

**THERMODYNAMICS  
TUTORIAL 15  
COMBUSTION**

This tutorial is set at QCF Levels 5 and 6

On completion of this tutorial you should be able to

- Analyse combustion processes in terms of stoichiometric, internal energy of reaction and enthalpy of reaction and formation.
- Apply First Law of thermodynamics to chemical reactions.
- Explain chemical dissociation and determine its effect in reactions involving perfect gases.

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6. *Energy Released by the Reaction*
7. *Dissociation*

Let's start by revising the basics.

## 1. Introduction

Combustion is the process of chemical reaction between fuel and oxygen (reactants). The process releases heat and produces products of combustion. The main elements which burn are:

*Carbon*

*Hydrogen*

*Sulphur*

The heat released by 1 kg or m<sup>3</sup> of fuel is called the calorific value.

The oxygen used in combustion processes normally comes from the atmosphere and this brings nitrogen in with it which normally does nothing in the process but makes up the bulk of the gases remaining after combustion.

The main elements in combustion are:

	Symbol	Atomic Mass	Molecular Mass	Product
Carbon	C	12		CO <sub>2</sub>
Hydrogen	H <sub>2</sub>	1	2	H <sub>2</sub> O
Sulphur	S	32		SO <sub>2</sub>
Oxygen	O <sub>2</sub>	16	32	
Nitrogen	N <sub>2</sub>	14	28	

If the water formed during combustion leaves as vapour, it takes with it the latent heat of evaporation and thus reduces the energy available from the process. In this case the calorific value is called the lower Calorific value (LCV). If the products cool down after combustion so that the vapour condenses, the latent heat is given up and the calorific value is then the higher calorific value (HCV).

Solid and liquid fuels are normally analysed by mass to give the content of carbon, hydrogen, sulphur and any other elements present. Often there is silica, moisture and oxygen present in small quantities which have some effect on process. The silica leaves slaggy deposits on the heat transfer surfaces in boilers.

Gaseous fuels are normally analysed by volumetric content and are in the main hydrocarbon fuels.

For purposes of calculation, the content of air is considered to be

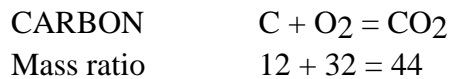
	Volumetric	Gravimetric
Oxygen	21%	23%
Nitrogen	79%	77%

The sulphur content of the fuel is considered to be a pollutant and so undesirable. The theoretically correct quantity of air or oxygen required to just exactly burn the fuel expressed as a ratio to the fuel burned, is called the **Stoichiometric Ratio**. In practice it is found that not all the oxygen in the reactant reaches the fuel elements and that excess air is required in order to ensure complete combustion. This results in oxygen appearing in the products. If too little air or oxygen is supplied, the result is incomplete combustion resulting in the formation of carbon monoxide CO instead of carbon dioxide CO<sub>2</sub>. The resulting products contain water H<sub>2</sub>O. Industrial equipment for measuring the contents of the products usually remove the water from the sample and the products are then called the dry products.

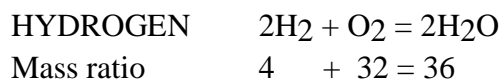
## 2. Combustion Chemistry

### 2.1 Solid and Liquid Fuels

In the case of solid and liquid fuels, we do the combustion of each element separately. The important rule is that you must have the same number of atoms of each substance before and after the process. This may be obtained by juggling with the number of molecules.



Hence 1kg of C needs 32/12kg of O<sub>2</sub> and makes 44/12kg of CO<sub>2</sub>



Hence 1kg of H<sub>2</sub> needs 8kg of O<sub>2</sub> and makes 9 kg of H<sub>2</sub>O



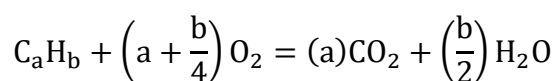
Hence 1 kg of S needs 1kg of O<sub>2</sub> and makes 2 kg of SO<sub>2</sub>.

## 2.2. Gaseous Fuels

Typical hydrocarbons are :

Methane	CH <sub>4</sub>
Ethane	C <sub>2</sub> H <sub>6</sub>
Propane	C <sub>3</sub> H <sub>8</sub>
Butane	C <sub>4</sub> H <sub>10</sub>
Pentane	C <sub>5</sub> H <sub>12</sub>
Hexane	C <sub>6</sub> H <sub>14</sub>
Heptane	C <sub>7</sub> H <sub>16</sub>
Octane	C <sub>8</sub> H <sub>18</sub>
Ethene	C <sub>2</sub> H <sub>4</sub> (Ethylene)
Propene	C <sub>3</sub> H <sub>6</sub> (Propylene)
Ethyne	C <sub>2</sub> H <sub>2</sub> (Acetylene)
Benzenol	C <sub>6</sub> H <sub>6</sub> (Benzene)
Cyclohexane	C <sub>6</sub> H <sub>12</sub>

The combustion equation follows the following rule

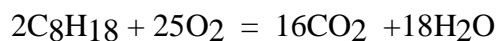
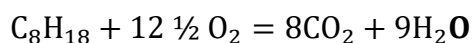
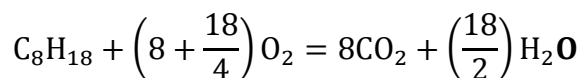


If this results in fractional numbers of molecules, then the whole equation may be multiplied up.

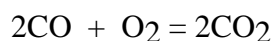
### WORKED EXAMPLE No. 1

Write out the combustion equation for C<sub>8</sub>H<sub>18</sub>

#### SOLUTION



There are other gases which burn and the main one to know about is Carbon Monoxide (CO) which is partially burned carbon. The equation for the combustion of CO is



### 3. Combustion by Mass

The only rule to be observed in deducing the quantities of each substance is the law of conservation of mass. The proportions of the mass are that of the molecular masses. This is shown in the following example.

#### WORKED EXAMPLE No. 2

A fuel contains by mass 88% C, 8% H<sub>2</sub>, 1% S and 3% ash (silica). Calculate the stoichiometric air.

#### SOLUTION

CARBON                      C + O<sub>2</sub> = CO<sub>2</sub>  
Mass ratio                    12 + 32 = 44

Hence 0.88kg of C need  $(32/12) \times 0.88 = 2.347$  kg of oxygen.

It makes  $(44/12) \times 0.88 = 3.227$  kg of carbon dioxide.

HYDROGEN                    2H<sub>2</sub> + O<sub>2</sub> = 2H<sub>2</sub>O  
Mass ratio                    4 + 32 = 36

Hence

0.08kg of hydrogen needs  $(32/4) \times 0.08 = 0.64$  kg of oxygen.

SULPHUR                      S + O<sub>2</sub> = SO<sub>2</sub>  
Mass ratio                    32 + 32 = 64

Hence 0.01kg of sulphur needs 0.01kg of oxygen and makes 0.02kg of sulphur dioxide.

Total Oxygen needed is  $2.347 + 0.64 + 0.01 = 2.997$ kg

Total Air needed is  $2.997/23\% = 13.03$ kg

The *Stoichiometric* air/fuel ratio is 13.03/1

### WORKED EXAMPLE No. 3

If the air supplied is 20% more than the stoichiometric value, find the analysis of the dry products by mass.

#### SOLUTION

If 20% excess air is supplied then the air supplied is:

$$120\% \times 13.03 = 15.637 \text{ kg}$$

Oxygen is also 20% excess so  $0.2 \times 2.997 = 0.599 \text{ kg}$  is left over.

Nitrogen in the air is  $77\% \times 15.637 = 12.04\text{kg}$

List of products

Nitrogen	12.04 kg	= 75.8%
Carbon dioxide	3.227 kg	= 20.3%
Sulphur dioxide	0.02 kg	= 0.1%
Oxygen	0.599 kg	= 3.8%
Total dry product	15.886 kg	= 100%

It is of interest to note that for a given fuel, the % of any product is a direct indication of the excess air and in practice the carbon dioxide and/or oxygen is used to indicate this. This is important in obtaining optimal efficiency in a combustion process.

### SELF ASSESSMENT EXERCISE No. 1

1. A boiler burns fuel oil with the following analysis by mass

80% C 18% H<sub>2</sub> 2% S

30% excess air is supplied to the process. Calculate the stoichiometric ratio by mass and the % Carbon Dioxide present in the dry products.

(15.62/1 14.9% CO<sub>2</sub>)

2. A boiler burns coal with the following analysis by mass

75% C 15% H<sub>2</sub> 7% S remainder ash

Calculate the % Carbon Dioxide present in the dry products if 20% excess air is supplied.

(16.5% CO<sub>2</sub>)

3. Calculate the % of each dry product when coal is burned stoichiometrically in air. The analysis of the coal is

80% C 10% H<sub>2</sub> 5% S and 5% ash.

(76.7%N, 22.5% CO<sub>2</sub> 0.8% SO<sub>2</sub>)

#### 4. Combustion by Volume

First we need to revise gas mixtures and understand the meaning of **Volumetric Content**. To do this we must understand Dalton's law of partial pressures and Avogadro's Law.

First let us define the kmol. A kmol of substance is the number of kg numerically equal to the apparent molecular mass. For example 12 kg of Carbon is a kmol, so is 32 kg of O<sub>2</sub> and 2 kg of H<sub>2</sub> and 28 kg of N<sub>2</sub>.

The molecular mass of a substance is expressed as kg/kmol so the molecular mass of O<sub>2</sub> for example is 32 kg/kmol.

**Avogadro's Law** states

1m<sup>3</sup> of any gas at the same pressure and temperature contains the same number of molecules. It follows that the volume of a gas at the same p and T is directly proportional to the number of molecules. From this we find that the volume of a kmol of any gas is the same if p and T are the same.

**Dalton's law** states:

The total pressure of a mixture is the sum of the partial pressures. The partial pressure is the pressure each gas would exert if it alone occupied the same volume at the same temperature.

Consider two gases A and B occupying a volume V at temperature T. Using the Universal gas law for each:

$$p_A V_A = \frac{m_A R_o T}{\tilde{N}_A} \quad p_B V_B = \frac{m_B R_o T}{\tilde{N}_B}$$

$\tilde{N}$  is the relative molecular mass.

$$\frac{p_A}{p_B} = \frac{m_A \tilde{N}_B}{m_B \tilde{N}_A} = \text{ratio of the kmol fractions}$$

$p_A$  and  $p_B$  are the partial pressures.

$V_A$  and  $V_B$  are the partial volumes. These are the volumes each gas would occupy if they were separated and kept at the original p and T. This concept is very useful in problems involving the combustion of gases. It also follows that the partial volumes are directly related to the partial pressures so that

$$\frac{V_A}{V_B} = \frac{p_A}{p_B}$$

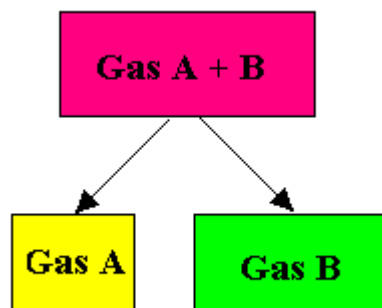


Figure 1



When not mixed the pressure is  $p$  and the volumes are  $V_A$  and  $V_B$ . Hence

$$\frac{pV_A}{T} = \frac{m_A R_o}{\tilde{N}_A} \quad p = \frac{m_A R_o T}{\tilde{N}_A V_A} \dots \dots (1)$$

$$\frac{pV_B}{T} = \frac{m_B R_o}{\tilde{N}_B} \quad p = \frac{m_B R_o T}{\tilde{N}_B V_B} \dots \dots (2)$$

Since (1) = (2) then

$$\frac{m_A R_o T}{\tilde{N}_A V_A} = \frac{m_B R_o T}{\tilde{N}_B V_B}$$

This shows that in a mixture, the partial volumes are in the same ratio as the kmol fractions which in turn are in proportion to the number of molecules of each gas.

When mixed they both have volume  $V$ , hence:

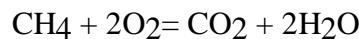
$$p_A = \frac{m_A R_o T}{\tilde{N}_A V_A} \dots \dots (3)$$

$$p_B = \frac{m_B R_o T}{\tilde{N}_B V_B} \dots \dots (4)$$

$$\frac{(3)}{(1)} \text{ gives } \frac{p_A}{p} = \frac{V_A}{V} \quad \text{and} \quad \frac{(4)}{(2)} \text{ gives } \frac{p_B}{p} = \frac{V_B}{V}$$

$$\frac{V_A}{V_B} = \frac{p_A}{p_B}$$

Consider the combustion of Methane.



Since the volumetric content of each gas is in the same ratio as the kmol fractions then volumetric content is in the same proportion as the molecules. Hence it needs 2 volumes of oxygen to burn 1 volume of methane.

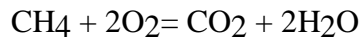
The volume of air needed is  $2 \div 21\% = 9.52$  volumes.

Hence it burn  $1 \text{ m}^3$  of methane we need  $9.52 \text{ m}^3$  of air for stoichiometric combustion. If the products are at the same  $p$  and  $T$  as the original reactants, we would obtain  $1 \text{ m}^3$  of carbon dioxide and  $2 \text{ m}^3$  of water vapour which would probably condense and cause a reduction in volume and/or pressure.

#### WORKED EXAMPLE No. 4

Calculate the % CO<sub>2</sub> in the dry products when methane is burned with 15% excess air by volume.

#### SOLUTION



Volume ratio      1      2      1      2

The stoichiometric air is  $2/21\% = 9.524 \text{ m}^3$

The actual air is  $9.524 \times 115\% = 10.95 \text{ m}^3$

Analysis of dry products

Nitrogen             $79\% \times 10.95$      $8.65 \text{ m}^3$

Carbon Dioxide                     $1.00 \text{ m}^3$

Oxygen     $15\% \times 2$                      $0.30 \text{ m}^3$

Total                                     $9.95 \text{ m}^3$

The % Carbon Dioxide =  $(1/9.95) \times 100 = 10\%$

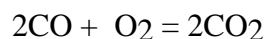
When the fuel is a mixture of gases, the procedure outlined must be repeated for each combustible gas and the oxygen deduced for the volume of each in  $1 \text{ m}^3$  of total fuel.

#### WORKED EXAMPLE No. 5

A fuel is a mixture of 60% Methane and 30% carbon monoxide and 10% oxygen by volume. Calculate the stoichiometric oxygen needed.

#### SOLUTION

As before, the volume of oxygen required to burn  $1 \text{ m}^3$  of methane is  $2 \text{ m}^3$ . To burn  $0.6 \text{ m}^3$  needs  $1.2 \text{ m}^3$  of oxygen. For carbon monoxide we use the combustion equation



Hence to burn  $1 \text{ m}^3$  of CO need  $0.5 \text{ m}^3$  of oxygen, so to burn  $0.3 \text{ m}^3$  needs  $0.15 \text{ m}^3$  of oxygen.

The total oxygen needed is  $1.2 + 0.15 = 1.35 \text{ m}^3$ . However there is already  $0.1 \text{ m}^3$  in the fuel so the **stoichiometric oxygen needed  $1.25 \text{ m}^3$**

## SELF ASSESSMENT EXERCISE No. 2

1. Find the air fuel ratio for stoichiometric combustion of Ethene by volume. (26.19/1)
2. Find the air fuel ratio for stoichiometric combustion of Butane by volume. (30.95/1).  
Calculate the % carbon dioxide present in the dry flue gas if 30% excess air is used. (10.6%)
3. Find the air fuel ratio for stoichiometric combustion of Propane by volume. (23.81/1)  
Calculate the % oxygen present in the dry flue gas if 20% excess air is used. (3.8%)

4. A gaseous fuel contains by volume :

5% CO<sub>2</sub>, 40% H<sub>2</sub>, 40% CH<sub>4</sub>, 15% N<sub>2</sub>

Determine the stoichiometric air and the % content of each dry product.

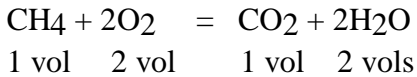
(4.76 m<sup>3</sup>, 89.7%,N<sub>2</sub> 10.3% CO<sub>2</sub>)

## 5. Relationship between Product and Excess Air.

It follows that if we can deduce the % product then given the figure, we can work backwards to determine the air or oxygen that was used.

### WORKED EXAMPLE No. 6

Consider the combustion of methane again.



### SOLUTION

Let the excess air be  $x$  (as a decimal)

The stoichiometric air is 9.52 vols. Actual air is  $9.52(1 + x)$

Dry Products:

Nitrogen	$0.79 \times 9.52(1 + x) = 7.524x + 7.524$
Oxygen	$2.000x$
Carbon Dioxide	$1.000$
Total	$9.524x + 8.524$

$$\% \text{ Carbon monoxide} = 100 \left\{ \frac{1}{9.524x + 8.524} \right\}$$

$$\% \text{ Oxygen} = 100 \left\{ \frac{2}{9.524x + 8.524} \right\}$$

For example if the %  $\text{CO}_2$  is 10% then the excess air is found as follows

$$10\% = 100 \left\{ \frac{1}{9.524x + 8.524} \right\}$$

$$0.1 = \frac{1}{9.524x + 8.524}$$

$$(9.524x + 8.524) = 10$$

$$9.524x = 1.476$$

$$\mathbf{x = 0.155 \text{ or } 15.5\%}$$

Similarly if the  $\text{O}_2$  is 10% then the excess air is 81% (show this for yourself)

If the analysis of the fuel is by mass, then a different approach is needed as in the following:

### WORKED EXAMPLE No. 7

An analysis of the dry exhaust gas from an engine burning Benzole shows 15% Carbon Dioxide present by volume. The Benzole contains 90% C and 10% H<sub>2</sub> by mass. Assuming complete combustion, determine the air/fuel ratio used.

### SOLUTION

1 kg of fuel contains 0.9kg of C and 0.1kg of H<sub>2</sub>. Converting these into kmol we have 0.9/12 kmol of C and 0.1/2 kmol of H<sub>2</sub>. For 1 kmol of dry exhaust gas we have

$$\begin{aligned} &0.15 \text{ kmol of CO}_2 \\ &Y \text{ kmol of excess O}_2 \\ &1 - 0.15 - Y = 0.85 - Y \text{ kmol of N}_2 \end{aligned}$$

$$\begin{aligned} &1 \text{ kmol of CO}_2 \text{ is } 44 \text{ kg} \\ &1 \text{ kmol of N}_2 \text{ is } 28 \text{ kg} \\ &1 \text{ kmol of O is } 32 \text{ kg} \\ &0.15 \text{ kmol of CO}_2 \text{ is } 0.15 \times 44\text{kg} \end{aligned}$$

This contains (12/44) carbon so the carbon present is  $0.15 \times 12$  kg  
The carbon in the fuel is 0.9 kmol per kmol of fuel. Hence the number of kmols of DEG must be

$$0.9/(0.15 \times 12) = 0.5$$

There are 0.5 kmol of DEG for each kmol of fuel burned.

The Nitrogen present in the DEG is  $0.85 - Y$  kmol per kmol of DEG. This has a mass of

$$28(0.85 - Y) \text{ per kmol of DEG}$$

The oxygen supplied to the process must be

$$(23.3/76.7) \times 28 \times (0.85 - Y) = 7.24 - 8.5Y \text{ kg per kmol of DEG.}$$

(Use precise proportions of air for accuracy).

The oxygen contained within the carbon dioxide is:  $(32/44) \times 0.15 \times 44 = 4.8$  kg per kmol DEG

1 kmol of CO<sub>2</sub> contains 44 kg and 32/44 of this is oxygen.

The oxygen in the CO<sub>2</sub> is hence  $32 \times 0.15$  kg per kmol DEG.

The excess oxygen is  $32Y$  kg per kmol DEG

Total oxygen in the products excluding that used to make H<sub>2</sub>O is

$$32 \times 0.15 + 32Y$$

The oxygen used to burn hydrogen is hence  $7.24 - 8.5Y - 32 \times 0.15 + 32Y$   
O<sub>2</sub> used to burn H<sub>2</sub> is

$$2.44 - 40.5Y \text{ kg per kmol DEG}$$

For 0.5 kmol this is

$$1.22 - 20.25Y \text{ kg}$$

To burn hydrogen requires oxygen in a ratio of 8/1. There is 0.1 kg of H<sub>2</sub> in each kmol of fuel so 0.8 kg of O<sub>2</sub> is needed. Hence

$$0.8 = 1.22 - 20.25Y$$

$$Y = (1.22 - 0.8)/20.25 = 0.0208 \text{ kmol per kmol DEG}$$

The nitrogen in the DEG is  $0.85 - Y = 0.829$  kmol per kmol DEG

The actual Nitrogen =  $0.829 \times 0.5 \times 28 = 11.61$  kg

The air supplied must be  $11.61/0.767 = 15.14$  kg per kg of fuel. A simple calculation shows the stoichiometric mass of air is 13.73 so there is 10.3% excess air.

### SELF ASSESSMENT EXERCISE No. 3

1. C<sub>2</sub>H<sub>6</sub> is burned in a boiler and the dry products are found to contain 8% CO<sub>2</sub> by volume. Determine the excess air supplied. (59%)
2. The analysis of the dry exhaust gas from a boiler shows 10% carbon dioxide. Assuming the rest is oxygen and nitrogen; determine the excess air supplied to the process and the % excess air. The fuel contains 85% C and 15% H<sub>2</sub>

(21.5 kg , 44.5%)

Now we will look at a complete example involving all the principles so far covered.

## 6. Energy Released by the Reaction

The contents of the fuel and air or oxygen prior to combustion are called the reactants. The resulting material is called the products. The process releases energy but the amount of energy depends upon the temperature before and after the reaction.

Consider a mixture of reactants at condition (1) which is burned and the resulting products are at condition (2). In order to solve problems we consider that the reactants are first cooled to a reference condition (0) by removing energy  $Q_1$ . The reaction then takes place and energy is released. The products are then brought back to the same reference conditions (0) by removing energy  $Q_2$ . The energy  $Q_1$  and  $Q_2$  are then returned so that the final condition of the products is reached (2).

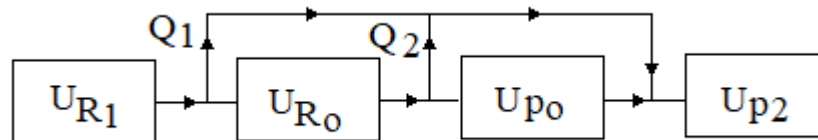


Figure 2

For constant volume combustion (closed system), we use Internal Energy. Balancing we have

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

The energy released by combustion is in this case the Internal Energy of combustion and this occurs at standard conditions of 1 bar and 25°C. This pressure is designated  $p^\theta$  and the internal energy of combustion is designated  $\Delta U^\theta$ . When this is based on 1 kmol it is designated  $\Delta u^\theta$

$$U_{p2} - U_{R1} = (U_{R0} - U_{R1}) + \Delta U_o^\theta + (U_{p2} - U_{p0})$$

The standard conditions chosen for the combustion are 1 bar and 25°C. At this temperature the internal energy of all gases is the same (-2 479 kJ/kmol). The figure is negative because the zero value of internal energy arbitrarily occurs at a higher temperature.

If the process is conducted in a steady flow system, enthalpy is used instead of internal energy. The reasoning is the same but  $U$  is replaced by  $H$ .

$$H_{p2} - H_{R1} = (H_{R0} - H_{R1}) + \Delta H_o^\theta + (H_{p2} - H_{p0})$$

$\Delta h_o^\theta$  may be found in the thermodynamic tables for some fuels. The figures are quoted in kJ per kmol of substance.

For the products In terms of kmol fractions  $h_{p0} = u_{p0} + n_p R_o T_o$

For the reactants In terms of kmol fractions  $h_{R0} = u_{R0} + n_R R_o T_o$

Where  $n$  is the kmols.

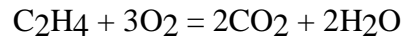
$$\Delta h_o^\theta = (u_{pO} + n_p R_o T_o) - (u_{RO} + n_R R_o T_o)$$

$$\Delta h_o^\theta = (u_{pO} - u_{RO}) - n_R R_o T_o + n_p R_o T_o$$

$$\Delta h_o^\theta = (u_{pO} - u_{RO}) + (n_p - n_R) R_o T_o$$

$$\Delta u_o^\theta = \Delta h_o^\theta + (n_p - n_R) R_o T_o$$

If the combustion produces equal numbers of kmols before and after, the pressure would be constant (assuming constant volume and no condensation).  $n_p = n_R$  so  $\Delta h_o^\theta$  is the same as the internal energy of reaction  $\Delta v_o^\theta$ . For example consider the combustion of ethylene.



In this case there are 4 kmols before and after. When this occurs, we may use the specific heat  $c_p$  to solve the problems.  $\Delta u_o^\theta = \Delta h_o^\theta = c_p \Delta T$

The specific heats are listed in the thermodynamic tables.

Note that in order to make the method of solution conform to standard data, the combustion equations should always be based on 1 kmol of fuel. The heat transfer  $Q_1$  is found either by use of the mean specific heat or by looking up the enthalpy of the gas at the required temperatures (enthalpy of formation) and deducing the change.

In general for a constant volume we should use  $\Delta u_o^\theta$  and  $C_v$  to solve problems.

For constant pressure with no work being done (e.g. a combustion chamber) we should use  $\Delta h_o^\theta$  and  $C_p$ .

Since tables only list  $\Delta h_o^\theta$  and  $C_p$  we may find

$\Delta u_o^\theta = \Delta h_o^\theta + (n_p - n_R) R_o T_o$  where  $T_o$  is 298.1 K and  $R_o$  is 8.314 kJ/kmol K and  $n$  is the number of kmols of product.

$$C_v = C_p - R = C_p - R_o / \text{molecular mass}$$



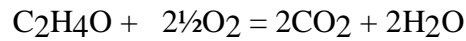
### WORKED EXAMPLE No. 8

1. A vessel contains  $0.2 \text{ m}^3$  of  $\text{C}_2\text{H}_4\text{O}$  and oxygen in its stoichiometric ratio. The mixture is at 1 bar pressure and  $25^\circ\text{C}$ . The mixture is ignited and allowed to cool back to  $25^\circ\text{C}$ . Determine
- The final pressure.
  - The amount of condensate formed.
  - The heat transfer.
  - The enthalpy of reaction per kmol of  $\text{C}_2\text{H}_4\text{O}$ .

The enthalpy of formation ( $\Delta h_o^\theta$ ) for the gases involved is shown below for a temperature of 298 K.

	Molecular mass. kg/kmol	Enthalpy of reaction (kJ/kmol)
$\text{CO}_2(\text{gas})$	44	- 393 520
$\text{H}_2\text{O}(\text{gas})$	18	- 241 830
$\text{H}_2\text{O}(\text{liquid})$	18	-285 820
$\text{O}_2(\text{gas})$	32	0
$\text{C}_2\text{H}_4\text{O}$	44	-52 630

## SOLUTION



mass ratio	44	80	88	36
kmol ratio	1	2½	2	1

$$p = 1 \text{ bar} \quad V = 0.2 \text{ m}^3 \quad T = 298 \text{ K}$$

$$V = 0.2 \text{ m}^3 = V_f + V_{\text{ox}} = 3\frac{1}{2} \text{ Volumes}$$

$$p = 1 \text{ bar} = p_f + p_{\text{ox}}$$

$$p_f = 1 \times (1/3.5) = 0.2857 \text{ bar}$$

$$p_{\text{ox}} = 1 \times (2.5/3.5) = 0.7143 \text{ bar}$$

Mass of fuel

$$m_f = \frac{pV\tilde{N}}{R_oT} = \frac{0.2857 \times 10^5 \times 0.2 \times 44}{8\,314.4 \times 298} = 0.1015 \text{ kg}$$

Mass of oxygen

$$m_{\text{ox}} = \frac{pV\tilde{N}}{R_oT} = \frac{0.7143 \times 10^5 \times 0.2 \times 32}{8\,314.4 \times 298} = 0.1845 \text{ kg}$$

$$\text{Total mass} = 0.286 \text{ kg}$$

$$\text{Mass of CO}_2 = (88/124) \times 0.286 = 0.203 \text{ kg}$$

$$\text{Mass of H}_2\text{O} = (36/124) \times 0.286 = 0.083 \text{ kg}$$

$$\text{Total mass} = 0.286 \text{ kg}$$

$$p(\text{CO}_2) = \frac{mR_oT}{\tilde{N}V} = \frac{0.203 \times 8\,314.4 \times 298}{44 \times 0.2} = 0.5716 \times 10^5 = 0.5716 \text{ bar}$$

Since condensate forms, the gas is saturated with water vapour.

Hence  $p(\text{vapour}) = p_g$  @ 28°C from the steam tables.

$$p(\text{vapour}) = 0.03166 \text{ bar}$$

$$\text{Total pressure} = 0.5716 + 0.03166 = 0.603 \text{ bar (answer (i))}$$

$$\text{Mass of vapour} = V/v_g$$

Where  $v_g = 43.4 \text{ m}^3/\text{kg}$  @ 28°C from tables.

$$\text{Mass of vapour} = 0.2/43.4 = 0.004608 \text{ kg}$$

$$\text{Mass of condensate formed} = 0.083 - 0.0046 = 0.0784 \text{ kg}$$

**Answer (ii)**

Now consider the reaction.

Since it starts and finishes at 25°C there is no initial cooling required ( $Q_1 = 0$ ).

## REACTANT

Fuel                      Mass = 0.1015 kg   kmol = 0.1015/44 = 0.00231 kmol  
Oxygen Mass = 0.1845 kg   kmol = 0.1845/32 = 0.00576 kmol

Enthalpy of formation for oxygen = 0  
Enthalpy of formation for C<sub>2</sub>H<sub>4</sub>O = -52 630 kJ/kmol  
H<sub>f</sub> = 0.00231(-52 630) = -121.4 kJ (Minus relative to higher point of reference)

## PRODUCTS

CO<sub>2</sub>   kmol = 0.203/44 = 0.00461 kmol  
H<sub>f</sub> = 0.00461 x (-393 520) = - 1 815.6 kJ

H<sub>2</sub>O (gas)              kmol = 0.0408/18 = 0.00227 kmol  
H<sub>f</sub> = 0.00227 x (-241 830) = - 548.1 kJ

H<sub>2</sub>O (water)           kmol = 0.0784/18 = 0.00436 kmol  
H<sub>f</sub> = 0.00436 × (-285 820) = - 1 244.9 kJ  
Total = -3 608 kJ

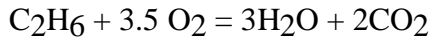
The change in enthalpy = -3 608 - (-121.4) = **-3 486.6 kJ = ΔH<sub>o</sub>**    **Answer (iv)**

Δh<sub>o</sub><sup>θ</sup> = -3 486.6/0.00231 = **1.509 GJ/kmol**    **Answer (v)**

### WORKED EXAMPLE No. 9

Air and Ethane ( $C_2H_6$ ) are mixed with twice the stoichiometric ratio at 600K in a vessel at 12 bar pressure. Determine the temperature and pressure after combustion assuming no energy losses. The enthalpy of combustion at 25°C is  $\Delta H_0 = -1\,427\,860$  kJ/kmol

### SOLUTION



kmol 1            3.5        3        2

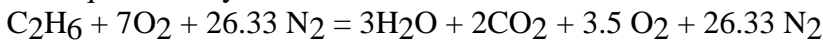
The air required =  $3.5/0.21 = 16.67$  kmol

Actual air = 33.33 kmol

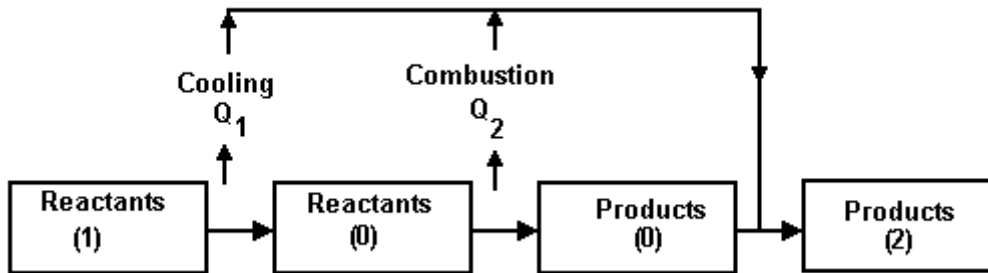
Nitrogen =  $0.79 \times 33.33 = 26.33$  kmol

Excess oxygen = 3.5 kmol

The equation may be rewritten as



The process may be idealised as follows



First find the enthalpy of the reactants. The mean temperature of the reactants relative to 25°C is  $\{(25+273) + 600\}/2 = 449$ K near enough 450K for the tables. We look up specific heats in the thermodynamic tables at 450 K. The temperature change from 25°C to 600 K is 302 K. We proceed to work out the heat transfer based on 1 kmol of fuel,  $Q_1$  as follows.

Table of values

$C_2H_6$              $C_p = 2.402$  kJ/kg K    mass = 1 kmol  $\times$  30 = 30 kg  
 $Q_1 = 30 \times 2.402 \times 302 = 21\,762$  kJ

$O_2$                  $C_p = 0.956$  kJ/kg K    mass = 7 kmol  $\times$  32 = 224 kg  
 $Q_1 = 224 \times 0.956 \times 302 = 64\,671.5$  kJ

$N_2$                  $C_p = 1.049$  kJ/kg K    mass = 26.33 kmol  $\times$  28 = 737.24 kg  
 $Q_1 = 737.24 \times 1.049 \times 302 = 233\,556$  kJ

Total  $Q_1 = -319\,989.7$  kJ per kmol of fuel (negative leaving system)

Next we repeat the process for the products to find  $Q_1 + Q_2$

In order to use a mean specific heat we must guess the approximate final temperature of the products. A good guess is always 2000 K so the mean of 25°C and 2000 K is near enough 1150 K. Using this we work out the heat transfer to the products with an unknown temperature change from 25°C to  $T_2$  of  $\Delta T$ .

$$\text{H}_2\text{O} \quad C_p = 2.392 \text{ kJ/kg K} \quad \text{mass} = 3 \text{ kmol} \times 16 = 48 \text{ kg}$$

$$Q = 48 \times 2.392 \times \Delta T = 114.8 \Delta T$$

$$\text{O}_2 \quad C_p = 1.109 \text{ kJ/kg K} \quad \text{mass} = 3.5 \text{ kmol} \times 32 = 112 \text{ kg}$$

$$Q_1 = 112 \times 1.109 \times \Delta T = 124.2 \Delta T$$

$$\text{N}_2 \quad C_p = 1.196 \text{ kJ/kg K} \quad \text{mass} = 26.33 \text{ kmol} \times 28 = 737.24 \text{ kg}$$

$$Q = 737.24 \times 1.196 \times \Delta T = 881.7 \Delta T$$

$$\text{CO}_2 \quad C_p = 1.270 \text{ kJ/kg K} \quad \text{mass} = 2 \text{ kmol} \times 44 = 88 \text{ kg}$$

$$Q = 88 \times 1.270 \times \Delta T = 111.76 \Delta T$$

Total  $Q_1 + Q_2 = 1232.5 \Delta T$  kJ per kmol of fuel (positive entering system)

$$Q_2 = -1427860 \text{ kJ/kmol of fuel (from question).}$$

Conserving energy we have  $1232.5 \Delta T = 1427860 + 319989.7$

Hence  $\Delta T = 1232.5 \text{ K}$  and  $T_2 = 1716 \text{ K}$  which is different from our original guess of  $2000 \text{ K}$  but more accurate.

Next we must repeat the last stage with a more accurate mean temperature.

Mean temperature =  $(298 + 1716)/2 = 1007 \text{ K}$ . Say  $1000 \text{ K}$ .

$$\text{H}_2\text{O} \quad C_p = 2.288 \text{ kJ/kg K} \quad Q = 48 \times 2.288 \times \Delta T = 109.8\Delta T$$

$$\text{O}_2 \quad C_p = 1.090 \text{ kJ/kg K} \quad Q_1 = 112 \times 1.09 \times \Delta T = 122.1\Delta T$$

$$\text{N}_2 \quad C_p = 1.167 \text{ kJ/kg K} \quad Q = 737.24 \times 1.167 \times \Delta T = 860.4\Delta T$$

$$\text{CO}_2 \quad C_p = 1.234 \text{ kJ/kg K} \quad Q = 88 \times 1.234 \times \Delta T = 108.6\Delta T$$

Total  $Q_1 + Q_2 = 1201\Delta T$  kJ per kmol of fuel (positive entering system)

Conserving energy we have  $1201\Delta T = 1427860 + 319989.7$

$\Delta T = 1455 \text{ K}$  and  $T_2 = 1753 \text{ K}$  which is different from our original guess of  $1716 \text{ K}$  but more accurate. The true answer is between  $1716$  and  $1753 \text{ K}$  and may be narrowed down by making more steps but two is usually sufficient.

Finally the pressure.  $p_1 V_1 / N_1 T_1 = R_0 = p_2 V_2 / N_2 T_2$  and the volumes are equal.

$$p_1 = 12 \text{ bar} \quad T_1 = 600 \text{ K} \quad N_1 = 4.5 \text{ kmol}$$

$$T_2 = 1753 \text{ K} \quad N_2 = 5 \text{ kmol}$$

$$p_2 = 12 \times 5 \times 1753 / (4.5 \times 600) = 38.9 \text{ bar}$$

### SELF ASSESSMENT EXERCISE No. 4

- The gravimetric analysis of a fuel is Carbon 78%, hydrogen 12%, oxygen 5% and ash 5%. The fuel is burned with 20% excess air. Assuming complete combustion, determine
  - the composition of the products.  
(72.6% N<sub>2</sub>, 17.3% CO<sub>2</sub>, 6.5% H<sub>2</sub>O and 3.6% O<sub>2</sub>)
  - the dew point of the products. (47°C)
  - the mass of water condensed when the products are cooled to 30°C. (0.67 kg)
- Carbon monoxide is burned with 25% excess oxygen in a fixed volume of 0.2 m<sup>3</sup>. The initial and final temperature is 25°C. The initial pressure is 1 bar. Calculate
  - the final pressure. (0.874 bar)
  - the heat transfer. (574.5 kJ)

Use your thermodynamic tables for enthalpies of reaction.

- Prove that the enthalpy and the internal energy of reaction are related by  
$$\Delta H_O = \Delta U_O + R_O T_O (n_P - n_R)$$
where  $n_P$  and  $n_R$  are the kmols of products and reactants respectively.

Ethylene (C<sub>2</sub>H<sub>4</sub>) and 20% excess air at 77°C are mixed in a vessel and burned at constant volume. Determine the temperature of the products. You should use your thermodynamic tables to find  $\Delta U_O$  or  $\Delta H_O$  and the table below. (Answer 2263 K)

T(K)	C <sub>2</sub> H <sub>4</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O
		U (kJ/kmol)			
298.15	-2 479	-2 479	-2 479	-2 479	-2 479
300	-2 415	-2 440	-2 440	-2 427	-2 432
400	-1 557	-297	-355	683	126
2 400		54 537	50 696	95 833	73 650
2 600		60 657	50 696	95 833	73 650
2 800		66 864	62 065	117 160	92 014
3 000		73 155	67 795	127 920	101 420

- An engine burns hexane (C<sub>6</sub>H<sub>14</sub>) in air. At a particular running condition the volumetric analysis of the dry products are
  - CO<sub>2</sub> 8.7%
  - CO 7.8 %
  - N<sub>2</sub> 83.5%

Calculate the air-fuel ratio by mass and find the stoichiometric ratio.  
(Answer 12.9 and 15.17)

## 7. Dissociation

At the high temperatures and pressures experienced in combustion, dissociation occurs. This results in some of the fuel not burning. CO is produced and in the case of hydrogen, some of it remains as hydrogen after the process even though oxygen is present. The reasons for this will not be covered here other than to say it is predicted by the 2nd law of thermodynamics and involves equilibrium in the chemical process.

When dissociation occurs, the energy released is reduced accordingly and if the amount of unburned fuel is known the previous examples may easily be modified to take account of it.

When hydrogen is burned, it can be shown that the partial pressures of the hydrogen, oxygen and water vapour present in the products are related by

$$k^\theta = \frac{p_{\text{H}_2\text{O}} p^\theta}{p_{\text{H}_2} (p_{\text{O}_2})^{1/2}}$$

The properties tables list values of  $\ln k^\theta$ .

Similarly when dissociation occurs in the formation of carbon dioxide, the relationship between the partial pressures of  $\text{CO}_2$ , CO and  $\text{O}_2$  is given by

$$k^\theta = \frac{p_{\text{CO}_2} p^\theta}{p_{\text{C}} p_{\text{CO}_2}}$$

Other similar equations for other combinations of products may be found in the tables.

### SELF ASSESSMENT EXERCISE No. 5

- Hydrogen is mixed with stoichiometric air at 25°C and burned adiabatically at constant volume. After combustion 6% of the hydrogen remains unburned. Determine the temperature and pressure of the products. (Answer the temperature is 2344K after two approximations)  
You need to find  $K^\theta$  in the tables. Also find  $\Delta H^\theta = 241\,800$  kJ/kmol. Deduce the partial pressures of the products as a fraction of  $p$  and then use  $K^\theta$  to solve  $p$ .
- A mixture of air and CO is burned adiabatically at constant volume. The air is 90% of the stoichiometric requirement. The mixture is initially at 5 bar and 400K. The only dissociation that occurs is  $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2$ .  
Show that the equilibrium constant at the final temperature  $T_2$  is

$$K_p = \frac{1.1212a}{(1-a)(0.9-a)^{1/2} \left(\frac{T_p}{T_R}\right)^{1/2}}$$

$a$  is the amount of  $\text{CO}_2$  kmol in the products per kmol of CO in the reactants.

If it assumed that initially  $T_2 = 2\,900$  K for which  $\log K_p = 0.649$ , the solution of the above equation gives  $a = 0.784$ . Check that at the assumed value of  $T_2$  given that the internal energy of reaction at  $T_0 = 298.15$  K is  $-281\,750$  kJ/kmol.

T (K)	U kJ/kmol			
	CO	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>
298.15	-2 479	-2 479	-2 479	-2 479
400	- 351	- 297	- 355	+ 683
2900	+65 715	+69 999	+64 924	+122 530