

COMBUSTION

Before attempting questions relating to the theory of the chief engineers syllabus it may be prudent for the student to revise the combustion theory associated with the Second engineer examination syllabus. The student should read the following and try the examples and then move to the chief engineer syllabus associated with the mol analysis of the combustion process.

CONTENTS:

- (a) Introductory notes
- (b) Atoms, elements and compounds
- (c) Atomic and molecular weights
- (d) Combustion equations including: the combustion of hydrogen, carbon and sulphur; stoichiometric air supply
- (e) The presence of oxygen in a fuel
- (f) The calorific value of a fuel
- (g) Higher and lower calorific values
- (h) Exhaust gas analysis
- (i) Conversion from volumetric to mass analysis and vice versa
- (j) Mol analysis of combustion processes

N.B.

Throughout the lesson various exercises donated by [Ex ...] have been arranged and should be completed by the student. These questions are only for guidance and do not require submission to the college.

(a) **INTRODUCTORY NOTES**

In the study of thermodynamics applied to heat engines it is realised that a heat engine requires two heat reservoirs for its successful operation. One is a high-temperature reservoir which transfers heat energy to the working fluid and the other is a low-temperature reservoir to which heat energy is rejected by the fluid.

In practice, the high-temperature heat transfer results from the combustion of a fuel which takes place in combustion chambers such as boiler furnaces and internal combustion engine cylinders.

Combustion is a chemical reaction which is accompanied by the release of energy. Such a reaction is termed an EXOTHERMIC reaction, whereas a chemical reaction which is accompanied by the absorption of energy is referred to as an ENDOTHERMIC reaction.

Fuels are substances containing mainly carbon and hydrogen, which on combining chemically with the oxygen in atmospheric air, will produce an exothermic reaction. The amount of energy released during the complete combustion of unit mass, or unit volume, of a fuel is termed its CALORIFIC VALUE. Fuels may also contain substances such as sulphur, nitrogen, oxygen and moisture, as well as some non-combustible matter which is usually classified as ash. The hydrogen in a fuel may be present in the uncombined or “free” form or in combination with part of the carbon in the fuel as “hydrocarbon”. Fuels may exist in solid, liquid or gaseous forms and we may state that, generally, solid fuels comprise coal, coke, wood and peat; liquid fuels comprise petroleum and shale oils and their distillates; and gaseous fuels comprise natural gas (mainly methane) coal gas, water gas and town gas.

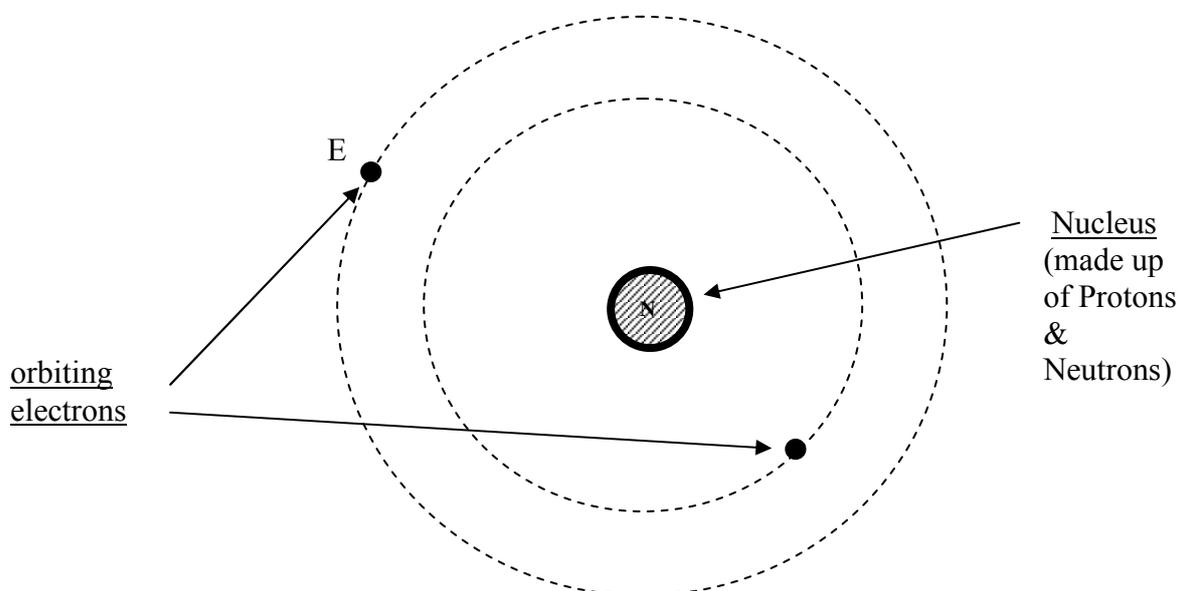
In this lesson, we shall confine our study to the combustion of solid and liquid fuels only.

(b) **ATOMS, ELEMENTS AND COMPOUNDS**

Before introducing the basic chemical equations used in a wide variety of combustion problems it is necessary that we know some simple chemistry related to combustion. The following notes should be of help and interest to the student.

Atoms may be considered to be made up of tiny particles called protons, neutrons and electrons. Protons are positively charged, electrons are negatively charged and neutrons carry no electrical charge at all. Fig 1 pictorially depicts the constitution of an atom

Fig. 1



It is seen that the centre of the atom (called the nucleus) has electrons orbiting around it, much like our own solar system where the planets are in orbit round the sun. The nucleus is composed of both protons and neutrons (except for the nucleus of the hydrogen atom which consists of just one proton) and hence the nucleus will have a positive charge.

Since each atom must be basically neutral in its charge, then the number of positively charged protons must be equal to the number of negatively charged electrons if the charge carried by a proton and an electron is the same.

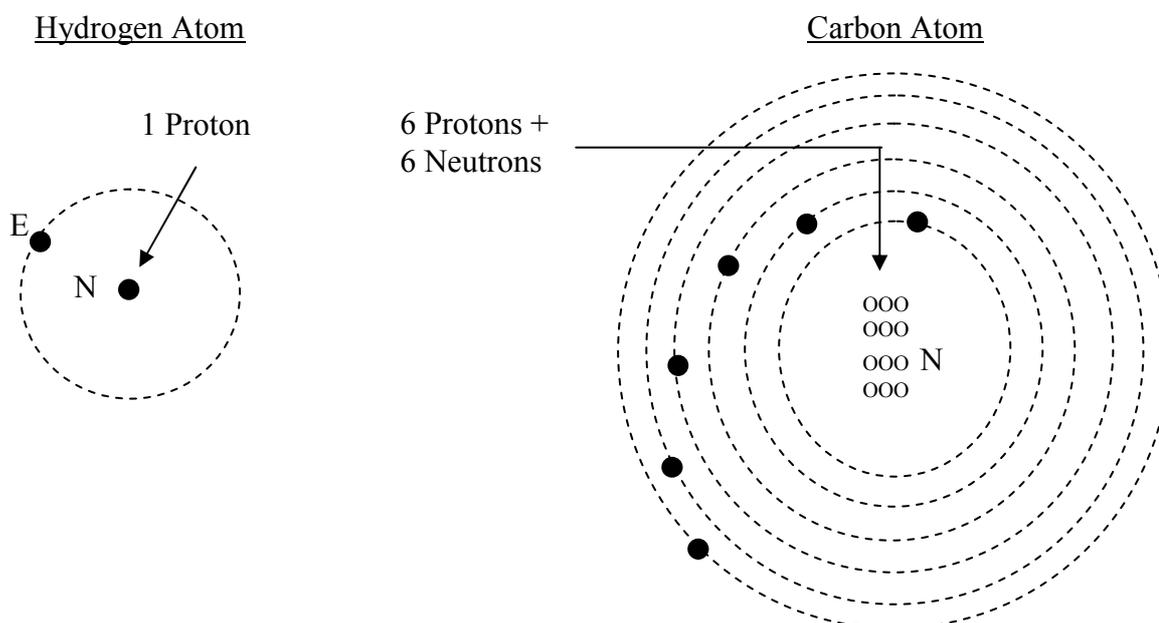
In most instances the number of neutrons is equal to the number of protons present in the nucleus, and the mass of a proton and neutron are approximately the same. By comparison, the mass of an electron is exceedingly small. Hence, it follows that the mass of an atom is related to the number of protons and neutrons present and this gives us a good measurement criteria for the so-called “atomic weight”.

i.e. the atomic mass may be expressed as:

$$= \text{number of protons} + \text{number of neutrons}$$

Fig. 2 illustrates the constitution of a hydrogen atom and a carbon atom.

Fig. 2



As can be seen from Fig. 2:

The HYDROGEN ATOM has only 1 proton, no neutrons with 1 orbiting electron whilst the CARBON ATOM has 6 protons, 6 neutrons and 6 orbiting electrons.

$$\begin{aligned} \text{Thus the atomic mass of hydrogen} &= 1 \\ \text{And the atomic mass of carbon} &= 6 + 6 = 12 \end{aligned}$$

Note that, in each case, the number of protons and electrons are balanced; hence the resulting charge of each atom is neutral.

Also note that the so-called “atomic mass” is a relative mass, not an absolute value.

ELEMENTS are substances which, so far, have not been resolved into other substance of simpler form. They are constituted only of themselves. There are some one hundred elements so far identified and each element is denoted by a symbol which is usually (but not always) the initial letter of the element. The symbol by itself indicates one atom of that element e.g. C → one atom of carbon; H → one atom of hydrogen; S → one atom of sulphur. However, in many elements, more particularly elementary gases, the atoms cannot exist singly but must be combined with at least

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one other atom to form a molecule of that element. All the elementary gases which are met with in combustion problems have two atoms per molecule and, to denote the number of atoms in the molecule, a small suffix number is added to the symbol. To denote the number of molecules, a large prefix number is used, so that:

$H_2 \rightarrow$ means 1 molecule of hydrogen comprising two atoms (here the prefix number 1 is omitted as in algebra)

$2O_2 \rightarrow$ means 2 molecules of oxygen, each molecule consisting of 2 atoms. Total number of atoms = $2 \times 2 = 4$

$3N_2 \rightarrow$ means 3 molecules of nitrogen consisting of 3×2 atoms.

It should be noted that most other elements such as carbon and sulphur (which exist as solids) and some elementary gases such as helium and neon are elements with molecules consisting of single atoms.

COMPOUNDS are chemical combinations of different elements. They are substances which can be resolved into simpler ones. Thus steam, water and ice are one and the same compound, each molecule of which consists of two atoms of hydrogen and one atom of oxygen. Its symbol, therefore, is H_2O and two molecules of water vapour would be written as $2H_2O$. Other compounds which are met with in combustion problems are:

Carbon dioxide	\rightarrow	CO_2	(1 atom of carbon with 2 atoms of oxygen)
Carbon monoxide	\rightarrow	CO	(1 atom of carbon with 1 atom of oxygen)
Sulphur dioxide	\rightarrow	SO_2	(1 atom of sulphur with 2 atoms of oxygen)

Also, a large group of fuels, called hydrocarbons, which have the general formula C_xH_y (x atoms of carbon with y atoms of hydrogen).

(c) ATOMIC AND MOLECULAR MASSES

An atom is a very tiny particle. A rough indication of the comparative size of an atom may be adjudged from the simile "As a cricket ball is to the earth, so is an atom to a cricket ball". Being so tiny, the actual or absolute mass of an atom of any element is extremely small and need not be considered here. As we have learned, the atomic "mass" which we use is a series of numbers indicating the sum of the number of protons and neutrons which constitutes the nucleus of the atom. They are really relative mass not absolute mass.

Hence, if we give hydrogen (the lightest element) the atomic mass value of 1, then we may give other elements atomic mass values which indicate how much "heavier" their atoms are than the atom of hydrogen.

e.g. oxygen has an atomic mass of 16. This means that the oxygen atom is 16 times heavier than the hydrogen atom.

Since molecules are made up of atoms, mass of a molecule of an element or a compound will be the sum of the atomic mass of its constituents. Thus, a molecule of

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the elementary gas hydrogen, which consists of two atoms (i.e. H_2) will have a molecular mass of $2 \times 1 = 2$. Similarly, a molecule of carbon dioxide (i.e. CO_2) will have a total mass of $(1 \times 12) + (2 \times 16) = 12 + 32 = 44$. This means, of course that 1 molecule of carbon dioxide is 44 times heavier than 1 atom of hydrogen, or 22 times heavier than 1 molecule of hydrogen.

The table below lists the atomic and molecular masses of some elements and compounds met with in combustion problems.

Substance		Symbol	Atomic Mass	Molecular Mass
Elements	Hydrogen	H_2	1	$2 \times 1 = 2$
	Carbon	C	12	$1 \times 12 = 12$
	Sulphur	S	32	$1 \times 32 = 32$
	Oxygen	O_2	16	$2 \times 16 = 32$
	Nitrogen	N_2	14	$2 \times 14 = 28$
Compounds	Water/Steam	H_2O	-	$(2 \times 1) + (1 \times 16) = 18$
	Carbon Dioxide	CO_2	-	$(1 \times 12) + (2 \times 16) = 44$
	Carbon Monoxide	CO	-	$(1 \times 12) + 1 \times 16 = 28$
	Sulphur Dioxide	SO_2	-	$(1 \times 32) + (2 \times 16) = 64$

Note that the symbol given to an element or compound is the symbol for the lowest form in which it can exist alone, e.g. hydrogen (like the other elementary gases oxygen and nitrogen) can only exist alone as a molecule, not as a single atom (hence " H_2 ") whereas carbon can exist alone as a single atom (hence "C").

(d) COMBUSTION EQUATIONS

When forming the following so-called combustion "equations", the following points should be remembered:

- (i) wherever the elementary gases appear on their own, we must credit them with 2 atoms/molecule i.e. they should always appear as O_2 , N_2 and H_2
- (ii) the number of atoms of each element must be the same on either side of the equation
- (iii) following directly from (ii) the total mass of the constituents on each side of the equation must be the same (... conservation of mass)

Keeping these points in mind we will now consider the combustion of the elements hydrogen, carbon and sulphur.

Combustion of Hydrogen

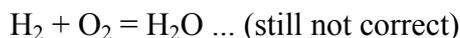
Consider hydrogen chemically reacting with oxygen to produce steam. This reaction is illustrated thus:

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Referring to item (i) above, this should be amended to:



Checking item (ii) above, in order to balance the number of oxygen atoms, there must be two molecules each of hydrogen and steam, such that:



(note that there are now four atoms of hydrogen and two atoms of oxygen on both sides of the equation).

If we now substitute the atomic mass of the elements in this equation we get:

$$2\text{H}_2 = 2 \times (2 \times 1) = 4$$

$$\text{O}_2 = 1 \times (2 \times 16) = 32$$

$$2\text{H}_2\text{O} = 2 \times \{(2 \times 1) + 16\} = 2 \times 18 = 36$$

i.e. $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ gives:

$$\begin{array}{rccccccc} \text{relative masses} & & 4 & + & 32 & = & 36 \dots \text{item (iii) verified} - \text{mass balance} \\ & & (\text{hydrogen}) & & (\text{oxygen}) & & (\text{steam}) \end{array}$$

$$\begin{array}{rccccccc} \text{dividing by 4} & & 1 & + & 8 & = & 9 \end{array}$$

this result may be interpreted thus:

for complete combustion, 1 kg of hydrogen requires 8 kg of oxygen to produce 9 kg of steam

or we can also express this combustion equation as follows:



ie

$$2 + \frac{1}{2} \times 32 (16) = 18$$

dividing by 2 we end up with the same result i.e.

$$1 + 8 = 9$$

thus for complete combustion, 1 kg of hydrogen requires 8 kg of oxygen to produce 9 kg of steam

Combustion of Carbon

Consider carbon chemically reacting with oxygen to produce carbon dioxide. The combustion equation gives:



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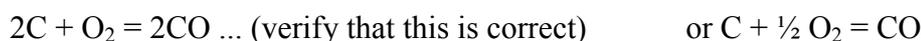
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relative masses $12 + 32 = 44$
or dividing by 12 $1 + 2\frac{2}{3} = 3\frac{2}{3}$

This result may be interpreted thus:

For complete combustion, 1 kg of carbon requires $2\frac{2}{3}$ kg of oxygen to produce $3\frac{2}{3}$ kg of carbon dioxide

If insufficient oxygen were supplied to the carbon, then some of the carbon may only burn to the lower oxide, namely carbon monoxide, and this reaction is stated thus:



relative weights $(2 \times 12) + 32 = 2 \times 28$
or $24 + 32 = 56$
and dividing by 24 $1 + 1\frac{1}{3} = 2\frac{1}{3}$

i.e. when carbon is burned to carbon monoxide, 1 kg of carbon requires $1\frac{1}{3}$ kg of oxygen to produce $2\frac{1}{3}$ kg of carbon monoxide

If carbon oxidises (or burns) to carbon monoxide then combustion is said to be incomplete. This should be readily appreciated since carbon monoxide is itself a combustible gas, as well as being highly toxic.

Let us, therefore, consider the combustion of carbon monoxide (CO) to carbon dioxide (CO₂).

The correct combustion equation for this reaction (which the student should verify for himself) is:



relative masses $(2 \times 28) + 32 = 2 \times 44$
or $56 + 32 = 88$
and dividing by 56 $1 + \frac{4}{7} = 1\frac{4}{7}$

i.e. 1 kg of carbon monoxide requires $\frac{4}{7}$ kg of oxygen to produce $1\frac{4}{7}$ kg of carbon dioxide

N.B. With reference to the above equations, dealing with the combustion of carbon, if we commence with 1 kg of C and burn it to CO we produce $2\frac{1}{3}$ kg of CO, using $1\frac{1}{3}$ of O₂.

To burn this $2\frac{1}{3}$ kg of CO to CO₂ we require a further

$$2\frac{1}{3} \times \frac{4}{7} = \frac{7}{3} \times \frac{4}{7} = 1\frac{1}{3} \text{ kg of } O_2$$

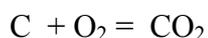
Thus, the total mass of O₂ required to burn 1 kg of CO₂

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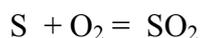
$$= 1\frac{1}{3} + 1\frac{1}{3} = 2\frac{2}{3} \text{ kg}$$

This, of course, is the same mass of O₂ as is required for the reaction:



Combustion of Sulphur

The normal oxidation of sulphur is illustrated thus:



$$\begin{array}{l} \text{relative weights} \quad 32 + 32 = 64 \\ \text{and dividing by } 32 \quad 1 + 1 = 2 \end{array}$$

i.e. 1 kg of sulphur requires 1 kg of oxygen to produce 2 kg of sulphur dioxide

Using the equations just derived, if we know the mass of the combustible elements in a fuel we should now be able to determine the amount of oxygen needed to completely burn unit mass of the fuel.

e.g. if a fuel consists of 85% carbon and 15% hydrogen, by mass, estimate the mass of oxygen and air required to completely burn 1 kg of the fuel.

Consider 1 kg of fuel

Mass of carbon present	= 0.85 kg
Mass of hydrogen present	= 0.15 kg
Mass of O ₂ required to burn 1 kg C (to CO ₂)	= 2 $\frac{2}{3}$ kg
Therefore “ “ “ 0.85 kg C (to CO ₂)	= 0.85 x 2 $\frac{2}{3}$ = 2.267 kg
“ “ “ 1 kg H ₂ (to H ₂ O)	= 8 kg
Therefore “ “ “ 0.15 kg H ₂ (to H ₂ O)	= 0.15 x 8 = 1.2 kg
Therefore mass of O ₂ required to completely burn 1 kg fuel	= 2.267 + 1.2
	= <u>3.467 kg</u> Ans

This is the mass of oxygen required. [17.03 kg]

In practice, however, we seldom supply pure oxygen. Instead we supply the abundant and cheaper air which contains the oxygen so necessary for combustion. It is usual to consider air as consisting of a mixture of oxygen and nitrogen in the following ratios:

By volume	:	21% O ₂ , 79% N ₂
By mass	:	23.3% O ₂ , 76.7% N ₂

Thus, for every 1 kg of air we supply, we are supplying only 0.233 kg of oxygen. Hence for every 1 kg of oxygen needed for combustion, we must supply $\frac{1}{0.233}$ kg of air.

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So, in the above example, if the mass of oxygen required is 3.467 kg, then the mass of air to be supplied will be $\frac{3.467}{0.233} = 14.8 \text{ kg}$

Points to be noted

1. The approximate gravimetric composition (i.e. composition by mass) of atmospheric air is more usually taken as 23% O₂ , 77% N₂. unless otherwise stated
2. For every 1 kg of air supplied although 0.23 kg is O₂ the much greater part, 0.77 kg, is N₂. Nitrogen is classed as an inert gas and so generally is assumed to take no part in the subsequent chemical reactions. Its presence dilutes the combustion products, limits the temperature obtained during combustion and makes it more difficult for the fuel and the oxygen to come into intimate contact.
3. When we refer to the “complete combustion” of a fuel we assume that:
 - (i) all the H₂ in the fuel burns to H₂O
 - (ii) all the C in the fuel burns to CO₂
 - (iii) all the S in the fuel burns to SO₂
4. The minimum amount of air which is supplied to produce the complete combustion of a fuel (as determined theoretically from the combustion equations), is known as the “Stoichiometric” air supply.

Thus, if more than the stoichiometric amount of air is supplied to a fuel, complete combustion will result but there will be excess oxygen present in the exhaust gases.

Conversely, if less than the stoichiometric requirement is supplied, then since there is insufficient oxygen present, incomplete combustion will result and some of the carbon in the fuel will only burn to carbon monoxide. Incomplete combustion, of course, will mean less energy released per unit mass of fuel burned. In practice, therefore, we should always ensure that a fuel is supplied with at least its stoichiometric amount of air. In fact depending upon the combustion equipment some degree of excess air is required

[Ex 1] Complete the following problem:

If the gravimetric analysis of a fuel gave 70% carbon, 25% hydrogen and 5% sulphur, calculate the stoichiometric mass of air required to burn 1 kg of the fuel. Assume the air consists of 23% O₂ by mass.

Consider 1 kg of fuel

Mass of carbon present	=
Mass of hydrogen present	=
Mass of sulphur present	=

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Mass of O ₂ required for the carbon	=	=
Mass of O ₂ required for the hydrogen	=	=
Mass of O ₂ required for the sulphur	= 0.05 x 1	= 0.05 kg
Therefore stoichiometric mass of O ₂ required	=	=
Therefore stoichiometric mass of air required	=	= kg Ans

(e) THE PRESENCE OF OXYGEN IN A FUEL

If oxygen is present in a solid or liquid fuel, it will probably be there in combination with some of the hydrogen or carbon, or both, or with some impurity in the fuel. To simplify calculations, it is generally assumed that all of the oxygen present is in combination with some of the hydrogen in the fuel in the form of water (H₂O). This means that some of the hydrogen in the fuel is rendered useless for combustion.

The hydrogen combustion equation earlier obtained, namely: $2\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}$, shows that the amount of hydrogen thus “fixed” is $\frac{1}{8}$ th of the mass of oxygen in the fuel. If this “fixed” amount of hydrogen is subtracted from the hydrogen in the fuel, the resulting amount is referred to as the “available” hydrogen and it is this reduced amount of hydrogen which is “available” for combustion.

$$\text{i.e. "available" hydrogen} = \text{hydrogen in fuel} - \text{"fixed" hydrogen} = \text{H}_2 - \frac{\text{O}_2}{8}$$

The presence of O₂ in the fuel not only affects the amount of air required but also affects the calorific value of the fuel. In both cases, a reduction occurs.

(f) THE CALORIFIC VALUE OF A FUEL

When a fuel burns in air, the combustible elements in the fuel (hydrogen, carbon and sulphur) chemically combine with oxygen in the air to produce chemical compounds (H₂O, CO₂ or CO and SO₂). In so doing exothermic reactions occur and the total amount of energy which is released when unit mass of the fuel is completely burned is called the “calorific value” of the fuel.

We can calculate the calorific value of a fuel provided we know the chemical composition of the fuel and the calorific values of the combustible elements.

e.g. It is known that when 1 kg of carbon burns to CO₂, the energy released during combustion is approximately 33.7 MJ. Also, when 1 kg of hydrogen burns to steam (H₂O) the amount of energy released is approximately 144 MJ: and when 1 kg of sulphur burns to SO₂, the release of energy is about 9.3 MJ. Accepting these values, if a fuel has a mass analysis of 75% carbon, 21% hydrogen and 4% oxygen, then its calorific value is able to be calculated in the following manner:

Considering 1 kg of fuel

Since O₂ is contained in fuel:

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$$\text{Available hydrogen} = \frac{0.21 - 0.04}{8} = 0.205 \text{ kg}$$

$$\begin{array}{l} \text{Therefore energy released by combustion of H}_2 = 0.205 \times 144 = 29.52 \text{ MJ} \\ \text{“ “ “ “ “ C} = 0.75 \times 33.7 = 25.28 \text{ MJ} \end{array}$$

$$\begin{array}{l} \text{Therefore calorific value of fuel} = 29.52 + 25.28 \\ = 54.8 \text{ MJ (per 1 kg fuel)} \end{array}$$

e.g. A fuel consists of 70% C, 20% H₂, 6% S and 4% O₂, by mass. Calculate its calorific value and the stoichiometric mass of air needed to burn 1 kg of the fuel. Take the c.v. of the elements as those given previously.

Consider 1 kg of fuel

$$\begin{aligned} \text{Available hydrogen} &= \frac{\text{H}_2 - \text{O}_2}{8} \\ &= \frac{0.2 - 0.04}{8} = 0.195 \text{ kg} \end{aligned}$$

$$\begin{array}{l} \text{Therefore energy released by combustion of H}_2 = 0.195 \times 144 = 28.08 \text{ MJ} \\ \text{“ “ “ “ “ C} = 0.7 \times 33.7 = 23.59 \text{ MJ} \\ \text{“ “ “ “ “ S} = 0.06 \times 9.3 = \underline{0.58 \text{ MJ}} \end{array}$$

$$\begin{array}{l} \text{Therefore total energy released} = \underline{52.25 \text{ MJ}} \\ \text{i.e. calorific value of fuel} = 52.25 \text{ MJ/kg} \quad \text{Ans} \end{array}$$

$$\begin{array}{l} \text{Mass of O}_2 \text{ required for the C} = 0.7 \times 2\frac{2}{3} = 1.867 \text{ kg} \\ \text{“ “ “ H}_2 = 0.2 \times 8 = 1.6 \text{ kg} \\ \text{“ “ “ S} = 0.06 \times 1 = \underline{0.06 \text{ kg}} \end{array}$$

$$\begin{array}{l} \text{Therefore total O}_2 \text{ required} = 3.527 \\ \text{But O}_2 \text{ present in the fuel} = \underline{0.04 \text{ kg}} \\ \text{Therefore stoichiometric O}_2 \text{ required from the atmospheric air} = \underline{3.487 \text{ kg}} \end{array}$$

this same figure for the O₂ required could have been obtained using “available” hydrogen, viz:

$$\begin{array}{l} \text{O}_2 \text{ for “available” hydrogen} = 0.195 \times 8 = 1.56 \text{ kg} \\ \text{And, as before:} \quad \text{O}_2 \text{ for the C} = 1.867 \text{ kg} \\ \quad \quad \quad \text{O}_2 \text{ for the S} = \underline{0.06 \text{ kg}} \\ \text{Therefore O}_2 \text{ from atmosphere} = \underline{3.487 \text{ kg}} \end{array}$$

Hence assuming air consists of 23% O₂ by means:

$$\text{Stoichiometric air required} = \frac{3.487}{0.23} = \underline{15.16 \text{ kg/kg fuel}} \quad \text{Ans}$$

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The student should note that since the cv of H₂ (namely 144 MJ/kg) is higher than any of the other combustible elements in a fuel, than a fuel which contains the greatest mass of H₂ will have the greatest cv. This is why, for example, the cv of a liquid fuel is greater than that of a solid fuel.

Note also that the use of empirical formulae may be used to determine both the calorific value of a fuel and the stoichiometric mass of air required, in a speedier manner than that illustrated in the previous example. If the student has understood the theory so far divulged, he should understand how the following formulae are derived.

Where C = mass of carbon present in 1 kg of fuel
H₂ = “ “ hydrogen “ “
S = “ “ sulphur “ “
O₂ = “ “ oxygen “ “

Therefore stoichiometric air = $\frac{100}{23} \left\{ 2\frac{2}{3} C + 8 \left(H_2 - \frac{O_2}{8} \right) + S \right\}$ kg/kg

and calorific value = $33.7 C + 144 \left(H_2 - \frac{O_2}{8} \right) + 9.3 S$ MJ/kg

the student should employ these formulae to verify the answers to the previous example

(g) HIGHER AND LOWER CALORIFIC VALUES
(often abbreviated as hcv and lcv)

We have seen that when a fuel is burned, H₂O is formed from the reaction between the oxygen and the hydrogen present. At room temperature this H₂O will exist as a liquid (water) even though when it was formed during the combustion process it existed as a superheated vapour (steam). Obviously, in cooling down to room temperature, the H₂O will release both sensible heat and latent heat as its temperature falls and as it changes its state from vapour to liquid. Hence, in order to extract the maximum amount of energy from a fuel, the combustion products must be permitted to cool down sufficiently so that water is formed.

In all the previous examples the value of 144 MJ/kg H₂ (i.e. the hcv of hydrogen) assumed this and consequently the calorific values of the fuels calculated were the maximum or gross values i.e. the hcv.

In practical cases, as in internal combustion engines and boiler plants, because of the relatively high temperatures of the exhaust gases, the H₂O present remains in the vapour phase until the gases are finally exhausted to atmosphere. Thus, the latent heat (or enthalpy of condensation) is unavailable and, as a result, the energy released by the fuel is correspondingly reduced to an amount referred to as the “lower calorific value” (lcv). The actual amount of unavailable energy varies with conditions

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(temperature and pressure) existing in the engine cylinder or boiler. The accepted allowance to be made for this unavailable energy is the enthalpy of evaporation (or latent heat) at a temperature of 25° C.

This is 2442 kJ or 2.442 MJ/kg of steam formed.

Since from every 1 kg of H₂ burned, 9 kg of H₂O (steam) are formed, then the calorific value of H₂ is reduced by:

$$9 \times 2.442 = 21.98 \text{ MJ}$$

$$\begin{aligned} \text{Therefore since the gross or hcv of H}_2 &= 144 \text{ MJ/kg} \\ \text{Then the net or lcv of H}_2 &= 144 - 21.98 \\ &= 122.02 \text{ say } 122 \text{ MJ/kg} \end{aligned}$$

e.g. using the values previously given, calculate the hcv and lcv of a fuel having a gravimetric analysis of 76% C and 14% H₂.

Per 1 kg fuel

$$\begin{aligned} \text{hcv} &= (0.76 \times 33.7) + (0.14 \times 144) \\ &= 25.54 + 20.16 \\ &= \underline{45.7 \text{ MJ/kg}} \quad \text{Ans} \end{aligned}$$

$$\begin{aligned} \text{lcv} &= (0.76 \times 33.7) + (0.14 \times 122) \\ &= 25.54 + 17.08 \\ &= \underline{42.62 \text{ MJ/kg}} \quad \text{Ans} \end{aligned} \quad [13.2\%]$$

$$\begin{aligned} \text{or lcv} &= (0.76 \times 33.7) + (0.14 \times 144) - (0.14 \times 9 \times 2.442) \\ &\quad \downarrow \qquad \qquad \qquad \downarrow \\ &\quad \text{hcv} \qquad \qquad \qquad \text{unavailable energy} \\ &= 45.7 - 3.08 \quad [33.54 \text{ MJ/kg}] \\ &= \underline{42.62 \text{ MJ/kg}} \quad (\text{as before}) \end{aligned}$$

Note that when solving problems in this lesson, where atomic and molecular mass and calorific values of elements and compounds have not been given in the question, they have been assumed. Likewise the composition of atmospheric air.

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[Ex 2] Complete the following problem:

The gravimetric analysis of a certain coal is 75% C, 6% H₂, 2.2% S, 3.2 % O₂ and the remainder is ash. For each kg of coal burned the amount of air actually supplied is 12 kg. Assuming that air consists of 23.3% O₂ by mass and taking the cv of the elements as given in the lesson notes, calculate:

- (i) the stoichiometric mass of air needed/kg coal
- (ii) the %age excess air supplied
- (iii) the hcv
- (iv) the lcv

Consider 1 kg coal

Mass of C	=	0.75 kg
Mass of H ₂	=	0.06 kg
Mass of O ₂	=	0.032 kg
Mass of S	=	<u>0.022 kg</u>
Σ	=	<u>0.864 kg</u>

Therefore by difference, mass of ash = 0.136 kg
Since O₂ is present in the fuel, then:

$$\begin{aligned} \text{“available” H}_2 &= \text{H}_2 - \frac{\text{O}_2}{8} = \\ &= \quad \quad \quad \text{kg} \end{aligned}$$

using the empirical formulae previously derived:

$$\text{mass of stoichiometric air} = \frac{100}{23.3} \left\{ 2\frac{2}{3} \text{C} + 8 \left(\text{H}_2 - \frac{\text{O}_2}{8} \right) + \text{S} \right\} \text{ kg}$$

=

=

$$= \dots\dots \text{kg/kg coal} \quad \text{Ans (i)}$$

$$\text{mass of air actually supplied} = 12 \text{ kg}$$

$$\text{therefore excess air supplied} = \quad \quad \quad =$$

$$\text{therefore \%age excess air supplied} =$$

$$= \dots\dots \text{Ans (ii)}$$

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$$\begin{aligned} \text{hcv} &= \{33.7 C + 144 (H_2 - \frac{O_2}{8}) + 9.3 S\} \text{ MJ/kg} \\ &= \\ &= \\ &= \dots\dots \text{ MJ/kg} \text{ Ans (iii)} \\ \text{and lcv} &= \\ &= \\ &= \dots\dots \text{ MJ/kg} \text{ Ans (iv)} \end{aligned}$$

Calorific values of solid and liquid fuels are determined experimentally by the use of a device known as a “Bomb Calorimeter”. Basically this consists of a strong, stainless steel vessel (the “bomb”) in which a measured fuel sample, held in a crucible, is burned completely in pure oxygen. Ignition is by means of an electrically heated wire. The energy which is released by the resulting exothermic reactions is calculated by measuring the temperature rise of the water which surrounds the bomb.

Since water surrounds the bomb, then it follows that the combustion products are finally cooled down such that the H₂O present will finally exist as liquid. This means, of course, that the calorific value so determined will be the hcv.

(h) **EXHAUST GAS ANALYSIS**

In practice, the efficiency of a continuous combustion process is ascertained by analysing the exhausting gases. In particular, the assessment of the CO₂ content of the gases provides a guide to the combustion performance. Exhaust or flue gas analysis is more particularly applicable to the combustion of fuel in a boiler since the air/fuel ratio is capable of wide control, which is not the case in internal combustion engines.

There are a number of methods which can be used to analyse the flue or exhaust gases, one of the most common being by chemical absorption, as used in the ORSAT apparatus. With this apparatus CO₂, CO and O₂ are extracted, in turn, from the gases, the reduction in volume of the exhaust gas as each constituent gas is absorbed is measured and represents the volume of the constituent gas which was present. This analysis is, of course, a volumetric analysis and the N₂ content is assumed by difference. Also, since any H₂O present in the exhaust gas would cool to the liquid state before reaching the apparatus, this analysis excludes the measurement of H₂O and is, consequently, referred to as a DRY GAS ANALYSIS.

A theoretical exhaust gas analysis may be obtained provided we know the gravimetric analysis of the fuel used and the mass of air supplied.

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e.g. If a certain fuel has a gravimetric analysis of 80% C, 12% H₂, 4% O₂, 3% S and the remainder incombustibles, and if 50% excess air is supplied, calculate per 1 kg of fuel burned, the mass of each constituent gas (including H₂O) present in the exhaust gases and resulting % mass analysis of the exhaust gases. Assume air contains 23% O₂ by mass.

Consider 1 kg fuel

First we must determine the stoichiometric mass of air required i.e. stoichiometric air needed = $\frac{100}{23} \left\{ \left(2\frac{2}{3} \times 0.8 \right) + 8 \left(0.12 - \frac{0.04}{8} \right) + 0.03 \right\}$

$$= \frac{100}{23} (2.133 + 0.92 + 0.03)$$

$$= \frac{100}{23} \times 3.083$$

$$= 13.4 \text{ kg/kg fuel}$$

Therefore excess air = $0.5 \times 13.4 = 6.7 \text{ kg/kg fuel}$

Therefore actual air supplied = $13.4 + 6.7 = \underline{20.1 \text{ kg/kg fuel}}$

Analysis of the exhaust gas

Since excess air has been supplied, then, as well as CO₂ (from C), H₂O (from H₂), SO₂ (from S) and N₂ (from air supplied) there will also be excess O₂.

$$\begin{aligned} \text{Mass of N}_2 \text{ present} &= 0.77 \times 20.1 \dots \text{ since } 77\% \text{ of air is N}_2 \\ &= \underline{15.48 \text{ kg}} \text{ (this is also the mass of N}_2 \text{ supplied)} \\ \text{Mass of O}_2 \text{ present} &= 23\% \text{ of excess air supplied} \\ &= 0.23 \times 6.7 = \underline{1.54 \text{ kg}} \\ \text{(or)} &= \text{mass of O}_2 \text{ supplied} - \text{mass of O}_2 \text{ used} \\ &= 0.23 \times 20.1 - 3.083 = 4.623 - 3.083 \\ &= 1.54 \text{ kg} \end{aligned}$$

since 1 kg of C requires 2 $\frac{2}{3}$ kg of O₂ to produce 3 $\frac{2}{3}$ kg of CO₂, then:

$$\begin{aligned} \text{mass of CO}_2 \text{ present} &= 3\frac{2}{3} \text{ C} = 3\frac{2}{3} \times 0.8 = \underline{2.93 \text{ kg}} \\ \text{(or)} &= \text{mass of C} + \text{mass of O}_2 \text{ for combustion of C} \\ &= 0.8 + 2.13 = 2.93 \text{ kg} \end{aligned}$$

since 1 kg of H₂ requires 8 kg of O₂ to produce 9 kg of H₂O, then:

$$\text{mass of H}_2\text{O present} = 9 \text{ H}_2 = 9 \times 0.12 = \underline{1.08 \text{ kg}}$$

(Note that with respect to the amount of H₂O formed, we must consider the total amount of H₂ present in the fuel, not just the “available” H₂, because it is of little

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consequence whether the O₂ for combustion comes from atmospheric air supply or from the fuel itself)

since 1 kg of S requires 1 kg of O₂ to produce 2 kg of SO₂, then:

$$\begin{aligned} \text{mass of SO}_2 \text{ present} &= 2S = 2 \times 0.03 = \underline{0.06 \text{ kg}} \\ \text{(or)} &= \text{mass of S} + \text{mass of O}_2 \text{ for combustion of S} \\ &= 0.03 + 0.03 = 0.06 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Therefore total mass of exhaust gases} &= 15.48 (\text{N}_2) + 1.54 (\text{O}_2) + 2.93 (\text{CO}_2,) \\ &\quad + 1.08 (\text{H}_2\text{O}) + 0.06 (\text{SO}_2) \\ &= \underline{21.09 \text{ kg}} \end{aligned}$$

from the principle of conservation of mass, this figure could be verified by the mass balance:

$$\begin{aligned} \text{mass of exhaust gases} &= \text{mass of air} + \text{mass of fuel} - \text{mass of incombustibles} \\ &= 20.1 + 1 - 0.01 \\ &= \underline{21.09 \text{ kg}} \text{ (this provides a useful check)} \end{aligned}$$

Percentage of masses of the constituent gases are therefore:

$$\text{CO}_2 = \frac{2.93}{21.09} \times 100 = 13.9\%$$

$$\text{H}_2\text{O} = \frac{1.08}{21.09} \times 100 = 5.1\%$$

$$\text{O}_2 = \frac{1.54}{21.09} \times 100 = 7.3\%$$

$$\text{SO}_2 = \frac{0.06}{21.09} \times 100 = 0.3\%$$

$$\begin{aligned} \text{N}_2 &= \frac{15.48}{21.09} \times 100 = 73.4\% \\ \Sigma &= \underline{100.0\%} \end{aligned}$$

N.B. The mass of any constituent gas formed in a combustion process must be equal to the sum of the mass of the element (from which the gas is formed) and the mass of the oxygen required to burn the element viz:

$$\begin{aligned} \text{Mass of carbon dioxide} &= \text{C} + 2\frac{2}{3} \text{C} &= 3\frac{2}{3} \text{C} \\ \text{Mass of steam} &= \text{H}_2 + 8 \text{H}_2 &= 9 \text{H}_2 \\ \text{Mass of sulphur dioxide} &= \text{S} + \text{S} &= 2 \text{S} \end{aligned}$$

Dry and wet gas analysis

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The exhaust gas analysis in the above example is a WET GAS analysis because it included the steam (H₂O) produced by the combustion of the H₂ in the fuel.

Practical gas analysers, such as the Orsat apparatus (mentioned earlier) do not indicate the presence of steam and so the analysis obtained is a DRY GAS analysis.

In the previous example the mass of wet gas formed per 1 kg of fuel burned was calculated as 21.09 kg, of which 1.08 kg was H₂O.

It follows, therefore, that the mass of dry gas was = 21.09 – 1.08
= 20.01 kg/kg of fuel

The percentage mass analysis of the dry gases may be found in a manner similar to that for the wet gases, and a tabulation is often preferred as follows:

Dry Gas	Mass (kg)	% Mass
CO ₂	2.93	$\frac{2.93}{20.01} = 14.6$
O ₂	1.54	$\frac{1.54}{20.01} = 7.7$
SO ₂	0.06	$\frac{0.06}{20.01} = 0.3$
N ₂	15.48	$\frac{15.48}{20.01} = 77.4$
$\Sigma = 20.01$		$\Sigma = 100.0$

Note that this analysis shows that the percentage of an individual dry product is greater than that of the same product shown in the wet gas analysis. The explanation, of course, is purely mathematical.

[Ex 3] Complete the following problem

A fuel consists of 70% C, 25% H₂ and 5% O₂ by mass.

If it is burned with 40% excess air supply, determine the percentage analysis of both the wet and dry exhaust gases. Assume air consists of 77% N₂ and 23% O₂ by mass.

Per 1 kg of fuel

$$\begin{aligned} \text{Stoichiometric mass of air required} &= \frac{100}{23} \left\{ 2\frac{2}{3} \text{C} + 8 \left(\text{H}_2 - \frac{\text{O}_2}{8} \right) \right\} \\ &= \\ &= \\ &= \dots \end{aligned}$$

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$$\begin{aligned} \text{mass of excess air} &= 0.4 x = \\ \text{of which } 0.77 x &= \dots \text{ kg is } N_2 \\ \text{mass of } CO_2 \text{ produced} &= 3\frac{2}{3} x C = 3\frac{2}{3} x = \dots \text{ kg} \\ \text{mass of } H_2O \text{ produced} &= 9 H_2 = 9 x = \dots \text{ kg} \\ \text{Therefore mass of wet exhaust} &= \text{excess } O_2 + N_2 + CO_2 + H_2O \\ \text{gases} &= \\ &= \dots \text{ kg} \end{aligned}$$

(CHECK: mass of air + mass of fuel = + =)

Wet gas analysis

$$\begin{aligned} \text{Total mass of wet gas} &= \text{ kg} \\ \text{Mass of } CO_2 &= \text{ kg} & \text{Therefore \% } CO_2 \text{ present} &= \dots = \dots \\ \text{Mass of } O_2 &= \text{ kg} & \text{Therefore \% } O_2 \text{ present} &= \dots = \dots \\ \text{Mass of } N_2 &= \text{ kg} & \text{Therefore \% } N_2 \text{ present} &= \dots = \dots \\ \text{Mass of } H_2O &= \text{ kg} & \text{Therefore \% } H_2O \text{ present} &= \dots = \dots \\ & & & \Sigma = \underline{100.0} \end{aligned}$$

Dry gas analysis

$$\begin{aligned} \text{Total mass of dry gas} &= - = \dots \text{ kg} \\ \text{Therefore \% of } CO_2 \text{ present} &= \dots = \dots \\ \text{Therefore \% of } O_2 \text{ present} &= \dots = \dots \\ \text{Therefore \% of } N_2 \text{ present} &= \dots = \dots \\ & \Sigma = \underline{100.0} \end{aligned}$$

(i) CONVERSION FROM VOLUMETRIC TO MASS ANALYSIS

Practical measurement of the dry exhaust gases usually yields a VOLUMETRIC analysis. It is sometimes desirable, however, to have a mass or gravimetric analysis and this may be achieved by conversion of the volumetric analysis in the manner shown below:

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e.g. Readings from an Orsat apparatus showed a boiler's dry flue gas to have the following volumetric analysis: 9% CO₂, 5% O₂, 4% CO and the remainder, assumed to be N₂, 82%.

Estimate the mass analysis of the dry flue gas.

N.B. The student may wonder how it is possible to have any CO existing in the presence of O₂. In theory it would appear unlikely, even impossible, but in practice this may occur. The reason is likely to be due to practical factors like faulty atomisation, perhaps a dirty or choked sprayer, or incorrect oil fuel temperature and/or pressure. So, remember, the presence of CO in an exhaust gas does not necessarily mean an insufficient air supply (i.e. a supply of air below the stoichiometric).

"Equal volumes of all gases, if at the same temperature and pressure, contain the same number of molecules". This is Avagadro's hypothesis which is now accepted as a law.

It follows from this law that since the molecular mass (M) of different gases vary, then the mass per unit volume (i.e. density) of any gas will depend upon its molecular mass.]

i.e. density \propto M , but density = $\frac{\text{mass}}{\text{volume}}$]

Therefore $\frac{\text{mass}}{\text{volume}} \propto M$

or $\frac{\text{relative mass}}{\text{relative volume}} = M$

hence, from this relationship we may write:

relative mass = relative volume x M

and relative volume = $\frac{\text{relative mass}}{M}$

Thus to convert a relative volume (or volume ratio) to a relative mass (or mass ratio) we simply MULTIPLY the relative volume of the gas concerned by its molecular mass (M). Returning to the solution of the example, a tabulation is preferred, via:

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Dry Gas	Relative Volume	M	Relative Mass	% Mass
CO ₂	9	44	9 x 44 = 396	$\frac{39600}{2964} = 13.4$
CO	4	28	4 x 28 = 112	$\frac{11200}{2964} = 3.8$
O ₂	5	32	5 x 32 = 160	$\frac{16000}{2964} = 5.4$
N ₂	82	28	82 x 28 = 2296	$\frac{229600}{2964} = 77.4$
$\Sigma = 100$			$\Sigma = 2964$	$\Sigma = 100.0$

- N.B. (i) The % volumes of the constituent gases may be used as their volume ratios or relative volumes.
- (ii) The conversion from a mass to a volumetric analysis is achieved by DIVIDING the relative mass of the gas concerned by its molecular mass (M).
- e.g. If a mass analysis of a dry flue gas gave 15% CO₂, 4% O₂ and 1% SO₂, remainder N₂, estimate the volumetric analysis.

Dry Gas	Relative Mass	M	Relative Volume	% Volume
CO ₂	18	44	$\frac{18}{44} = 0.409$	$\frac{40.9}{3.3} = 12.4$
CO	4	32	$\frac{4}{32} = 0.125$	$\frac{12.5}{3.3} = 3.8$
O ₂	1	64	$\frac{1}{64} = 0.016$	$\frac{116}{3.3} = 0.5$
N ₂	77	28	$\frac{77}{28} = 2.75$	$\frac{275}{3.3} = 83.3$
$\Sigma = 100$			$\Sigma = 100$	$\Sigma = 100$

[Ex 4] Complete the following problem

The gravimetric analysis of a fuel gave 82% C, 11% H₂, 5% O₂ and the remainder ash. For every kg of fuel burned 15 kg of air were supplied.

- Estimate:
- (i) % excess air supplied
 - (ii) mass and volumetric analyses of the wet exhaust gases
 - (iii) hcv of the fuel

(j)

Chief Engineer Syllabus

The combustion theory associated with chief engineer examinations often involves an analysis based on molar volumes when defining molar volumes it may also be prudent to define the Universal Gas Constant R_0

THE UNIVERSAL GAS CONSTANT (R_0)

$$pV = mRT \text{ for } m \text{ kg of gas } \dots$$

Or $pV = RT$ for one kg of gas(1)

Where R is constant for a particular gas -- different gases have differing numerical values of "R".

The Molar Volume

A quantity of gas where mass is equal to its molecular mass in kilograms is referred to as the "kilogram mole" or the kilo mol or simply the mole.

- e.g. 1mole of O_2 has a mass of 32 kg
- 1mole of H_2 has a mass of 2 kg
- 1mole of N_2 has a mass of 28 kg
- 1mole of CO_2 has a mass of 44 kg

hence if the volume of 1 mole of gas is given by V_0 , then we can rewrite equation (1) as

$$pV_0 = MRT \dots \dots \dots (2)$$

where M is the molecular mass and V_0 is the molar volume.

Avagadro's Law states that at the same temperature and pressure, equal volumes of all gases contain the same number of molecules.

It follows then that the volume of one mole of all gases (V_0) is the same at the same temperature and pressure.

From equation (2) $\frac{pV_0}{T} = MR$

And since p, V_0 , and T are constant for each gas then the product MR must also be a constant.

This constant is referred to as the universal gas constant and is denoted by " R_0 "

$$\underline{R_0 = MR}$$

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From (2) we can write :-

$$PV_o = R_o T \dots \text{for one kilogram mole of gas}$$

For n moles of gas we have,

$$PV_o n = nR_o T \quad \text{but } V_o n = V$$

Therefore

$$\underline{PV = nR_o T} \rightarrow$$

Experiment shows that an average value of the molar volume V_o of any gas is about 22.4136 m^3 at standard temperature and pressure (1.01325 bar, 0°C .)

Therefore from $PV_o = R_o T$

$$\text{Then} \quad \frac{1.01325 \times 10^5 \times 22.4136}{273 \times 10^3} =$$

$$= \underline{8.3143 \text{ kJ/kgmolK}}$$

Summary

$$PV = mRT$$

$$PV = nR_o T$$

from

$$R = R_o/M$$

hence

$$\mathbf{n = \text{no of kgmols} = m/M}$$

Note also..... Molar Heat capacities

$$K_p = M.C_p \quad \text{units kJ/kmol K}$$

$$K_v = M.C_v$$

Since $C_p - C_v = R$ then $MC_p - MC_v = MR$

Hence $K_p - K_v = R_o$

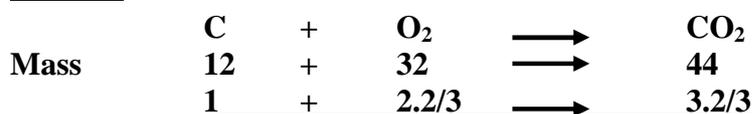
Also $K_p/K_v = \gamma$

Combustion Processes and Thermo-chemical Equations for combustion

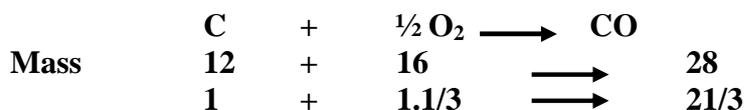
Combustion is defined as a process in which an oxidant is rapidly reacted with a fuel to liberate thermal energy. The product(s) of this reaction normally being in the form of high temperature gases. For all marine engineering applications the oxidant is the oxygen in the air. Most marine fuels in use are hydrocarbons and as such their main constituents are the elements of carbon and hydrogen which can be in a liquid solid or gaseous form. Often these hydrocarbon fuels also contain contaminants, which do not oxidise or if they do give a very small release in thermal energy. A typical example of this is sulphur which when burnt can have a detrimental effect on the local environment i.e. sulphurous acid production.

Equations for combustion (revisited)

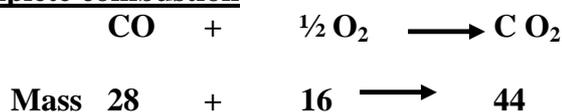
Carbon



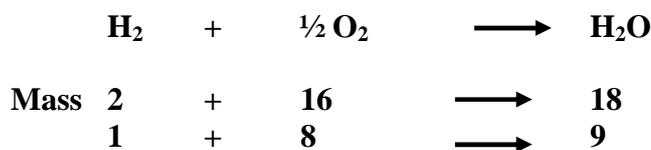
Incomplete combustion of carbon



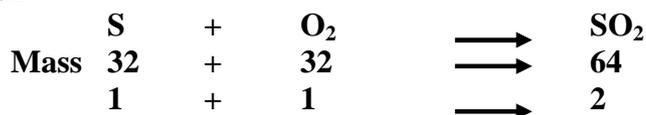
to complete combustion



Hydrogen



Sulphur



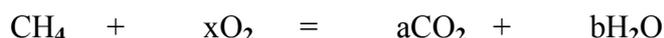
Most combustion problems are involved in the determination of the quantities of air required to complete the combustion process. Often the determination of stoichiometric conditions is the first stage in the process of evaluating the quantity of air required for complete

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combustion. An approach to the solution of combustion problems, which lends itself to the further development of combustion analysis, is to use an approach known as the kg mol or kmol method.

Consider the stoichiometric combustion of methane with x mol of oxygen.



We can see that this equation does not balance and we must thus complete a carbon, hydrogen and oxygen balance by applying the unknown quantities ie equating the atoms on one side of the equation to the atoms on the other side of the equation

Carbon

1 atom on lhs of equation = a atoms on the rhs of the equation
hence a = 1

Hydrogen

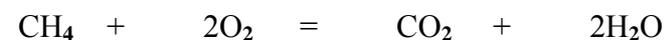
4 atoms on lhs of equation = 2b atoms on the rhs of the equation
hence b = 2

Oxygen

2x atoms on the lhs of the equation = 2a + b atoms on the rhs of the equation

$$2x = 2 + 2 = 4 \quad \text{hence } x = 2$$

thus the equation becomes



ie 1mol of methane requires 2 mols of oxygen to produce 1 mol of CO₂ and 2 mols of water vapour.

ie 1 volume of methane requires 2 volumes of oxygen to produce 1 volume of CO₂ and 2 volumes of water vapour

We can treat all combustion processes in a similar manner by balancing the combustion equation. If the combustible constituents are quoted as percentage mass analysis the general rule is to convert this mass into kmols by dividing each mass by the molecular mass of the particular constituent. (ie $n = m/M$) Consider the following example

Ex 1

A fuel consists of 86% carbon, 13% hydrogen and 1% sulphur by mass. Determine the mass of air required to burn the fuel stoichiometrically

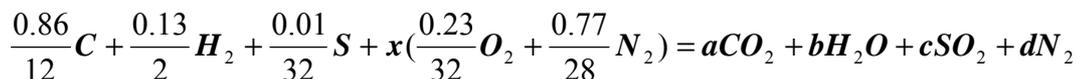
To use the mol method we must set up a combustion equation converting our mass analysis into a mol analysis. Let us consider that the requirement is for the supply of x kg of air for one kg of fuel. The equation can simply be written as follows:

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0.86kg of carbon + 0.13 kg of hydrogen + 0.01kg of sulphur + x kg of air will produce Carbon Dioxide + water vapour + Sulphur dioxide and Nitrogen (no part in combustion).

We must put this equation into the form of a chemical equation which involves converting the masses into k mols ie $n = m/M$. We must remember that air contains 23% O_2 and 77% N_2 by mass. The equation can thus be written as follows:



This equation is now set out in the form of the chemical equation similar to the burning of methane which was discussed previously. We now need to balance the equation by considering each constituent of the equation on the left hand side of the equation.

Carbon balance

Equate the carbon atoms on the lhs to those on the rhs

$$\frac{0.86}{12} = a = 0.071667$$

Hydrogen balance

Equate the hydrogen molecules on each side of the equation

$$\frac{0.13}{2} = b = 0.065$$

Sulphur balance

Equate the sulphur atoms on each side of the equation

$$\frac{0.01}{32} = c = 3.125 \times 10^{-4}$$

Oxygen balance

Equate oxygen molecules on each side of the equation

$$\frac{0.23x}{32} = a + \frac{b}{2} + c \quad \text{can you see why we have } \frac{b}{2} \text{ it's because we are equating molecules}$$

and the O in H_2O is only an atom ie half a molecule

$$\text{thus } \frac{0.23x}{32} = 0.071667 + \frac{0.065}{2} + 3.125 \times 10^{-4}$$

$$x = \underline{\underline{14.54 \text{ kg/kg of fuel supplied}}}$$

a simpler way to calculate the stoichiometric air supply would be to utilise the mass analysis equation previously derived in the initial revision notes

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$$\text{i.e. } mass_{air} = \frac{100}{23} (2.667C + 8H_2 + 1S) \text{ Stoic hom etric}$$

$$mass_{air} = \frac{100}{23} \{ (2.667 \times 0.86) + (8 \times 0.13) + (1 \times 0.01) \}$$

$$= \underline{\underline{14.54 \text{ kg/kg of fuel supplied}}} \text{ as above.}$$

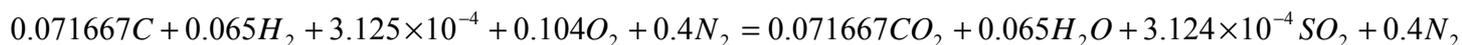
The mol method seems much more complicated in this simple example but we will find this process much easier for the more complex problems

To complete the combustion equation we will need to continue with the nitrogen balance

Nitrogen balance

Equate the nitrogen molecules on each side of the equation

$$\frac{0.77x}{28} = d = 0.4 \quad \text{thus the final combustion equation can be written as}$$



We can easily find the percentage volumetric analysis of the combustion products by using the ratio of each combustion product mol to the ratio of the total number of mols from this we can also find a percentage mass analysis. Consider the following table of combustion products.

Product	n(mols)	%Vol	M(molecular mass)	Mass(m)= n.M	% mass
CO ₂	0.071667	$\frac{0.071667}{0.537} \times 100 = 13.34$	44	$0.071667 \times 44 = 3.153$	$\frac{3.153}{15.54} \times 100 = 20.28$
H ₂ O	0.065	$\frac{0.065}{0.537} \times 100 = 12.1$	18	1.17	$\frac{1.17}{15.54} \times 100 = 7.53$
SO ₂	3.125×10^{-4}	0.058	64	0.02	0.129
N ₂	0.4	74.5	28	11.2	72.05
SUM	0.537	99.998	-----	15.54	99.99

Let's try another example

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Ex 2

Coal of mass analysis 90% carbon, 3% Hydrogen, 2% Oxygen, 1% nitrogen 1% sulphur and 3% ash is burned with an air to fuel ratio of 13.6 kg/kg fuel.

Determine:

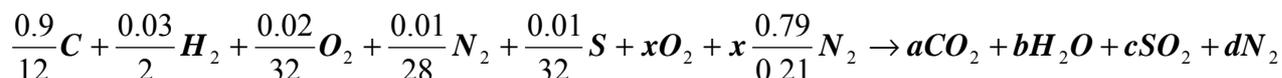
- a) the percentage excess air supplied
- b) the percentage by mass of SO₂ in the dry exhaust gas.

Atomic mass relationships H=1 C=12 N=14 O=16 S=32

Air contains 21% by volume

In this question we must only use the information provided namely that the air contains 21% oxygen by volume.

Let's look at the stoichiometric equation. Where x = no of kmols of O₂ supplied



Carbon balance

$$\frac{0.9}{12} = a = 0.075$$

Hydrogen balance

$$\frac{0.03}{2} = b = 0.015$$

Sulphur balance

$$\frac{0.01}{32} = c = 3.125 \times 10^{-4}$$

Oxygen balance

$$\frac{0.02}{32} + x = a + \frac{b}{2} + c = 0.075 + \frac{0.015}{2} + 3.125 \times 10^{-4}$$

$$x = 0.0821875$$

To find the mass oxygen and the mass of nitrogen supplied we must multiply each by its molecular mass.

hence 1 kg of fuel requires 0.0821875 X 32 = 2.63kg of oxygen for combustion and the

process will also be supplied with $\frac{0.79}{0.21} \times x$ mols of nitrogen =

$$\frac{0.79}{0.21} \times 0.0821875 \times 28 = 8.657 \text{ kg}$$

Total air supplied stoichiometrically is 2.63 + 8.657 = 11.287kg

$$\text{Percentage excess air} = \frac{\mathit{Air}_{actual} - \mathit{Air}_{stoich}}{\mathit{Air}_{stoich}} = \frac{13.6 - 11.287}{11.287} = 20.49\%$$

To find the percentage mass of sulphur dioxide we need to know the number of mols of SO₂ produced in the combustion process. Even though the actual process is supplied with excess

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air this will not change the amount of SO₂ produced. Hence we can take this value from the stoichiometric combustion equation. i.e. 3.125X 10⁻⁴ mols of SO₂ produced. **THUS BY MULTIPLYING THIS VALUE BY THE MOLECULAR MASS OF SO₂ WE CAN DETERMINE THE MASS OF SO₂ IN THE COMBUSTION PRODUCTS.**

$$mass_{SO_2} = 3.125 \times 10^{-4} \times 64 = 0.02kg$$

$\%_{SO_2} \text{ mass} = \frac{0.02}{14.6} \times 100 = 0.13699$ where the total mass of combustion products(14.6) is the mass of air supplied plus the mass of fuel supplied

Nitrogen balance

$$\frac{0.79}{0.21}A = 0.82B$$

∴ **eq(4) From these equations we can solve for the unknowns**

$$A = 0.218B$$

subs eq(1), eq(2) and eq (4) into eq(3)

$$A = 0.1B + 0.08B + \frac{a}{2} = 0.18B + \frac{a}{2}$$

$$A = 0.18(0.833x) + \frac{a}{2} = 0.15x + \frac{1-x}{4} = 0.218B$$

∴

$$0.218(0.833x) = 0.15x + 0.25 - 0.25x$$

∴

$$0.1816x = 0.25 - 0.1x$$

∴

$$x = \frac{0.25}{0.2816} = 0.8878 \text{kg} / \text{kg}_{\text{fuel}}$$

Thus the percentage composition of the fuel is 88.78% carbon and 11.22% Hydrogen.

The percentage excess air can be determined by considering the excess oxygen in the exhaust gas and the actual oxygen supplied. To determine this we need to find the value of A and of B This can be achieved by solving the equations further.

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$$B = 0.833x = 0.833 \times 0.8878 = 0.74 \text{ mols}$$

$$A = 0.218B = 0.218 \times 0.74 = 0.1613 \text{ mols}$$

\therefore

$$n_{\text{air supplied}} = \frac{0.1613}{0.21} = 0.7682 \text{ mols}$$

$$m_{\text{air supplied}} = 0.7682 \times M_{\text{air}}$$

where

m = mass .. and ... M = molecular .. mass

also

$$\text{Excess } O_2 = 0.08 \times B = 0.08 \times 0.74 = 0.0592 \text{ mols}$$

$$n_{\text{air excess}} = \frac{0.0592}{0.21} = 0.2819 \text{ mols}$$

$$m_{\text{air excess}} = 0.2819 \times M_{\text{air}}$$

$$\text{Stoichio}_{\text{air}} = \text{air}_{\text{supplied}} - \text{air}_{\text{excess}}$$

$$\%_{\text{excess}} = \frac{m_{\text{air excess}}}{\text{Stoichio}_{\text{air}}} \times 100 = \frac{0.2819 M_{\text{air}}}{(0.7682 M_{\text{air}} - 0.2819 M_{\text{air}})} = 57.97\%$$

Gaseous Fuels

The previous examples have involved the analysis of solid and liquid hydrocarbons where the analysis of the fuel is by mass. Gaseous fuels are still hydrocarbons but their constituents are analysed by volume. This makes the combustion equation a little easier in that the percentage volumes can be directly related to mols. The solution of the problem to determine the products analysis is exactly the same as described in the previous examples. Consider the following examples:

Ex 4

Natural gas consists of 93% CH₄, 3% C₂H₆, 1% CO, and 3% N₂. Determine the volumetric flow rate of air to be supplied to burn 5m³ /s of fuel when the mixture of the reactants is at 1 atmosphere and 56°C.

Note air contains 21% oxygen and 79% Nitrogen by volume

The stoichiometric combustion equation can be set up in terms of 1 mol of fuel supplied with x mols of air



Carbon – balance

$$0.93 + (2 \times 0.03) + 0.01 = a = \underline{1.0}$$

Hydrogen – balance

$$(0.93 \times 4) + (0.03 \times 6) = (b \times 2) \dots \dots \dots \text{worked – in – atoms – H}$$

$$b = \underline{1.95}$$

Oxygen – balance

$$\frac{0.01}{2} + 0.21x = a + \frac{b}{2} \dots \dots \dots \text{worked – in – molecules – O}_2$$

$$\frac{0.01}{2} + 0.21x = 1 + \frac{1.95}{2}$$

$$x = 9.381 \text{ mols}_{\text{air}} / \text{mol}_{\text{fuel}}$$

hence since the reactants are at the same temperature and pressure then

1m³ of fuel will require 9.381 m³ of air to burn the fuel stoichiometrically

5m³ of fuel will require 46.95 m³ of air