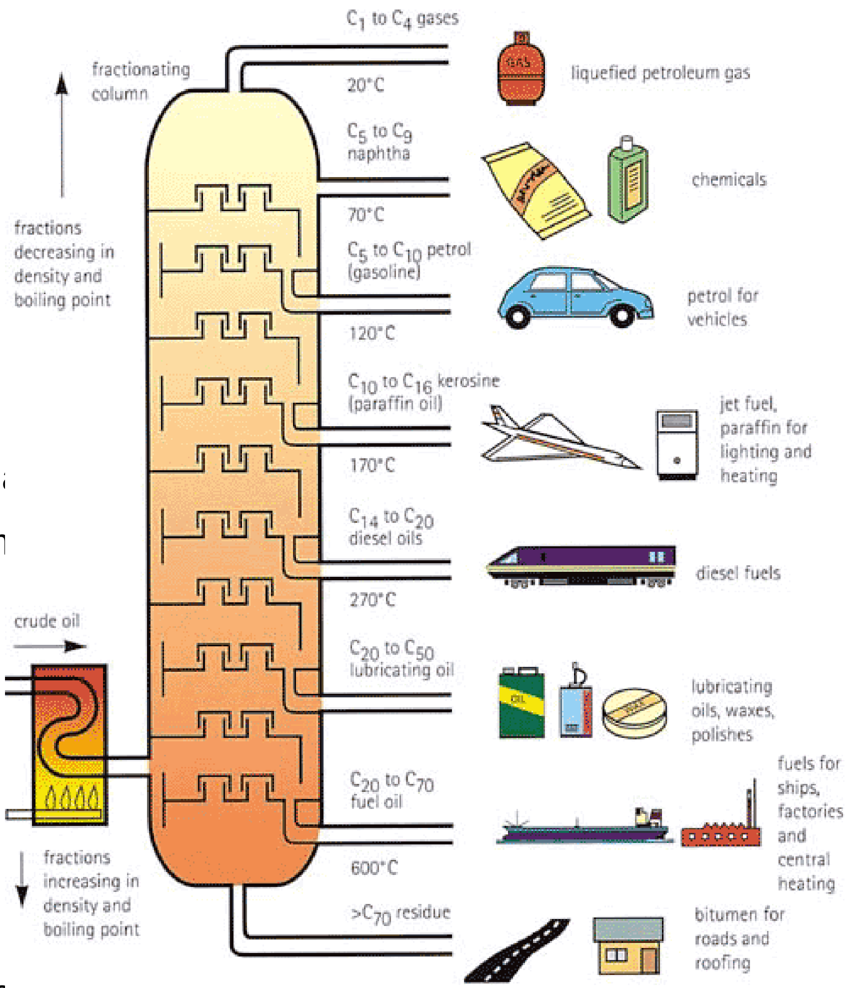
Fuels & Thermochemistry | Topic Notes

Fuel and Heats of Reactions.

- Crude Oil is a fossil fuel and formed from the bodies of tiny sea creatures that died millions of years ago, as the layers of mud and slit grew thicker over the years, the decay caused by bacteria slowly turned these bodies into crude oil and natural gas.
- It is separated into a number of useful mixtures through a process called Fractional Distillation.



- This involves heating the crude oil and separating the various mixtures on the basis of their boiling points, each one of these useful mixtures is called a fraction.
- The crude oil is heated in the furn and enters the fractionating colum a partially vapourised mixture.
- The fractionating column is a tall cylindrical tower containing a series of trays to help collect the condensed liquids.
- Maintained at high temperature at the bottom and the temperature column.
- The larger hydrocarbons with higher boiling points turn to liquids near the bottom of the column.
- The smaller hydrocarbons remain as gases and rise up along the column.

- Different fractions condense at different levels in the fractionating column.
- **R**eal - Refinery gas, bottled for sale as domestic gas, fuel **C1 - C4**
- **P**eople - Petrol or light gasoline, motor fuel **C5 - C10**
- **N**ever - Naphtha - petrochemical industry, medicines, plastics, solvents and synthetic fibres **C7 - C10**
- **K**ick - Kerosene - aviation fuel and in stoves **C10 - C14**
- **D**irty - diesel oil, fuel in trucks, buses, trains and some cars **C14 - C19**
- **L**ittle - Lubricating oil - reduces wear of engines **C10 - C35**
- **F******** - Fuel Oil - ships, power stations and heating plants **C30 - C40**
- **B******** - bitumen - road surfacing/tar, waterproofing and roofing. **C35 <**

Lubricating Oil, Bitumen and Fuel Oil are the **residue fractions**, these are the fractions that are left over when the more volatile fractions boil off.
Mercaptens are sulfur compounds that are added to odourless gases such as refinery gases so that gas leaks can be detected.

Octane Number is a measure of a fuels tendency to resist knocking or auto ignition measured on a scale of 100 being assigned to 2,2,4 trimethylpentane and 0 being assigned to heptane.

- The early explosion of the petrol air mixture in the car’s cylinder is auto ignition or ‘knocking’, the engine can lose power and the cylinders can be damaged as a result, the pistons vibrate and a metallic noise is heard.

- **The shorter the alkane chain the higher the ON rating**
- **The more branched the alkane chain, the higher the ON rating**
- **Cyclic compounds have a higher ON than straight chain compounds**

Tetraethyl lead was used in 1920’s as an anti-knock additive, lead pollution from car exhausts had the potential to cause health damage. This lead to ‘unleaded petrol’

Lead compounds are toxic and poison metal catalysts in the catalytic converter which means they can no longer reduce levels of pollutants in exhaust fumes.

Isomerisation

Involves changing straight chain alkanes into their isomers.

- The alkanes are heated in the presence of a suitable catalyst and this causes chains to break. When they do they are allowed to rejoin together and as a result they are more likely to become branched chain alkanes as opposed to straight chain alkanes.
- The straight chain alkanes are then again recycled over a suitable catalyst that converts them to branched chain alkanes
- **Pentane and hexane**

Catalytic Cracking

Involves the breaking down of long chain hydrocarbon molecules to short chain hydrocarbon molecules for which there is a greater demand.

- Short chain hydrocarbons are used in petrol - huge demand, they tend to be highly branched which also increases the octane number.
- Involves heating heavier fractions in the presence of a catalyst
- A common reaction is when an alkane is converted into an alkene and a branched alkane. If you split a saturated alkane atleast one product is unsaturated.
- Alkenes are important feedstock for petrochemicals industry - polythene, polypropene etc...

Reforming or Dehydrocyclisation

Involves the use of catalysts to form ringed compounds.

- Straight chain alkanes are converted to cycloalkanes and then cycloalkanes are converted to aromatic compounds. Petrol contains 3/4% benzene - high ON.

Adding Oxygenates

any fuel that contains oxygen in its molecules, eg. methanol, ethanol, MTBE (methyl tertiary butyl ether).

Increases octane number AND gives rise to very little pollution. They are **cleaner fuels** than hydrocarbons as there are less carbon monoxide in exhaust of cars (Brazil, ethanol)

Hydrogen gas is another fuel. There are 2 methods of manufacturing it:

(I) **Steam reforming of natural gas** - CH4 + H20 = 3H2 +CO, reacting methane with steam in presence of suitable catalyst.

(II) **Electrolysis of water** - H20 -------> H2 +0.502, more expensive because of high electricity costs

Burning hydrogen is very environmentally friendly - only by product is water, used to manufacture ammonia, hydrogenating vegetable oils in making margarine.
hydrogen forms an **explosive mixture** with air so there are problems with storage and transport.

ΔH

Thermochemistry

Exothermic - any chemical reaction that produces heat is exothermic and is represented by **-** delta H. MINUS DELTA H. e.g. burning of food inside the body, the reaction of sodium dichromate and ethanol.
Endothermic - a reaction that takes in heat - + Delta H. e.g. sherbert with water

Heat of reaction is the heat change that takes place when the number of moles of reactants indicated in the balanced equation for the reaction react completely.

Thermochemical equations must be balanced, the value of delta H must be written and the states of reactants and products must be given, e.g. gas, liquid etc...

Heat of combustion is the heat change that takes place when 1 mole of a substance is completely burned in excess oxygen.
(general term)

important notes:

- C + 1/2O2 --------> CO delta H = -111kJmol^-1 This is not the heat of combustion because when carbon is COMPLETELY burned in excess oxygen it forms carbon DIOXIDE not carbon monoxide.
- Heat of combustion is measured using a **bomb calorimeter.**
- Small steel container with a screw on cap, the sample is placed in the crucible, the bomb is placed in the container of water (calorimeter), oxygen is pumped into the bomb and the sample is ignited by the electric wires.
- Bomb calorimeters also compare the efficiency of various fuels and gives the kilogram calorific value of substances with a variable composition (coal, petrol, peat).

The kilogram calorific value of a fuel is the heat energy produced when 1kg of the fuel is completely burned in oxygen.

Bond energy is the energy required to break one mole of covalent bonds and to separate the neutral atoms completely from each other.

Heat of neutralisation is the heat change that takes place when 1 mole of H+ ions from an acid react with 1 mole of OH- ions from a base.

Heat liberated = M X C X (T1-T2)
C = specific heat capacity.
REMEBER MASS IS IN KILOGRAMS

- **When 200 cm^3 NaOH solution was added to 200 cm^3 of a 0.4M sulfuric acid solution, a neutral solution was produced and temperature increased by 5.5 degrees.**
- **C of neutral solution = 4.2 kJ kg^-1 degrees celsius to the -1.**
- **Density is 1g/cm^-3**

C =4.2 X 1000= 4,200 Joules
Plastic container is used because plastic has a NEGLIGIBLE specific heat capacity, i.e. we can assume the container itself doesn't absorb heat.

Mass of the solution = 1 gram per cm^3 density X (200+200)cm^3 = 400g = 0.4KG

Heat liberated = M X C X temp rise = 0.4 X 4,200 X 5.5 = 9,240 Joules
Number of moles of H2SO4 Liberated = (volume X Molarity) divided by 1000 = (200 X 0.4)/ 1000 = 0.08 Moles
0.08 Moles of H2SO4 Liberates 9240 joules
1 mole liberates 9240/0.08 joules/ 115,000 joules

115,000 joules is 115.5 KJ
H2SO4 + 2NaOH ------> Na2SO4 + H20
i.e. 2H+ + 2OH- -----> 2H2O
Heat of neutralisation is when 1 mole of H+ Ions react with 1 mole OH- ions, here there are 2 moles.

115.5/2 = -57.75 KJ molˆ-1
Heat of neutralisation is half the heat of reaction here

The heat of formation of a compound is the heat change that takes place when one mole of a compound in its standard state is formed from its elements in their standard states.

Standard state is at 25 degrees and at 1 atmospheric pressure or 101 KPa

$2C + H_2$ ------> C_2H_2 deltaH= 233kJmol^-1   you will be required to write down heats of formation and sometimes fractions will be necessary.
$1/2N_2 + 3/2H_2$ -----> NH_3

Hess's Law states that if a chemical reaction takes place in a number of stages, the sum of the heat changes in the separate stages is equal to the heat change if the reaction is carried out in 1 stage.

A   ----->   B ------> C -----> D

Delta H of A --> D = deltaH of A-->B + DeltaH of B-->C + DeltaH of C--->D

May be used indirectly to measure the heat of reaction of a chemical reaction that may be difficult to measure.

1. Calculate heat of formation of a compound using other heats of formation and one heat of reaction

(i) $C + O_2$ ----> CO_2 deltah= -393
(ii) $H_2 + 1/2O_2$ --> H20 deltah=-286
(iii) $CH_4 + 2O_2$ --> CO_2 + H20 deltah=-879

calculate the heat of formation of methane.

what we need: $C + 2H_2$ ----> CH_4 deltaH= ?????

Start by introducing C - $C + O_2$ ---> CO_2 deltah=-393

introduce $2H_2$ by multiplying (ii) by 2 : $2H_2 + O_2$ ---> 2H20 deltah= **-572**

add both equations here

C + 2H2 +202 ----> CO2 + 2H20 deltah = -393-572 = -965

We need CH4 on right hand side so REVERSE equation (iii) and add to the previous equation:

reversed - CO2 + 2H20 ----> CH4 + 2O2 deltah= +879

Add **-** CO2 + 2H2 + 202 +2H20 + C ---> CH4 + 2H20 + CO2 + 202

this leaves us with

C + 2H2 ----> CH4 deltaH = -965 + 879 = -86

2. Calculate Heat of reaction using heats of formation of reactants and products.

This is the same as above except a more complex equation IS GIVEN to us with heats of formation of its elements.

Sources of Hydrocarbons

Hydrocarbons

- compounds consisting of hydrogen and carbon only, bonded together covalently.
- important as fuels and feedstock for the chemical industry.

Coal, Natural Gas and Petroleum

- sources of hydrocarbons
- formed from the compacted remains of dead plants of animals which have been fossilised
- crude oil and natural gas = marine animals and plants

Decomposition as Methane Sources

- anaerobic decay - animal waste, vegetation, rubbish dumps

Hazards of Methane Production

- extremely explosive

Structure of Aliphatic Hydrocarbons

Aliphatic

- hydrocarbons which do not contain a benzene ring

Homologous Series

- a homologous series is a family of organic compounds with the same general formula, similar chemical properties, gradations in physical properties, and each member differs by a CH_2 unit

No. of Carbons	Root
1	Meth
2	Eth
3	Prop
4	But
5	Pent
6	Hex
7	Hept
8	Oct
9	Non
10	Dec

Alkanes - names, structural formulas, isomers (to C-5)

- -ane
- C_nH_{n+2}
- saturated (only single bonds)
- making isomers: shorten chain by one, add methyl group to an inner carbon
- tetrahedral shape

Alkanes - physical properties

- lower (up to butane) - gases @ rt
- middle (up to C_{15}) - liquids @ rt
- high (C_{15+}) - waxy solids @ rt
- longer chains → stronger van der Waals' → higher boiling point
- non-polar - cyclohexane and methylbenzene

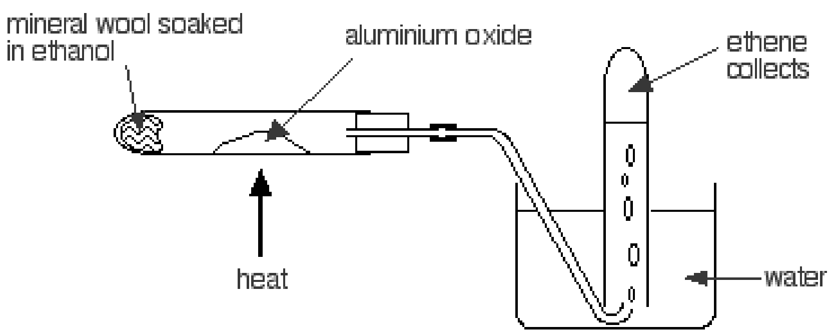
Alkenes - names, formulas, isomers to C-4

- C_NH_{2N}
- C = C (unsaturated)
- lowest member is ethene
- isomers of butene: but-1-ene, but-2-ene, 2-methylpropene

- lower - gases,
- higher - liquids or solids
- non-polar or slight polarity
- longer chains →stronger van der Waals' →higher boiling point

Prep and Properties of Ethene

- ethanol is dehydrated using hot aluminium oxide (white powder)
- non-polar so collected by displacement of water
- $C_2H_5OH \longrightarrow C_2H_4 + H_2O$



(III) combustion: sooty, smoky flame. Limewater ⟶ milky

(IV) unsaturation: bromine water ⟶ cloudy

(V) unsaturation: acidified potassium manganate(VII) ⟶ cloudy

Alkynes - Ethyne / Acetylene

(VI) C_2H_{2N-2}

(VII) C≡C (unsaturated)

(VIII) lowest member is ethyne

(IX) longer chains → stronger van der Waals' → higher boiling point

(X) lower - gases,

(XI) higher - liquids or solids

(XII) non-polar or slight polarity

(XIII) uses: cutting metal and welding - oxyacetylene torch

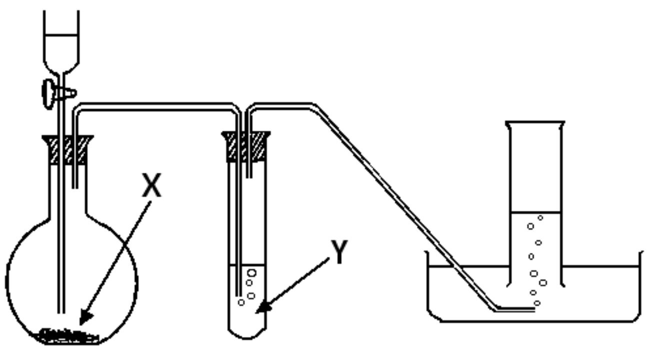
Prep and Properties of Ethyne

(XIV) impurities: calcium sulfide & calcium phosphide ⟶ phosphene, hydrogen sulfide

(XV) acidified copper sulfate soln to remove impurities

(XVI) calcium dicarbide & water

(XVII) $CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$



2.

(iv) liquid in dropping funnel = water

(v) X = calcium dicarbide

(vi) Y = acidified copper sulfate soln

(vii) colourless, sweet smell

(viii) combustion: explosive, basic

(ix) unsaturation: bromine water

(x) unsaturation: potassium manganate(VII)

Aromatic Hydrocarbons

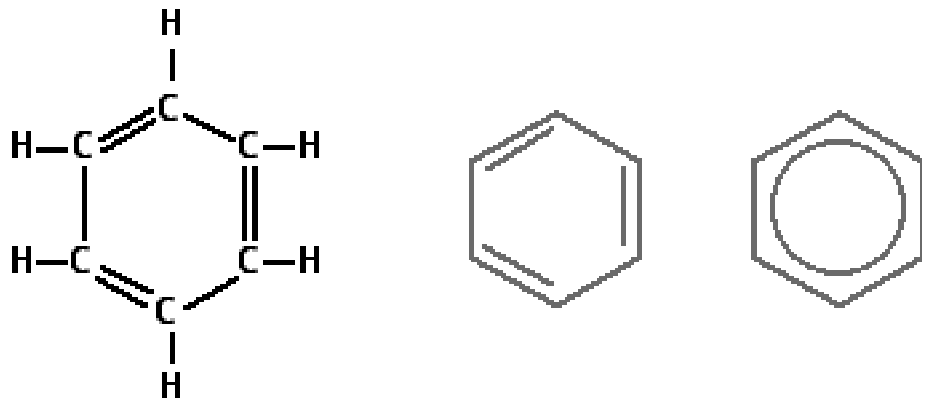
Structure of Benzene, Methylbenzene and Ethylbenzene

(xi) carbon-carbon bonds are intermediate between single and double bonds

(xii) (due to) delocalised pi electron cloud

(xiii) note: benzene is carcinogenic

3.



4. Benzene depicted in three ways

Uses of Aromatic Compounds

- methyl benzene - industrial solvent - dissolves non-polar solvents
- martius yellow - dye
- folic acid - pharmaceuticals
- morphine - pain killer
- diuron - herbicide
- phenolphthalein & methyl orange - acid-base indicators
- aspirin - pain killer (non-carcinogenic)

Physical Properties

- non-polar
- lower - liquids
- higher - solids