# *ICE CH. 5*

# Thermochemistry of Fuel & Stoichiometric

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## *Fuels:*

Fuel is any material when burnt will produce heat energy. Various fuels commonly used are as follows:

## Liquid Fuels:

Liquid fuels are widely used for I.C.E. Practically all liquid fuels have two basic combustible elements; carbon and hydrogen, present separately or in a combination called hydrocarbons, there are principal commercial types of liquid fuels:

The oxygen contained in the air unites chemically with carbon, hydrogen and other elements in fuel to produce heat. The amount of heat liberated during the combustion process depends on the amount of oxidation of the constituent of fuel and the nature of fuel. In order that the combustion of fuel may take place with high efficiency.

## *Petroleum and its Derivatives*

They are easy to handle, store, and burn and have nearly constant heating values. They are usually a mixture of hydrocarbons that may be represented by the molecular formula of the form $C_nC_m$, where *m* is a function of *n* that depends upon the family of the hydrocarbon.

## **Combustion of Fuels:**

Combustion of fuel is accomplished by mixing fuel with air at elevated temperature:

*Fuel + Air → Products of Combustion + Heat*

Following conditions must be fulfilled:

1. The amount of air supplied should be sufficient.
2. The air and fuel should be thoroughly mixed.
3. The temperature of the reactants should be high enough to ignite the mixture.
4. Sufficient time should be available to burn fuel completely

## Combustion Chemistry; Chemical Equation:

The chemical equation shows how the atoms of the reactants are arranged to form products. Before the chemical equation can be written it is necessary to know the number of atoms of elements in the molecules of the reactants and products.

During combustion process the atoms are rearranged to form new molecules, and the total number of atoms of each element is unchanged. A chemical equation expresses the principle of the conservation of mass in terms of the conservation of atoms

**The mole:** is the unit of measurement in the International System of Units (SI) for amount of substance, and has the unit symbol **mol**.

The mole is widely used in chemistry as a convenient way to express amounts of reactants and products of chemical reactions. For example, the chemical equation

**$2\ H_2 + O_2 \rightarrow 2\ H_2O$** implies that **2** mol of dihydrogen (**$H_2$**) and 1 mol of dioxygen (**$O_2$**) react to form **2** mol of water (**$H_2O$**).

*i- Combustion of Carbon:* $C + O_2 \rightarrow CO_2$

1 kmol $C$ + 1 kmol$O_2 \rightarrow$ 1 kmol$CO_2$

12 kg C + 32 kg$O_2$ $\rightarrow$ 44 kg$CO_2$

If any of the reactants or products is in solid or liquid phase, the volume occupied by them can be neglected. It follows that:

0 vol. $C$ + 1vol $O_2$ $\rightarrow$1 vol.$CO_2$

If *insufficient* oxygen is present for all carbon to burn to carbon dioxide, some will burn to carbon monoxide, then:

$C + 1/2O_2 \rightarrow CO$

*ii- Combustion of Hydrogen*

$H_2 + 1/2\ O_2 \rightarrow H_2O$

1 kmol $H_2$ + 1/2 kmol $O_2$ $\rightarrow$ 1 kmol $H_2O$

2kg $H_2$ + 16 kg $O_2$ $\rightarrow$ 18kg $H_2O$

1 vol. $H_2$ + 1/2 vol. $O_2$ $\rightarrow$ vol. $H_2O$ (vapour)

In most engineering combustion systems the necessary oxygen is obtained by mixing the fuel with air (except rockets) and it is necessary to use accurate and consistent analysis of air by mass and by volume. It is usual in combustion calculations to take air as (23.3% $O_2$, 76.7% $N_2$) by mass, and (21% $O_2$, 79%$N_2$) by volume. The small traces of other gases in dry air are included in the nitrogen, which is sometimes called "*atmospheric nitrogen*".

| Substance | Formula | M | State | Btu/$lb_m$ | kJ/kg |
|---|---|---|---|---|---|
| Carbon | $C$ | 12.011 | solid | 0 | 0 |
| Oxygen | $O_2$ | 32.000 | gas | 0 | 0 |
| Hydrogen | $H_2$ | 2.016 | gas | 0 | 0 |
| Nitrogen | $N_2$ | 28.016 | gas | 0 | 0 |
| Sulfur | $S$ | 32.060 | solid | 0 | 0 |
| Carbon monoxide | $CO$ | 28.011 | gas | −1697.6 | −3948.3 |
| Carbon dioxide | $CO_2$ | 44.011 | gas | −3846.7 | −8946.8 |
| Water | $H_2O$ | 18.016 | liquid | −6825.7 | −15,875.5 |
| | | | vapor | −5774.6 | −13,430.8 |
| Methane | $CH_4$ | 16.043 | gas | −2007.8 | −4669.8 |
| Ethane | $C_2H_6$ | 30.070 | gas | −1211.3 | −2817.3 |
| Propane | $C_3H_8$ | 44.097 | gas | −1013.1 | −2356.3 |
| Butane | $C_4H_{10}$ | 58.124 | gas | −933.7 | −2171.6 |
| Octane | $C_8H_{18}$ | 114.230 | liquid | −941.4 | −2189.5 |
| | | | vapor | −785.1 | −1826.0 |
| Nitric oxide | $NO$ | 30.008 | gas | −1298.8 | −3020.8 |
| Nitrogen dioxide | $NO_2$ | 46.008 | gas | −315.3 | −733.3 |
| Sulfur dioxide | $SO_2$ | 64.060 | gas | −1992 | −4632.8 |

The moisture or humidity in atmospheric air varies over wide limits, depending on meteorological conditions. Its presence in most cases simply implies an additional amount of inert material. The molar mass of $O_2$ can be taken as 32 kg/kmol, and that of $N_2$ as 28 kg/kmol and air 29 kg/kmol. Since oxygen is accompanied by nitrogen when air is supplied for combustion, then this nitrogen should be included in the combustion equation, it will appear on both sides of the equation. With one mole of $O_2$ there are 79/2=3.762moles of N2, Hence:

$$C + O_2 + \frac{79}{21}N_2 \rightarrow CO_2 + \frac{79}{21}N_2$$

Also

$$H_2 + \frac{1}{2}(O_2 + \frac{79}{21}N_2) \rightarrow H_2O + \frac{1}{2}\times\frac{79}{21}N_2$$

A frequently used quantity in the analysis of combustion process is the *air-fuel ratio* A/F. it is defined as the ratio of the mass of air to the mass of fuel for a combustion process.

$$A/F = \frac{m_a}{m_f} = \frac{mass\ of\ air}{mass\ of\ fuel}$$

The mass m of a substance is related to the number of moles n through the relation: $m = nM$, where M is the *molar mass*.

The reciprocal of A/F ratio is called the *fuel-air ratio*. The minimum amount of air needed for the complete combustion of a fuel is called the stoichiometric or theoretical air. In actual combustion processes, it is common practice to use more air than the stoichiometric amount. The amount of extra air than the stoichiometric is called (***excess air***).

Amount of air less than stoichiometric amount is called (*deficiency of air*).

***Equivalence ratio:*** is the ratio of the:

$$\frac{\text{actual fuel– air ratio}}{\text{stoichiometric fuel–air ratio}}$$

***Mixture strength:***

Sometimes this ratio is given in term of A/F ratio and called

$$Mixture\,strength = \frac{Stoichiometric\ A/F\ Ratio}{Actual\ A/F\ Ratio}$$

$$Equivalence\,ratio = \frac{Actual\,(F/A)\,ratio}{Stoich.\,(F/A)\,ratio} = \phi$$

$$\phi = \frac{(F/A)\,actual}{(F/A)\,stoich} = \frac{(A/F)\,stoich}{(A/F)\,actual}$$

*Where:*

- $\phi = 1$: stoichiometric
- $\phi < 1$: lean (week) mixture- excess of air.
- $\phi > 1$: rich mixture- deficiency of air.

A general reaction equation of a hydrocarbon fuel for stoichiometric condition with air is given by:

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 + 3.762\left(n + \frac{m}{4}\right)N_2 \rightarrow nCO_2 + \frac{m}{2}H_2O + 3.762\left(n + \frac{m}{4}\right)N_2$$

The composition of a hydrocarbon fuel $C_nH_m$ are carbon and hydrogen, n and m can be determined for 1 kg of fuel as follows:

$$\frac{Weight\ of\ C\ in\ fuel}{Weight\ of\ fuel} = \frac{C}{1} = \frac{12n}{12n + 2.02\frac{m}{2}} = \frac{12n}{12n + m}$$

**Exhaust and Flue Gas Analysis:**

The products of combustion are mainly gaseous. When a sample is taken for analysis it is usually cooled down to a temperature which is below the saturation temperature of the steam present. The steam content is therefore not included in the analysis, which is then quoted as the analysis of *dry products*. Since the products are gaseous, it is usual to quote the analysis by volume. An analysis which includes the steam in the exhaust is called a *wet analysis*.

**Example (3 – 1):**

Find the stoichiometric A/F ratio for the combustion of ethyl-alcohol ( $C_2H_5$ OH) in a petrol engine. Calculate the A/F ratios for 0.9&1.2 equivalence ratios(ϕ). Determine the wet and dry analyses by volume of the exhaust gas for each equivalence ratio.

**Solution:**

Combustion equation of ethyl-alcohol is:

$$C_2H_5OH + 3O_2 + 3\times\frac{79}{21}N_2 \rightarrow 2CO_2 + 3H_2O + 3\times\frac{79}{21}N_2$$

One mole of fuel has a mass of $(2\times12+16+6) = 46$ kg

Mass of air required for complete burning of one mole of fuel is:

$$\left(3\times 32+3\frac{79}{21}\times 28\right)=412.0\,kg$$

$$\therefore \text{Stoichiometric A/F ratio}=\frac{412}{46}=8.96/1$$

$$Equivalence\ ratio(\phi)=\frac{(A/F)stoich.}{(A/F)actual}$$

$$0.9=\frac{8.96}{(A/F)_{actual}}$$

$$(A/F)_{\text{actual}}=8.96/0.9=9.95$$

$$\text{Volumetric A/F ratio}=3\times(1+3.762)=14.3$$

For $\phi = 0.9$; air supplied is 1/0.9 = 1.11 times as much air supplied for complete combustion, then: combustion equation becomes:

$$C_2H_5OH + 1.11\left(3O_2 + 3\times\frac{79}{21}N_2\right) \rightarrow 2CO_2 + 3H_2O + 0.11\times 3O_2 + 1.11\times 3\times\frac{79}{21}N_2$$

i.e. The total number of moles of products = 2+3+0.33+12.54 =17.87.

Hence wet analysis is:

Total dry moles = 2+0.33+12.54=14.87

Hence dry analysis is:

$$\frac{2}{17.87}\times 100 = 11.20\%\ CO_2; \qquad \frac{3}{17.87}\times 100 = 16.80\%\ H_2O$$

$$\frac{0.33}{17.87}\times 100 = 1.85\%\ O_2; \qquad \frac{12.54}{17.87}\times 100 = 70.20\%\ N_2$$

For $\phi = 1.2$:

$$\text{Actual A/F ratio} = \frac{8.96}{1.2} = 7.47:1$$

This means that 1/1.2 = 0.834of the stoichiometric air is supplied. The combustion cannot be complete & is usual to assume that all the hydrogen is burned to $H_2$O, since $H_2$atoms have a greater affinity for oxygen than $C$ atoms. The carbon in the fuel will burn to $CO$ and $CO_2$:

$$C_2H_5OH + 0.834(3O_2 + 3\text{x}3.762N_2) \rightarrow \text{a}\,CO_2 +$$

$$\text{b}\,CO + 3H_2\text{O} + 0.834 \times 3 \times 3.762N_2$$

C balance: 2 = a + b

O balance: 1+2 × 0.834 × 3=2a+b+3

Subtracting the equations gives: a=1.004

and then: b =2 – 1.004 =0.996

i.e. The products are:1.004 moles $CO_2$ + 0.996 moles $CO$+3 moles $H_2$ + 9.41 moles $N_2$. The total moles of products = 1.004+0.996 +3+9.41 =14.41

Hence wet analysis is:

$$\frac{1.004}{14.41}\times 100 = 6.97\%\ CO_2; \qquad \frac{0.996}{14.41}\times 100 = 6.91\%\ CO$$

$$\frac{3}{14.41}\times 100 = 20.8\%\ H_2O; \qquad \frac{9.41}{14.41}\times 100 = 65.3\%\ N_2$$

The total dry moles =

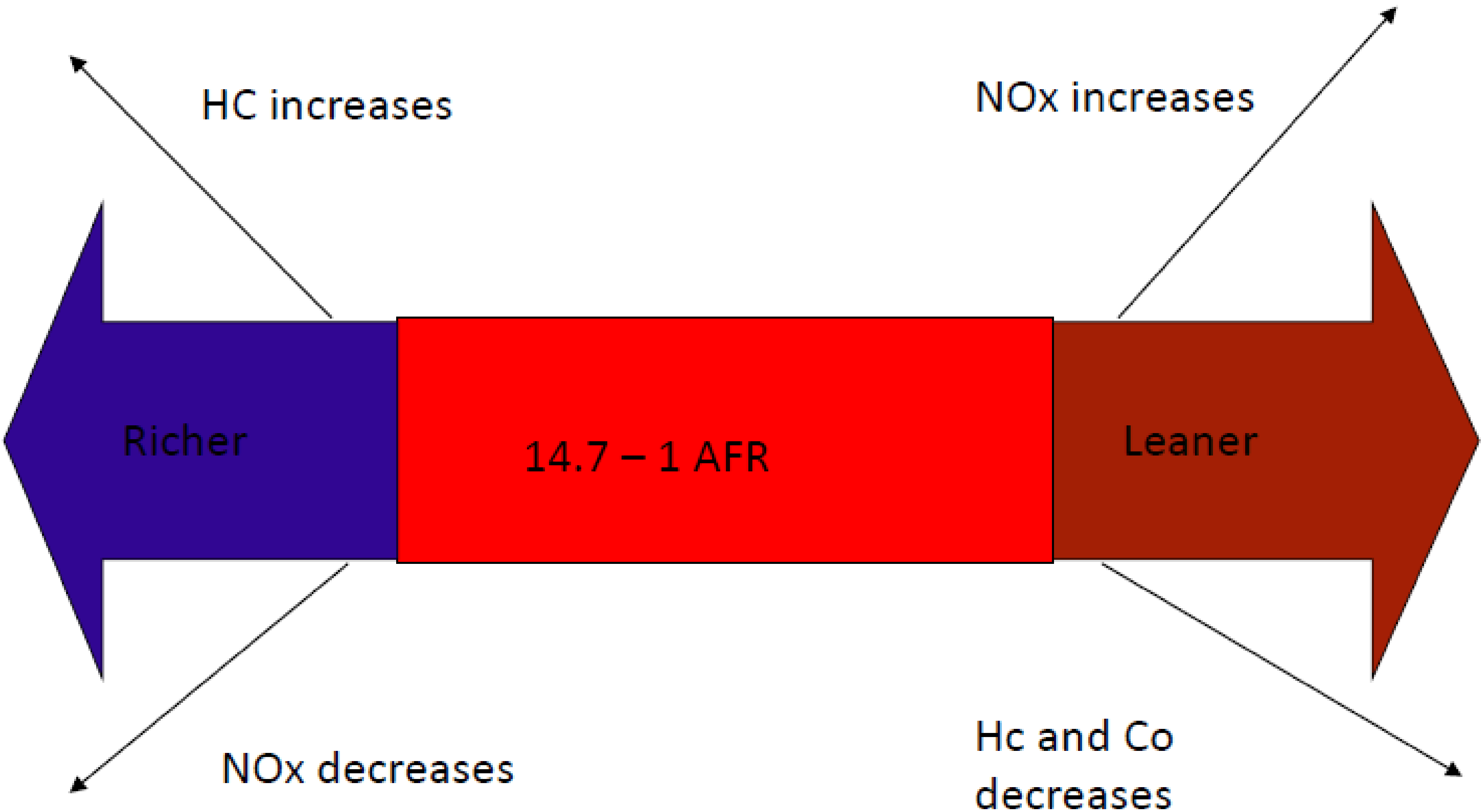
1.004+0.996+9.41=11.41

Hence dry analysis is:

$$\frac{1.004}{11.41}\times 100 = 8.80\%\ CO_2; \qquad \frac{0.996}{11.41}\times 100 = 8.73\%\ O_2$$

$$\frac{9.41}{14.41} = 82.47\%\ N_2$$

# Exhaust Gasses



Determine the air fuel ratio on both a molar and mass basis for the complete combustion of octane, $C_8H_{18}$, with (a) the theoretical amount of air (b) 50% excess air.

**Solution**

**(a) It is conveniently to conduct the calculation on the basis of 100 kg of dry product.**

$$C_8H_{18} + a\left(O_2 + 3.76N_2\right) \rightarrow bCO_2 + cH_2O + d\,N_2$$

$C$: $b=8$

$H$: $2c=18$

O: $2a=2b+c$

N: $2 \times 3.76a=2d \rightarrow 3.76a=d$

Solving these equations, $a = 12.5$, $b=8$, $c=9$, $d=47$. The balanced chemical equation is,

$$C_8H_{18}+(12.5)(O_2+3.76)N_2 \rightarrow 8CO_2+9H_2O+47\,N_2$$

$$\overline{AF}=\frac{12.5+12.5\times 3.76}{1}=59.5\,\frac{kmol(air)}{kmol\,(fuel)}$$

The air fuel ratio expressed on a mass basis is

$$AF=\overline{AF}\left(\frac{M_{air}}{M_{fuel}}\right)=59.5\left(\frac{28.97}{114.22}\right)=15.1\,\frac{kg\,(air)}{kg\,(fuel)}$$

**(b)**

$$C_8H_{18}+1.5(12.5)(O_2+3.76\,N_2)\rightarrow bCO_2+cH_2O+d\,N_2+eO_2$$

**Example 3.4**

Methane, $CH_4$, is burned with dry air. The molar analysis of the products on a dry basis is $CO_2$, *9.7%*, *CO*, *0.5%*, $O_2$, *2.95%* and $N_2$, *86.85%*. Determine (a) the air fuel ratio on both molar and a mass basis, (b) the percent theoretical air.

**Solution**

**(a)**

$$aCH_4 + b(O_2 + 3.76)N_2 \rightarrow 9.7CO_2 + 0.5CO + 2.95O_2 + 86.85N_2 + cH_2O$$

$C$: $9.7+0.5=a$

$H$: $2c=4a$

$O$: $2b=(9.7)(2)+0.5+2(2.95)+c$

Solving this set of equations gives $a=10.2$, $b=23.1$, $c=20.4$. The balanced chemical equation is

$$10.2CH_4 + 23.1(O_2 + 3.76)N_2 \rightarrow 9.7CO_2 + 0.5CO + 2.95O_2 + 86.85N_2 + 20.4H_2O$$

The air fuel ratio on a molar mass is

$$\overline{AF} = \frac{23.1 + 23.1 \times 3.76}{10.2} = 10.78\,\frac{kmol(air)}{kmol\,(fuel)}$$

The air fuel ratio expressed on a mass basis is

$$AF = \overline{AF}\left(\frac{M_{air}}{M_{fuel}}\right) = 10.78\left(\frac{28.97}{16.04}\right) = 19.47\,\frac{kg\,(air)}{kg\,(fuel)}$$

(b)

The balanced chemical equation for the complete combustion of methane with the theoretical amount of air is

$$CH_4 + a\left(O_2 + 3.76\right)N_2 \rightarrow bCO_2 + cH_2O + d\,N_2$$

Applying the conservation of mass principles, results in four equations among the four unknowns

C: $b=1$

H: $2c=4$

O: $2a=2b+c$

N: $2 \times 3.76a=2d \rightarrow 3.76a=d$

Solving these equations, the balanced chemical equation is

$$CH_4 + 2\left(O_2 + 3.76\right)N_2 \rightarrow CO_2 + 2H_2O + 7.52\,N_2$$

The theoretical air fuel ratio on a molar basis is

$$\overline{AF}_{theo} = \frac{2 + 2 \times 3.76}{1} = 9.52 \frac{kmol(air)}{kmol\,(fuel)}$$

The percent theoretical air is then found from

## Example 3.3

Determine the molar analysis of the products of combustion when octane, $C_8H_{18}$ is burned with 200% theoretical air, and determine the dew point* of the products if the pressure is 100 kPa.

## Example 3.6 (4.3)

An unknown hydrocarbon fuel, $C_xH_y$ was allowed to react with air. The analysis of product gases by volume gave: $CO_2$ 12.1%, $O_2$ 3.8% and $CO$ 0.9%. Determine (a) the chemical equation for the actual reaction, (b) the composition of the fuel, (c) the air fuel ratio during the test, and (d) the excess or deficiency of air used.