MMME2047 THERMOFLUIDS

Topic 5. Combustion Reactions; part 1

Aim of this section

Despite a dedication to finding sources of energy from 'renewable' resources, there is an ongoing commitment to burning things to make a hot energy source – at least this is being continued with biologically resourced fuels, like biogas, biomass or biofuel. These fuels are composed of hydrocarbons, just as were the oil and gas which have financed and fuelled the astronomical advance of mankinds progression since the 1960s. It is the engineering profession's responsibility to make the use of these fuels as efficient as possible. The starting point is understanding how the hydrogen and carbon are broken apart and burned in the atmosphere, consuming oxygen, to work out how much air is required and what happens if there is too much or too little air for the fuel.

Aim: learn to calculate the amount of air consumed when common hydrocarbon fuels are burned.

Objectives: work out mass and volume proportions of gases in a gas mixture; calculate properties of a mixture of gases; understand stoichiometric combustion; understand the idea of excess air supply and fuel rich combustion and the production of carbon monoxide in air starved combustion; calculate air to fuel ratio for excess air situations; calculate the amount of air by mass and by volume required to burn an amount of fuel.

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1. Gas mixtures

Gas mixtures are of interest because gases have many uses – apart from air conditioning, gas balloons, and processing gas atmospheres, combustion always produces gases and we concentrate here on combustion products from all fuels as well as on mixtures of combustible gases.

Symbols here:

c_v specific, $\therefore$ lower case

$\widetilde{m}$ molar mass, kg/kmol

R specific gas constant, but capital!

Values of these properties of individual gases, can be used to provide a value for a mixture of gases, which then helps to treat it as a bulk gas rather than having to consider separate parts.

- Two ways of looking at gas mixtures – by mass fractions and by volume fractions.

- **Law of partial pressures and internal energy** leads to mass or gravimetric analysis.

- Using it enables calculation of properties of a mixture, i.e. *h, c_v, c_p, R, $\widetilde{m}$, s.*

- **Law of partial volumes** leads to volumetric and molar analysis

Gas mixtures are interesting for combustion chemistry calculations, which is our focus. The mixture of fuel and air reacts and produces a mixture of product gases, which consist mainly of carbon dioxide and water vapour. Nitrogen is drawn in with the air, but for our purpose is considered to not react – but its presence in the mixture must be registered because it informs us of how much volume and mass of air is supplied which in turn defines the size of any combustion equipment we may design for it.

Incidentally gases and volatile liquids are interesting in several instances, for example: refrigeration, carbon dioxide can be used as a refrigerant it is R744 in the ASHRAE designation table of refrigerants (https://www.ashrae.org/technical-resources/standards-and-guidelines/ashrae-refrigerant-designations); some gases are very dense, sulphur hexa-fluoride (SF_6) is used in electrical switch gear due to its dielectric properties, but it is very dense; some liquids combust for power generation, e.g. petrol (approximate formula is octane, C_8H_{18}) and diesel (approximate formula is $C_{12}H_{23}$).

2. Gibbs-Dalton Law of partial pressures

The fuller version of the law of partial pressures is the empirical Gibbs-Dalton law – it includes internal energy. Suppose there are 'i' gas components completely mixed and occupying a volume V at temperature T and in a vessel at pressure p, the law of partial pressures is:

$$p = \sum_i p_i$$

where p is the pressure of the mixture of gases and p_i is the pressure of a particular gas species, here called i, which may be any gas such as oxygen, O_2, hydrogen, H_2 etc, if that gas species were isolated in the same volume of the entire mixture of gases.

The law also accounts similarly for the internal energy of the gas mixture as:

$$U = \sum_i U_i = \sum_i m_i u_i$$

where U is the internal energy of the mixture of gases and $m_i u_i$ is the internal energy of a particular gas species.

3. Amagat's Law of partial volumes

Similar to the law of partial pressures, but completely distinct and not to be confused with it, is the law of partial volumes.

The volume of a mixture of gases is equal to the sum of the volumes of the individual constituents when each exists alone at the pressure and temperature of the mixture.

$$V = \sum_i V_i$$

where V is the volume of the mixture of gases and V_i is the volume of a particular gas species in the mixture, if it were at the pressure of the gas mixture and isolated on its own.

Since by Avogadro's law, there is an equal volume occupied by equal number of moles of any gas, regardless of its mass, this can also be written as:

$$n = \sum_i n_i$$

where n is the total number of moles of gas in the mixture and n_i is the number of moles of a particular species in the mixture.

This is the alternative way of thinking – a gas at the pressure of the mixture will have a particular volume.

4. Difference between mass and volume fractions

Consider hydrogen and oxygen mixing, pictured by volume, at constant pressure & temperature:
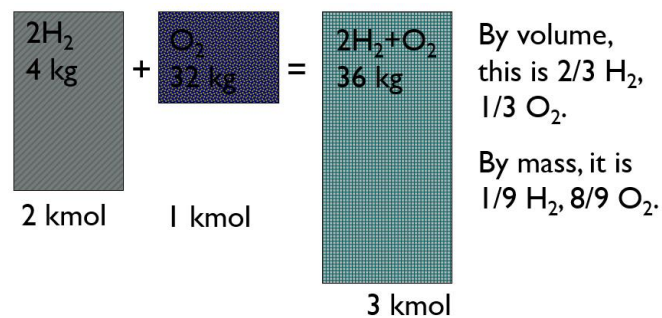
At same p and T, 1 kmol of any gas occupies the same volume - regardless of mass – as 1 kmol of any other gas. This shows us that the effect of molecular weight can be vastly different volume and mass fractions of gases in a mixture. This is based on Avogadro's law which is that the same number of atoms or molecules of different gases have the same volume at a given state. Here we see 2 times the amount of hydrogen molecules as there are of oxygen molecules, so the volume of oxygen is half the volume of the hydrogen. The sum of the two gases if mixed (not burned) is then 3 times the volume of the oxygen. The masses however tell a different story – because the same number of atoms or molecules do not have the same mass unless they have the same atomic mass number. The atomic mass number is found in the periodic table of elements for each atom type, and the molecular mass of a compound of more than one atom type is the sum of the atomic masses of the atom types by their relative quantity in the molecule. We see here that hydrogen has an atomic mass of 1 g·mol^{-1} or 1 kg·kmol^{-1} and the result of this is a diatomic molecule (H_2) molecular mass of 2 g·mol^{-1}; likewise oxygen has atomic mass 16 g·mol^{-1}. Avogadro number is the number of atoms or molecules in a mole of a gas, and 1 mole is the measure of the number of atoms in exactly 12 g of carbon-12, ^{12}C, the most abundant isotype of carbon on Earth.

5. Equation of state in terms of n for a perfect gas

The gas law for a component of a gas mixture is either p_iV or $pV_i = mRT$. We know that the number of moles is the actual mass divided by the molar mass:

$$n = {}^m\!/\!{\widetilde{m}}$$

so:

$$mR = m\frac{\widetilde{R}}{\widetilde{m}} = n\widetilde{R}$$

Therefore $p_iV = pV_i = n_i\widetilde{R}T$

Both partial pressure and partial volume can consider molar analysis.

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Formula for the relation between partial pressure and partial volume and molar fraction

For the mixture as a whole, considered as a perfect gas $pV = n\tilde{R}T$. Use the equation of state for a perfect gas for the constituent gas with partial pressure p_i, and the mixture at pressure p, and divide:

$$\frac{p_iV}{pV} = \frac{n_i\tilde{R}T}{n\tilde{R}T} \rightarrow \frac{p_i}{p} = \frac{n_i}{n}$$

Combine with the partial-pressure/partial-volume relation formula:

$$\frac{p_i}{p} = \frac{n_i}{n} = \frac{V_i}{V}$$

in which $\sum p_i = p$; $\sum V_i = V$; $\sum n_i = n$.

This eqaution shows us the important fact that volume fraction is equal to molar fraction. Consider a reaction (if we burned the mixture in the previous section) $2H_2+O_2\rightarrow 2H_2O$. The molar fraction of H_2 in the reactants is 2/3. This is also its volume fraction, and after the reaction, the volume of the gases has decreased to 2/3rds of its volume prior to combustion. Usually we have a volumetric analysis and a reaction to consider in combustion related calculations. And that is why the laws of partial pressure and partial volume are very useful for this section.

6. **Derived properties of the gas mixture**

The other properties of a mixture of gases can be derived from the properties of the individual gas species in the mixture from these laws, as shown below for h,cv, cp, R and $\tilde{m}$ using the law of partial pressures and the law of partial volumes.

by the law of partial pressures

a) enthalpy

$$H = U + pV$$

and since by the law of partial pressures, each gas species is considered to occupy the whole volume of the mixture:

$$H = \sum_i U_i + \sum_i p_i\tilde{V}, therefore\ H = \sum_i H_i$$

b) specific heat at constant volume

$$m(u_2 - u_1) = \sum_i m_i(u_{2i} - u_{1i}), therefore\ mc_v(T_2 - T_1) = \sum_i m_i c_{vi}(T_2 - T_1)$$

and by dividing through by m(T$_2$-T$_1$)

$$c_v = \sum_i \frac{m_i}{m}c_{vi}$$

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c) specific heat at constant pressure

$$m(h_2 - h_1) = \sum_i m_i(h_{2i} - h_{1i}) \ therefore \ mc_p(T_2 - T_1) = \sum_i m_i c_{pi}(T_2 - T_1)$$

again dividing through

$$c_p = \sum_i \frac{m_i}{m} c_{pi}$$

d) specific gas constant

$$R = \sum_i \frac{m_i}{m} c_{pi} - \sum_i \frac{m_i}{m} c_{vi} \ therefore, R = \sum_i \frac{m_i}{m}(c_{pi} - c_{vi}) \ and, R = \sum_i \frac{m_i}{m} R_i$$

It can be seen that the law of partial pressures has led to the analysis of the gas mixture in terms of mass fractions of each of the species, m_i/m.

other useful derivations related to gas constant

e) molar mass of the mixture

Starting with:

$$R = \sum_i \frac{m_i}{m} R_i = \sum_i \frac{m_i}{m} \frac{\tilde{R}}{\tilde{m}_i}$$

and using the relationship between the specific gas constant and the molar or universal gas constant:

$$R = \frac{\tilde{R}}{\tilde{m}}$$

where the wavy line above indicates molar, or per mol, and $\tilde{R}$ is the universal gas constant, for every gas, 8.314 J/molK, and we get by equating the two terms and cancelling the $\tilde{R}$ term:

$$\frac{1}{\tilde{m}} = \sum_i \frac{m_i}{m} \frac{1}{\tilde{m}_i}$$

and thus the molar mass of the gas mixture, $kg \cdot kmol^{-1}$ or $g \cdot mol^{-1}$ is determined.

Some useful molar masses to remember are:

O_2, 32 $g \cdot mol^{-1}$, N_2, 28 $g \cdot mol^{-1}$, H_2O, 18 $g \cdot mol^{-1}$, CO_2, 44 $g \cdot mol^{-1}$, CO, 28 $g \cdot mol^{-1}$. Obviously these are just the sum of the atomic masses of the atoms comprising the molecules. It is important to remember that oxygen and nitrogen exist in the natural state as *diatomic* molecules and not as atoms – it is a more stable energy condition to be a bonded pair.

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f) another way of getting the molar mass by partial volumes

Since:

$$\tilde{m} = \frac{m}{n}, and, m = \sum_i m_i n_i, therefore, \tilde{m} = \sum_i \frac{n_i}{n} \tilde{m}_i$$

and by Avogadro we know that the ratio by number of moles is the same as the ratio by volume:

$$\frac{n_i}{n} = \frac{V_i}{V}$$

g) gas constant by partial volumes

$$R = \frac{\tilde{R}}{\tilde{m}}; rearrange: \tilde{m} = \frac{\tilde{R}}{R}$$

and using the relation above for the mass in terms of fraction of moles

$$\frac{\tilde{R}}{R} = \sum_i \frac{n_i}{n} \frac{\tilde{R}}{R_i} and \frac{1}{R} = \sum_i \frac{n_i}{n} \frac{1}{R_i}$$

h) conversion between fractions by mass and by mole (volume)

gas law for constituent i, by partial volume (where pressure and temperature are those of the mixture):

$$pV_i = n_i \tilde{R} T = \frac{m_i}{\tilde{m}_i} \tilde{R} T$$

and for the mixture as a whole:

$$pV = \frac{m}{\tilde{m}} \tilde{R} T$$

divide the first by the second:

$$\frac{V_i}{V} = \frac{m_i}{m} \frac{\tilde{m}}{\tilde{m}_i} \quad or, \quad \frac{m_i}{m} = \frac{\tilde{m}_i V_i}{\tilde{m} V} = \frac{\tilde{m}_i n_i}{\tilde{m} n}$$

or the other way:

$$\frac{m_i}{m} = \frac{\tilde{m}_i n_i}{\tilde{m} n} \rightarrow \frac{n_i}{n} = \frac{m_i}{m} \frac{\tilde{m}}{\tilde{m}_i}$$

therefore knowing the volume fraction and the molar masses of the gases the mass fraction can be derived.

7. volumetric and molar analysis

The analysis from the Law of Partial Pressures is GRAVIMETRIC, that is the analysis of gas mixtures by measurement of the constituents by mass.

Similarly, the analysis from the Law of Partial Volumes leads to VOLUMETRIC composition of gases in the mixture, i.e. measurment by volume.

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e.g. the volumetric composition of air is approximately

79% N_2, 21% O_2 by volume.

i.e. in $1m^3$ of air, the <u>partial</u> volumes of N_2 and O_2 are $0.79m^3$ and $0.21m^3$.

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Volumetric analysis is directly related to molar analysis, and molar analysis is standard chemical equation balancing.

This data can be found in the tables of data, which will be issued in both exams, Thermodynamic and Transport Properties of Fluids by Rogers and Mayhew. On the last page there is a section on 'For approximate calculations with air'.

So for a quick calculation for air it is ok to assume c_p = 1005 J/kgK, R=287 J/kgK and γ=1.4 and $\tilde{m}$=29 kg/kmol.

Molar analysis

By definition, this is the same as the volumetric analysis but using mole fractions.

<u>Definitions</u>:

    a) 1 mol of a substance contains an ***Avogadro number*** of molecules, N_A = 6.022×10^{23} mol^{-1}.

    b) 1 **mole** (1 mol) of gas has a mass in g equal to its molecular weight.

    c) 1 mol of any perfect gas occupies the same volume V at a given P and T as 1 mol of any other perfect gas (e.g. the standard atmosphere condition, V=22.4 litres (i.e. $0.0224m^3$) at T=0°C and p=1 atmos).

    d) Usually it is more convenient to quantify in kmol.

*Formula for the **relation between partial pressure and partial volume**.*

Partial pressures and partial volumes are **alternative** ways of describing the mixture.

Either a component occupies

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p_i at V or V_i at p

But not V_i at p_i.

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Using the gas law, considering a perfect gas:

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By partial pressure, $p_i V = m_i R_i T$

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By partial volume, $pV_i = m_i R_i T$

Divide to give:

$$\frac{V_i}{V} = \frac{p_i}{p}$$

This equation shows that proportions by volume are equal to proportions by pressure. So if a gas occupies 10% of volume of a mixture, it's partial pressure will be 10% of the mixture pressure.

8. **Combustion chemistry**

Fuels produce energy by reacting with *oxidisers*. The oxidiser is commonly atmospheric air. The fuel may be a solid (e.g. coal), a liquid (e.g. petrol ~octane C_8H_{18}) or a gas (e.g. natural gas ~methane CH_4).   If sufficient energy is provided to initiate a *reaction*, then the oxygen will react with the *hydro-carbon* fuel in combustion. We want to calculate the amount of *air required* to burn a fuel and the *composition* of the *products* of combustion.

Chemical equations are done by atom combinations and consider molecule reactions. But they are also molar – i.e. each number of atoms in an equation represents the number of moles because of Avogadro's analysis, you can scale up or down by the number of atoms or molecules involved because the number of moles represents the number of atoms or molecules.

9. **Molar reaction equations**

The analysis of a combustion process, begins by the formulation of the chemical equation which shows how the atoms of the <u>reactants</u> are combined to form the <u>products</u>.

Examples $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

 $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
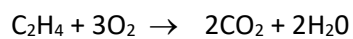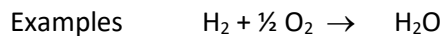
On the left hand side are the reactants and on the right hand side are the products. The reaction can actually go both ways depending on the temperature, but we consider complete combustion, which is at the end of the process where the most stable condition for these reactions is on the right hand side.

By the *law of conservation of mass*, the number of atoms of each element is the same at the beginning as at the end of any chemical reaction. i.e. the number of atoms of *reactants* = the number of atoms of *products*.

The *reaction equations* are *MOLAR* (equivalent to volume for gases) equations which *define* the number of atoms of each element from reactants = atoms in products of combustion and *conserve* Mass of reactants = mass of products.

Usually the number of moles of reactants *will not* equal the number of moles of products.
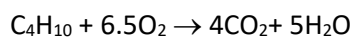
How to balance equations:

        e.g. butane $C_4H_{10} + xO_2 \rightarrow aCO_2 + bH_2O$
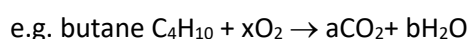
Count atoms and balance on each side of the equation:

C: 4 = a

H: 10 = 2b; b=5

O: 2x = 2a + b; x=6.5

Therefore:

$C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O$

The atoms in each molecule swap around and rearrange themselves to be with preferred partners. That rearrangement leads to a release of energy in a combustion reaction – the desired product.

10. Mass of molecules in reaction equations

Consider the reaction of hydrogen and oxygen to make water: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

In terms of the number of moles of reactants, there is 1 mol of H_2 and ½ a mol of O_2; on the right hand side there is 1 mol of H_2O. From the perspective of mass, the mass on the left hand side is 1 mol of H_2, i.e. 2g of H_2 (hydrogen has an atomic mass of 1 g/mol) and ½ mol of O_2, i.e. 16g (oxygen has an atomic mass of 16 g/mol) of O_2 making a total of 18g. On the right hand side there is 1 mol of water or 18g of water, given that the water is made up of two atoms of H and one atom of O, and the proportion per mole of water will be the same as for the single molecule.