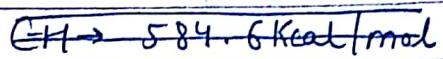
$$\Delta H_{Rxn.} = \sum \Delta H_c \text{Reactants} - \sum \Delta H_c \text{products}$$



Determination of enthalpy of rxn. with Bond energies

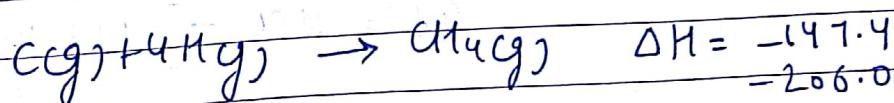
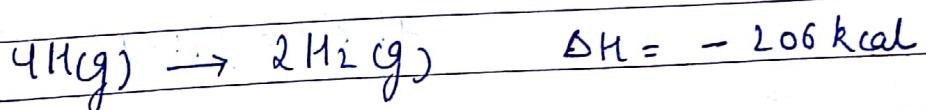
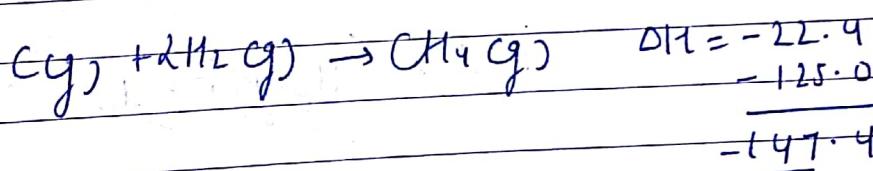
$$\Delta H_{Rxn.} = \frac{\text{Sum of Bond energies of Reactants}}{\text{Sum of Bond energies of Products.}}$$

Qn) from the following info. calculate energy of CH and CC bonds, energy absorb in dissociation of ethane into gaseous atoms is 584 Kcal/Moles



$$\Delta H_{\text{rxn}} = \frac{\text{sum of Bond energies of Reactants}}{\text{of products}} - \frac{\text{sum of Bond energies}}$$

$$= (\text{C-C}) + 6(\text{C-H}) - 0$$



$$\Delta H_{\text{rxn}} = 0 - 4[\cancel{353} \text{ C-H}]$$

$$88.35 = \frac{353.4}{4} = \underline{\underline{\text{C-H}}}$$

88.35

$$+584.6 = C-C + 6(35.54) \\ = C-C + 530.41$$

$$54.56 \text{ kJ/mol} = C-C$$

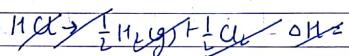
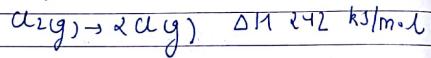
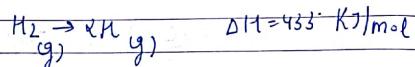
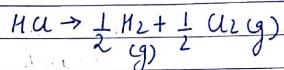
Ques)

Calculate bond energy of H-Cl given that
 H-H bond energy is equal to 433 KJ/mol
 Cl-Cl bond energy is 242 KJ/mol

$$\Delta H_f (\text{HCl}) = -91 \text{ KJ/mol}$$

$$H-H = 433 \text{ KJ/mol}$$

$$Cl-Cl \rightarrow 242 \text{ KJ/mol}$$



$$91 \text{ KJ} = (H-Cl) - \left[\frac{1}{2} \times 433 + \frac{1}{2} \times 242 \right]$$

$$91 = HCl - [121 + 121] \quad [121 + 121 = 242]$$

$$= HCl - 337.5$$

$$428.5 = HCl$$

$\frac{1 \text{ mole}}{\text{mol}}$

FUELS

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- Petroleum is a mixture of thousands of different types of hydrocarbons (crude oil)
 - * light sweet crude oil - (more content of petrol, kerosene) more mixture of hydrocarbons
 - * heavy sweet crude oil - more viscous, not used in industry

→ sweet = sulphur %

→ Petroleum = rocks + oil

→ oil producing countries (Shell gas)
 Saudi Arabia, Russia, U.S., Iran, China

→ shell gas comes from sedimentary rocks (US + China)
 Cost decreases, crude oil is extracted from these (Ankleswar Gujarat), more combustible, good quality

→ Petroleum Hydrocarbon structures -

Paraffins - (Alkanes)

Aromatic - (4n+2, Hückel's Rule)

Naphthenes - (Cyclic alkane) [looks like aromatic but follows Hückel's Rule]

→ Composition of petroleum -

C \rightarrow 80-70%

H \rightarrow 15-16

S, N, O & Cl (1%)

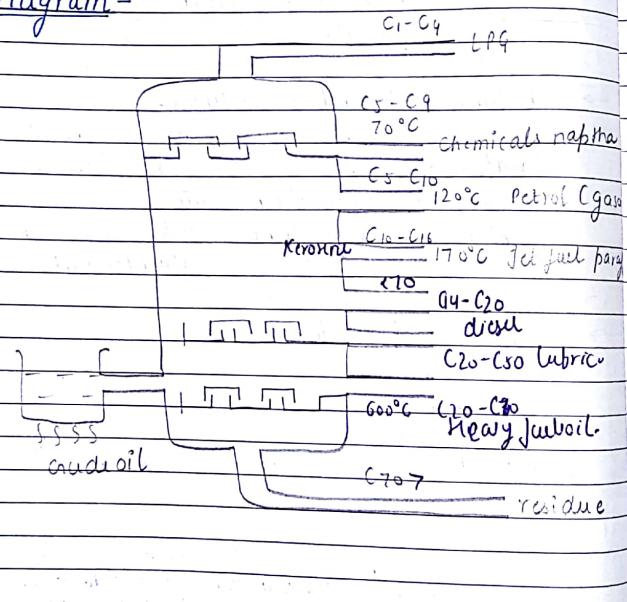
(Hetero atom)

Grade oil					
Hydrocarbons			Non-Hydrocarbons		
Aliphatic	Aromatic	Naphthalene			Metals
25%	17%	50%	8%	1%	3%

Fractional Distillation of Petroleum-

- fractionating tower
- as petroleum is a mixture of substance with different boiling points
- Petrol : $40 - 120^{\circ}\text{C}$
- Kerosene : $180 - 250^{\circ}\text{C}$
- Diesel : $250^{\circ}\text{C} - 320^{\circ}\text{C}$
- naphtha : flammable liquid having low B.P.
- bitumen : last product of petroleum (coaltar)

Diagram-



Grade oil: Petroleum derived from well field

Desalting: water washing to remove impurities

Refining: [fractional distillation] distillation on the basis of boiling point

Reforming: conversion reaction to alter molecular structure

Blending: Mixing of cheap chemicals into petrol eg: alcohol to obtain max commercial character to reduce the price of petrol.

* petrol vehicle is more better: gum deposit is less
* biodiesel more viscous, creates gum deposits

Octane Number-

• octane number signifies the quality of gasoline in automobile engines

→ for grading gasoline (Petrol)

Isooctane = 100 (branching in structure)

n-heptane = 0

→ the % of iso-octane present in the mixture of iso-octane and n-heptane has same knocking property as fuel itself.

→ More the octane number, better the fuel efficiency.

⇒ Reasons for opting the blend of iso-octane and n-heptane

• the different hydrocarbons is gasoline

straight chain paraffins

Iso-paraffins

Naphthalene

Aromatics

• for the same carbon no., straight chain paraffin have higher octane number.

• Olefins also have high O.N. but they cause gum deposits in the fuel tank and are not desirable.

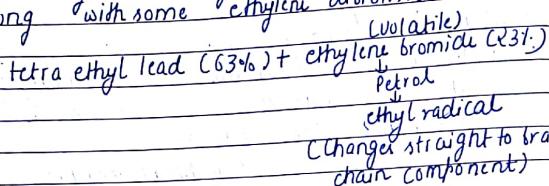
• Aromatic have high O.N. but their content is being

Knocking: When the fuel air mixture undergoes classmate self ignition due to heating and compression of unburned fuel which dissipates its energy by hitting the cylinder walls and piston which results in rattling sound.

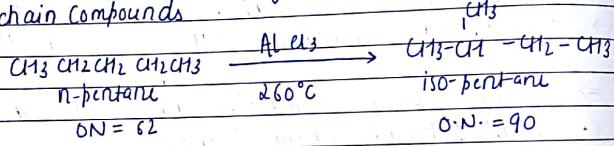
→ TEL give rise to Pb and Pbo which decrease the explosive reaction which decreases engine life. These particulate act as free radical chain inhibitors as they arrest the propagation of two explosive chain reactions responsible for knocking.

Imp - Methods to increase O.N. -

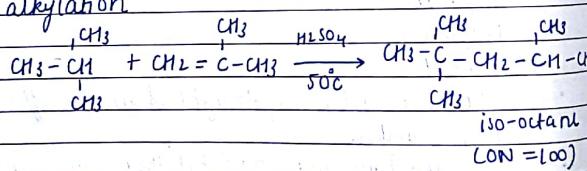
1) By adding antiknocking agent e.g. TEL (about 1.0-3.0 ml/gallon) along with some ethylene dibromide.



2) Isomerisation converts straight chain compounds to branched chain compounds.



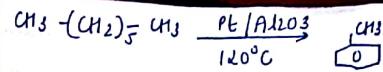
3) By alkylation.



4) By aromatisation

straight chain compound to aromatic compounds.

5)



(Grade oil)
By cracking : reducing chain length and convert to good quality fuel.

• Liquid phase

• Vapour phase

* Liquid phase cracking temp : 920°C - 600°C
pressure : 6-10 atm

* Vapour phase cracking temp : 600 - 800°C
pressure : 3.5 - 10 atm

→ BTX (Benzene, toluene, xylyne)

→ CETANE NUMBER of $(\text{C}_{16}\text{H}_{34})_n$

• for grading diesel oil

• normal paraffins have highest cetane no. followed by naphthenes, iso paraffins, olefins and aromatics

• for grading oil

$n\text{C}_{16}\text{H}_{34}$ Hexadecane (Octane) = 100
 α -methyl naphthalene = 0

• The % of cetane present in the mixture of cetane and α -methyl naphthalene which has the same ignition property as the fuel itself.

• More the cetane number, better the fuel efficiency
Premium value : 65 (45-60)

→ Flash point is the minimum temp. at which the sample gives sufficient vapours which forms an ignition mixture with air, giving a flash when a flame is applied to it. It is called flash point.

At flash point, the vapours may cease to burn when the source of ignition is removed.

Flash point of a flammable liquid is the lowest temp. at which there will be enough flammable vapour to ignite when an ignition source is applied.

16th
January,
H.J.



Fuel- Any substance which on combustion gives heat which can be consumed for domestic or industrial purposes is known as fuel.
classified as primary / natural & secondary / artificial.

Characteristics of Good fuel-

1) Calorific value - The amount of heat generated by complete combustion of unit mass or volume of a fuel is known as calorific value.
units calories/gm

A good fuel will have high calorific value.

Qn) The enthalpy of Combustion of methane is -890 kJ and enthalpy of combustion of ethane is -15597 kJ. Which one is better fuel.

Heat liberated per gram is,

890	1559.7	So good
16	30	fuel is
- 55.62 kJ	519.77	L.I.U.

- 2) Ignition Temperature - The min temp. required to start combustion or burning of fuel.
Good fuel has should be have moderate Ignition Temperature.
- 3) Rate of Combustion -
The rate of Combustion is Moderate.
- 4) Moisture Content -
In solid fuel - There should be moisture content up to 8 to 10%. (low) If high it will decrease calorific value and increase cost of transportation.
- 5) It should Not produce harmful chemicals.
- 6) It should Not have non combustible substances.
(Mainly in solid fuel such as coal)
- 7) Fuel should be easy to store and easy to transport.
- 8) It should be cheap.

Comparison of Solid liquid and gaseous fuels

	Solid	Liquid	Gaseous
1) cheap		cheap Costly	Costliest
2) Transport is easy		Transport is easier than gas	Difficult
3) Easy to store		Easy to store than gas	Difficult
4) Ash is produced		No Ash	No Ash
5) Max. Smoke		Less smoke than solid	No smoke
6) Efficiency/calorific value	low	More than solids	Max
7) Max. Ignition temp.		Moderate	less

→ Determination of Calorific Value-
there are two types of Calorific value

① High Calorific value (HCV)
or

Gross C.F. (GCV)

② Low C.F. (LCV)
or

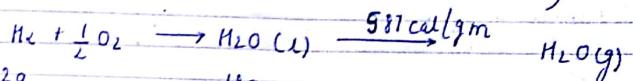
Net C.F. (NCV)

Gross C.F.V. - The calorific value measured in a closed calorimeter where the vapours are not allowed to escape the system.
calories/gm.

(Latent heat of condensation of water is included)

Net C.F.V. - The calorific value measured in open calorimeter where vapours are allowed to escape from system hence the measured calorific value is less than the expected value.

(Latent heat of condensation of water is not included)



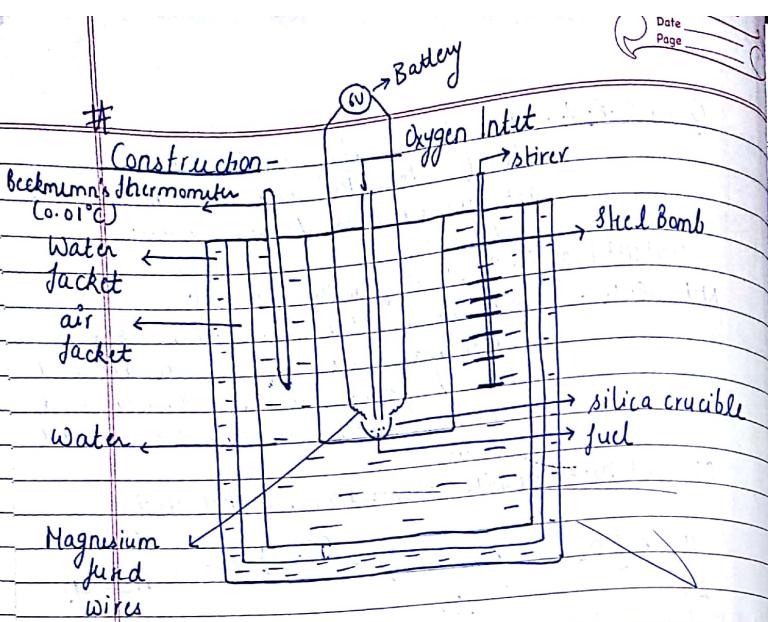
$$\begin{array}{ll} 2g & 18g \\ 1g & 9g \\ 11g & 9 \times 11g \end{array}$$

$$9 \times 587 \times 11 \text{ cal}$$

$$NCV = GCV - 9 \times 11 \times 587$$

$$NCV = GCV - 0.09 \times 11 \times 587$$

→ Bomb Calorimeter - The apparatus used for calculating the calorific value of solid fuel.



Working / Principle -

Bomb calorimeter is a type of constant volume calorimeter used to find the heat of combustion of the reaction. Bomb calorimeters have to withstand a large amount of pressure. Electrical energy is used to ignite the fuel; as the fuel is burning, it will heat up the surrounding layer, which expands and escapes through the tube that leads the air out of the calorimeter. When the air is escaping through the calorimeter, the change in temperature of water allows (it will also heat the water outside the tube) for calculating calorific content of the fuel.

Air jacket / water jacket \rightarrow to prevent heat transmission b/w inside and outside.

Magnesium fund wires \rightarrow to generate the spark.

Stirrer \rightarrow to maintain a same temperature throughout.

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Calculation -

Let the weight of fuel taken = n g

Initial temp. = T_1

Final temp. = T_2

Gross calorific value = HCV (HCV)

Mass of water taken = w g

water equivalent of container = w g

Heat evolved by fuel = $HCV \times n$ calorie

Heat absorbed = Heat given

$HCV \times n = \text{Heat absorbed by water} + \text{Heat absorbed by container}$

$$= w \times s \times (T_2 - T_1) + w \times s \times (T_2 - T_1)$$

$$3^{\circ}Q = ms \Delta T$$

$$= (w + w)(T_2 - T_1) \text{ Calorie } (s=1) \text{ cal/gm}$$

$$HCV = \frac{(w+w)(T_2 - T_1)}{n}$$

The following are included in the Corrections in Bomb Calorimeter -

- 1) Heat given by cotton thread : cotton thread Correction
- 2) Heat given by Mg fun wire : fun wire correction.
- 3) Heat given during formation of : Acid Correction
 HNO_3 and H_2SO_4
- 4) Cooling Correction (The rise in temp. is more than the actual rise in temp.)

$$HCV \times n = (W+w)(T_2 - T_1 + \text{cooling}) - (\text{cotton thread correction} + \text{fun wire correction} + \text{acid correction})$$

$$HCV = (W+w)(T_2 - T_1 + \text{cooling}) - (\text{cotton thread correction} + \text{fun wire correction} + \text{acid correction})$$

Amount of fuel

(Qn) The following data in bomb calorimeter experiment were obtained,

$$\text{wt. of crucible} = 3.649 g$$

$$\text{wt. of crucible + fuel} = 4.678 g$$

$$\text{water equivalent} = 510 g$$

$$\text{water taken} = 2100 g$$

$$* \text{Rise in temp} = 2.5^\circ C$$

$$\text{Cooling Correction} = 0.047^\circ C$$

$$F.W \text{ of Correction} = 3.8 \text{ cal}$$

Acid Correction = 62.5 cal

C.T. Correction = 1.6 cal

Calculate GCV and LCV if fuel containing 6.5% of Hydrogen (Latent heat of Vapourisation 587 cal/g)

$$\rightarrow G.C.V = \frac{(2200 + 570)(2.3 + 0.047) - (1.6 + 3.8 + 62.5)}{(4.67g) - (3.649)}$$

$$= \frac{(2770)(2.347) - (68)}{1.029}$$

$$= \frac{6501.19 - 68}{1.029} = \frac{6433.19}{1.029} \rightarrow 6251.88 \text{ calories/gm}$$

$$\begin{aligned} L.C.V &= G.C.V - 0.09 \times 587 \times 11\% \\ &= 6251.88 - 0.09 \times 587 \times 6.5\% \\ &= 6251.88 - 343.39 \\ &= 5908.49 \text{ calories/gm} \end{aligned}$$

Analysis of fuel - Coal -

at industrial unit	the coal can be analyzed by two methods
① Proximate analysis	→ % of Moisture
② Ultimate analysis	→ % of Volatile Component → % of Ash → % of fixed Carbon → % of Carbon → % of Hydrogen → % of Nitrogen → % of Sulphur

→ proximate analysis-

- Determination of % of Moisture - (8 to 14% of Moisture should be there)

$$\text{wt. of coal sample crucible} = w_1 \text{ g}$$

$$\text{wt. of Crucible + coal} = w_2 \text{ g}$$

$$\text{wt. of coal} = (w_2 - w_1) \text{ g}$$

Heat coal + crucible in hot air oven at $100-110^{\circ}\text{C}$, for 1 hour

$$\text{wt. of crucible fuel of heating} = w_4 \text{ g}$$

$$\% \text{ Moisture} = \frac{w_2 - w_4}{(w_2 - w_1)} \times 100$$

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$$\text{Weight of crucible} = w_1 \text{ g}$$

$$" " \text{ crucible + sample} = w_2 \text{ g}$$

$$" " \text{ Sample} = w_2 - w_1 \text{ g}$$

- ① 1. Moisture

$$\text{weight after heating (Crucible + sample)} = w_4 \text{ g}$$

- ② 1. of Volatile Component

Heat sample in Muffle furnace at $920 \pm 25^{\circ}\text{C}$ for seven minutes (with lid on crucible)

Why we are keeping lid over the crucible in determination of volatile component?

The lid helps to prevent the direct contact of fuel sample with oxygen and hence prevents combustion.

$$\text{Let the weight of sample} \xrightarrow{+ \text{Crucible}} = w_5 \text{ g}$$

$$\% \text{ Volatile Component} = \frac{(w_4 - w_5)}{(w_2 - w_1)} \times 100$$

- ③ Determination of Ash-

Heat $750 \pm 20^{\circ}\text{C} \rightarrow$ Muffle furnace \rightarrow 30 minutes [without lid]

Let the weight of crucible and sample = w_6

$$\% \text{ ash} = \frac{(w_6 - w_1)}{(w_2 - w_1)} \times 100$$

Ques A coal sample was analyzed as follows: exactly 1.40g of sample was weighed in silica crucible. After heating for 1 hr. at 110°C the residue weighed 1.10g. The crucible next was covered with a lid and strongly heated for 1 min. at 950°C. The residue weighed 1.00g. The crucible was heated without cover. The last residue weighed 0.21g. Calculate the result of above analysis.

$$\% \text{ of sample} = 1.40 \text{ g}$$

$$\begin{aligned}\% \text{ Moisture} &= \left(\frac{1.40 - 1.10}{1.40} \right) \times 100 \\ &= \frac{0.30}{1.40} \times 100 \\ &\Rightarrow 21.42\% \end{aligned}$$

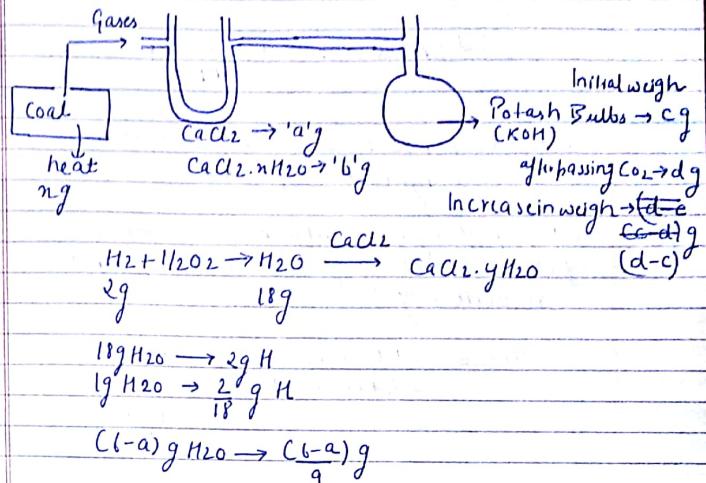
$$\begin{aligned}\% \text{ Volatile Component} &= \left(\frac{1.10 - 1.00}{1.40} \right) \times 100 \\ &\Rightarrow \frac{1}{14} \times 100 \\ &= 7.142\% \end{aligned}$$

$$\% \text{ Ash} = \left(\frac{0.21}{1.40} \right) \times 100 \\ = 15.1.$$

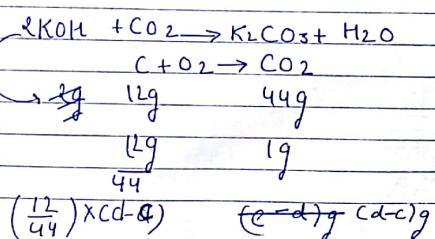
$$\% \text{ of Carbon} = 100 - (21.42 + 7.14 + 15) \\ = 56.44\%$$

ULTIMATE ANALYSIS-

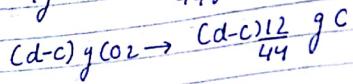
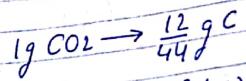
① Determination of % of C and H →



$\% \text{ of Hydrogen} = \frac{\text{Amount of H2O formed or Increase in weight of U-tube}}{9 \times \text{amount of Coal}} \times 100$



44 g of CO_2 is obtained from 12 g C



$$\% \text{ C} = \frac{\text{Increase in wt. of P.B.}}{\text{weight of coal}} \times 100$$

Ques) 0.2475 g of organic substance on combustion give 0.4950 g of CO_2 and 0.2025 g H_2O . Calculate % of C and H?

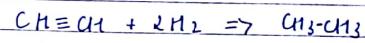
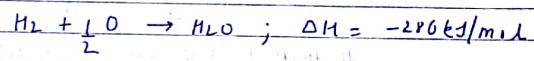
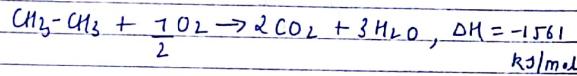
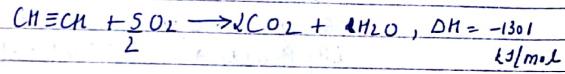
$$\begin{aligned}\% \text{ C} &= \frac{0.4950 \times 12 \times 100}{0.2475 \times 44} = \frac{594}{10.89} \\ &= 54.54 \%\end{aligned}$$

$$\begin{aligned}\% \text{ H} &= \frac{0.2025 \times 100}{0.2475 \times 9} \\ &= 9.09 \%\end{aligned}$$

20th January, 2017

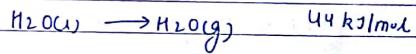
Chemistry Tutorial

Ques) Standard heat of combustion acetylene, ethane and Hydrogen are -1301 kJ/mol , -1561 kJ/mol , -286 kJ/mol respectively. calculate heat of hydrogenation of acetylene.



$$\begin{aligned}-1301 + 1561 + 2(-286) \\ \Rightarrow -312 \text{ kJ/mol}\end{aligned}$$

Ques) An athlete is given 100 g Glucose of energy equivalent to 1560 kJ. He utilises 50% of the gained energy in an event. In order to avoid storage of energy in body calculate the wt. of H_2O he would have to perspire. Enthalpy of evaporation of water is 44 kJ/mol .



$$\frac{1560}{2 \times 44} \times 18$$

$$\Rightarrow 319.0909 \text{ kJ}$$

Ques) Using the data given below calculate bond energies of C-C and C-H bonds

$$\Delta H_{\text{Combustion}} \text{ C}_2\text{H}_6 = -372 \text{ kcal/mol}$$

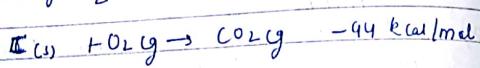
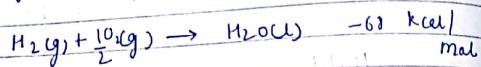
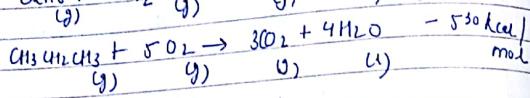
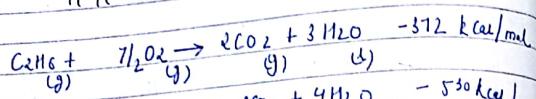
$$\Delta H_{\text{comb}} \text{ propane} = -530 \text{ kcal/mol}$$

$$\Delta E(\text{Cgr}) \rightarrow \text{C}_2\text{H}_6 \quad 172 \text{ kcal/mol}$$

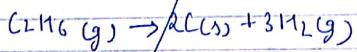
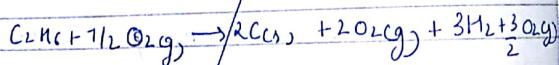
$$\Delta H_f \text{ H}_2\text{O}(l) \rightarrow -68 \text{ kcal/mol}$$

$$\Delta H_f \text{ CO}_2(g) \rightarrow -94 \text{ kcal/mol}$$

$$\text{H-H} = 104$$

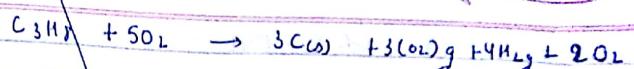


$$2(-94) + 3(-68) = -372$$



$$+ (104) \text{ kcal/mol} \quad | \quad \text{C-C} + 6 \times \text{C-H} = 10$$

$$2(\text{C-C}) + 6(\text{C-H}) = 20$$



~~$$3(-94) + 4(-68) - 530 \\ = 554 - 530 \\ = 24 \text{ kJ}$$~~

~~$$3\text{C-C} + 8\text{C-H} = 24$$~~

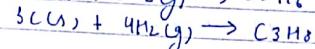
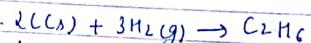
~~$$3(10 - 5\text{C-H}) + 8\text{C-H} = 24$$~~

~~$$30 - 9\text{C-H} + 8\text{C-H} = 24$$~~

~~$$-\text{C-H} = -6$$~~

~~$$\text{C-H} = 6 \text{ kJ/mol}$$~~

C-C



$$\Delta H_f \text{ C}_2\text{H}_6$$

$$\Delta H_f \text{ C}_3\text{H}_8$$

$$\Delta H_{\text{Rxn}} = \sum \text{H}_f \text{ prod} - \sum \text{H}_f \text{ reactants}$$

$$-372 = 2(-94) + 3(-68) - [\Delta H_f \text{ C}_2\text{H}_6 + 0]$$

$$-530 = 3(-94) + 4(-68) - [\Delta H_f \text{ C}_3\text{H}_8 + 0]$$

$$\Delta H_{\text{Rxn}} = \sum \text{H}_f \text{ prod} - \sum \text{H}_f \text{ reactants}$$

$$\Delta H_{\text{Rxn}} = [2(172) + 3(104)] - [2\text{C-C} + 6 \times \text{C-H}]$$

$$-372 + 3(-68) - 530 = [2(172) + 3(104)] - [2\text{C-C} + 6 \times \text{C-H}] \\ -20 = 656 - [2\text{C-C} + 6 \times \text{C-H}]$$

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$$676 = C-C + 6CH$$

$$\Delta H_{rxn} = [3(172) + 4(104)] - [2(C-C + 8CH)]$$

$$3(694) + 4(-68) + 530 = [3(172) + 4(104)] - [2(C-C + 8CH)]$$

$$-24 = 932 - [2(C-C + 8CH)]$$

$$2CC + 8CH = 956$$

$$C-C + 4CH = 478$$

$$676 = 478 - 4CH + 6CH$$

$$198 = 2CH$$

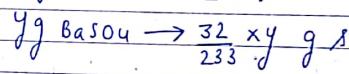
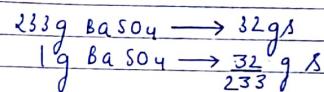
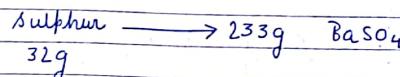
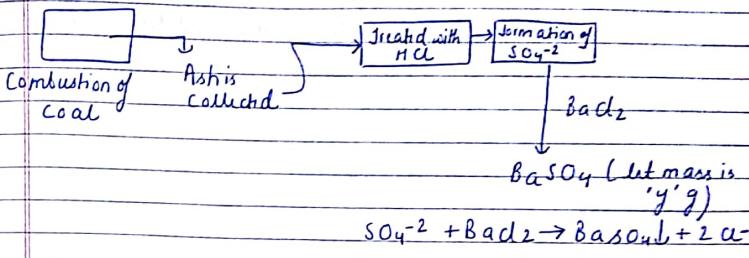
$$99 = CH \quad (\text{B.E.})$$

$$\begin{array}{rcl} C-C & = & 478 - 4CH \\ & = & 2478 - 4(99) \\ & = & 82 \quad (\text{B.E.}) \end{array}$$

"Summary"

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Determination of % Sulphur in coal-



$$\boxed{\% \text{ Sulphur} = \frac{32 \times \text{Amount of BaSO}_4 \text{ formed} \times 100}{233 \times \text{Amount of Coal}}}$$

(Ques) 1.275g of Coal sample was heated the ash is treated with Conc. HCl and the sulphate formed is reacted with BaCl_2 solution. 1.116g of BaSO_4 was obtained. Calculate % of Sulphur!

$$\begin{aligned} \% \text{ Sulphur} &= \frac{32 \times 1.116 \times 100}{233 \times 1.275} \\ &= \underline{\underline{12.02\%}} \end{aligned}$$

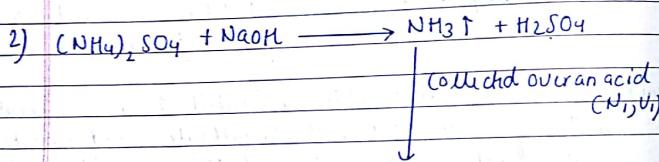
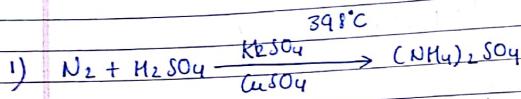
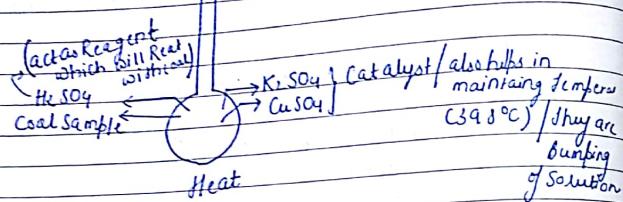
Important

Determination of % of Nitrogen -

Kjeldahl's Method

It is known as such because Kjeldahl's flask is used here.

long necked flask



- Fertilized in the presence of H₂SO₄ to form ammonium sulphate (NH₄)₂SO₄.

1 g eq. of N₂ will give 1 g eq. of (NH₄)₂SO₄

- The (NH₄)₂SO₄ is treated with an alkali (NaOH/KOH) to form ammonia (NH₃).

- The ammonia formed is collected over a known concentration and a known volume of acid (H₂SO₄/HCl)
- Let the initial concentration of acid is, N₁
Let the initial volume of acid is, V₁

The unreacted acid is treated with a known concentration of base.

Let the conc. of base used for back titration = N₂
Let the volume of base used = V₂

$$\text{No. of } \frac{\text{mL}}{\text{g eq.}} \text{ of base used} = N_1 V_2$$

$$\text{Initial no. of } \frac{\text{mL}}{\text{g eq.}} \text{ of acid taken} = N_1 V_1$$

$$\text{No. of } \frac{\text{mL}}{\text{g eq.}} \text{ of acid left after reaction with NH}_3 = N_1 V_2$$

$$\begin{aligned} \text{No. of } \frac{\text{mL}}{\text{g eq.}} \text{ of acid used for NH}_3 &= N_1 V_1 - N_1 V_2 \\ &= N_1 (V_1 - V_2) \end{aligned}$$

$$\text{No. of } \frac{\text{g eq.}}{\text{g eq.}} \text{ of nitrogen} = \frac{N_1 (V_1 - V_2)}{1000}$$

$$\text{g of Nitrogen present} = \frac{N_1 (V_1 - V_2) \times 14}{1000}$$

$$(\text{No. of g eq.} = \frac{\text{Mass}}{\text{eq. wt.}})$$

Let amount of Coal taken = n g

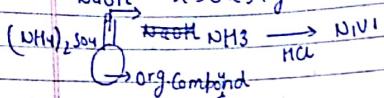
$$\boxed{\text{do of N present} = \frac{N_1 (V_1 - V_2) \times 14 \times 100}{1000 \times n}}$$

$$\therefore \text{% of N} = \frac{N_1 (V_1 - V_2) \times 1.4}{\text{Amount of Coal taken}}$$

Ques) 0.257 g of an organic compound was heated with conc. sulphuric acid and then distilled with excess of strong alkali like ammonia.

Gas evolved was absorbed in 50 ml of N/10 HCl which required 23.2 ml of N/10 NaOH for neutralization at the end of operation determine % of Nitrogen?

$$\text{NaOH} \rightarrow n = 0.257 \text{ g}$$



$$\text{Milliequi. of HCl initial} = N \times V = \frac{1}{10} \times 50 = 5$$

" " HCl reacted with NaOH = Milliequi. of HCl remained after reaction with NH₃

$$= \frac{5}{10} \times 23.2 \\ = 1.10 \times 23.2 \\ \Rightarrow 2.32$$

$$\text{Milliequi. of HCl reacted with NH}_3 = 5.00 - 2.32 \\ \Rightarrow 2.68$$

$$\% \text{ of N} = \frac{2.68 \times 14 \times 1000}{1000 \times 0.257} \\ = 2.68 \times 1.4 \\ = 0.457 \\ = 14.59922$$

Ques) 0.4 g of an organic compound was hydrolyzed and NH₃ evolved was absorbed into 50 ml of semi-normal of sulphuric acid. The residual acid solution was diluted with distilled water and volume was made up to 150 ml. 20 ml of this diluted solution required 31 ml of N/20 NaOH for complete neutralisation. Calculate % of N?

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$$\text{Milliequi. of H}_2\text{SO}_4 \text{ initially present} = 50 \times \frac{1}{2} = 25$$

$$\text{Milliequi. of NaOH reacted} = 31 \times \frac{1}{20}$$

$$\Rightarrow \frac{25}{20} = 1.25$$

$$20 \rightarrow 1.52 \\ 1 \rightarrow 0.052 \\ 20$$

$$150 \rightarrow 1.52 \times \frac{150}{20} \rightarrow 11.4 \text{ milliequi.}$$

$$\text{Normality of H}_2\text{SO}_4 \rightarrow 11.4 \rightarrow 0.076$$

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$$\text{Lit. Volume of H}_2\text{SO}_4 \text{ used for NH}_3 = n \text{ ml}$$

$$\text{Lit. Volume of H}_2\text{SO}_4 \text{ left} = (50 - n) \text{ ml}$$

$$\text{Milliequi. of H}_2\text{SO}_4 \text{ left} = (50 - n) \times \frac{1}{2}$$

$$(50 - n) \frac{1}{2} = 150 \times 0.076$$

$$20 \times 0.076 = 31 \times \frac{1}{20}$$

$$n = \frac{31}{400} \Rightarrow 0.0778$$

$$(50 - n) = 300 \times 0.0778$$

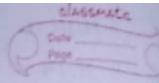
$$50 - 23.34 = n$$

$$ml \times 6.66 = n$$

$$\text{Milliequi. of H}_2\text{SO}_4 \text{ used for NH}_3 = 26.66 \times \frac{1}{2} \Rightarrow 13.33 \text{ ml}$$

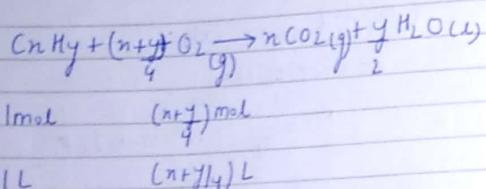
$$1.0 = \frac{13.33 \times 1.4}{0.4} \Rightarrow 46.655$$

Important (8th Std Maharashtra)



Combustion-

- the gas we study combustion at S.T.P (0°C, 1 atm)
- In a fuel C, H, S undergoes combustion. N never undergoes combustion.
- The amount of oxygen present in air is a) 23% by wt.
b) 21% by volume
- The molecular wt. of air is 28.97 g/mol

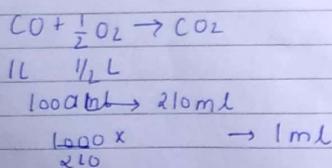


CO₂ 1 Mol of gas occupies 22.4 L.

Ques 1) Calculate the Vol. of air required for complete combustion of 1L of CO?

Ques 2) Calculate wt. and volume of air required to burn 1kg of C?

Ans 1)

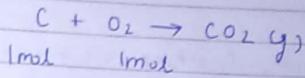


$$\left(\frac{1000}{210} \times 500 \right) \rightarrow 500 \text{ ml}$$

$$\frac{500}{210} L = 2.38$$

$=$

Ans 2)



$$\text{Mole of C g} \rightarrow \frac{1000}{12} \text{ mol}$$

$$\text{" of O}_2 \text{ req} \rightarrow \left(\frac{1000}{12} \right) \text{ mol}$$

$$\text{wt. of O}_2 \text{ req} \rightarrow \left(\frac{1000}{12} \right) \times 32 \text{ g}$$

34
11.59 kg

30th January, 2017

Knocking - is a metallic sound due to ignition of fuel.

Octane No. - is a no. by virtue of that we can measure the virtue quality of petrol.

Stuttering

→ High Octane no. less the knocking.
iso-octane h-pentene = 0
Octane No. → 100
normal Octane No. → 0-10

lot of compound have octane No. = 100; ie. it known as RON (R research octane no.)

branched has high octane no. because it can be vapourised much easily than straight chain.

Mixing of Petrol and air take place at same time and it comes from carburetor to combustion chamber.

2,2,4 trimethylpentane → iso-octane
Normal Octane → C₈H₁₈

only one solid hydrocarbon - Bituminous.

C-tane No. - is used to determine the quality of diesel.



Octane No. = 100 Octane (Mixa Octane)

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Straight chain has high C-tane No.

branched chain has low C-tane No.

(because we want that whose boiling point is high)

Diesel have high Naphthalene No.



α-Methyl Naphthalene
C-tane No. = 0

Anything that help in increasing C-tane No. is called C-tane booster.

Reforming is a process which can increase the efficiency of either petrol or diesel.

- ① Cracking - breaking of bigger H-C into smaller H-C at 500-600°C and 15-20 atm is called cracking.
- ② Catalytic cracking -
 - (i) cyclisation
 - (ii) Aromatization
- ③ Isomerisation -
- ④ Dimersisation -
- ⑤ Hydrocracking -

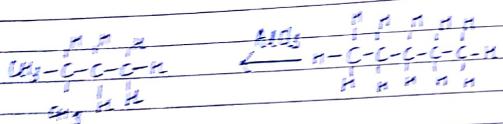
catalytic cracking - cracking by a catalyst



Conjugated compound in aromatic compound
is called aromatization.

→ Isomerization is a process by which we can change one isomer into another and it takes place in presence of any acid. Catalyst frequently used is acid.
 AlCl_3 , HgCl_2 , ZnCl_2

Recently acid.
Decomposition of two different catalyst.



Disproportionation - taking in between any type of Lewis acid. at optimum isomerization.

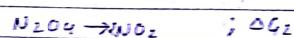
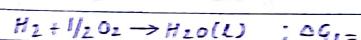
Pyrocracking - Removal of sulfur.

2nd February, 2017

Assignment -
Gude oil -
and
fractional distillation
(With diagram)

Chemical Kinetics -

$\Delta G < 0$, spontaneity



$\Delta G_1 < \Delta G_2$
∴ $\text{H}_2\text{O(L)}$ is more spontaneous by thermodynamics
but the rate of its own is very slow



Rate = The Rate of disappearance of reactants
or
The Rate of appearance of products

$$= -\frac{1}{a} \frac{dA}{dt} = -\frac{1}{b} \frac{dB}{dt} = +\frac{1}{c} \frac{dC}{dt} = +\frac{1}{d} \frac{dD}{dt}$$

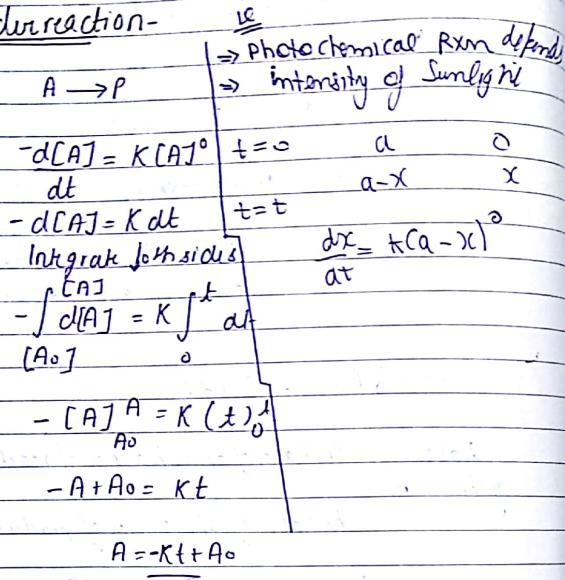
Order -

→ The sum of power of to which concentration term are raised
or sum of stoichiometric coefficient of the
reactants in the Rate determining step.

Molecularity -
The no. of atoms or molecule colliding in a chemical reacns.

→ Order can be zero, negative and fraction.
→ Molecularity is always a natural no.

Zero order reaction-



for t_{1/2}

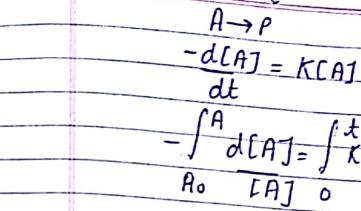
$$A = A_0/2$$

$$K = \text{mols/l.u.s.c.}$$

$$A = A_0 e^{-kt} = \frac{A_0}{2}$$

$$2 = e^{-kt}$$

First order Reaction-



$$-\left[\ln[A] \right]_0^A = K(t)_0^{-1}$$

$$\ln[A_0] - \ln[A] = Kt$$

$$\ln[A_0] - Kt = \ln[A]$$

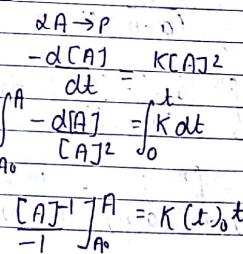
$$\frac{\ln[A_0]}{A} = Kt$$

$$\frac{A_0}{A} = e^{Kt}$$

$$A_0 e^{-Kt} = A$$

$$K = \text{mols/l.sec}$$

Second order Rxn.



$$\frac{1 - 1}{A_t - A_0} = kt$$

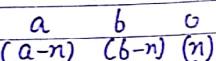
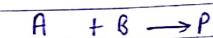
Put, at $A_t = a-n$
 $A_0 = a$

$$\frac{1}{(a-n)} - \frac{1}{a} = kt$$

$$\frac{a - a+n}{(a)(a-n)} = kt$$

$$(n) = (a)(a-n)kt$$

2nd order rxn. with two diff. reactants



$$(a-n) \quad (b-n) \quad (n)$$

$$dn = (k)(a-n)(b-n)$$

dt

$$\int_0^n dn = \int_0^t Kdt$$

$$\frac{1}{(b-a)} \int_0^n \frac{(b-a) - n + n}{(a-n)(b-n)} dt = \int_0^t Kdt$$

$$\frac{1}{(b-a)} \int_0^n \frac{(b-n) - (a-n)}{(a-n)(b-n)} dn = \int_0^t Kdt$$

$$\frac{1}{(b-a)} \int_0^n \frac{1}{(a-n)} - \frac{1}{(b-n)} dn = \int_0^t Kdt$$

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$$\frac{-1}{(b-a)} \left[\ln(a-n) - \ln(b-n) \right]_0^n = kt$$

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$$\checkmark \quad \frac{-1}{(b-a)} \left[\ln(a-n) - \ln(b-n) - (\ln a - \ln b) \right] = kt$$

$$\frac{-1}{(b-a)} \left[\ln \left(\frac{a-n}{b-n} \right) - \ln \left(\frac{a}{b} \right) \right] = kt$$

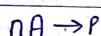
$$\frac{-1}{(b-a)} \ln \left[\frac{a-n}{b-n} \times \frac{b}{a} \right] = kt$$

$$-\ln \left[\frac{b(a-n)}{a(b-n)} \right] = (b-a)kt$$

$$\frac{b(a-n)}{a(b-n)} = e^{-(b-a)kt}$$

$$\ln \left[\frac{a(b-n)}{b(a-n)} \right] = (b-a)kt$$

Rate expression for nth order



$$-d[A] = K[A]^n$$

Integrate both sides

$$- \int_{A_0}^{AT} \frac{d[A]}{[A]^n} = K \int_0^t dt$$

Integrate both sides

$$- \int_{A_0}^{AT} \frac{d[A]}{[A]^n} = K \int_0^t dt$$

$$-\left[\frac{[A_t]}{[A_0]} \right]^{\frac{n+1}{n-1}} = Kt$$

$$-\left[\frac{[A_t]}{[A_0]}^{\frac{n+1}{n-1}} - [A_0]^{-\frac{n+1}{n-1}} \right] = Kt$$

Factors affecting Rate of Reaction.

- ① **Temperature** - Rate of reaction will increase on increasing temperature due to increase in no. of effective Collisions.
- ② **Nature of Reactants** - More the reactivity of Reactants more the rate of Rxn.
- ③ **Effect of Surface area** - More the surface area per unit Volume, more the no. surface area molecules, higher the surface energy, higher the reactivity.
- ④ **Pressure** - (No effect of pressure on solids or liquids)
On increasing pressure no. of effective collision increases, and hence rate of Rxn increases.
- ⑤ **Catalyst** - Catalyst provides an alternate path lowering the activating energy of the rxn.

3rd February, 17

Ques) In first order Rxn. it takes the reactant 40.5 minutes to be 25% decomposed. Calculate Rate constant?

$$\frac{75}{100} A_0 = -K (A_0 - 5)$$

Ans^R

$$\ln \left(\frac{A_0}{A_0 - 5} \right) = K (40.5)$$

$$\ln \left(\frac{4}{3} \right) = K (40.5)$$

$$7.1 \times 10^{-3} = K \text{ min}^{-1}$$

Ques) Show that for a first order reaction, the time required for 99.9% completion of Rxn. is 10 times to the time required for 50% completion?

$$t = \frac{1}{K} \ln \left(\frac{A_0}{A} \right)$$

$$t_{50} = \frac{1}{K} \ln \left(\frac{A_0}{A_0 - 50} \right) = \frac{1}{K} \ln (2) = 10.693 \text{ min}$$

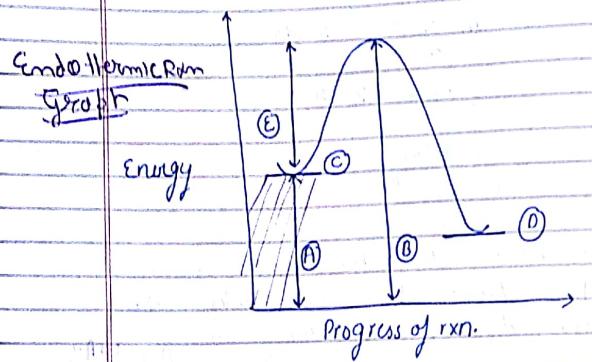
$$t_{99} = \frac{1}{K} \ln \left(\frac{A_0}{A_0 - 99} \right) = \frac{1}{K} \ln \left(\frac{100}{1} \right) = 6.9071 \text{ min}$$

$$\therefore t_{50} = 10 \times t_{99}$$

Collision theory

According to this theory the reactant molecules undergo effective collision to form products. The two necessary conditions for effective collisions are proper orientations of molecules, the molecules should have minimum amount of energy known as activation energy.

* average velocity is considered for Collision theory



→ Activation energy
Ant → threshold energy
Min energy that molecule must acquire

Ferrhenius Equation-

Arrhenius equation is used for establishing relationship b/w Rate Constant and Temperature.

$$\rightarrow K = A e^{-\frac{E_a}{RT}}$$

Rate $\propto p \times f \times Z$ → collision frequency.
Probability of effective collision b/w the molecules → fraction of molecules having threshold energy
Take natural log

$$\ln K = \ln A - \frac{E_a}{RT}$$

at T_1 ,

$$\ln K_1 = \ln A - \frac{E_a}{RT_1}$$

at T_2 ,

$$\ln K_2 = \ln A - \frac{E_a}{RT_2}$$

$$\therefore \frac{\ln(K_2)}{K_1} = -\frac{E_a}{R} + \frac{E_a}{RT_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Ques) Rate constant of 1st order rxn is $5.7 \times 10^{-5} \text{ mol}^{-1} \text{ L mc}^{-1}$ at 25°C . & 1.64×10^{-4} at 40°C ? calculate activation energy? A?

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \left(\frac{1.64 \times 10^{-4}}{5.7 \times 10^{-5}} \right) = \frac{E_a}{8.314} \left[\frac{1}{313} - \frac{1}{298} \right]$$

$$\ln \left(\frac{1.64}{5.7} \right) = \frac{E_a}{8.314} \left(\frac{313 - 298}{313 \times 298} \right)$$

$$1.05681 \times 8.314 \times 313 \times 298 = E_a$$

$$\frac{1.05681 \times 8.314 \times 313 \times 298}{15} = 54.635 \text{ kJ}$$

$$\ln(57 \times 10^{-5}) = \ln(A) - \frac{54.635}{8.31 \times 298}$$

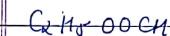
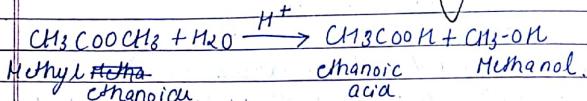
$$1.740 + 2.303x - 5 + 22.06 = \ln(A)$$

$$1.740 - 11.515 + 22.06 = \ln(A)$$

$$\frac{12.285}{C} = A$$

$$216,420.19 \rightarrow A$$

Pseudo first order Reaction



Ethyl Ethanoate

3rd Jcb, 11

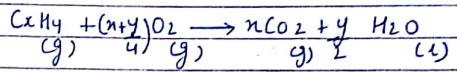
Tutorial

discuss

see

ex

Ques) 16 Cubic cm of Gaseous Hydrocarbon was exploded with excess of O₂. The contraction was 48 c.c. There is a further contraction of 48 c.c. on treatment with KOH. What is Molecular formula of HC?



$$16 \quad \frac{(\text{x+y})}{4} \cdot 16 \quad \text{n} \times 16$$

$$\begin{aligned} 16n &= 48 \\ n &\approx 3 \end{aligned}$$

$$\frac{16 + 16n + 16y}{4} - 16n = 48$$

$$16 + 4y = 48$$

$$4y = 32$$

$$y = 8$$

$$\text{C}_3\text{H}_8$$

* Some important formulas for calculating order of rxn:

$$(a) K = \frac{2.303}{t} \log \left(\frac{V_0 - V_t}{V_0 - V_0} \right) \quad (\text{for 1st order rxn})$$

$$(b) K = \frac{2.303}{t} \log \left(\frac{V_0 - V_{\infty}}{V_t - V_{\infty}} \right) \quad (\text{for optical rotation})$$

$$(c) \frac{(t_1 t_2)}{(t_1 t_2)} = \left(\frac{R_2}{R_1} \right)^{D-1} \quad [R_1 \text{ is the conc. and } n \text{ is the order of rxn}]$$

$$\left(\frac{t_1}{t_2} \right) = \left(\frac{C_2}{C_1} \right)^{n-1}$$

Ques) Find the order of reaction of the time of which completion for a certain reaction is formed to change from 50% to 25% and conc. to 0.5 M.

$$\frac{(50)}{25} = \left(\frac{1}{0.5}\right)^n =$$

$$(2) = (2)^n =$$

$$n-1 = 1$$

$$n = 2$$

Steady State Approximations (ΔS_{f})

$$\frac{d[I]}{dt} = 0$$

Rate of formation of Intermediate = Rate of decomposition of Intermediate.

→ Method to determine the rate when the slowest step is not given

→ SSA sets the chance in conc. of reactions Intermediate to zero. The SSA assumes that that the conc. of reaction intermediate remains ~~not~~ constant throughout the reaction. The conc. of reaction intermediate is considered to be steady because the intermediates are being produced as fast as they are consumed.

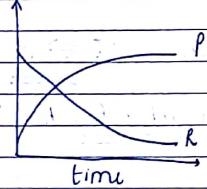
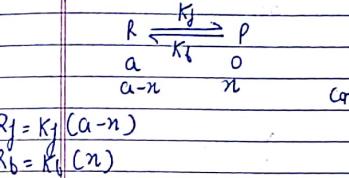
→ When the slowest step is not given, which is the rate determining step, otherwise can use the S.S.A to judge the rate determining step.

Complex Reactions

The reaction in which the particular reaction is not in one particular step. If we:

- Rversible Reaction
- Parallel Reaction
- Chain Reaction
- Consecutive Reaction.

(a) Rversible Reactions:



at equilibrium; $n = n_e$ = Product conc. at equilibrium

$$R_f = R_b \Rightarrow K_f(a-n) = K_b(n)$$

$$K_f(a-n) = K_b(n)$$

$$K_b = K_f(a-n) / n_e$$

Net rate of Rxn. in forward reaction direction :

$$\frac{dx}{dt} = (R_f - R_b)$$

$$= K_f(a-n) - K_b(n)$$

$$= K_f(a-n) - K_f(a-n) \frac{n}{n_e}$$

$$\Rightarrow K_f(a-n) \left[1 - \frac{1}{n_e} \right] \geq 0$$

$$\Rightarrow \frac{K_f}{n_e} \left[x_e(a-n) - (a-n)n_e \right]$$

$$= \frac{K_f}{n_e} [a x_e - x_e n_e - a n_e + n_e n_e] = \frac{K_f}{n_e} [a x_e - a n_e]$$

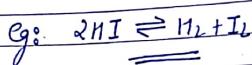
Ques

$$\frac{dx}{dt} = K_1 \frac{a(x_c - x)}{n_e}$$

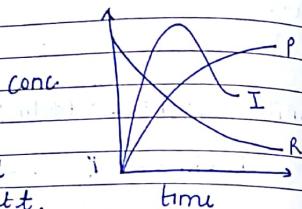
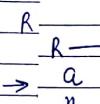
Separating the integral and
doing integration we get

$$\ln \left(\frac{x_c}{x_c - n_e} \right) = K_1 \frac{at}{n_e}$$

$$K_1 = \frac{n_e}{at} \ln \left(\frac{x_c}{x_c - n_e} \right)$$



(b) Consecutive Reaction:



Rate of Consumption of Reactant

$$-\frac{dx}{dt} = K_1 [n]$$

$$-\frac{dn}{[n]} = K_1 dt$$

$$-[\ln[n] - \ln[n_0]] = K_1 t (t=0)$$

$$\ln[n] - \ln[n_0] = K_1 t$$

$$\ln(n/n_0) = -K_1 t$$

Rate of formation of intermediate (I) = $\frac{dy}{dt}$

$$\frac{dy}{dt} = K_1 [n] - K_2 [y]$$

$$\frac{dy}{dt} = K_1 a e^{-K_1 t} - K_2 y$$

this is my first order differential equation

linear

whose solution is

$$y = \frac{K_1 a}{(K_2 - K_1)} \left[e^{-K_1 t} - e^{-K_2 t} \right]$$

condition for mass conservation

$$a = x + y + z \quad | \quad z = a - x - y$$

Substituting these values

$$z = a - \frac{a}{(K_2 - K_1)} a e^{-K_1 t} - \frac{K_1 a}{(K_2 - K_1)} \left[e^{-K_1 t} - e^{-K_2 t} \right]$$

$$= \frac{a}{K_2 - K_1} \left[(K_2 - K_1)(1 - e^{-K_1 t}) - (K_1 e^{-K_1 t} - K_1 e^{-K_2 t}) \right]$$

$$= \frac{a}{(K_2 - K_1)} \left[(K_2 - K_1 e^{-K_1 t}) - (K_1 - K_1 e^{-K_2 t}) \right]$$

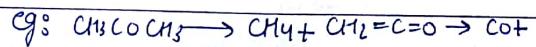
case ① $K_1 \gg K_2$; $e^{-K_1 t} \ll e^{-K_2 t}$

$$z = \frac{a}{K_2 - K_1} \left[-K_1 + K_1 e^{-K_2 t} \right]$$

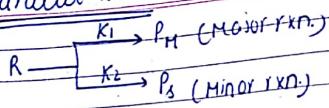
$$= a \left[1 - e^{-K_2 t} \right]$$

case ② $K_1 \ll K_2$; $e^{-K_1 t} \gg e^{-K_2 t}$

$$z = a(1 - e^{-K_1 t})$$



(c) Parallel Reaction



$$\text{Rate of formation of } P_M = \frac{d[P_M]}{dt} = K_1[R]$$

$$\text{Rate of formation of } P_S = \frac{d[P_S]}{dt} = K_2[R]$$

$$\text{Overall decomposition of } R = -\frac{d[R]}{dt}$$

$$-\frac{d[R]}{dt} = \frac{d[P_M]}{dt} + \frac{d[P_S]}{dt}$$

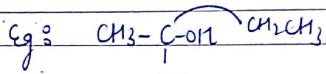
$$= K_1[R] + K_2[R]$$

$$-\frac{d[R]}{dt} = (K_1 + K_2)[R]$$

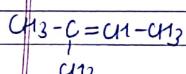
On integration

$$\ln\left(\frac{[R]}{[R_0]}\right) = -(K_1 + K_2)t$$

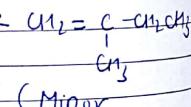
\Rightarrow



\equiv



(Major)



(d) Chain Reactions

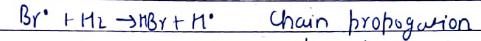
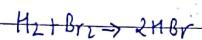
Chain initiation:

chain propagation

chain retardation

chain termination

Overall reaction is:



$$\begin{aligned} B &= K_1 A_0 \left[e^{-K_1 t} - e^{-K_2 t} \right] & A \approx A_0 e^{-K_1 t} \\ \frac{dB}{dt} &= K_1 A_0 \left[-K_1 e^{-K_1 t} + K_2 e^{-K_2 t} \right] & A_0 = [A] + [B] + [C] \\ &\quad \downarrow \quad \downarrow \\ &-K_1 e^{-K_1 t} + K_2 e^{-K_2 t} = 0 \end{aligned}$$

$$K_2 e^{-K_2 t} = K_1 e^{-K_1 t}$$

$$\ln(K_2 e^{-K_2 t}) = \ln(K_1 e^{-K_1 t})$$

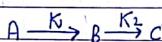
$$\ln K_2 + \ln e^{-K_2 t} = \ln K_1 + \ln e^{-K_1 t}$$

$$\frac{\ln(K_2)}{K_1} = -K_1 t + K_2 t$$

$$\frac{\ln(K_2)}{K_1} = (K_2 - K_1)t$$

$$\frac{1}{(K_2 - K_1)} \frac{\ln(K_2)}{K_1} = t$$

Steady state Approximation



if $K_1 \gg K_2$

$$B = \frac{K_1 A_0}{K_2 - K_1} \left[e^{-K_1 t} - e^{-K_2 t} \right]$$

$$= \frac{K_1 A_0}{-K_1} \left[-e^{-K_2 t} \right]$$

$$B = A_0 e^{-K_2 t}$$

if $K_2 \gg K_1$

$$\begin{aligned} B &= \frac{K_1 A_0}{K_2 - K_1} \left[e^{-K_1 t} - e^{-K_2 t} \right] \\ &= \frac{K_1 A_0 e^{-K_1 t}}{K_2} \\ B &= \frac{K_1 [A]}{K_2} \end{aligned}$$

Type ① Two step rxn -

1st step slow; apply SSA on intermediate

Type ② More than two steps rxn - we don't know which is faster/slow
Apply SSA on Intermediate

first step is rapid

Type ③ Equilibrium followed by two slow steps (Two step rxn.)
Apply SSA on Intermediate

Type ④ Multiple equilibrium we don't know which is fast or slow
Apply SSA.

How to identify which are Intermediate?

1) All free radical, carbocation, carbonanion are intermediate

2) Anything other than product + Reactant are intermediate.

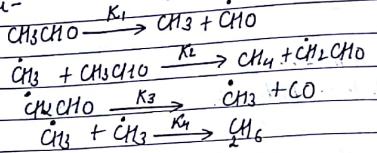
3) Necessary conditions that Intermediate should consume.

16th February, 17

Steady State Approximation (SSA) -

- Qn.) The decomposition of acetaldehyde can be written as
 $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$
 Prove that the following rate expression can be obtained
 $\frac{d[\text{CH}_4]}{dt} = K_2 [\text{CH}_3\text{CHO}]^{1/2}$ by following rxn mechanism.

Mechanism -



$$\frac{d[\text{CH}_4]}{dt} = K_2 [\cdot\text{CH}_3] [\text{CH}_3\text{CHO}]^{1/2} \quad (4)$$

Apply SSA on $\cdot\text{CH}_3$

$$\frac{d[\cdot\text{CH}_3]}{dt} = 0 = K_1 [\text{CH}_3\text{CHO}] - K_2 [\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - K_3 [\cdot\text{CH}_2\text{CHO}] - 2K_4 [\cdot\text{CH}_3]^2 \quad (1)$$

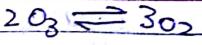
Apply SSA on $\cdot\text{CH}_2\text{CHO}$

$$\frac{d[\cdot\text{CH}_2\text{CHO}]}{dt} = 0 = K_2 [\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - K_3 [\cdot\text{CH}_2\text{CHO}] \quad (4)$$

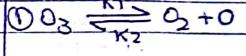
$$[\text{CH}_3\text{CHO}] = \frac{K_2 [\cdot\text{CH}_3][\text{CH}_3\text{CHO}]}{K_3}$$

Put in eq. (1)

$$K_1 [\text{CH}_3\text{CHO}] - K_2 [\cdot\text{CH}_3]$$



Add eqn. (1) & (2)



$$0 = K_1 [\text{CH}_3\text{CHO}] - 2K_4 [\cdot\text{CH}_3]^2$$

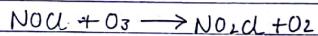
$$2K_4 [\cdot\text{CH}_3]^2 = K_1 [\text{CH}_3\text{CHO}]$$

$$[\cdot\text{CH}_3] = \sqrt{\frac{K_1 [\text{CH}_3\text{CHO}]}{2K_4}} \quad (3)$$

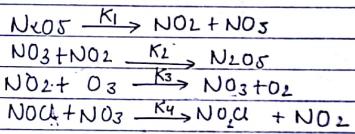
Put (3) in (4)

$$\frac{d[\text{CH}_4]}{dt} = K_2 [\cdot\text{CH}_3][\text{CH}_3\text{CHO}] \left(\frac{K_1}{2K_4} \right)^{1/2}$$

- Qn.) The effect of adding NO_2 to the rxn. was studied and the mechanism proposed is



Mechanism -



Show that it leads to following rate expression -

$$-\frac{d[\text{NO}_2]}{dt} = \left(\frac{K_1 K_3 K_4}{K_2} \right)^{1/2} [\text{NO}_2]^{1/2} [\text{O}_3]^{1/2} [\text{NO}_3]^{1/2}$$

$$\frac{d[N_{O_4}]}{dt} = -K_4 [N_{O_3}] [N_{O_4}] \quad (1)$$

Applying SSA on N_{O_3}

$$\frac{d[N_{O_3}]}{dt} = 0 = K_1 [N_{2O_5}] - K_2 [N_{O_2}] [N_{O_3}] + K_3 [N_{O_2}] [O_3] - K_4 [N_{O_4}] \quad (2)$$

Applying SSA on N_{O_2}

$$\frac{d[N_{O_2}]}{dt} = 0 = K_1 [N_{2O_5}] - K_2 [N_{O_2}] [N_{O_3}] - K_3 [N_{O_2}] [O_3] + K_4 [N_{O_4}] \quad (3)$$

Add (2) & (3)

$$0 = 2K_1 [N_{2O_5}] - 2K_2 [N_{O_2}] [N_{O_3}] - K_4 [N_{O_4}]$$

$$[N_{O_2}] = \frac{2K_1 [N_{2O_5}] - K_4 [N_{O_4}] [N_{O_3}]}{2K_2 [N_{O_3}]} \quad (4)$$

Put in (2)

$$0 = K_1 [N_{2O_5}] - K_2 \left(\frac{2K_1 [N_{2O_5}] - K_4 [N_{O_4}] [N_{O_3}]}{2K_2 [N_{O_3}]} \right) + K_3 [O_3] \left(\frac{2K_1 [N_{2O_5}] - K_4 [N_{O_4}] [N_{O_3}]}{2K_2 [N_{O_3}]} \right)$$

~~$$0 = K_1 [N_{2O_5}] - \frac{K_1 [N_{2O_5}]}{2} + \frac{K_4 [N_{O_4}] [N_{O_3}]}{2} + K_2 \frac{[O_3] [N_{2O_5}]}{K_2 [N_{O_3}]} - \frac{K_4 K_3 [O_3] [N_{O_4}]}{2K_2} - \frac{K_4 [N_{O_4}] [N_{O_3}]}{2K_2}$$~~

$$\frac{K_4 [N_{O_4}] [N_{O_3}]}{2} = \frac{K_1 K_3 [O_3] [N_{2O_5}]}{K_2} - \frac{K_4 K_3 [O_3] [N_{O_4}]}{2K_2} \quad (5)$$

$$0 = K_1 [N_{2O_5}] - K_2 \frac{[N_{O_3}]}{2} \frac{2K_1 [N_{2O_5}]}{K_2 [N_{O_3}]} + \frac{K_3 [O_3] K_1 [N_{2O_5}]}{K_2 [N_{O_3}]} - K_4 [N_{O_4}] [N_{O_3}]$$

$$0 = K_1 [N_{2O_5}] - K_2 \frac{[N_{O_3}]}{2} \frac{K_1 [N_{2O_5}]}{K_2 [N_{O_3}]} - K_4 [N_{O_4}] [N_{O_3}]$$

$$K_4 [N_{O_4}] [N_{O_3}]^2 = \frac{K_3 K_1 [O_3] [N_{2O_5}]}{K_2} \quad (6)$$

$$[N_{O_3}] = \left(\frac{K_3 K_1 [O_3] [N_{2O_5}]}{K_2 K_4 [N_{O_4}]} \right)^{1/2}$$

Put in (1)

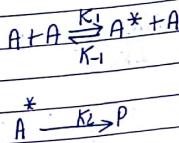
$$\frac{d[N_{O_4}]}{dt} = -K_4 [N_{O_4}] \left(\frac{K_3 K_1 [O_3] [N_{2O_5}]}{K_2 K_4 [N_{O_4}]} \right)^{1/2}$$

$$-\frac{d[N_{O_4}]}{dt} = \left(\frac{K_4 K_3 K_1 [N_{O_4}] [O_3] [N_{2O_5}]}{K_2} \right)^{1/2}$$

$$-K_4 [N_{O_4}] [N_{O_3}]$$

Important

Application - Lindeman Unimolecular Collision Theory



According to the theory two molecules collide with each other and one of the molecules give energy to the other molecule to make it energized. This energized molecule either degenerates back or get converted to product. The reaction will be as above.

There will be a time lag b/w formation of product and degeneration of energized molecule.

$$\frac{dP}{dt} = K_2[A^*] \quad \text{--- (1)}$$

dt

Apply SSA on A^*

$$\frac{d[A^*]}{dt} = K_1[A]^2 - K_1[A^*][A] - K_2[A^*] = 0 \quad \text{--- (2)}$$

$$[A^*] = \frac{K_1[A]^2}{K_1[A] + K_2} \quad \text{--- (3)}$$

Put (3) in (1)

$$\frac{dP}{dt} = \frac{K_2 K_1 [A]^2}{K_1[A] + K_2}$$

Unimolecular

classmate
cont 750

Effect of Pressure on order of Reaction -

at high pressure the molecules are close to each other and the rate of degeneration of energized molecule will be greater than rate of conversion to product. Therefore

$$K_1[A] \gg K_2$$

$$\frac{dP}{dt} = \frac{K_1 K_2 [A]^2}{K_1[A]} = \frac{K_1 K_2 [A]}{K_1} = K_1' [A]$$

So the rxn. is 1st Order

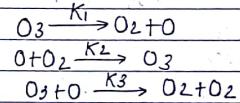
At low pressure,

$$K_2 \gg K_1[A]$$

$$\frac{dP}{dt} = \frac{K_1 K_2 [A]^2}{K_2} = K_1[A]^2$$

So the rxn. is 2nd Order

(Q) For the decomposition of ozone (O_3) is $O_3 \rightarrow O_2 + O$. The following mechanism has been proposed.

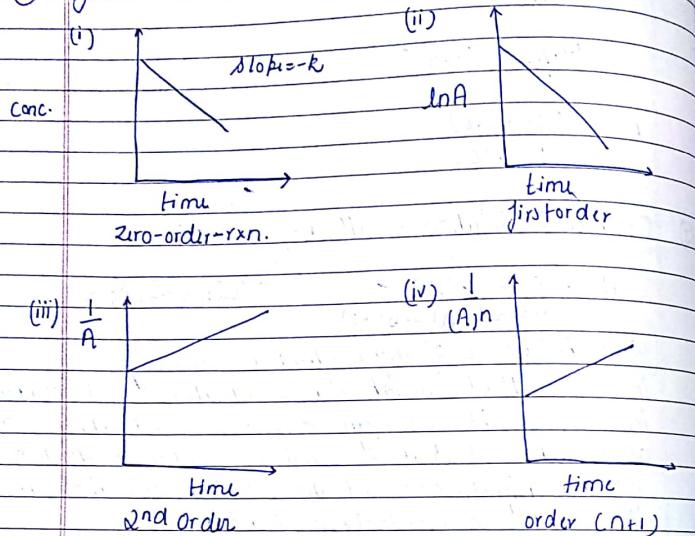


Find the rate of rxn. with respect to O_2 .

$$n = 1 + \log \left[\frac{(t_{1/2})_1}{(t_{1/2})_2} \right]$$

$$\log \left(\frac{1}{2} \right)$$

5 Graphical Method Unimolecular

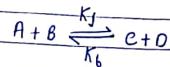


Ques) Determine rate constant of zero, 1st, 2nd order by graphical method?

24th february, 17

CHEMICAL-EQUILIBRIUM

classmate
Date _____
Page _____



law of Mass action

$$\text{Rate} \propto [A][B]$$

$$(Rate)_f = k_f [A][B]$$

$$(Rate)_b = k_b [C][D]$$

$$Q = K_c$$

$$Q > K_c$$

$$Q < K_c$$

equilibrium

more forward reaction
more backward reaction

$$\text{Rate}_f = \text{Rate}_b$$

$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

Le Chatelier's Principle -

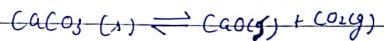
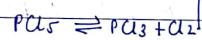
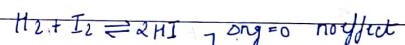
in equilibrium
when a stress is applied to a system than the system will move in the direction where stress can be nullified.

1) Temperature -

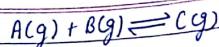
On increasing T. For endothermic forward
For exothermic backward

2) Pressure -

Pressure \uparrow , Volume \downarrow $\frac{n}{V} \uparrow$ (conc.)



$\Delta n > 0$
backward direction



$$\Delta n_g < 0$$

forward reaction

3) Effect of addition of inert gas -

Constant
Volume
(no effect)

Volume \uparrow $\frac{n}{V} \downarrow$
 $\Delta n_g = 0$
 $\Delta n_g > 0$ forward
 $\Delta n_g < 0$ backward

4) Effect of addition of Reactants & Products -

Reactants - forward
Products - backward



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}; K_p = \frac{P_c^c P_d^d}{P_a^a P_b^b}; K_n = \frac{n_c^c n_d^d}{n_a^a n_b^b}$$

$$K_p = \frac{(P_{n_c})^c (P_{n_d})^d}{(P_{n_a})^a (P_{n_b})^b}$$

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT$$

$$P = CRT$$

$$K_p = (C_c RT)^c \times (C_d RT)^d$$

$$(C_a RT)^a \times (C_b RT)^b$$

$$= C_c^c C_d^d (R^{cd-ab}) (T)^{cd-ab}$$

$$C_a^a C_b^b$$

$$K_p = K_c (RT)^{\Delta n}$$

$$\rightarrow K_p = \frac{(P_{n_c})^c (P_{n_d})^d}{(P_{n_a})^a (P_{n_b})^b} \Rightarrow \frac{x_c^c x_d^d}{x_a^a x_b^b} \times (P)^{\Delta n}$$

$$K_p = P \times$$

$$K_p = K_n (P)^{\Delta n}$$

Relation b/w Pressure & degree of dissociation -

For homogeneous equilibrium,

$$\textcircled{1} \quad \underline{\Delta n_g = 0} \quad A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

Initial	a	b	0	0
Change	(a-x)	(b-x)	x	x
Equi.	-x	-x	+x	+x

$$\text{Total Moles at equilibrium} = a+b$$

Let total pressure P

$$n_A = \frac{(a-n)}{a+b}$$

$$\chi_B = \frac{(b-n)}{a+b}$$

$$n_C = \frac{n}{a+b}$$

$$n_D = \frac{n}{a+b}$$

$$K_p = \frac{p_A \times p_C}{p_B \times p_D}$$

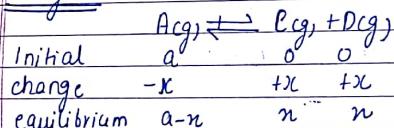
$$= \frac{p_A \times p_C}{p_B \times p_D} = \frac{P \times \left(\frac{a-n}{a+b} \right) \times P \times \left(\frac{n}{a+b} \right)}{P \times \left(\frac{b-n}{a+b} \right) \times P \times \left(\frac{n}{a+b} \right)}$$

$$K_p = \frac{\chi_C^2}{\chi_B \chi_D}$$

$\rightarrow K_p$ is independent of Pressure.

so degree of dissociation is independent of Pressure.

(2) $\Delta n > 0$



$$\text{Total Moles} = a+n$$

$$\chi_A = \frac{a-n}{a+n}$$

$$\chi_C = \frac{n}{a+n}$$

$$\chi_D = \frac{n}{a+n}$$

Let total Pressure = P

$$K_p = \frac{p_A \times p_C}{p_B \times p_D}$$

$$= \frac{p_A \times p_C}{p_B \times p_D} = \frac{P \times \frac{a-n}{a+n} \times P \times \frac{n}{a+n}}{P \times \frac{b-n}{a+n} \times P \times \frac{n}{a+n}}$$

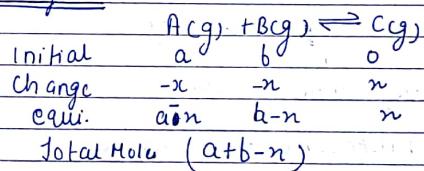
$$= \frac{P \chi_C^2}{(a-n)(a+n)}$$

$$K_p = \frac{P \chi_C^2}{(a-n)(a+n)}$$

$$\chi^2 \propto 1/P$$

\rightarrow therefore when pressure is increased degree of dissociation is decreased.

(3) $\Delta n < 0$

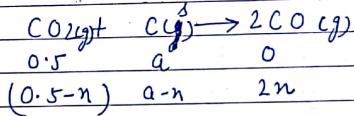


$$\Delta G = -RT \ln K_p$$

Temp (T) - Kelvin
 $R = 8.314 \text{ Joules}$

Qn) Bulk struct Rxn. dynamics Qn 9

Qn) A vessel at 1000 K contain CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted to CO on addition of graphite. Calculate value of equilibrium constant and change in free energy if total pressure at equilibrium is 0.89 atm.



$$\text{Total Pressure} = 0.5 + n$$

$$0.8 = 0.5 + n$$

$$0.3 = n$$

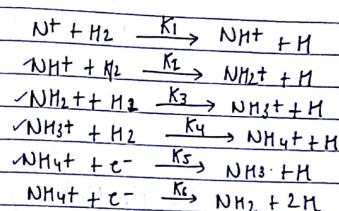
$$K_p = \frac{(2n)^2}{(0.5-n)} = \frac{(0.6)^2}{0.2} = \frac{0.36}{0.2} = \frac{18}{5} = 3.6$$

$$\Delta G = -8.314 \times 1000 \times \ln(1.8) \\ = -4.88 \text{ kJ/mol}$$

24th February, 2017

tutorial

Qn) A possible ion molecule reaction for synthesis of ammonia is shown below



Find the reaction rate in terms of ammonia. Consider $\text{N}^+, e^-, \text{H}_2$ as stable components

intermediates $\text{NH}^+, \text{NH}_2^+, \text{NH}_3^+, \text{NH}_4^+$

$$\frac{d[\text{NH}_3]}{dt} = K_5 [\text{NH}_4^+] [e^-] \quad (5)$$

apply SSA on NH_4^+

$$\frac{d[\text{NH}_4^+]}{dt} = 0 = K_4 [\text{NH}_3^+] [\text{H}_2] - K_5 [\text{NH}_4^+] [e^-] \quad (4)$$

Apply S.S.A on NH_3^+ also,

$$\frac{d[\text{NH}_3^+]}{dt} = 0 = K_3[\text{NH}_2^+] \cdot [\text{H}_2] - K_4[\text{NH}_3^+][\text{H}_2] \quad \text{--- (3)}$$

Apply S.S.A on NH_2^+ also,

$$\frac{d[\text{NH}_2^+]}{dt} = 0 = K_2[\text{NH}_3^+][\text{H}_2] - K_3[\text{NH}_2^+][\text{H}_2] \quad \text{--- (4)}$$

Applying S.S.A on NH_3^+

$$\frac{d[\text{NH}_3^+]}{dt} = 0 = K_1[\text{N}^+][\text{H}_2] - K_2[\text{NH}_3^+][\text{H}_2] \quad \text{--- (2)}$$

from (3) and (2)

$$+ K_3[\text{NH}_2^+][\text{H}_2] = K_1[\text{N}^+][\text{H}_2]$$
$$[\text{NH}_2^+] = K_1[\text{N}^+]$$

Put in (3)

$$0 = K_3 \times K_1[\text{N}^+][\text{H}_2] - K_4[\text{NH}_3^+][\text{H}_2]$$

$$[\text{NH}_3^+] = K_1[\text{N}^+]$$

Put in (4)

$$0 = K_4[\text{H}_2]K_1[\text{N}^+] - K_5[\text{NH}_3^+][\text{e}^-] - K_6[\text{NH}_3^+][\text{e}^-]$$

$$0 = K_1[\text{H}_2][\text{N}^+] + (K_5[\text{e}^-])$$

$$[\text{NH}_3^+] = K_1[\text{H}_2][\text{N}^+]$$

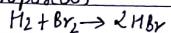
$$+ K_5[\text{e}^-] + K_6[\text{e}^-]$$

Put in (5)

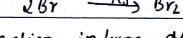
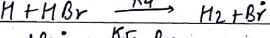
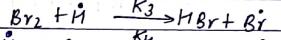
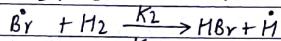
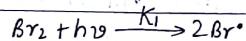
$$\frac{d[\text{NH}_3^+]}{dt} = K_5[\text{e}^-] K_1 [\text{H}_2][\text{N}^+] \quad \text{--- (5)}$$

$$= \frac{K_1 K_5}{(K_5 + K_6)} [\text{H}_2][\text{N}^+]$$

Ques) What for the formation of HBr , the following mechanism has been proposed,



Mechanism-



Find reaction in terms of HBr , rate

Intermediates are Br^\bullet , H^\bullet ,

$$\frac{d[\text{HBr}]}{dt} = K_2[\text{H}_2][\text{Br}^\bullet] + K_3[\text{Br}_2][\text{H}^\bullet] - K_4[\text{HBr}][\text{H}^\bullet]$$

Apply S.S.A. on $[\text{Br}^\bullet]$

$$\frac{d[Br^{\cdot}]}{dt} = 2K_1[Br_2] - K_2[H_2][Br^{\cdot}] + K_3[Br_2][H^{\cdot}] \\ + K_4[H^{\cdot}][HBr] - 2K_5[Br^{\cdot}]^2 \quad (1)$$

Apply S.S.A on $[H^{\cdot}]$

$$\frac{d[H^{\cdot}]}{dt} = K_2[H_2][Br^{\cdot}] - K_3[H^{\cdot}][Br_2] - K_4[H^{\cdot}][HBr] \quad (2)$$

Add (1) and (2)

$$2K_1[Br_2] - 2K_5[Br^{\cdot}]^2 = 0$$

$$\left(\frac{2K_1[Br_2]}{K_5}\right)^{1/2} = [Br^{\cdot}]$$

$$\therefore [H^{\cdot}] = K_2[H_2] \left(\frac{2K_1[Br_2]}{K_5}\right)^{1/2}$$

$$= K_3[Br_2] + K_4[HBr]$$

$$\frac{d[HBr]}{dt} = K_2[H_2] \left(\frac{2K_1[Br_2]}{K_5}\right)^{1/2} + K_3[Br_2]K_2[H_2] \left(\frac{2K_1[Br_2]}{K_5}\right)^{1/2} \\ - K_4[HBr]K_2[H_2] \left(\frac{2K_1[Br_2]}{K_5}\right)^{1/2}$$

$$= K_3[Br_2] + K_4[HBr]$$

$$\frac{d[HBr]}{dt} \Rightarrow K_3K_2[H_2][Br_2](x) + K_4[HBr]K_2[H_2](x)$$

$$+ K_3K_2[H_2][Br_2](x) - K_4K_2[H_2][HBr](x)$$

$$= K_3[Br_2] + K_4[HBr]$$

$$\Rightarrow 2[K_3K_2[H_2][Br_2]x - K_4K_2[H_2][HBr]x]$$

$$= K_3[Br_2] - K_4[HBr]$$

$$\Rightarrow 2[K_2][H_2]x$$

$$= 2K_2[H_2] \left(\frac{K_1[Br_2]}{K_5}\right)^{1/2}$$

$$\Rightarrow 2K_3K_2[H_2][Br_2] \left(\frac{K_1[Br_2]}{K_5}\right)^{1/2}$$

$$= K_3[Br_2] + K_4[HBr]$$

$$\Rightarrow 2K_3K_1\left(\frac{K_1}{K_5}\right)^{1/2}[H_2][Br_2]^{3/2}$$

$$= K_3[Br_2] + K_4[HBr]$$

$$= K[H_2][Br_2]^{3/2}$$

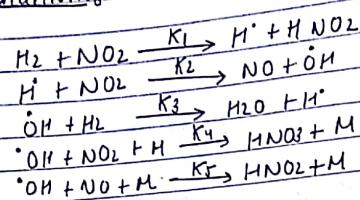
$$= [Br_2] + K^1[HBr]$$

Ques)

for the Reaction



Mechanism:



Prove -

$$\frac{-d[NO_2]}{dt} = \frac{K_1 K_3 [NO_2] [H_2]}{K_4 [NO_2] [H] + K_5 [NO] [M]}$$

$\frac{d[NO_2]}{dt}$ Intermediate are;
 H^+, OH^-

$$\frac{d[NO_2]}{dt} \rightarrow -K_1 [H_2] [NO_2] - K_2 [H^+] [NO_2] \\ - K_4 [OH^-] [NO_2] [H]$$

Apply SSA on $[H^+]$;

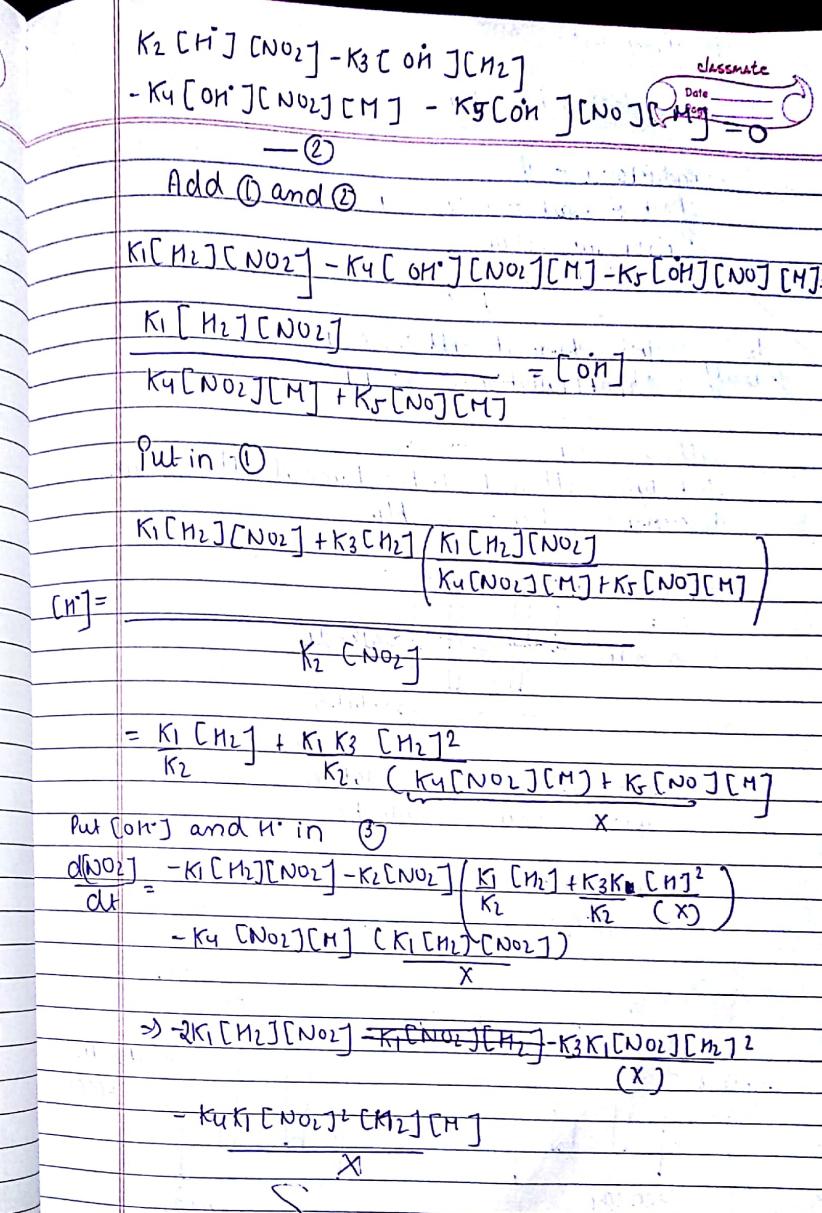
$$\frac{d[H^+]}{dt} = 0$$

$$K_1 [H_2] [NO_2] - K_2 [H^+] [NO_2] + K_3 [OH^-] [H_2] = 0$$

— ①

Apply SSA on $[OH^-]$;

$$\frac{d[OH^-]}{dt} = 0$$



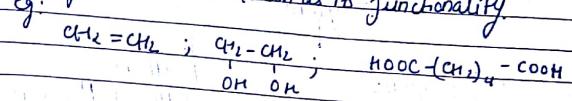
* excess NaNH_2 works similar to alcoholic KOH .

27th April, 2017

POLYMERS (20 marks)

Polymers are large macro molecules obtained by repetitive combination of small molecules called as monomers.

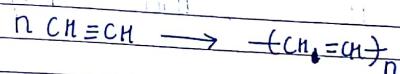
A molecule can behave as monomer if it has atleast two binding sites which is known as its functionality.



Draw structure of polythene?

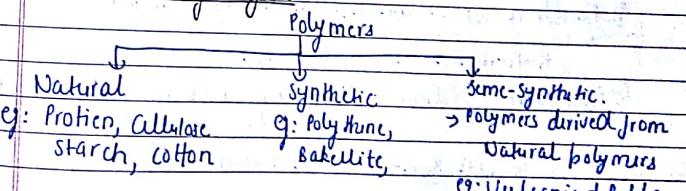


Polyacetylene

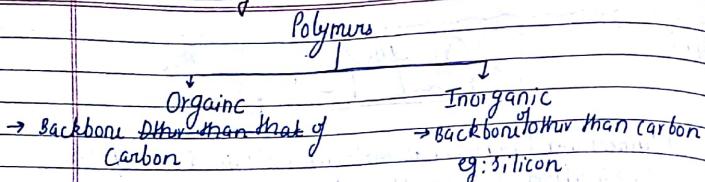


Classification of Polymers:

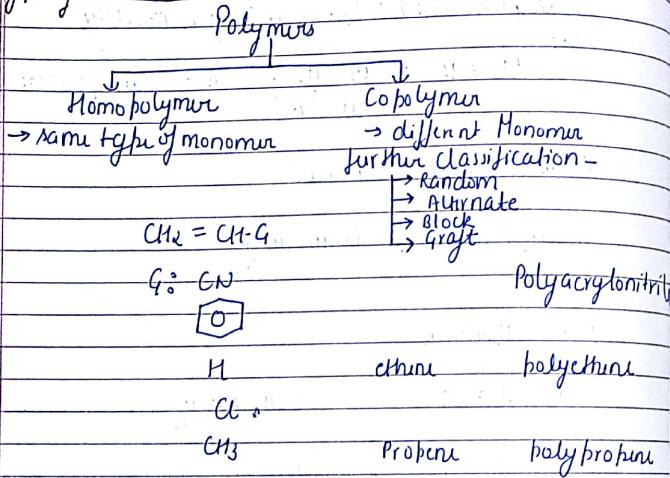
① On the basis of origin :



(2) On the basis of Backbone chain:

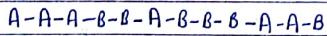


(3) Type of Monomer:

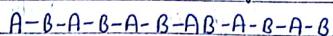


A, B Monomer

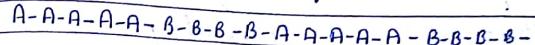
① Random copolymer - A, B randomly arranged



② Alternate copolymer - Monomeric units are alternatively arranged.

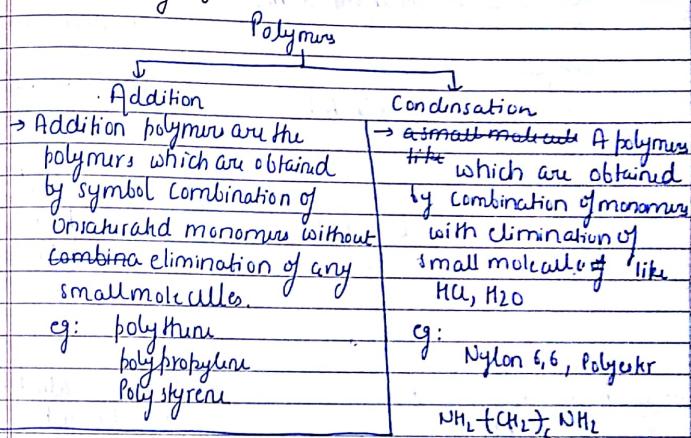


(3) Block polymer - Repetition of blocks



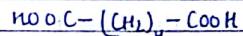
④ Graft Polymer - It generally has one long chain of single monomeric unit grafted with small chain of another monomeric unit.

(4) On the basis of Synthesis:

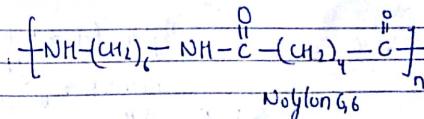


Monomers

Polyester: diols, dicarboxylic acids



(Adipic acid)



Nylon 6,6

⑤ On the basis of thermal properties

Polymers

Thermoplastic
 → Polymers which are soft on heating, hard on cooling and can be remoulded again and again.
 → low degree of cross linkage

Thermosetting
 the polymer becomes hard on cooling and cannot be remoulded again.
 → high degree of Cross linkage

 straight chain

 cross-linked

 branched

Flexibility

Cross Straight

branched

Coz branches
has less

Packing

Efficiency.

→ weak bonds are present in cross linkage
 e.g.: H bonding
 → low Mechanical strength
 → low Melting point

→ Strong Covalent bond are present
 → high Mechanical Strength
 → high Melting Point

Tyton 6-6 → Ropes,
ty Records
Nylon 6, 6 → Brushes, Brisks
 $\text{C}_{60}(\text{CH}_2)_2-\text{C}_60$

Amorphous

Amorphous - the polymers in which polymeric chains are randomly arranged or are entangled b/w each other.
 → low Melting point
 e.g.: low density polythene (laminations)



Crystalline

the polymers in which polymeric chains have regular arrangement.
 → high Melting point.

e.g.:
 high density polythene

⑥ On the basis of utility: (final Application)

Polymers

↓ Plastic

The polymers which have final application on hard materials are called as Plastic.

↓ Fibre

The polymers which have too firm & length of fiber original diameter

e.g.: Cotton

Polyester

Ghillion, Silk, Nylon 66

↓ Elastomer

The polymers which can be stretched several times to their original length and they regain their original length on removal of stress.

e.g.: elastoids

Rubbers

↓ Resins

The polymers which show adhesive property at high temp.

e.g.: epoxides

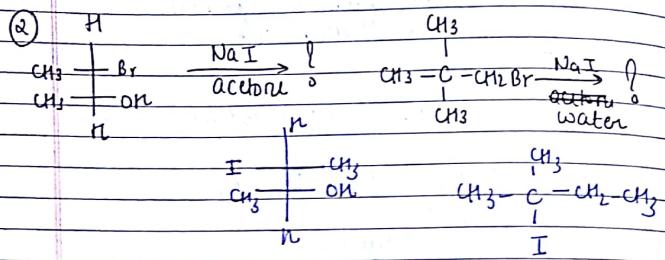
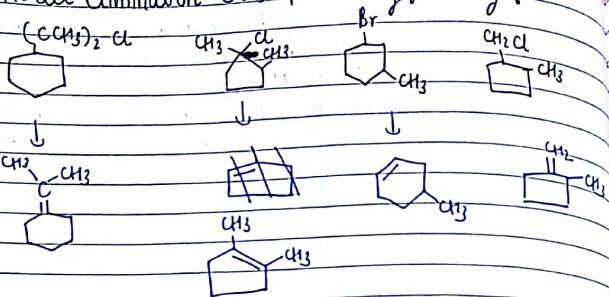
PF resins

e.g.: Natural Rubber, Buna N, Buna S

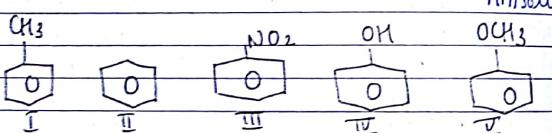
21st April, 2017

Tutorial

1) Write all elimination (E^2) products of following?



3) Decreasing order of Reactivity for electrophilic substitution reaction

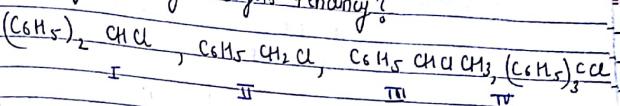


$IV > II > I > III > I > II > III$

electro
negativity
 $O - H$ More
 $O - C$ Less] So More l.p. available to O in
 $O - H$.

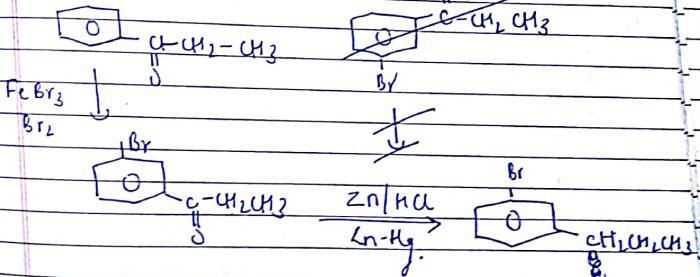
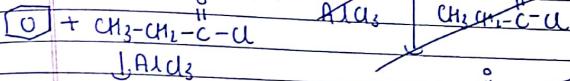
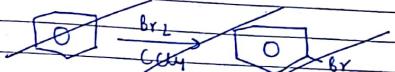
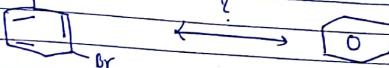
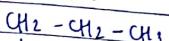
action almost Non polar solvent.
 $H_2O \rightarrow S_{N}1$ or E^2
 $DMSO \rightarrow S_{N}2$

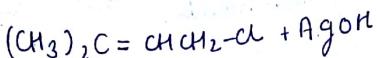
4) Increasing order of solvolysis tendency?



~~$I < II < III < IV$~~

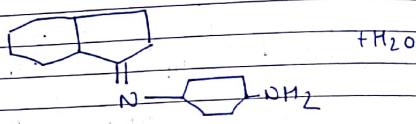
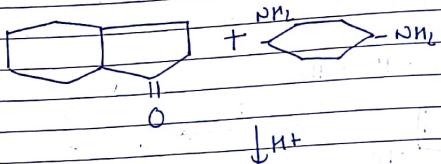
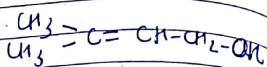
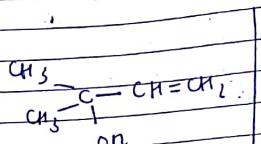
$II < III < I < IV$





A + B
85% 15%

(Ag Cl)



26th April, 2017

Polymerisation Techniques:

Bulk Polymerisation:-

In this technique we take monomer in its liquid state and add initiator to start polymerization. We don't need any solvent in this technique. E.g. Free radical polymerisation of styrene.

classmate
Date _____
Page _____

- Mol wt.
- Mechanism of Addition Polymer
- Biodegradation Polymer
- Conducting Polymer

Disadvantage:

- Due to absence of solvent the mixture becomes highly viscous which cause difficulty in stirring the mixture.
- Due to high viscosity, chain termination is difficult, we obtain polymer of high molecular wt. distribution.
- The reaction is too vigorous that sometimes lead to explosion even.

Advantages:

- Polymer of high quality is obtained.
- No separation is required.
- We are not using any solvent so process is economical.

Solution Polymerisation:

In this technique we dissolve monomer in a suitable solvent, for poly vinyl chloride we dissolve vinyl chloride in dichlorobenzene at low temperature. Initiator is added to start polymerisation. The polymer is separated from solvent.

Advantages:

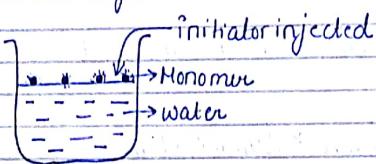
- i) Due to presence of solvent, the mixture is not so much viscous therefore can be stirred easily.
- ii) Presence of solvent enables dissipation of heat so chances of explosion are reduced.
- iii) Chain termination is easier.
- iv) No molecular distribution. Almost same type of polymer are made.

Disadvantages:

- i) Polymers are not pure.
- ii) Separation of solvent and polymer is needed.
- iii) Not so economical (\because solvent is used).

Suspension Polymerisation - (Bead / Pearl)

This technique is used for water insoluble monomer.



In this technique we used water as medium. The monomer is spread over the surface of water in the form of droplets. We add surfactants and stir the mixture continuously to prevent collapsing of droplets. Initiator is injected in each individual

droplet. The polymer can be separated easily from water and surfactant can be rinsed off by water.

Advantages:

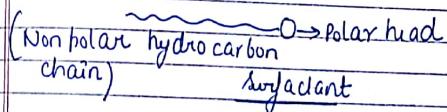
- Economical as water is used as medium.
- Easy separation of Polymer.
- Purity of Polymer is high.
- Heat liberated can be controlled.

Disadvantages:

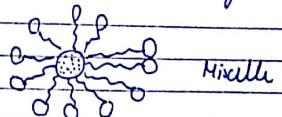
- We cannot control the size of the polymer precisely.

Emulsion Polymerisation:

This technique is also used for water insoluble monomer. We take water as medium and add monomer to it. Here also we use surfactants or emulsifiers but at high concentration as compared to suspension polymerisation.

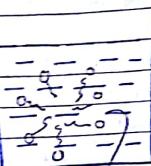


If taken in small amount they are dissolved in water but after certain conc. (CMC) they form Micelle.



In this method we use water soluble initiator.

We can control the size of Polymer by controlling the ratio of Monomer and water.



✓ Misalki

The polymerisation occurs at the centre of each misalki can be controlled by controlling the ratio (size of polymer) of monomer and water.

The polymer can be filtered off and emulsion can be removed by repetitive washing with water.

Polymer of high purity is obtained.

28th April, 17

Average Molecular weight

Due to high variation in molecular wt of each polymeric chain we take average molecular wt.

It can be calculated in two ways -

$$① \text{ Number average molecular wt. } (\bar{M}_n) = \frac{\sum n_i M_i}{\sum n_i}$$

No. of chain	fraction No:	Mol-wt.	Contribution in molecular wt.
n_1	$n_1 / \sum n_i$	M_1	$n_1 M_1 / \sum n_i$
n_2	$n_2 / \sum n_i$	M_2	$n_2 M_2 / \sum n_i$
n_3	$n_3 / \sum n_i$	M_3	$n_3 M_3 / \sum n_i$
\vdots	\vdots	\vdots	\vdots
n_i	$n_i / \sum n_i$	M_i	$n_i M_i / \sum n_i$
$\sum n_i$			$\sum n_i M_i / \sum n_i$

= 10,500

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Ques 3)

		Mw	
10	molecules	5,000	
20	"	10,000	$\overline{M}_n = ?$
25	"	15,000	$\overline{M}_w = ?$
20	"	20,000	
5	"	25,000	

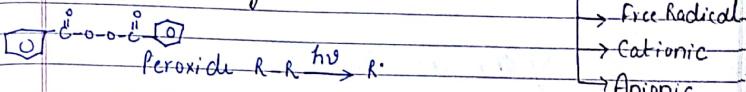
Polydispersity Index ($PDI = \frac{\overline{M}_w}{\overline{M}_n}$)

$$PDI = \frac{\overline{M}_w}{\overline{M}_n} = \frac{91,818.181}{55,000}$$

Ans 3)

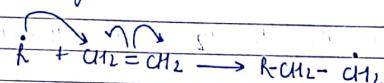
$$\begin{aligned}\overline{M}_n &= \frac{\sum n_i M_i}{\sum n_i} \\ &= \frac{(10 \times 5000) + (20 \times 10000) + (25 \times 15000)}{(10 + 20 + 25 + 20 + 5)} \\ &= \frac{50,000 + 2,00,000 + 375,000}{80} \\ &= \frac{4,00,000 + 125,000}{80} \\ &\Rightarrow\end{aligned}$$

Mechanism of Addition Polymerisation



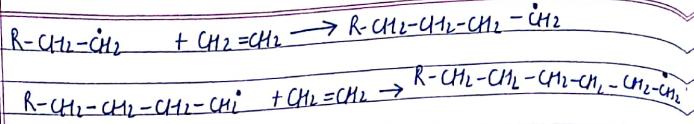
① Initiation -

In this step the initiator attacks on a monomer to form a new free radical.

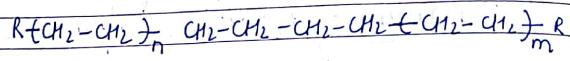
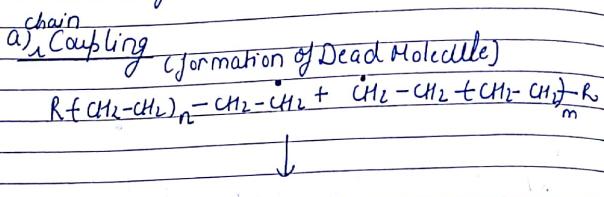


② Propagation:

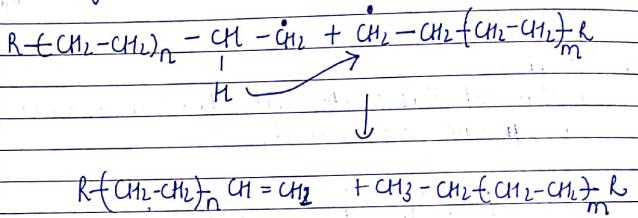
The free radical generated during initiation will attack on other monomeric unit to generate a new free radical and the process continues till termination.



③ Termination
In free radical Polymerisation termination can occur by

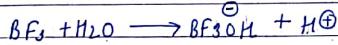


b) By disproportionation-

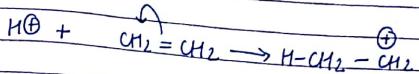


Cationic Polymerisation:

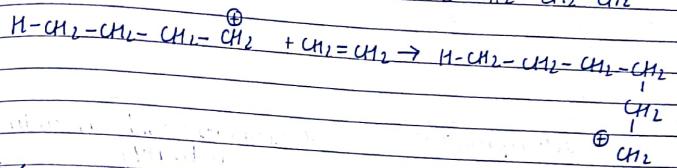
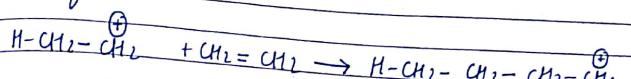
Generally we take acid for polymerisation



① Initiation -



② Propagation -



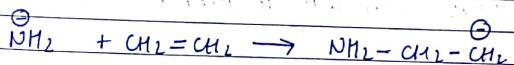
③ Termination:

- a) By combination with counter ion.
- b) Reverse of initiation

Anionic Polymerisation -



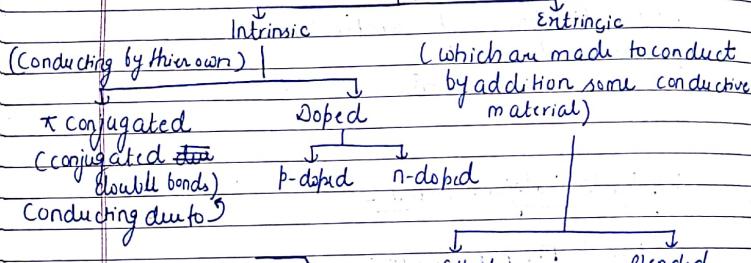
① Initiation :



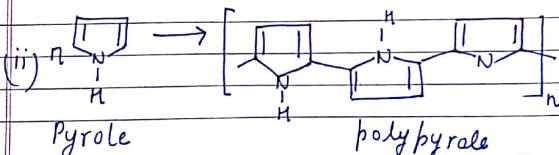
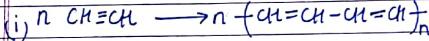
28th April, 2017

(the polymers which can conduct electricity)

Conducting polymers

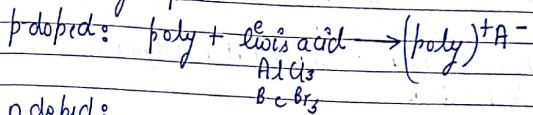


① π -conjugated polymer \rightarrow eg: Polyacetylene

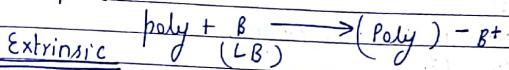


(iii) polyaniline

② Doping: The conductivity of polymers is increased by adding dopant.



n -doped:



① Filled:

The conducting polymers generated by addition of some filler to a non-conducting polymer are known as filled conducting polymers. e.g. carbon nanotubes, carbon black, metal oxides.

② Blended (mix): The conducting polymers which are obtained by blending a conventional polymer with a conducting polymer.

The maximum amount of filler which can be added to a polymer is known as percolation limit.

Applications of conducting polymers-

- optical fibres
- Biosensors, sensors
- Rechargeable batteries
- target drug delivery system.

Biodegradable polymers:

The polymers which can be degraded by microorganisms due to their enzymatic activities are known as biodegradable polymers.

Factors affecting biodegradable polymers.

- Temperature
- pH
- Presence of microorganisms.
- Humidity
- Nature of substrate

- There should be some hydrolysable bonds.
- It should be amorphous.
- There should be a functional group like -OH.
- Low melting point.

e.g. polyhydroxy butyrate

poly lactic acid

Advantages of Biodegradable Polymers-

- Ecofriendly
- Easy disposal

Disadvantage-

- Expensive
- Short shelf life
- Can't be used for storage operations for long period.

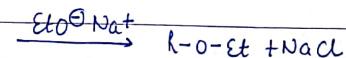
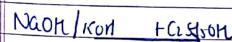
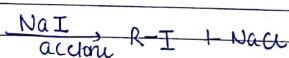
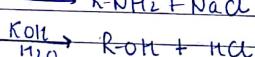
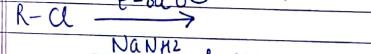
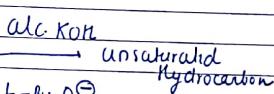
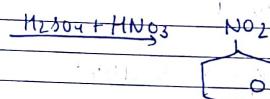
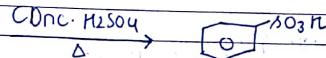
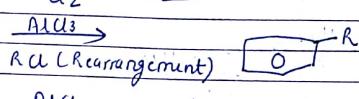
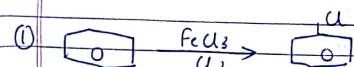
(Study More from book if possible)

Mitoff / Moving Boundary — 1 Numerical

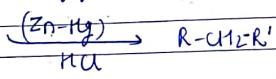
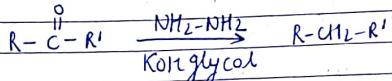
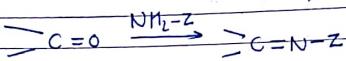
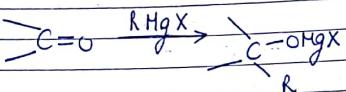
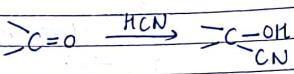
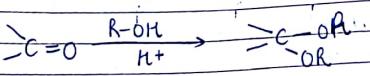
[derivations]

[Corrosion]

[Sacrificial cathode]
[types of corrosion]



R-OH $\xrightarrow[\Delta]{\text{Conc. H}_2\text{SO}_4}$ unsaturated Hydrocarbon

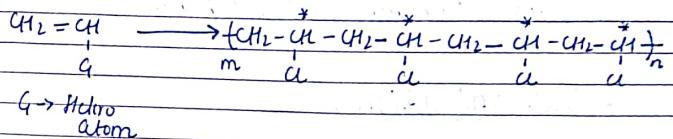


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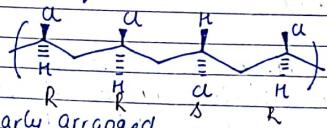
Tutorial

Tacticity:

The different configurational arrangement of stereo atom in a long polymeric chain is known as tacticity.



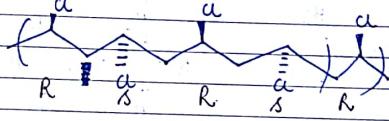
i) Atactic arrangement:



→ irregularly arranged.

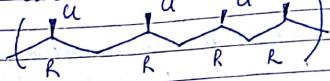
In this, the stereo atom is irregularly arranged above the plane and below the plane leading to irregularity in the configuration of chiral carbon.

ii) Syndiotactic:



The configuration of chiral carbons is alternate.

iii) Isotactic-



All the Hydrogen atoms on each carbon atom are either above the plane or below the plane.

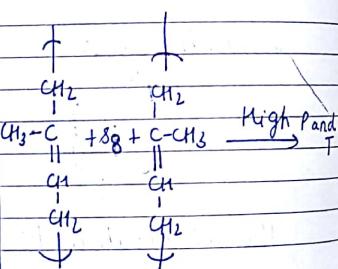
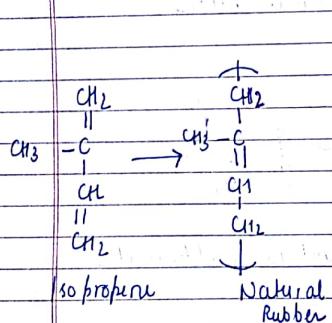
* Vulcanization :

'Vulcan' = Roman god of fire.

Good year \rightarrow 1839
(Scientist)

The process of heating rubber with sulphur or any vulcanization agent at high temperature and pressure is known as vulcanization.

This process brings cross linkage b/w two polymeric chains.



The other examples of vulcanising agents are Mg, ZnO
 $\text{Mercaptans}, \text{Alkoxides}, \text{Crown ethers}$
(sulphur containing compound)
↓
used in LPG.

→ 100% oxygenated compounds

→ 100% aliphatic hydrocarbons

→ 100% branched hydrocarbons

→ 100% saturated hydrocarbons

→ 100% aromatic hydrocarbons

→ 100% cyclic hydrocarbons

→ 100% branched hydrocarbons

→ 100% saturated hydrocarbons

→ 100% aromatic hydrocarbons

→ 100% cyclic hydrocarbons

→ 100% branched hydrocarbons

→ 100% saturated hydrocarbons

→ 100% aromatic hydrocarbons

→ 100% cyclic hydrocarbons

→ 100% branched hydrocarbons

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