Subject : fuel combustion	**موضوع: احتراق وقود**
Weekly Hours: Theoretical: 2	**الساعات الأسبوعية: نظري :2**
Tutorial: 1	**مناقشة: 1**
Experimental : 1	**عملي:1**
Units: 4	**الوحدات : 4**

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2.	**Molecular structure of fuel**	**البناء الجزيئي للوقود**	**.2**
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Fuel and Combustion

Fuel........ syllabus

1. Introduction.
2. Chemical composition and molecular structure of petroleum fuel.
3. Refining processes of petroleum.
4. Fuel for spark ignition engines.
5. Fuel for compression ignition engines.
6. Liquefied Petroleum Gas (LPG) for Spark Ignition Engines.
7. Alternative fuels...... alcohol fuel.

1. Introduction

Petroleum oil is generally considered to be formed from animal and vegetable debris accumulating in sea basins or may have been decomposed by anaerobic bacteria under reducing conditions, so that most of oxygen was removed, or oil may have been distilled from the partially decayed debris by heat generated by earth movement.

Petroleum has established its status as the primary transportation fuel through its use with automobiles. The foremost attribute of a fuel is the release of thermal energy through chemical reaction called combustion.

* General Requirements of an Automobile Fuel

1. High power output. Higher power output is affected by the following characteristics of fuel.
   a. Calorific value: heat of combustion
   b. Thermal efficiency
   c. Inlet temperature
2. Low consumption
   a. Calorific value
   b. Thermal Efficiency.
3. Low pollution.
   a. Inlet temperature.
   b. Volatility
   c. Ignition temperature.

Beside that, the reaction characteristics of the fuel should be such that the rate of pressure and temperature rise inside the cylinder due to combustion is moderate and reduce the possibility of large mechanical and thermal stresses in the components of the engine. Other requirements are:

- High thermal stability.
- Low deposit forming tendencies.
- Good fire safety.
- Low toxicity.
- Easy transfer, handle & storage.
- Easy starting under various working conditions.

2. Chemical composition and molecular structure of fuels

All liquid fuels that used for internal combustion engines have two combustible elements carbon and hydrogen, with percentage of about (86% c & 14% H_2) by weight, present separately or in combination called hydrocarbons. There are three principle commercial types of liquid fuel.

1. Refined products of petroleum

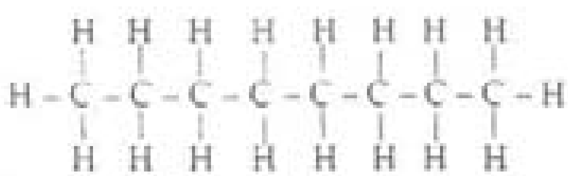
The refined product of petroleum fuel, which mainly consists of gasoline, kerosene, gas oil and fuel oil, are the major source of liquid fuel at the present time. The specific characteristics of a particular fuel vary widely with its composition. They are arranged into families based on their chemical formula and their molecular structure.

a. Paraffins (C_nH_{2n+2}):

In normal paraffins the valence of each carbon is fully utilized in combining by a single bond with other carbon atoms and with hydrogen atoms. Paraffins are, therefore, saturated hydrocarbons and very stable in character. Paraffins are further classified as straight chain and branched chain.

1. Straight chain paraffins

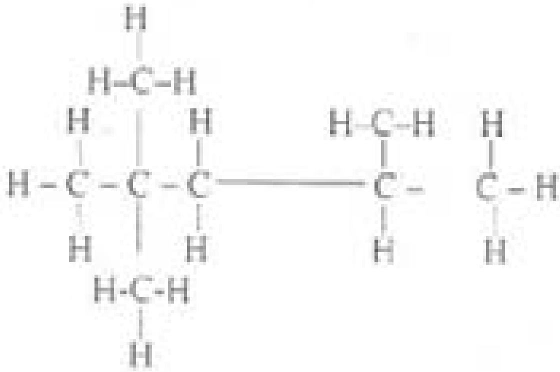
Here the carbon are bonded in a straight chain. For example n-octane (C_8H_{18}) is written as:



Meth. 1
Eth. 2
Prop. 3
But. 4
Pent. 5
Hex. 6
Hept. 7
Oct. 8

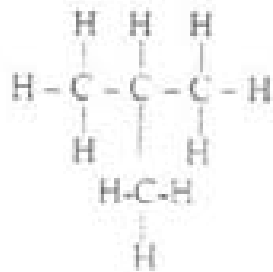
2. Branched chain paraffin

Another group of the paraffin family consists of carbon atoms bonded in branched chain. For example Iso- octane (C_8H_{18}) but its molecular structure and physical and chemical characteristics are different of normal octane (n-octane) C_8H_{18}.



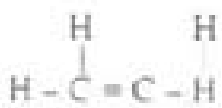
iso- octane

iso- butane



b. Oleffins (C_nH_{2n})

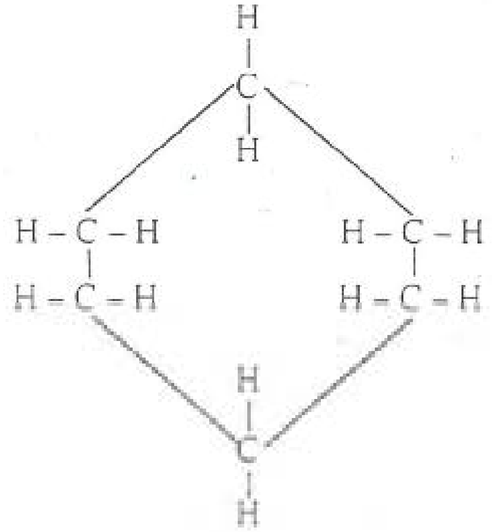
These compounds are similar to paraffins with one or more double carbon and, therefore, they are unsaturated. For example ethene C_2H_4



ethene

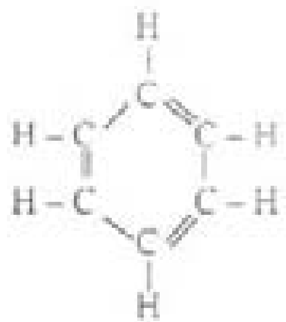
c. Naphthenes (C_nH_{2n}) Cycloparaffins

The general formula of naphthenes is (C_2H_4) like that of the oleffins but these hydrocarbons have ring structure, so that they are saturated compounds and they tend to be stable. For example cyclo-hexane (C_6H_{12}).

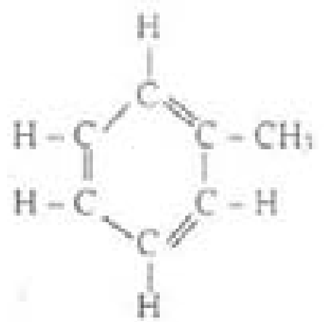


d. Aromatics (C_nH_{2n-6}) benzene derivative

These are ring structure compounds based on benzene ring. For example benzene (C_6H_6).



Other members of this family are formed by replacing H molecules by organic radical (CH_3). For example toluene (C_7H_8)



These are unsaturated hydrocarbons but the nature of their strong bonds makes their stable compared to other unsaturated families.

2. Benzol

Benzol is obtained as a by product of high temperature coal carbonization and consists of benzene (C_6H_6) and toluene (C_7H_8).

3. Alcohols

Alcohol's are formed by replacing one or more H molecules of paraffins group by OH radical. For example methyl–alcohol CH_3OH ethyl- alcohol (C_2H_5OH).

```
     H
     |
H – C – OH        methyl – alcohol
     |
     H

     H   H
     |   |
H – C – C – OH    ethyl – alcohol
     |   |
     H   H
```

Alcohols can be manufactured from grains, molasses and other waste products. Alcohols are generally used as blending agent (10 to 15%) with gasoline or petrol. Also it can be blend with gas oil.

* General characteristics of Hydrocarbons

The heat of combustion of the fuel decrease as the carbon hydrogen ratio, in the molecule, increase. Therefor, in the refined petroleum group, Paraffin have the highest heat of combustion and aromatics have the lowest heat of combustion.

Alcohol have lower heat of combustion than refined petroleum product due to the presence of OH group in the molecule.

- The self- ignition temperature of the fuel decrease as the carbon hydrogen ratio, in the molecule, decrease. Therefor Paraffins have the lowest self- ignition temperature and aromatics have the highest self-ignition temperature.
- In general as the number of atoms, in the molecule increase, the boiling point rises. Thus fuels with fewer number of atoms in the molecule are more volatile.
- Ignition delay of fuel increase as the carbon hydrogen ratio increase. Therefor paraffin's have low ignition delay and aromatics have comparatively high ignition delay. In the same family the more

complex structure of the molecule the higher is the ignition delay. So that branched chain paraffins have higher ignition delay than straight chain paraffins.

- The anti- knock quality of fuel used in spark ignition engines improves with increase in ignition delay of the fuel. Therefor, paraffin's offer less resistance to detonation while the aromatics offer better resistance. Also branched chain paraffin's are more resistant to detonation than straight chain paraffin's. Alcohol due to their complex structure have high anti-knock quality.
- The anti-knock quality of compression ignition engines fuel improve with decrease in ignition delay. Therefore paraffins are better fuel and aromatics are least desirable. Within the paraffin group the straight chain paraffin's with larger number of atoms in the molecule are considered to be best for compression ignition engines.

3. Refining Processes of fuel

The Process of separation is carried out in refineries by a process known fractional distillation. Fractional distillation process is based on the fact that the constituents of crude petroleum have different boiling points.

The products of refining processes are:

1. Natural gas (CH_4) with traces of other light hydrocarbons (boiling point(-70)→ (-40)).
2. Liquefied petroleum-gas (LPG): Mainly C_3H_8 C_4H_{10} with other light hydrocarbons (boiling point (-40)→(-30)) [calorific valve 10750-11080 kcal/Kg].
3. Naphtha: A mixture of number of hydrocarbons (boiling point (30→ 170) with specific gravity (0.675-0.7). (octane number 50-55) and (H.c.v 11000 Kcal/Kg). Used in internal combustion engines
4. Gasoline: A mixture of various hydrocarbons (boiling point 30-200 C^o). (Specific gravity 0.7-0.78), (octane number 88-93), and (H.c.v 10500 Kcal/Kg). Used in internal combustion engines.
5. Kerosene: Is heavier than gasoline (boiling point 250-300). (specific gravity 0.78-0.85) and (H.c.v 10900 Kcal/Kg). Used in gas turbines and jet engines.
6. Gas- oil: A fuel which it lie between kerosene and diesel fuel. (boiling point 200-370c^o), (specific gravity 0.84), (cetane number 53-58), (diesel index 53-55) and (calorific value 10800 Kcal/Kg) used in internal combustion engines.
7. Diesel Fuel: (specific gravity 0.87), (Diesel index 50) and (H.c.v 10500 Kcal/Kg). Used in tractor trains.

4. Isomerisation

Isomerisation is process by which the atoms of carbon and hydrocarbon in normal hydrocarbons are re- arranged to produce a more complex structure (iso- structure) of higher antiknock value. Isomerisation is used to:

1.Convert n- butane into iso-butane for alkylation.
2.Convert n- pentane and n- hexane into iso- paraffins to improve knock rating of highly volatile gasoline.

5. Reforming.

Reforming is a process for convert low- octane gasoline or naphtha by reaction with hydrogen so it can be called hydro-forming.

6. Super-fractionation

Super-fractionation is a method for separation of branched chain alkanes from their isomers the normal a lkanes, which are poor in anti-knock properties, the separated branched chain alkanes are used for blending to produce high octane number gasoline's.

7. Blending

Blending is the process of obtaining a product of desired quality by mixing certain products in some suitable proportions.

4. Fundamentals of automotive fuels

1. Fuel for spark ignition engines (gasoline)

Gasoline is a mixture of various hydrocarbons within a range of 4-10 carbon number and a boiling point range of 35-200°c it is colorless and transparent as manufactured, but by regulation, leaded gasoline is dyed orange to indicate toxicity. Gasoline is the fuel for spark ignition engines in which the three properties of particular importance are:
1. Stability
2. Volatility
3. Anti-knock quality

1. Stability

The stability of a fuel is its resistance to degradation and decomposition. Degradation is essentially caused by oxidation of gasoline with air (auto-oxidation), and its octane number will decrease. Q. 1

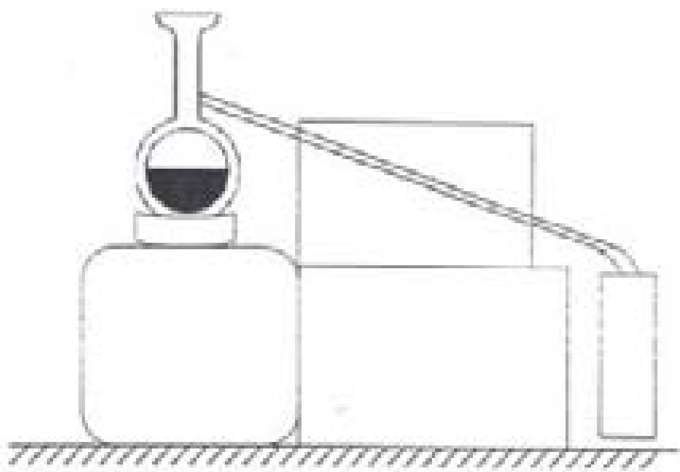
The most troublesome among all products arising from oxidation of gasoline is the high molecular-weight gum that forms as a result of oxidation polymerization and condensation of olefinic components. Gum is normally soluble in gasoline, but it tend to be left behind and deposit in the carburetor and other fuel system components as the gasoline evaporate. Antioxidants are added to improve oxidation stability.

2. Volatility

The volatility of a liquid in general is its tendency to evaporate under a given set of conditions. Gasoline should remain in completely liquid form in the fuel supply system from the fuel tank to the carburetor or injector and immediately vaporize when sprayed toward the combustion chamber.

If the fuel supply system is exposed to heat from the engines gasoline may boil, evolving babbles of vapor that interrupt liquid gasoline flow and causing vapor lock. On the other hand if gasoline has low volatility and does not evaporate readily, it stays partly in liquid form on the walls of the intake manifold. The fuel for internal combustion engines is a blend of different hydrocarbons. Volatility, therefore depends on the fractional composition of the fuel.

The usual method of measuring fuel volatility is by distilling the fuel in a distillation device at atmospheric pressure and in the presence of its own vapor.



* The 10 percent evaporation in the distillation curve is very important in all gasoline specification because it must be low enough for easiness starting of the engine but not too low to prevent vapor lock formation.

* From the temperature of different fuels it has been observed that the temperature of 20 percent evaporation gives an indication of its warning up time.

* The acceleration of the engine improves with lower evaporation temperature from 40 to 60 percent evaporation of fuel. Also it has been observed that, for satisfactory distribution, about 60 percent of fuel should evaporate in the manifold. Therefore the temperature at which 60 percent fuel evaporator should be the manifold temperature.

* The temperature at which 90 percent fuel evaporates gives an indication of the tendency of the fuel for smoke combustion. A high 90 percent temperature will also produce crank-case oil dilution with unburned fuel.

* The fuels for diesel engines have very low volatility. The fuel is injected inside the combustion chamber near the end of compression when the air temperature is well above the maximum temperature of evaporation of the fuel, therefore the volatility characteristics of fuel have very little effect on the performance of the engine.

3. Anti-knock quality

The antiknock quality of a fuel is its resistance to detonation. The factors that affect the tendency of the fuel to detonate in the engine cylinder are: chemical characteristics of hydrocarbons, air-fuel ratio, ignition timing, dilution, effectiveness of jacket cooling, atmospheric conditions and compression ratio.

* Knock measurement

Intensity of knock is usually measured by a bouncing pin type vibration meter or knock meter.

The pin is mounted on the engine so that a diaphragm connected to one end of the pin is directly exposed to combustion pressure.
When knock occurs the pin will bounce and close the two open contact points. The reading of the knock meter is depend on the time of contact.

* Octane number

Octane number of fuel is defined as the percentage by volume of iso-octane in a mixture of ico-octane (C_8H_{18} with 100 octane number) and n-heptane (C_7H_{16} with zero octane number) which will match the detonation intensity of the fuel when the comparison of detonation intensity is made in a standardized test engine under special conditions.

* Determination of octane number

To determine the octane number of fuel a single cylinder standard engine of the type C.F.E. (Cooperating Fuel Research) or Ricardo type with variable compression ratio is used. The test engine run under standard conditions with standard (reference) fuel blended from ico-octane and n-heptane.

If the running of the test engine with a sample gasoline makes the engine knock at a compression ratio that matches with a volume percentage blend of standard fuel the octane number of the sample gasoline equals the percentage of iso-octane.

The octane number measured in this case called research octane number R.O.N. where the test is carried out under relatively mild operating conditions (low engine speed and low mixture temperature).

Another test carried out under more severe operating conditions (high engine speed and higher mixture temperature) is called motor octane number (M.O.N.)

In general the research octane rating can be related to antiknock quality of the fuel when used in engine which is highly loaded at low speeds. The motor octane rating is more indicative of antiknock performance at high speeds and part throttle.

The octane number obtained by motoring method are lower than that obtained research method, because the end gas temperatures are appreciably higher in motor method due to sever test conditions.

The higher the octane number of a gasoline the higher the compression ratio can be of the engine it fuels, thus improving thermal efficiency and increasing power output.

*** Sensitivity**

Sensitivity of a fuel is the difference between research octane number and motor octane number, that is:

$$Sensitivity = RON\text{-}MON$$

The higher the sensitivity the poorer the gasoline performance under sever conditions.

*** Performance number (PN)**

The octane scale fails to serve with fuels that resist knock more than iso-octane. In order to extend the octane scale the knock resistance of a fuel is measured in terms of performance number (PN) which is the ratio of the knock-limited indicated mean effective pressure (Klimep) of test fuel to knock-limited indicated mean effective pressure of iso-octane i.e.

$$PN = \frac{Klimep\ of\ test\ fuel}{Klimep\ of\ iso\text{-}octane}$$

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Another attempt to extend the octane scale for motor gasoline is Wiese method which is:

$$ON = 100 + \frac{PN - 100}{3}$$

*** Knock Inhibitors**

Chemical compound like tetraethyl lead (TEL), iron carbonyl and nickel carbonyl appreciably increase the knock resistance of gasoline engines fuel when a small quantity is added to the fuel (0.2→1.5ml/liter of gasoline). This additive produce cylinder deposit and poisonous emission through exhaust. Therefore, the amount of compound added per liter restricted.

When TEL is added with iso-octane the knock resisting property of the mixture is higher than that of iso-octane. This fuel cannot be rated according to the octane number scale. The resistance of fuel in this case be expressed in terms of iso-octane + TEL (ml/liter).

2. Fuel for compression ignition engines (gas oil)

Gas oil is a petroleum distillate with a boiling point range between 200 and 370°c. The three critical properties of gas oil are 1-stability, 2-fluidity, and 3-Ignition quality.

1. Stabillity

If gas oil undergoes degradation through auto-oxidation, macromolecular gum is formed as in the case of gasoline. Gas oil soluble gum, if present in minor amount, and will not cause trouble but in large amounts, it will clog fuel in section nozzles and interrupt fuel supply. The stability is depend on the content of the compounds containing sulfur, nitrogen and oxygen as will as olefins.

hydrogen remove the compounds responsible for degradation resulting in a stable gas oil.

2. Fluidity

At low temperatures deposits of wax contained in gas oil clog the piping of fuel supply system. Also hydrocarbon components of high molecular weight have poor fluidity and cause lock of fuel supply at low temperature. Generally speaking. Gas oil tend to have poor fluidity at low temperatures if they contain higher amounts of heavy fractions or they contain higher amounts of normal paraffin's for the same molecular weight. Also the viscosity and surface tension of the fuel influence the degree of atomization of combustible mixture. which in turn influence the physical part of the ignition delay period

3. Ignition quality

The hydrocarbon components in gas oil have low ignition points ranging from (200 to 300)°c .the abnormal combustion (knocking) also occur in compression ignition engines but in ways different of knocking in spark ignition engines .

*** Abnormal combustion in compression ignition engines [knocking]**

An excessive large fraction of fuel may accumulate in the combustion space before actual ignition if the ignition lag is too large or if the rate of fuel in section is too high. When this large fraction of fuel take part in combustion it cause the pressure rise to be very high resulting in a compression waves in the gases. The gas vibration due rapid rate of pressure rise causes the engine to vibrate and result in very rough running of the engine and producing objectionable noise and excess stressive on engine structure. This phenomenon is called 'diesel knock'

*** The tendency of diesel knock can be reduced by the following**

1- Increase the temperature of air at the end of compression. This can be achieved by increasing the compression ratio or by increasing the inlet temperature of charge. Starting of injection near the top dead center.
2- Increasing pressure of charge at the beginning of combustion by super charging.
3- Increasing the temperature of combustion chamber wall specially where the fuel jet tends to impinge.
4- Decreasing the r.p.m or injection rate. Decrease in r.p.m or injection rate reduce the amount of fuel taking part in the period of rapid combustion.
5- Using fuel of better ignition quality . i.e. higher cetane number fuel.

*** Cetane number**

The straight chain hydrocarbon cetane ($C_{16}H_{34}$) is considered as the best high-speed diesel fuel known, and is given a rating of (100). While the aromatic hydrocarbon methyl-naphthalene is given a rating of 0. The cetane number of a diesel oil is the percentage by volume of a cetane in a cetane /methyl-naphthalene mixture that has the same performance in a standard compression ignition engines as that of the fuel.

* **Determination of cetane number**

1. Ignition delay test

The test is carried out at constant speed and load. The delay time is measured for the oil under test with an electronic delay meter and compared with the standard reference fuels having delay periods shorter and larger than that of the sample fuel. The cetane number is obtained by interpolation.

2. Throttling test

The engine is run at the lowest load which gives steady conditions. A surge chamber and throttle device is attached to the engine intake port. This device reduce the surge chamber pressure and increase the delay period until a misfire occurs, which indicated by a paff of white smoke. The air pressure at this point is related to the delay period and is a function of the cetane number. By bracketing the pressure for misfire of the sample fuel with reference fuels of higher and lower quality, the cetane value can be calculated.

As the octane number gives a measure of resistively to ignition, the cetane number gives a measure of spontaneous ignition tendency, so that a reverse correlation holds between them.

The ignition quality of oil can be improved with a higher content of normal paraffins, but in the field performance, it may degrade due to the loss of low-temperature fluidity.

- high speed diesels hot < 50
- medium speed diesels hot < 53
- slow speed diesels hot < 51

- pentane (C_5H_{12}) 218°C
- cetane ($C_{16}H_{34}$) 235°C (hexadecane)
- toluene (C_7H_8) 550°C
- benzene (C_6H_6) 580°C

Diesel index

An alternative method of expressing the quality of diesel fuels is by use of the "diesel index", which does not necessitate the use of a test engine.

$$\text{Diesel index} = \text{aniline point in } ^\circ F \times \frac{API\ gravity}{100}$$

This can only be used as a rough guide to cetane numbers and is not applicable to fuels containing additions for ignition quality improvement.

*** Aniline point**

This is the lowest temperature at which the oil is completely miscible with an equal volume of aniline for a good quality diesel oil the aniline point is > 22°C.

$$A.P.I.\ gravity = \frac{141.5}{sp.gr\ at 15.6^{\circ}C} - 131.5$$

This gives a higher result for paraffin oils than for aromatics hence its use in the diesel index formula.

5. Liquefied petroleum gas (L.P.G)

LPG is a general term for hydrocarbons that are gases at ordinary atmospheric temperature and pressure but can be readily liquefied by compressing or cooling. By liquefaction, the volume of LPG reduce to 1/250 of the gaseous phase, making it convent to store and handle. LPG has a simple composition, as it consists essentially of propane and butane which have carbon number of 3-4.

LPG is used in the spark ignition engines as a substitute for motor gasoline.

The fuel system of LPG engine is partly different from that of gasoline engine. It consists of a fuel cylinder, a solenoid valve a regulator (vaporizer), and carburetor. The solenoid valve opens only when the engine ignition switch is turned on to allow LPG to be supplied from the cylinder to the regulator, wherein it is heated by air or hot water and vaporize. Completely vaporized LPG is then mixed uniformly with air in the carburetor before the mixture is induced to the combustion chamber. Thus, LPG combustion implementation occurs with a nearly uniform fuel-air mixture that reduces deposit, such as soot, on the combustion chamber walls. Further, LPG does not cause fuel dilution of engine oil.

The fuel consumption of LPG is found to be 10% less than that of gasoline. The reason for this is that LPG generates the maximum engine torque at a higher air-fuel ratio, a leaner mixture condition which is a result of LPG air-fuel mixture being more uniformly distributed in the combustion chamber.

The LPG fuel has a comparative disadvantage relative to gasoline, the power output is less. In case of gasoline engine the evaporation of the fuel caused the fuel-air mixture to cool and increase its density, while in LPG engines the fuel is preheated and vaporized in a heat exchange-pressure regulator before it mixed with air in the carburetor, resulting in a relatively high mixture temperature and a low mixture density. Consequently for LPG the weight of fuel supplied to the engine is less than gasoline, further, its calorific value (885 $kcal/m^3$) is less than gasoline (928 $kcal/m^3$). Low power output is the result.

The calorific value by weight for LPG is 10 750-11080 kcal/kg, while for gasoline is 10500kcal/kg.

6. Alternative fuels

The importance of reduce pollution, scarcity of existence of petroleum in some countries, fears of fuel shortage, energy crises, and cost increase of the petroleum fuels have generated intense interest in alternative fuels, especially non-petroleum fuels, for engines.

Alcohols are one of these alternative fuels. They have been used as a fuels for internal combustion engines since their invention. Alcohols do seems to be among the most promising alternative fuels to replace conventional fuels for automobiles.

*** Alcohols structure**

Alcohols are compound of the general formula ROH where R is any alkyl or substituted alkyl group. The group may e primary, secondary or tertiary, it may be open chain or cyclic: it may contain a double bond as show in the following examples:

CH_3CH_2OH	$H_2C=CH-CH_2OH$	$CH_2-CH-CH_2$ (each carbon bearing OH: OH OH OH)
ethyl-alcohol	allyl-alcohol	glycerol

*** Physical properties of ethyl alcohol (ethanol)**

Ethyl alcohol is the most common type of alcohols, this compound burns with non-luminous flame, without soot, and forms CO_2 & H_2O. pure ethanol is colorless liquid with an ethereal odor. Ethanol is not labeled poisonous whereas methanol is poisonous due its toxic oxidation products. Ethanol is an excellent solvent for many compounds like fates, oils, and faty acids.

* **Sources of alcohols**

Alcohols were first obtained from natural products which will be considered as organic compounds produced by living organisms, also alcohols can be produced from agriculture products and/or wastes. For industrial sources of alcohols there are two principle ways to get the simple alcohols by hydration of alkenes obtained from the cracking of petroleum and by fermentation of carbohydrates.

* *Approaches* of the practical utilization of alcohols is I.C.E. several factors must be taken into account before deciding the method by which the engine fueled with alcohol. Two of these factors are; the quality of alcohol; and the engine design. The following approaches can be used:

1. Alcohol fumigation
2. Dual injection
3. Spark ignition of alcohol.
4. Alcohol containing ignition improves
5. Alcohol petroleum fuel solution
6. Alcohol petroleum fuel emulsion

Combustion

Syllabus:-

- *Mixture.*
- *Combustion ………….. Introduction.*
- *Chemical equation of combustion.*
- *Stiochiometry.*
- *Combustion analysis.*
- *First low of thermodynamics applied to combustion processes.*
- *Internal energy and enthalpy of combustion.*
- *Enthalpy of formation.*
- *Calorific value of fuels.*
- *Efficiency of combustion systems.*
- *Dissociation.*
- *Equilibrium constant.*
- *Pollution.*

1- Mixture

***Introduction**: -* *Any homogeneous mixture of gases can be regarded as a single substance if the constituents do not react chemically with one another and are in fixed proportion by weight . the properties of such a mixture can be determined experimentally just or for a single substance , and they can be tabulated or related algebraically in the some way .*
Air is the common example of a mixture. It can be assumed invariable for most purposes and air is usually treated as a single substance. As air is such a common fluid, its properties have been determined by direct measurement.

The combustion of air which air tables are usually based is as follows:-

Components	Chem. symbol	Molecula.weight	Vol.analysis%	Grovimetric.analysis%
Oxygen	O_2	31.999	20.95	23.14
Nitrogen	N_2	78.013	78.09	75.53
Argon	Ar	39.984	0.93	1.28
Carbon dioxide	CO_2	44.01	0.03	0.05

Neglecting all other gases but oxygen and nitrogen, the combustion af air on which air tables are usually is:-

		Mol. weight %	Vol. analysis %	Grov. analysis %
Oxygen	O_2	32	21	73.3
Nitrogen	N_2	28	79	76.7
Nitrogen/oxygen		—	3.76/1	3.29/9

**** Dalton's law and the Gibbs-Dalton law.***

**** Dalton's law:-*** *"The pressure of a mixture of gases is equal to the sum of the partial pressures of the constituents when each exists alone at the volume and temperature of the mixture".*

i.e $$P = \sum p_i \quad \text{……………………. (1)}$$

Where pi is the partial pressure of a constituents i .

***Gibbs-Dalton law:-** "the internal energy, enthalpy, and entropy of gases mixture are respectively equal to the sum of the internal energies, enthalpies, and entropies of the constituents".*

$mu = \sum mui$ -----------------------(2)
$mh = \sum mhi$ ------------------------(3)
$ms = \sum msi$ --------------------- (4)

**** Amagat's law: -** "The volume of a mixture is equal to the sum of the volume of the individual constituents when each exist along at the pressure and temperature of the mixture "*

$V = \sum vi$ -------------------- (5)

**** Avogadro's law: -** " The number of moles of any gas is proportional to the volume of the gas at a given pressure and temperature ". Then*

$n = \sum ni$ -------------------- (6)

Where ni is the number of moles of a constituents i .

**** The gas constant (R) and specific heat (Cv,Cp) of a gaseous mixture** .*

It can be assumed that a mixture of perfect gases obeys all the perfect gas laws . to find the gas constant from the mixture in terms of the gas constant of the constituents we can use the equation of state (p v= mrt) both for the mixture and the for the constituents .

$Pv = mrt$ and $Piv = MiRit$ -------------------- (7)

$\sum piv = \sum mi\, Rit$ ------------------------ (8)

$V \sum pi = T \sum mi\, Ri$ --------------- (9) but $P= \sum pi$ (eq.9) there for

$Pv = T\sum mi\, Ri$ ---------------- (10) but $Pv = MRt$ (eq.7) then

$T \sum mi\, Ri = mRt$ ---------------- (11) re- arrange eq.11 gives :-

$R= \sum mi / m\ Ri$ ----------------- (12)

Where mi/m is the mass fraction of a constituents.
For a perfect gas $U = Cvt$ ---------------- (13)
Combine eq.(13) will eq.(2) get $Cv = \sum mi /m\ Cvi$ ---------------- (14)

Also for a perfect gas $h = Cpt$ ----------------- *(15)*
Combine eq.(15) with eq.(3) get

$Cp = \sum mi/m\ Cpi$ --------------------- *(16)*

From equ's (14 &16) we can obtain that

$Cp-Cv = R$ ------------------------ *(17)*

The specific heat (Cv & Cp) can be exported in terms of mole and the known as (molar heats) and denoted by :-

Cv & Cp where

$Cv = MCv$ & $Cp = MCp$ ------------------- *(18)*

$Cp - Cv = R_0$ --------------------- *(19)*

Also it can be proved that

$Cv = \sum ni/n\ Cvi$ & $Cp = \sum ni/n\ Cpi$ ------------------ *(20)*

**** Molecular weight of a mixture:-***

From equation (7) we can write that :-

$M = Pv/Rt$ & $mi = Piv/Rit$ ----------------*(21)*

By conservation of mass

$M = \sum mi$ --------------- *(22) and for a perfect gas we have*

$R = R_0/M$ --------------------- *(23) where* R_0 *is the universal gas constant and M is the molecular weight.*

Using equ's (21,22&23) it can be proved that for a mixture the molecular weight M is :-

$M = \sum Pi/p\ Mi$ --------------------- *(24)*

** Eq (7) can be written in term of moles then*

$Pv = nR_0T$ & $PiV = niR_0T$ --------------------- *(25)*

$PiV/Pv = niRoT/nRoT$ ---------------------*(26)*

$Pi/P = ni/n$ ----------------- *(27). It can be easily be improved that*

Pi/P = Vi/V , there for eq.(27) can be written as

$$P_i/P = n_i/n = V_i/V = Y_i$$

-------------- (28

Example-1-

A vessel of volume 0.4m^3 contains 0.45 kg of CO and 1kg of air at 15C. Calculate the partial pressure of each constituent, the total pressure in the vessel, the gas constant of the mixture and the volumetric analysis of the mixture?

Solution:-

*Mass of O_2 = 23.3 /100 *1 = 0.233 kg , M of O_2=32*

*Mass of N_2 = 76.7 /100 *1 = 0.767 kg , M of N_2 =28 , M of CO = 28*

**PiV= mRiT , Ri = Ro/Mi .: Pi = mRiT/V*

.: PO_2 = 43.59 kn/m^2

PN_2 = 164 kn/m^2

PCO = 96.2 kn/m^2

**P = ∑ pi = 303.8 kn/m^2*

**R = ∑ mi/m Ri --→ mO_2/m , mN_2/m , mCO/m m=mO_2 + mN_2 + mCO*

** ni = mi/Mi , n=∑ni ---→ Volumetric analysis --→ ni/n * 100 = result*

Example-2-

A mixture of 1 mole Co_2 and 3.5 mole of air are contained in a vessel at 1 bar and 15c. Calculate:

a) The mass of Co_2, O_2 and N_2 and the total mass.
b) The percentage carbon content by mass .
c) The apparent molecular weight and the gas constant for the mixture .
d)The specific volume of the mixture .

<u>Solution:-</u>

a- Volumetric analysis of air is 21% O_2 & 79%N_2

$nO_2 = 0.21 * 3.5 = 0.735$ mol O_2
$nN_2 = 0.79 * 3.5 = 2.765$ mol N_2
$mi=niMi$ --→

$mCO_2 = 1*44 = 44$ kg
$mO_2 = 0.735 * 32 = 23.55$ kg
$mN_2 = 2.765 * 28 = 77.5$ kg

$m = \sum mi = 145.05$ kg

b)
$\% C = 12/145.05 * 100 = 8.27 \%$

c)
$n = \sum ni = 4.5$

$M = \sum ni/n\ Mi = 32.2$

$R = Ro/M = 0.2581$ ks/kg k

d)
$Pv = RT$ ---→ $V= RT/P = 0.7435$ m3/kg

Example -3-

The gas in an engine cylinder has a volumetric analysis of 12% CO_2 , 11.5 % O_2 & 76.2% N_2 , the temperature at the beginning of expansion is 1000C and the gas mixture expands reversibly through a volume ratio of 7/1 according to allow PV1.25 =c . Calculate the work done, the heat flow per kg of gas and the gage of entropy per kg of mixture

Note: - Cp from table are

constituent	Cp (ks /kg k)
CO_2	1.235
O_2	1.088
N_2	1.172

Solution:-

For poly tropic process the work done (w) is

$W= R\,(T1-T2) / n-1$

For 100 mde of the mixture

$mCO_2 = 12 * 44 = 528$ kg $\quad mCO_2/m = 0.174$

$mO_2 = 11.5 * 32 = 368$ kg $\quad mO_2 /m = 0.121$

$mN_2 = 76.5 * 28 = 2140$ kg $\quad mN_2 / m = 0.705$

$m= \sum mi = 3036$ kg

$R = \sum mi/m\, Ri = 0.2739$ kj/kg k

$T_2/T_1 = (V_1/V_2)^{n-1}$

$\rightarrow T_2 / 1000 +273 = (1/7)^{1.25-1}$

$--\rightarrow T_2 = 783.2$ k

$.: W = 536.3$ kj/ kg

$Q = Du + W$ *where* $Du = Cv\,(T_2- T_1)$

$Cv = Cp – R$ *where* $Cp =\sum mi/m\, Cpi = 1.173$ kj/kg k

$.: Cv = 1.173 – 0.2739 = 0.899$ kj/kg k

$.: Q = - 440.3 + 536.3 = 96$ kj / kg *heat supplied .*

The change in entropy can be establish referring to the figure the change in entropy between 1 & A

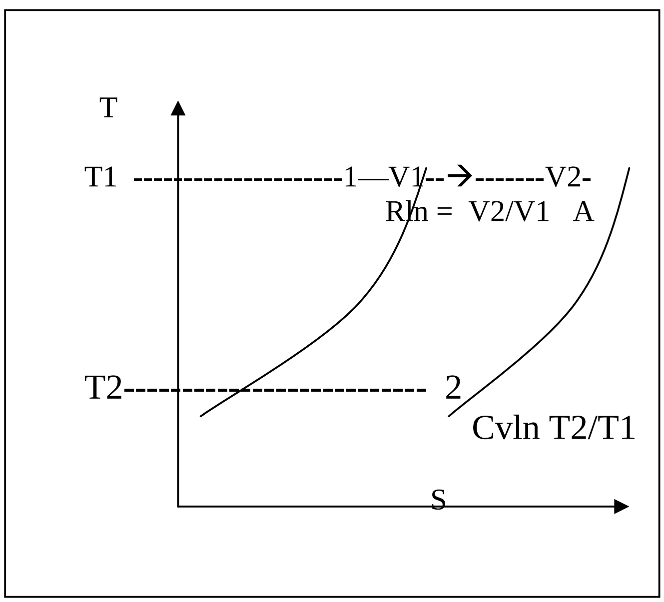
(Iso thermal process) is

$SA – S_1 = Rln\, V_2/V_1 =0 .533$ ks/kg k

The change in entropy between A & 2 is

$SA –S_2\, Cv\, ln\, T_2/T_1 = 0.436$ ks/kg k

$.: S_2 –S_1 = 0.097$ ks/kg k



Example-4-

A procedure gas has the following volumetric analysis 29% CO , 12% H_2 , 3% CH_4 , 4% CO_2 and 52% N_2 calculate the values of Cp , Cv, cp and cv for the mixture .

Note Cp : For the constituents are

Constituent	Cp (Ks/ kmol k)
CO	29.27
H_2	28.89
Ch_4	35.8
CO_2	37.22
N_2	29.14

$Cp = \sum ni/n\ Cpi = 29.676$ kj/k mol k

$Cp - Cv = Ro$ ------→ $Cv = Cp - Ro = 21.362$ ks/kmol k

$M = \sum ni/n\ Mi = 25.2$

The $cp = Cp/M = 1.178$ Ks/ kg k

$cv = Cv/M = 0.847$ Ks/ kg k

2- Combustion

Introduction: - *The term combustion refers to the fairly rapid reaction, usually accompanied by a flame, which accurse between a fuel and an oxygen carrier such as air. The molecules of fuel and air have a carbon amount of energy stored in the bonds between their constituent atoms. In the new molecules formed by a reaction , this (chemical) energy as at a lower level and the energy release can be transferred to the surrounding , in the form of heat . Combustion is there for said to be an (exothermic) reaction.*

**** Fuels: -*** *Most common fuels consist mainly of hydrogen and carbon whether the fuel is solid (e.g. coal), liquid (e.g. petroleum) or gaseous (e.g. natural gas). For solid and liquid fuels the analysis is usually quoted as a percentage by mass of each chemical element in the fuel. The analysis of a gaseous fuel is usually given in terms of the percentage by volume of each gas.*

3- Chemical Equations of Combustion

In any purely chemical reaction the pressure is simply based on the arrangement of atoms to form a new molecule, and the total number of atoms of each element is unchanged. A chemical equation expresses the principle of the conservation of mass in terms of the conservation of atoms.

** **Consider the reaction***

$C + O_2$ ---------→ CO_2
12kg C + 12 KgO_2 ---------→ 44 kg CO_2
1kmol C + 1 kmol O_2 -------→ 1 kmol CO_2
1 Vol C + 1 Vol O_2 --------→ 1 vol CO_2

$2H_2 + O_2$ ------→ 2h_2O
4kg H_2 + 32Kg O_2 -------→ 36 Kg H_2O
2 kmol H_2 + 1 kmol O_2 -------→ 2 Kmol H_2O
2 Vol H_2 + 1Vol O_2 ---------→ 2 Vol H_2O

If the gases are considered ideal, then according to Avogadro's hypothesis:"All gases contain the same number of molecules per unit volume at the same pressure and temperature". This implies that:
1 kmol of any gaseous sub stance occupies the same volume.
For example 44 kg of CO_2, 32 Kg of O_2, and 16kg of CH_4 will occupy a volume of 22.4 m_3 at NTP.
It should be clearly understood that in any reaction the mass is conserved but the number of moles or volume may or may not be conserved, for example

2CO + O_2 ---------→ 2CO_2
2Vol .+2Vol. -----------→ 2 Vol..
56kg + 32kg --------→ 88 kg

4- Combustion Stoichiometry:-

Stoichiometry means complete combustion
Of chemically correct mixture. The principle reaction of combustion for any fuel is

$C+O_2$ --→ CO_2 Called Stoichiometric equation of combustion
C+ 0.5 O_2 ------→ CO
CO + 0.5 O_2 -----→ CO_2
H2 + 0.5 O_2 -----→ H_2O
S + O_2 -----→ SO_4

$CH_4 + 2O_2$ ------→ $CO_2 + 2H_2O$
Since the most common oxidize is air which is a mixture of 21% O_2 & 79% N_2 (on volume or mole bases) i.e. 1 kmol of O_2 is accompanied by 79/21 = 3.76 kmol of N_2

.: the above equation become :-

$C+O_2 + 3.76\ N_2$ --------→ $CO_2 +3.76\ N_2$ ……….. And so other equation

The minimum amount of air required for complete combustion of a fuel is known as (theoretical air).
The fuel rich mixture, or mixture with less than Stoichiometry air give in complete combustion , that result m some quantity of undesirable carbon monoxide (CO) in the exhaust gases and also some loss of heat energy .

** Theoretical air required for complete combustion.*

If the fuel composition is known the requirement of O_2 or air can be calculated as follows:-

1- On mass bases.

12 kg of C require 32 kg of O_2 to form 44 kg of CO_2 or:

1kg C + 32/12 kg O_2 --------→ 44/12 kgCO_2 or

1kg C + 8/3 kg O_2 ---------→ 11/3 kg CO_2

4kg 2 H_2 + 32 KgO_2 ---------→ 36kg H_2O or

1kg H_2 + 8 Kg O_2 --------→ 9kg H2O

<u>In general</u>

1kg CmH_4 + [(m+n/u)22/12m+n] kgO_2 -----------→ 44m/12m+n kg CO_2 + 9n /12m+n kgH_2O

2- On mole bases:-

1kmol C+1kmol O_2 -------→ 1kmol CO_2

1Kmol H_2 + 0.5 Kmol O_2 --------→ 1kmol H_2O

<u>In general</u>

1 kmol CmHn + (m+n/4) kmol O_2 + 3.26 (m+n/4) kmol N_2 ------→ m kmol CO_2 + n/2 Kmol H_2O + 3.76 (m+n/4) kmol N_2 .

Note: - The theoretical amount of air required for complete combustion can be calculated using the following formula.

*(M $_{thea.}$)Air = 4.31 *32/ Mf (m+n/4) kg/kg of fuel*

Where mf is the molecular weight of fuel, m is the number of moles of carbon, and n is the number of mole of hydrogen.

Notes: - To find the Stoichiometric amount of air for complete combustion of a fuel:-

1- *If the analysis of a fuel is given by mass, then*

*a- Determine the **mass** of oxygen required for each constituent, from this; find the total mass of oxygen by adding all the separate masses required.*

*b- Subtract any oxygen which may be **(m)** the fuel since their does not have to be supplied.*

c- Stoichiometric mass of air = O_2 required / 0.233 kg

2- *If the analysis of a fuel is given by volume or mole, then*

*a- Determine the **volume** of oxygen required for each constituent, from this; find the total volume of oxygen by adding all the separate volumes required.*

b- Subtract any oxygen which may be(m) the fuel since their does not have to be supplied.

c- Stoichiometric volume of air = O_2 required / 0.21 mole or vol.

Non – Stoichiometric Mixture:-

The term weak and rich are used where, respectively, O_2 & fuel are available in excess of these Stoichiometric proportions. It is possible to have complete combustion to CO_2 & H_2O with a weak mixture the excess O_2 appearing in the products side of chemical equation , it is however , impossible to have complete combustion of a rich mixture .

An example of incomplete combustion is:

$$C_8H_{18} + a\,O_2 + 3.76\,a\,N_2 \text{ --------}\rightarrow b\,CO_2 + d\,CO + e\,H2O + f\,H_2 + 3.76\,a\,N_2$$

a) The percentage of excess air:

$$Px = \text{actual } A/F - \text{Stoichiometric } A/F \,/\, \text{Stoichiometric } A/F$$

b) Mixture strength (MS):

$$MS = A/F\ (\text{Stoichiometric}) / A/F\ (\text{actual})$$

***c) Equivalence ratio (Ø) :** is the ratio of the theoretical air –fuel ratio $(A/F)_{Theo}$ to the actual air-fuel ratio $(A/F)_{act}$*

$$Ø = (A/F)_{Theo} / (A/F)_{act}$$

***d) Relative air/fuel ratio (λ):** Opposite of equivalence ratio*

$$\lambda = \text{actual } A/F / \text{Stoichiometric } A/F \qquad \lambda = 1/Ø$$

A correlation between the equivalence ratio, relative air-fuel ratio, and mixture strength and percentage excess air can be expressed in the form.

$$Px = (\lambda-1) * 100\% = 1-Ø/\,Ø * 100\% \qquad or$$

$$Px = 1-Ms/Ms * 100\%$$

5- Combustion Analysis:-

One of the primary objects in combustion analysis is the determination of the amount of air required to burn a fuel and to determine the amount of the products of combustion which will have been formed. Some analysis made by mass, some made by volume, which others of analysis both by mass and by volume. An analysis which includes the steam in the exhaust is called a wet analysis and that without steam is called dry analysis. The following examples will give an indication of the above cases.

Example(1) *:- A fuel consists of 72% carbon , 20% hydrogen and 8% oxygen by mass , determine the stoichiometric mass of air required to completely burn 1kg of the fuel*

Solution:-

$C + O_2$ ----------→ CO_2

12Kg + 32Kg ----------→ 44Kg

1Kg + 32/12 Kg --------→ 44/12 Kg

1kg C required 8/3 O_2 ----------→ .: *0.72 Kgc required*

*0.72 *8/3 = 1.92 kg*

$H2 + 0.5\ O_2$ ---------→ H_2O *or* $2H_2 + O_2$ -----------→ $2H_2O$

2Kg + 16Kg -------→ 18kg

9kg + 8kg ---------→ 9kg --------→ .: 0.2kg H_2 *need*

*0.2 *8 =106 kg*

The total amount of O_2 *required to complete combustion of C & H is then 1.92 * 1.6 = 3.52 kg*
Of O_2 *but there is 0.08 kg of* O_2 *available in the fuel so that this amount of O2 must subtract from the total amount of air required. The amount of* O_2 *required becomes 3.52 – 0.08 = 3.44 kg* O_2.

The amount of air by mass associated with this amount of oxygen is = 14.8 kg/kg of fuel

** For the same example calculate A/F if the fuel contain only 0.80 carbon & 0.20 hydrogen*

Example (2):- *Determine the stoichiometric mass of air required to completely burn 1kg of heptane* (C_7H_{16})

Solution:-

The chemical equation is

$C_7H_{16} + 11O_2$ ---------→ $7CO_2 + 8H_2O$

$12*7+1*16 + 11*32$ ----------→ $7[12 + 16*2] + 8[2+16]$

$[100+352$ -----------→ $308 + 144] / 100$

$1 + 3.52$ ------------→ $3.08 + 1.44$

.: 1 kg of C_7H_{16} requires 3.52 kg of O_2 which is associated with the amount of air equal to 7.52/0.232 = 15.17 kg/kg fuel .

Example(3) :- *The analysis of a supply of coal gar is H2 49.4% , CO 18% , CH4 20% , C4H8 2% , O2 0.4 % ,N2 6.2% and CO2 4% , calculate the stoichiometric A/F ratio . Find also the wet and dry analysis of the products of combustion if the actual mixture is 20% weak .*

* بما انه لم يذكر شئ ، اذا تؤخذ النسب كنسب مولية .

Solution: - *The example can be solved by a tabular method, for CH4*

$CH_4 + 2O_2$ ----------→ $CO_2 + 2H_2O$

1mole CH_4 + 2mole O_2 --------→ 1mole CO_2 + 2mole H_2O

1mole of CH_4 require 2mole of O_2 for complete combustion
.: 0.2 mole of CH_4 require

0.2 * 2 = 0.4 mole of oxygen. The equation become →

$0.2\ CH_4 + (0.2*2)O2$ ----------→ $0.2\ CO_2 + (0.2*2)\ H_2O$

Combustion	*Percentage*	*Equation*	*O_2 moles/mole of fuel*	*CO_2*	*H_2O*
H_2	0.494	$2H_2+O_2 \rightarrow 2H_2O$	0.247	---	0.494
CO	0.18	$2CO + O_2 \rightarrow 2CO_2$	0.09	0.18	---
CH_4	0.2	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	0.4	0.2	0.4
C_4H_8	0.02	$C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$	0.12	0.08	0.08
O_2	0.004	----	-0.004	---	---
N_2	0.062	-----	---	---	---
CO_2	0.04	-----	---	0.04	---

Total 0.853 0.5 0.974

.: The amount of air required is 0.853/0.21 = 4.06 moles / mole of fuel

*For a mixture which is 20% weak the A/F is Actual A/F ratio = 4.06 + 20/100 * 4.06 = 4.872/1*

The amount of nitrogen associated with a mount of air is

*4.872 * 0.79 = 3.85 moles/ mole fuel*

*Excess oxygen = 4.872 * 0.21 – 0.853 = 0.171 moles / mole fuel*

The total N_2 in products is 3.85 + 0.062 = 3.912 moles / mole of fuel

.: The analysis by volume of the wet and dry products is

Products	*Moles/mole of fuel*	*% by vol . (dry)*	*% by vol.(wet)*
CO_2	0.5	10.9	9.0
H_2O	0.974	----	17.5
O_2	0.171	3.72	3.08

N_2	3.912	85.4	70.4
	Total wet 5.557 **- H2O 0.974** **Total dry 4.583**	100	100

** **The Orsat apparatus:-***
The orsat apparatus is a device commonly used in the laboratory to determine the volumetric composition of products of combustion. It consists essentially of three absorption vessels filled with different reagents. These are:-

***a-** Potassium hydroxide (KOH) for the absorption of carbon dioxide (CO_2).*

***b-** Pyrogallic acid in potassium hydroxide (or caustic so do) for the absorption of oxygen (O_2).*

***c-** Cuprous chloride solution for the absorption of carbon monoxide (CO).*

The gases must be absorbed in the above order, since the pyrogallic acid solution will absorb CO_2 as well as O_2. Also cuprous chloride will absorb CO_2. O_2 and CO.

The sample of exhaust gas is drawn into measuring burette by lowering the leveling bottle containing water. This known volume of sample at atmospheric temperature and pressure is forced in succession into of the reagent bottles which contain the absorbents.

The volume is measured after each absorption process by returning the sample to the burette and bringing it to atmospheric pressure with the aid of the leveling bottle.
The change in volume after a particular constituents has been absorbed is then the partial volume of that constituents in the original sample. The gas which remains is assumed to be nitrogen.

The apparatus gives an analysis of the dry products of combustion in order to ensure this, a V-tube containing calcium chloride or some other drying agent is sometimes fitted in the beginning of the sample intake tube.

Example (4):-

An orsat analysis of the dry exhaust from an internal combustion engine gane 12% CO_2, 2% CO, 4% CH_4, 1% H_2, 4.5 % O_2 and 76.5% N_2. Calculate the proportions by mass of carbon to hydrogen in the fuel.

Solution:-

*N_2 in dry exhaust gas = 0.765 * 28 = 21.42 kg/mole*

*O_2 associated with this amount of nitrogen is 0.233*21.42 / 0.767 = 6.5 kg/mole*

O_2 accounted for in the dry exhaust gas = 32 [0.32 + (0.02/2) + 0.045] = 5.6 kg / mole

.: O_2 burned to H2O = 6.5 – 5.6 = 0.9 kg/mole

$H_2 + 0.5O_2$ ------→ H_2O

[2Kg + 16Kg ---------→ 18Kg H_2O] / 2

1Kg + 8 ------→ 9Kg H_2O

.: H_2 burned to H_2O = 0.9/8 = 0.1125 Kg / mole

*H_2 accounted for in the dry exhaust gas = 1 [0.04*4) + (0.01 *2)] = 0.18 kg / mole*

.: H_2 in the fuel 0.18 + 0.1125 = 0.2925 kg / mole

Mass of carbon in the fuel = 12[0.12+0.02+0.04] = 2.16 kg / mole
.: Ratio of C to H_2 in the final = 2.16 / 0.292 = 7.38 /

6- Dissociation

Consider the reaction

$CO+1/2\ O_2$ ---------→ CO_2

When these reactions proceed in the direction indicated by the arrow it is accompanied by a release of energy and know as an exothermic reaction. The reaction can be preceding in the reverse direction it sufficient energy is supplied to molecules of CO_2. Actually in combustion products some CO_2 molecules to receive sufficient energy in collision for this to occur.

CO_2 ---→ $CO + 1/2\ O_2$

There fore the reaction equation can be written or

$CO + 1/2\ O_2$ ←----→ CO_2

The reversed reaction is accompanied by absorption of energy and it is termed as an endothermic reaction. it is found that at any particular temperature and pressure the proportions of CO_2 , CO & O_2 adjust themselves until the two reaction proceed at the same rate , i.e number of CO_2 molecules being formed is equal to the number of CO_2 molecules dissociating . Therefore a state of stable chemical equilibrium is existing.

It is only at high temperatures, above 1500 k, that a conceivable proportion of the CO_2 molecules must dissociate to provide an equilibrium mixture.

Similar case apply equally to H_2O molecules in combustion products

$H_2+1/1\ O_2$ ←--------→ H_2O

For any hydrocarbon fuel burning in air, the products contain an equilibrium mixture of CO_2, CO & O_2 and equilibrium mixture of H_2O, H_2 & O_2.

The pressure of CO & H_2 indicates that not all the chemical energy in the fuel is released.

7- Equilibrium Constant (Dissociation constant) K:-

The stoichiometric reaction of hydrocarbon fuel with air is given by:

$C_mH_n + A(O_2 + 3.76\,N_2) \longrightarrow mCO_2 + n/_2\,H_2O + A*3.76N_2$

When a dissociation of CO_2 and H_2O is occur then the above equation becomes:-

$C_mH_n + A(O_2 + 3.76\,N_2) \longrightarrow aCO_2 + b\,CO + d\,H_2O + e\,H_2 + f\,O_2 + A*3.76N_2$

In Chemical reaction the chemical equilibrium is reached when the rate of brake up of product molecules is equal to that of formation.

The determination of the proportions of the various substances at chemical equilibrium is based open a relationship of the partial pressures. In general, for the reaction:

$aA + bB \longleftrightarrow aC + d\,D$

There exists the relationship $\dfrac{P_c\,P_d}{P_A\,\,P_B} = K$

Where a.b.c & d are the respective of moles of the relationship a,b,c & d

Pi is the partial pressure of the substances A, B, C and D (in atmosphere unit).

And K: is the equilibrium constant which is a function of the temperature

Example (5):-

1- $CO + 1/2O_2 \longleftrightarrow CO_2$ $\quad K = \dfrac{Pco_2}{Pco\,PO_2}$ $atm^{-1/2}$

2- $2CO + O_2 \longleftrightarrow 2CO_2$ $\quad K = \dfrac{Pco_2}{Pco\,PO_2}$ $atm\text{-}1$

3- $CO_2 \longleftrightarrow CO + 1/2O_2$ $\quad K = \dfrac{PO_2\;Pco}{Pco_2}$ $atm^{-1/2}$

4- $H_2 + 1/2\,O_2 \longleftrightarrow H_2O$ $\quad K = \dfrac{PH_2O}{PH_2\,PO_2}$ $atm^{-1/2}$

5- $2H_2 + O_2 \longleftrightarrow 2H_2O$ $\quad K = \dfrac{PH_2O}{PH_2\,PO_2}$ $atm\text{-}1$

$H_2O \leftarrow\text{-----}\rightarrow 1/2H_2 + OH$ $K = \boxed{\dfrac{P_{H_2}\, P_{OH}}{P_{H_2O}}}$ $atm^{-1/2}$

In the combustion of hydrocarbon fuels both of the above reactions may occur simultaneously and another equilibrium constant can be define

$CO_2 + H_2 \leftrightarrow CO + H_2O$ $K = \boxed{\dfrac{P_{CO}\, P_{H_2O}}{P_{CO_2}\, P_{H_2}}}$

***Equilibrium Constant (Dissociation constant) K:**

The stoichiometric reaction of hydrocarbon fuel with air is given by:

$C_mH_n + A\,(O_2 + 3.76\,N_2) \text{--------}\rightarrow mCO_2 + n/_2\,H_2O + A*3.76N_2$

When a dissociation of CO_2 *and* H_2O *is occur then the above equation becomes:-*

$C_mH_n + A(O_2 + 3.76\,N_2) \text{------}\rightarrow aCO_2 + b\,CO + d\,H_2O + e\,H_2 + f\,O_2 + A*3.76N_2$

In Chemical reaction the chemical equilibrium is reached when the rate of brake up of product molecules is equal to that of formation. The condition of equilibrium during a reversible combustion process can be studied by mean of a device known as the ''vant hoff equilibrium box'' as shown in the fig below:

Consider the general reversible combustion process

α *moles A + b moles B* $\leftarrow\text{----}\rightarrow$ *c moles C + d moles D*

The work done during an isothermal expansion by a perfect gas between state 1 & 2 is given by:

$W = mRT \ln\ P_1/P_2 = nR_ot \ln P_1/P_2$ --------------(1)

Where n= the number of moles R_o *= universal gas constant*

For the system of "Vant hoff "the work input on A is

$W_A = a\, R_oT \ln P_1/P_A$ ---------- (2)

And the net work output of the systems is:

$W = W_A + W_B + W_C + W_D$ ---------------- (3)

$= R_o t\, [\, a\ln(P_1/P_A) + b\ln(P_1/P_B) + c\ln(P_C/P_1) + d\ln(P_D/P_1)\,]$ ------------- (4)

$= R_o t\, [\, \ln \qquad + \ln P_1{}^{a+b+c+d}\,]$ -----------------(5)

Suppose that in a second similar system in the same surroundings the pressure in the equilibrium box is P' then it will have a net work out put W' given by:

$W' = R_oT\, [\, \ln \qquad + \ln P'^{\,a+b+c+d}\,]$ ---------------(6)

Where $P' = P'_A + P'_B + P'_C + P'_D$ ---------------- (7)

Either W=W' or W≠W'. if W≠W' the system producing the lesser work can be reversed and the two systems can be coupled together . The combined system will then operate in a cycle and produce a net a mount of work while exchanging heat with a single reservoir of uniform temperature T. this contradicts the second law of "thermodynamics " and so W=W' and follow that

$$\frac{P_C\, P_D}{P_A\, P_B} = \frac{P_C\, P_D}{P_A\, P_B} = K \text{ ------------------(8)}$$

Example 1:-

The products from the combustion of stoichiometric mixture of CO and O_2 *are at pressure of 1 atm and certain temperature. The products analysis shows that 35 percent of each Kmol of* CO_2 *is dissociated. Determine the equilibrium constant for this temperature, and hence find the percentage dissociated when the products are the same temperature but compressed to atmosphere.*

Solution: - *The combustion equation for this reaction is:*

$CO + 1/2\, O_2$ ----------→ $a\, CO_2 + b\, CO + d\, O_2$

C balance $1 = a+b$ ---------- (1)

O_2 *balance* $1 + 1/2 * 2 = 2a + b + 2d$ ------------- (2)

It was given that 0.35 of each Kmol of CO_2 *is dissociated Pi i.e. CO in products is 0.35 = b Kmol , substitute in eq.1 becomes :*

$1 = a + 0.35$ ------→ $a = 1 - 0.35 = 0.65$ *Kmol*

Eq.2 becomes

$2 = 2*0.65 + 0.35 + 2d$

.: $d = 0.35 / 2 = 0.175$ *Kmol*

.: *The combustion equation for this reaction becomes :*

$CO + 1/2O_2$ --------→ $0.65\ CO_2 + 0.35\ CO + 0.175\ O_2$

The stoichiometric equation or equilibrium equation is

$CO + 1/2O_2$ ←-----→ CO_2

$K = P_{CO_2} / P_{CO} + P_{O_2}$, $P_i = n_i / n * P$, $n = 0{,}65 + 0{,}35 + 0.175 = 1.175$

.: $P_{CO_2} = 0.65 / 1.175 *1 = 0.552$ *atm*

.: $P_{CO} = 0.35 / 1.175 *1 = 0.298$ *atm*

.: $P_{O_2} = 0.175/1.175 *1 = 0.149$ *atm*

.: $K = 0.553 / 0.298 * (0.149)^{1/2} = 4.81$ atm^{-1}

At any pressure P the partial of any constituents Pi will be $P_i = (n_i/n)P$ *where n = total mole of products* $n = a+b+c+d$ *from equ.1* $a = 1-b$

From equ.1 &2 $d = b/2$ *substitute these for n*

.: $n = 1 + b/2$

.: $P_{CO_2} = 1-b *p / 1+b/2$ $P_{CO} = b / 1+b/2 *P$ $P_{O_2} = b/2 *p / 1 +b/2$

$$.: K = \frac{\frac{(1-b)}{(1+b/2)}}{(b/1+b/2) + (b/2 /1+b/2)^{1/2}} * \frac{P}{P * P^{1/2}}$$

Since the temperature is unchanged, K will still equal 4.81 atm^{-1} *substitute this in the above equation at P= 10 atm and solve it to get* $b = 0.185$ *Kmol CO*

.: $a = 1 - 0.185 = 0.815$ & $d = 0.185 /2 =$

Example (2):- *A combustible mixture of CO and Air which is 10% rich is compressed to pressure of 8.82 bar and a temp of 282 c . The mixture is ignited and combustion occurs adiabatically at constant volume. When the maximum temp is attained analysis shows 0.228 moles of CO present for each moles of CO supplied. Show that the maximum temp reached is 2677 C. if the pressure at this temperature is now doubled calculate the amount of CO percent .*

Solution: - *Actual A/F = stoichiometric A/F – 10/100 stoi A/f*

$$= 100/100 - 10/100 = 0.9$$

The stoi equ. Is $CO + 0.5O_2 \text{------}\rightarrow CO_2$

The combustion equation for the reaction is

$$CO + 0.9 * 0.5 (O_2 + 3.76 N_2) \text{------}\rightarrow a\ CO_2 + b\ CO + d\ O_2 + 1.71\ N_2$$

C balance $1= a+b$ --------- (1)

O_2 balance $1+ 0.91 * 0.5 *2 = 2a + b + 2\ d$ ------------ (2)

$b = 0.228$, from equ1 $a= 0.772$

From equ2 $C= 0.069$

.: The combustion equation become

$$CO + o.455\ O_2 + 1.71\ N_2 \text{--------}\rightarrow 0.772\ CO_2 + 0.228\ CO + 0.06\ O_2 + 1.71\ N_2$$

The stoichiometric equation is

$CO +0.5\ O_2 \leftarrow\text{--}\rightarrow CO_2$ and $K= Pco2 / Pco * Po2$

$Pi = ni* P / nt$

$ni = a+b+d = 0.772 + 0.228 + 0.069 + 1.71 = 2.779$ moles

At ignition $pi = 8.28 / 1.013 = 8.175$ atm

$T_1 = 282 + 273 = 555$ K

$P_1V = n1R_oT_1$, $P2V = n2R_oT_2$

$n_1 = 1+ 0.455 + 1.71 = 3.165$ moles

V= constant .: $P_2 = P_1\ n_2/n_1 * T_2 / T_1 \Rightarrow P_2 = 38.1$ atm

Assuming that $T_2 = 2677 + 273 = 2950$ K

.: $P_{CO_2} = 0.772 * 38.1 / 2.779 = 10.584$

$P_{CO} = 0.228 * 38.1 / 2.779 = 3.125$

, $P_{O_2} = 0.069 * 38.1 / 2.779 = 0.946$

Substitute these in K equ get K= 3.48 from tables it was found that for the reaction of $CO + 0.5\, O_2 \leftrightarrow CO_2$ K is equal to 3.5 at 2950 K so that the assumption of T2 2950 is true.

If the pressure is now doubled it because 76.2 atm

$P_i = n_i * P / n$ from equ1 $b = 1-a$

From equ 1&2 $C = 0.455 - 0.5\, a$

.: $n = n_2 = 3.165 - 0.5\, a$

.: $P_{CO_2} = a / 3.165 - o.5a$

$P_{CO} = 1-a / 3.165 - 0.5a \quad * 76.2$

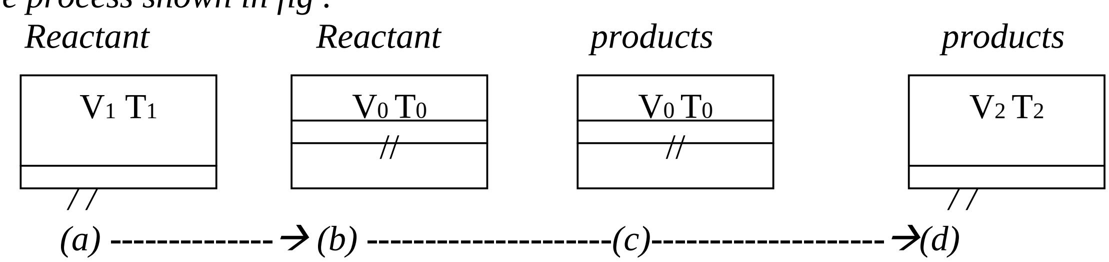
$P_{O_2} = 0.455 - 0.5a / 3.165 - 0.5a$

$$.: K = P_{CO_2} / P_{CO} * P_{O_2} = \frac{a/3.165-0.5A}{(1-a / 3.165-0.5a)\,(0.415 - 0.5a/3.165-0.5a)} \quad * P / P * P^{1/2}$$

K= 3.48 , P = 76.2 solve for this values get a>0.99 which indicate that the amount of CO at this condition is negligible .

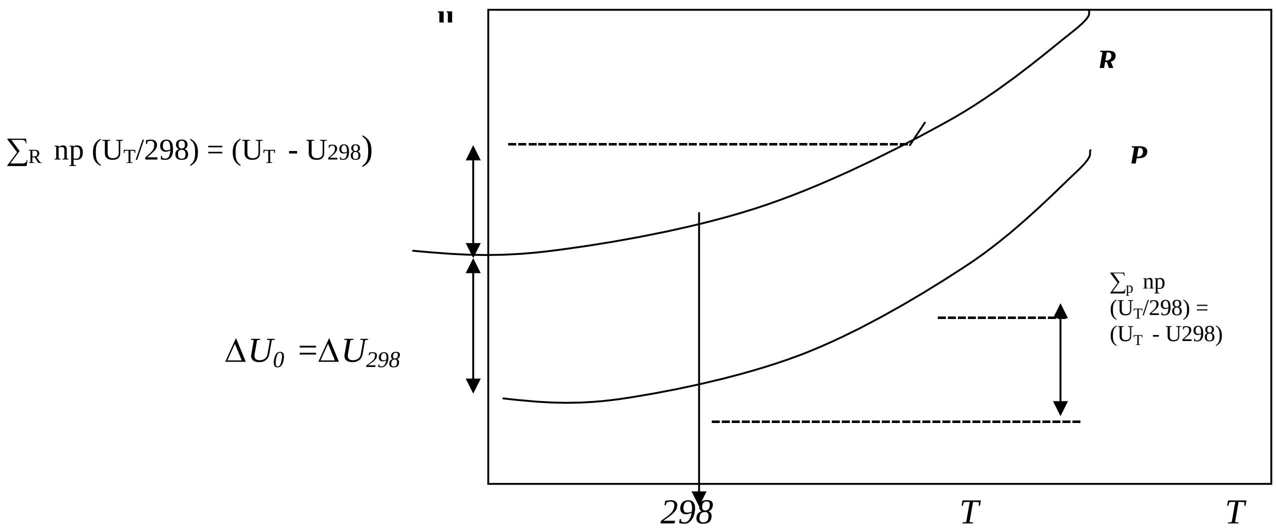
First law of thermodynamic applied to combustion processes.

The first law of thermodynamic applies to any system , and the non-flow and steady flow energy equations deduced from this law must be applicable to system undergoing combustion processes consider a non-flow combustion process , starting with a mixture of fuel and air at state (V_1 , T_1) and ending with products and state (V_2 , T_2) . it consist of three process shown in fig .



حيث تؤخذ المتفاعلات وتحول الى الحالة (T_0, V_0) بواسطة الاجزاء (a b) والذي لايتضمن تفاعلا كيمياويا كان ترفع درجة حرارتها ويقل حجمها عن طريق الانضغاط الناتج عن حركة المكبس الى اعلى وعندما تكون المتفاعلات في الحالة (V_0,T_0) يحصل التفاعل الكيميائي والذي يكون عادة تفاعل باعث للحرارة (exoth) ويحصل هذا التفاعل عند ثبوت الحجم ولذلك فلا مشغل ينجز في هذه الحالة . ان هذا التفاعل سوف يولد النواتج (products) والتي سوف تكون ايضا بالحالة (V_0,T_0) وذلك لان النظام يمر ضمن عملية انعكاسية ولذلك يمكن حساب الغير بالطاقة الداخلية($\Delta u0$) بين المتفاعلات والنواتج وذلك عن طريق قياس الحرارة المنتقلة .

ان عملية الاحتراق هي تفاعل كيميائي باعث للحرارة كما قلنا ولارجاع النظام الى نفس حالته لابد من طرح بعض الحرارة (Q) خارج النظام ولذلك سوف تكون قيمتها سالبة وسوف يكون هناك نقصان باطاقة الداخلية للنظام برغم كون المتفاعلات والنواتج كلاهما عند نفس الحالة من ناحية الحجم ودرجة الحرارة (V_0,T_0) . ان تفسير ذلك هو ان كل جزيئة تمتلك طاقة كامنة مخزونة في الاواصر بين الذرات المكونة لها وان هذه الطاقة والتي يمكن ان نسميها الطاقة الكيميائية هي اقل لجزيئات النواتج منها لجزيئات المتفاعلات . ولذلك فان في اجزاء ثبوت الحجم تحرر الطاقة الى الجو على شكل حرارة . وقد لوحظ من التجارب بان التغيير بالطاقة الداخلية هنا وعند الضغوط الاعتيادية يعتمد على درجة الحرارة (T_0) بشكل اساسي وليس على الحجم (V_0) .



For this process and from the fig. we can write:-

$(U_{p2} - U_{R1}) = (U_{p2} - U_{p0}) + (U_{p0} - U_{R0}) + (U_{R0} - U_{R1})$ ----------------(1)

Where the suffixes (P&R) refers to reactant & products

Suffixes (1, 2) refer to initial and final states. Because the process (bc) occurs at constant volume, no works is done and the non-flow energy equation can be written as below:-

$Q_{R0,p0} = (U_{p0} - U_{R0}) = \Delta U_0$ ----------------(2)

The term (U_{p0}-U_{R0}) is called internal of combustion at (T_0) and it is symbolized by (ΔU_0). Or it is called constant volume heat of combustion at (T_0) and it can be obtained measuring the heat transferred in a constant volume calorimetric process.

Equation (1) now can be written in the form:

$(U_{p2} - U_{R1}) = (U_{p2} - U_{p0}) + \Delta U_0 + (U_{R0} - U_{R1})$ --------------- (3)

- ملاحظة في عمليات الاحتراق يحتوي خليط المتفاعلات والنواتج اعتياديا على غازات وابخرة عند ضغوط منخفضة والتي يمكن اختراق سلوكها على ان سلوك الغازات التاحة المثالية (perfect gases)

Assuming no change of phase occurs during the process (db) (cd) , then the first term and third term of equation (3) can be calculated .

$(Up_2-Up_0) = \sum_p \; mi\ cvi\ (T_2-T_1) \sum_p \; mi\ cvi$ ------------------(4)

$(U_{R0}-U_{R1}) = \sum_R \; mi\ cvi\ (T_0-T_1) = (T_0-T_1) \sum_R mi\ cvi$ ---------------------(5)

Where mi is the mass of constitutes (i).

Cvi is the mean specific heat at constant volume of constitutes (i).

* ملاحظة في حالة مرور احد المكونات بتغير في الطور عند مدى درجات الحرارة من $T_0 \rightarrow T_1$ او $T_0 \rightarrow T_2$ فيجب في هذه الحالة ادخال الـ Ufg واحتسابها عند الجمع .

Similar consideration lead to the establishment of an equivalent equations for the change of enthalpy between reactant : at (T_1) and products at (T_2), then :-

$(Hp_2-H_{R1}) = (Hp_2-Hp_0) + (Hp_0-H_{R0}) +(H_{R0}- H_{R1})$ --------------(6)

$(Hp_2-H_{R1}) = (Hp_2-Hp_0) +\Delta U_0 + (H_{R0}- H_{R1})$ -----------------(7)

In the same way of determination of the first and third terms of equation (3) , the first and third terms of equation (7) can be calculated :-

$(Hp_2-Hp_0) = \sum_p \; mi\ cpi(T_2-T_0) = (T_2-T_0) \sum_p \; mi\ cpi$ --------------(8)

$(U_{R0}-U_{R1}) = \sum_R \; mi\ cpi\ (T_0-T_1) = (T_0-T_1) \sum_R mi\ cpi$ ---------------------(9)

Where mi is the mass of constitutes (i).

Cpi is the mean specific heat at constant pressure of a constitutes (i).

ملاحظة في حالة مرور احد المكونات بتغير في الطور عند مديات ودرجات الحرارة اعلاه فيجب ادخال الـhfg ضمن الحسابات .

The term ΔU_0 is called the enthalpy of combustion at (T_0) or the constant pressure heat of combustion at (T_0) , and it can be obtained by measuring the heat rejected during a steady *flow combustion process carried out at temperature (T_0) for both reactants & products then :*

$Q_{R1,P0} = (H_{p0}-H_{R0}) = \Delta H_0$ ------------------------(10)

Where W=0 & the kinetic energy is negligible. Or it can be calculated as follows:-

$\Delta H_0 = (H_{p0}-H_{R0}) =(U_{p0}+PV_{po}) - (U_{R0}+PV_{p0})$ -----------------(11)

$\Delta H_0 =\Delta U_0 + (PV_{p0} - PV_{R0})$ -------------------(12)

Bat for gaseous reactants products we can write

$PV = nR0T$ --------------- (13) then

$\Delta H_0 = \Delta U_0 + R_0T_0 (np - n_R)$ -------------------- (14)

Where (np&n_R) are the number of moles of reactants & products gaseous respectively.

For Solid and liquid constituents the N terms are negligible compared with the internal energy term. Then

$\Delta H_0= \Delta U_0$ ----------------- (15)

- ملاحظة : يلاحظ من المعادلة (14) بانه اذا كانت عدد مولات المتفاعلات والنواتج متساويا اي $np=nR$ فان ($\Delta H0=\Delta U_0$) .

ملاحظة ان قيم كل من (ΔH_0 ΔU_0) ترد عند درجة الحرارة (T_0) والتي تساوي (25درجة) وتكون لكل 1kgاو لكل 1Kmol من الوقود وعند حساب(ΔH_0)(ΔU_0) مختبريا لايهم كم من المواد الموجودة ولم يدخل التفاعل مثل النتروجين او الاوكسجين الفائض وذلك لان التغير بالطاقة الداخلية او التغير في الانثالبي سوف يكون مساويا الى الصفر نظرا لاعادة النواتج الى درجة حرارتها الابتدائية .
وعند ورود كل (ΔH_0)(ΔU_0) يجب تحديد الطور لاي من مكونات المتفاعلات او النواتج لانه على سبيل المثال تكون (ΔH_0) لهيدروكاربون معين في الحالة االسائلة اقل منها له في الغازية بمقدار الطاقة الكامنة للتبخر عند درجة حرارة (T_0) .

Enthalpy of formation (ΔH_{f0}):- The enthalpy of formation is the increase in enthalpy when a compound is formed from its constituent's elements in their natural from and at standard conditions. For calculation purpose:-

$\Delta H_0 = \sum_p ni\, \Delta h_{foi} - \sum_R ni\, \Delta h_{foi}$

ملاحظة :- انثالبي التكوين : هي الزيادة في الانثالبي عندما يتكون المركب من عناصره المكونة له في حالتها الطبيعية وعندما تكون في الظروف القياسية فمثلا يكون الاوكسجين بحالته الطبيعية O_2والنتروجين N_2 والكاربون C اذ كان بصورة كرافيت فتكون انثالب التكوين لهم صفر ولكن اذا تحول الكاربون الى الطور الغازي فتكون هناك قيمة لانثالبي التكوين .

Example (2) :-

Calculate the enthalpy of condition at STD of enthalpy alcohol (C_2H_5OH) using the following data :-

$C_2H_5OH + 3O_2 \text{-----}\rightarrow 2CO_2 + 3H_2O$

$\Delta H_0 = \sum_p ni\ \Delta h_{foi}\ -\ \sum_R ni\ \Delta h_{foi}$

$\sum_p ni\ \Delta hfoi = 2(-393.443) + 3(-241.783)$

$= -1512235\ KJ$

$\sum_R ni\ \Delta h_{foi} = 1(-281,102)+3*0$

$= -281.102\ \ KJ$

$.\!:\ \ \Delta H_0 = -1512235 - (-281102) = -1231133\ \ KJ/Kmol$

Example: *- The enthalpy of combustion of ethane (C_2H_6) at 25c is -47590 KJ/Kg when all the products is gaseous phase find*

a) *The corresponding internal energy of combustion.*
b) *The enthalpy of combustion at 540c.*

Also calculate the heat transferred when 0.2 kg of ethane is burn at constant pressure in a cylinder containing 0.4Kg of dry air. The temperature of the reactants and products being 40c and 440c respectively.

The relevant mean specific heats at constant pressure for the range 25c to 540 c in KJ/Kg are C_2H_6 2.8 ; O_2 0.989 ; CO_2 1.049 ; H_2O (VOP) 1.987 ; $N_2$1.066 and for the range 25c to 40c in KJ/Kg K are C_2H_6 1.788 ; O_2 0.919 ; N_2 1.04

Solution:-

a- *The Stiochiometric equation is*

$C_2H_6 + 3.5\ O_2 + 3.5 * 3.76\ N_2 \text{------}\rightarrow 2CO_2 + 3H_2O + 13.16N_2$

$\Delta H_0 = \Delta U_0 + R_0T_0\ (np-n_R)$

$.\!:\ \ \Delta U_0 = \Delta H_0 - R_0T_0\ (np-n_R)$

$n_p = 2+3+13.16 = 18.16$ *Kmol*

$n_R = 1+3.5+13.16 = 17.66$ *Kmol*

$np - n_R = 0.5$ *Kmol*

$R_0 * T_0 * (np - n_R) = 8.314 * 298 * 0.5 = 1238.786$ *KJ*

Since ΔH_0 *is given in KJ/Kg in the value 1238.786 KJ must be divided by the molecular weight of ethane which is equal to 12*2+6 = 30 then*

$1238.786/30 = 41.292 KJ/Kg$

$.: \Delta U_0 = - 47590 – 41.292 = - 47631.292$ *KJ/Kg*

b) $\Delta H_{540} = Hp_{540} – H_{R25} = (Hp_{540} - Hp_{25}) + (\Delta H_{25}) + (H_{R25} - H_{R540})$

The combustion equation in terms of mass is:-

$30Kg\ C_2H_6 + 112Kg\ O_2 + 368.48N_2$ ------→ $88Kg\ CO_2 + 54Kg\ H_2O + 368.48\ Kg\ N_2$

On the basis of 1kg of C_2H_6 *the combustion equation become:-*

$1kg\ C_2H_6 + 3.733kg\ O_2 + 12.282kg\ N_2 = 2.933kgCO_2 + 1.8kg\ H_2O + 12.282Kg\ N_2$

$(H_{p540} – H_{p25}) = \sum_p mi\ cpi\ (540 – 25)$

$= [(2.933 * 1.049) + (1.8*1.987) + (12.282*1.066)] * 515$

$= 10169.153$ *KJ/Kg*

$(H_{R25} – H_{R540}) = \sum_R mi\ cpi\ (25- 540)$

$= [(1*2.8) + (3.733 * 0.989) + (12.282*1.066)] * -515$

$= - 10086.042$ *KJ/Kg*

$\Delta H_0 = - 47590$

$.: \Delta H_{540} = 10169.153 +(- 47590) + (-10086.042)$

$= -47506$ *KJ/Kg*

Another method to compute ΔH_{540}; from tables

$\Delta H_{540} = (H_{p540} - H_{p25}) + \Delta H_{25} + (H_{R25} - H_{R540})$

For products and from tables

H in KJ/Kg at 298 K are CO_2 913.8, H_2O (vop) 840.5; N_2 728.4

H in KJ/Kg at 813 k are CO_2 23750 ; H_2O 18830 ; N_2 15790

For reactants from tables h in KJ/Kg at 25 C

C_2H_6 1281; O_2 731.5

& at 540 C are C_2H_6 42710; O_2 16600

$H_{p540} - H_{p25} = 2(23750 - 913.8) + 3(18830 - 840.5) + 13.16\ (15790 - 728.4)$

$= 297841.55$ KJ / 30 = 9928.05 KJ/Kg of fuel

$H_{R25} - H_{R540} = 1(1281 - 42710) + 3.5(731.5 - 16600) + 13.16\ (15790 - 728.4)$

$= -\ 294521.4$ KJ/ 30 = -9817.38 KJ / Kg of fuel

.: $\Delta H_{540} = 9928.05 - 47590 - 9817.38$

$= -\ 47479.33$ KJ/Kg

$Q = (H_{p540} - H_{R40}) = (H_{p540} - H_{p25}) + \Delta H_{25} + (H_{R\,25} - H_{R40})$

The Stiochiometric equation for 0.2 kg of C_2H_6 is

0.2kg C_2H_6 + 0.747kg O_2 + 2.456 kg N_2 -----→ 0.587kg CO_2 + 0.36 kg H_2O + 2.456 kg N_2

But 4 kg of air is consist of

4*0.233 kg O_2 = 0.932kg O_2 &

4*0.767 = 3.068 kg N_2

.: *the actual equation of combustion of 0.2 kg of C_2H_6 with 4kg of air is*

0.2kg C_2H_6 + 0.932kg O_2 + 3.068kg N_2 --------→ 0.587 kg CO_2 + 0.36 kg H_2O + 0.185 kg O_2 + 3.068 kg N_2

.: $H_{p540} - H_{p25} = \sum_p m_i\, c_{pi}\ (540-25)$

$= [(0.587 * 1.049) + (0.36 * 1.987) + (0.185*0.989) + (3.068 * 1.066)] * 515 = 2464$ KJ

$H_{R25} - H_{R40} = \sum_R m_i \, c_{pi} \, (25-40)$

$= [(0.2 * 1.788) + (0.932 * 0.919) + (3.068 * 1.04)] * -15 = -66$ KJ

.: $Q = 2464 + (0.2 * - 47590) + (-66) = -7120$ KJ

- كطلوب اعادة الجزء الاخير عن طريق اخذ قيم H من الجداول .

8- Calorific value of fuels:-

Calorific values are defined in term of the number of heat units liberated when unit mass of fuel is burnt completely in a calorimeter under specified conditions. The calorific values and their relation to ΔU_0 are given below:-

1- Gross (higher) calorific value at constant value.
$Q_{gr,v}$ *(≈ - ΔU_{25} with H_2O in liquid phase) H.C.V.*

2- Net (lower) calorific value at constant volume.
$Q_{net,v}$ *(≈ - ΔU_{25} with H_2O in vapor phase) L.C.V.*

3- Gross (higher) calorific value at constant pressure.
$Q_{gr,p}$ *(≈ - ΔH_{25} with H_2O in liquid phase)*

4- Net (lower) calorific value at constant pressure.
$Q_{net,p}$ *(≈ - ΔH_{25} with H_2O in vapour phase)*

ملاحظة :- من المعتاد ان تكتب القيمة الحرارية ككمية موجبة حتى لو كانت الحرارة مفقودة حيث النظام .

**The difference between the higher & lower calorific values can be calculated as follows:-*

1- At constant volume $(Q_{gr,v} - Q_{net,v}) = m_w U_{fg}$ -------------(1)

2- At constant pressure $(Q_{gr,p} - Q_{net,p}) = m_w h_{fg}$ ----------------(2)

Where m_w = mass of water produced /kg of fuel burnt U_{fg} & h_{fg} is the internal energy & enthalpy of evaporation and it should be taken from tables at 25C.

Example-1-:- *The ultimate analysis of a fuel is 86% C & 14% H_2 and its calorific value ($Q_{gr,v}$) was found to be 46890 KJ/Kg . Calculate other three calorific values.*

Solution:-

*1kg of fuel produce 0.86*44/12 = 3.15 kg CO_2 & 0.14* 18/2 = 1.26 kg H_2O*

At 25C U_{fg} of water = 2304 KJ/Kg and

H_{fg} = 2442 KJ/Kg (from table)

$Q_{net,v} = Q_{gr,v} - m_w U_{fg}$

$= 46890 – 1.26 * 2304 = 43987$ KJ/Kg .

$\Delta H_0 = \Delta U_0 + pv = \Delta U_0 + nR_0T_0 = (np – n_R)(R_0T_0) \Rightarrow Q_{gr,p} = Q_{gr,v} – R_0T_0 (np-n_R)$

$N_p = nCO_2 = mCO_2/MCO_2 = 3.25/44$, $n_R = nO_2 = mO_2/MO_2$

$mO_2 = 0.86 * 8/3 + 0.14 * 8 = 3.41 \Rightarrow nO_2 = 3.41/32$

$Q_{gr,p} = 46890 – 8.314 * 298 (3.15/44 – 3.41/32) = 46977$ KJ/Kg

$Q_{net,p} = Q_{gr,p} – m_w h_{fg}$

$= 46977 – 1.26 * 2442$

$= 43900$ KJ/Kg

Example-2-:- *Determine the L.C.V of liquid Octane C_8H_{18}*

Solution:-

L.C.V = - ΔH_0

$C_8H_{18} + 12.5\ O_2 \dashrightarrow 8\ CO_2 + 9H_2O\ (_{vop})$

$\Delta H_{298} = m\Delta h298 = \sum_p m\ h_{fg} - \sum_R m\ h_{fg}$

$= [8(-393522 + 9(-241827)] – [1(-249952)+12.5(0)]$

$= -5074667$ KJ/Kmol

Hence L.C.V. = 5074667/114 = 44514.6 KJ/Kg

*Where 114 is the molecular weight of octane (12*8+1*18=114)*

***Combustion Efficiency: - The** combustion efficiency is defined as the ratio between the heat transfer and work out put & the energy of the fuel supplied which is equal to its lower calorific value .i.e.*

$$\eta_{co} = \text{heat transfer / fuel energy supplied} = q/L.C.V$$

$$\eta_{co} = \text{work output / fuel energy supplied} = W/L.C.V$$

***Example-1-:-** Liquid octane fuel and air are supplied to an industrial heater at a temperature of 300K. The burner operates at atmosphere pressure and excess air of 25% is used in order to ensure complete combustion. If the flue gas leave the heater at a temperature of 400K, estimate the heat transfer occurring in the heater (per unit mass of fuel) and hence determine the efficiency of combustion.*

Solution:-

The actual chemical equation is:-

$$C_8H_{18} + [12.5+(12.5*0.25)][O_2+3.76N_2] \text{-----}\rightarrow 8CO_2 + 9H_2O + 3.125O_2 + 58.75N_2$$

$$Q - W = \Delta H \quad (W \rightarrow 0)$$

$$Q = \Delta H$$

$$\Delta H = (Hp_{400} - Hp_{25}) + \Delta H_0 + (Hp_{25} - Hp_{300})$$

$$\Delta H = \sum_p mi\ h_{400/298} + \Delta H_0 + \sum_R mi\ h_{298/300}$$

$$\sum_p mi\ h_{400/298} = 8(4008) + 9(3452) + 3.125(3092) + 58.75(2971)$$

$$= 535141.87\ KJ$$

$$\Delta H_0 = \sum_p mi\ h_{f0} - \sum_R mi\ h_0$$

$$= [8(-393522) + 9(-241827)] - [1(-249952) - 12.5(0)]$$

$$= -5074667\ KJ$$

$$\sum_R mi\ h_{298/300}$$

1- For C_8H_{18} $h298_{/300} = nCP\ (298-300) = 1*195.1*2 = -390.2\ KJ$

2- For O_2 $h_{298/300}$ *= [12.5+(12.5*0.25)] (-54) = -843.75 KJ*

3- For N_2 $h_{298/300}$ *= [12.5+{12.5*0.25)] * 3.76 * (-54) = - 3172.5 KJ*

.: $\sum_R mi\ h_{298/300}$ *= -390.2 – 843.75 – 3172.5*

= - 4406.45 KJ

.: ΔH *= 535143.87 – 5074667 – 4406.45 = - 454392.5 KJ*

*q = Q/m = 4543929.5 / 1 * 114 = 39859.03 KJ/Kg of fuel*

L.C.V = ΔH_0 */ m = - 5074667 / 1*114 = 44514.622 KJ/Kg*

.: η_{co} *= 39859.03 / 44514.622 = 89.5%*