ESO201A

Lecture#26

(Class Lecture)

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First Law Application to Chemically Reacting Systems

Fuels and Combustion

Fuel

- Any material that can be burned to release thermal energy is called a fuel.

- Most familiar fuels consist of primarily hydrogen and carbon. They are called hydrocarbon fuels and are denoted by the general formula C_nH_m.

- Fuels exist in all phases, some examples being coal, gasoline and natural gas.

Coal

- The main constituent of coal is carbon.
- Coal also contains varying amounts of oxygen, hydrogen, nitrogen, sulfur (also spelled as sulphur), moisture and ash.
- It is difficult to give an exact mass analysis for coal since its composition varies considerably from one geographical area to the next and even within the same geographical location.

Liquid Hydrocarbon Fuels

- Although liquid hydrocarbon fuels are mixtures of many different hydrocarbons, they are usually considered to be a single hydrocarbon for convenience.

- For example, gasoline is treated as octane, C_8H_{18}, and the diesel fuel as dodecane, $C_{12}H_{26}$.

- Another common liquid hydrocarbon fuel is methyl alcohol, CH_3OH, which is also called methanol and is used in some gasoline blends.

Gaseous Hydrocarbon Fuel

- Natural gas which is a mixture of methane and smaller amounts of other gases, is often treated as methane, CH_4, for simplicity.

- On vehicles, natural gas is stored either in the gas phase at pressures of 150 to 250 atm as CNG (compressed natural gas), or in the liquid phase at $-162^{\circ}C$ as LNG (Liquefied natural gas).

- Liquefied petroleum gas (LPG) is a byproduct of natural gas processing or the crude oil refining. It consists mainly of propane (C_3H_8) and thus LPG is usually referred to as propane. LPG is used as a fuel for cooking in India. It is also used in vehicles.

Combustion

- A chemical reaction during which a fuel is oxidized and a large quantity of energy is released is called <u>combustion</u>.

- The oxidizer most often used in combustion is air.

- On a mole or volume basis, dry air is composed of 21% O_2 and 79% N_2.

Therefore, each mole of oxygen entering a combustion chamber is accompanied by $0.79/0.21 = 3.76$ mole of nitrogen.

That is,

$$1 \text{ kmol } O_2 + 3.76 \text{ kmol } N_2 = 4.76 \text{ kmol air}$$

Ignition Temperature

The fuel must be brought above its ignition temperature to start the combustion. In air the ignition temperature of gasoline is approximately 260°c, 400°c for carbon, 580°c for hydrogen, 610°c for carbon monoxide, and 630°c for methane.

Balancing of Chemical Reaction Equations

- Chemical reaction equations are balanced on the basis of the conservation of mass principle (or the mass balance), which can be stated as follows:

  The total mass of each element is conserved during a chemical reaction. Thus, total mass of the reactants is equal to total mass of the products.

- However, the total number of moles is not conserved during a chemical reaction. Thus, total number of moles of reactants is not equal to total number of moles of products.

Air-Fuel Ratio

- Air-Fuel ratio (AF) is usually expressed on a mass basis and is defined as the ratio of the mass of air to the mass of fuel for a combustion process. That is,

$$AF = \frac{m_{air}}{m_{fuel}}$$

- 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 air-fuel ratio is called the <u>fuel-air ratio</u> (FA).

- $$(AF)_{mole} = \frac{N_{air}}{N_{fuel}}$$

Hence, $$(AF)_{mass} = \frac{m_{air}}{m_{fuel}} = \frac{N_{air} M_{air}}{N_{fuel} M_{fuel}} = (AF)_{mole} \frac{M_{air}}{M_{fuel}}$$

Theoretical and Actual Combustion Processes

Complete Combustion

A combustion process is complete if all the carbon in the fuel burns to CO_2, all the hydrogen burns to H_2O, and all the sulfur (if any) burns to SO_2.

Incomplete Combustion

A combustion process is incomplete if the combustion products contain any unburned fuel or components such as C, H_2, CO, OH or free O_2.

Reasons for Incomplete combustion

- Insufficient oxygen
- Insufficient mixing in the combustion chamber during the limited time that the fuel and oxygen are in contact. This can happen even when excess oxygen is present in the combustion chamber.
- Dissociation of water vapour into H_2 and O_2 as well as into H, O and OH at very high temperatures.

Stoichiometric or Theoretical Air

- The minimum amount of air needed for the complete combustion of a fuel is called the stoichiometric air or theoretical air.

- For example, the theoretical combustion of methane is

$$CH_4 + 2(O_2 + 3.76\,N_2) \longrightarrow CO_2 + 2H_2O + 7.52\,N_2$$

Notice that the products of the theoretical combustion contain no unburned methane and no C, H_2 CO, OH or free O_2.

Percent Excess Air or Percent Theoretical Air

- In actual combustion processes, it is common practice to use more air than the stoichiometric amount to increase the chances of complete combustion or to control the temperature of the combustion chamber.

- The amount of air (by mass) in excess of the stoichiometric amount is called excess air.

- The amount of excess air is usually expressed in terms of the stoichiometric air as percent excess air or percent theoretical air (by mass).

- For example, 50% excess air is equivalent to 150% theoretical air.

- $(AF) = (\text{Percent theoretical air})\,(AF)_s$

Deficiency of Air

- Amounts of air less than the stoichiometric amount are called deficiency of air and are often expressed as percent deficiency of air.
- For example, 90% theoretical air is equivalent to 10% deficiency of air.

Equivalence Ratio

- The amount of air used in combustion processes is also expressed in terms of the equivalence ratio, which is the ratio of actual fuel-air ratio to the stoichiometric fuel-air ratio.

- Thus, equivalence ratio, ϕ, is :

$$\phi = \frac{(FA)_{actual}}{(FA)_{stoichiometric}}$$

$$= \frac{(AF)_{stoichiometric}}{(AF)_{actual}}$$

In short,

$$\phi = \frac{FA}{(FA)_s} = \frac{(AF)_s}{AF}$$

Note : ϕ is the reciprocal of percent theoretical air.

Thus, 150% theoretical air means that the air actually supplied is 1.5 times the theoretical air and $\phi = 2/3$.

Example Problem #1

Calculate the theoretical air-fuel ratio for the combustion of octane, C_8H_{18}. $M_{air} = 28.97$ kg/kmol, $M_{octane} = 114.2$ kg/kmol

Solution

The combustion equation is

$$C_8H_{18} + 12.5\,O_2 + 12.5\,(3.76\,N_2)$$
$$\rightarrow 8\,CO_2 + 9\,H_2O + 47.0\,N_2$$

The air-fuel ratio on a mole basis is

$$(AF)_{mole} = \frac{12.5 + 47.0}{1}$$
$$= 59.5 \text{ kmol air/kmol fuel}$$

The air-fuel ratio on a mass basis is

$$(AF)_{mass} = \frac{m_{air}}{m_{fuel}} = \frac{N_{air}\,M_{air}}{N_{fuel}\,M_{fuel}}$$
$$= (AF)_{mole}\,\frac{M_{air}}{M_{fuel}}$$
$$= \frac{(59.5)(28.97)}{114.2}$$
$$= 15.09 \text{ kg air/kg fuel}$$

Example Problem #2

Methane (CH_4) is burned with atmospheric air. The analysis of the products on a dry basis is as follows:

CO_2	10.00 % by volume
O_2	2.37
CO	0.53
N_2	87.10
	100.00 %

Calculate the air-fuel ratio and the percent theoretical air and determine the combustion equation.

Solution

The following equation can be written for 100 kmol of dry products.

$$a\,CH_4 + b\,O_2 + c\,N_2 \rightarrow 10.0\,CO_2 + 0.53\,CO + 2.37\,O_2 + 87.1\,N_2 + d\,H_2O$$

Nitrogen (N2) balance : $c = 87.1$

Since all nitrogen comes from air

$$\frac{c}{b} = 3.76$$

$$\Rightarrow b = \frac{c}{3.76} = \frac{87.1}{3.76} = 23.16$$

Carbon (C) balance : $a = 10.00 + 0.53$
$= 10.53$

Hydrogen (H2) balance : $d = 2a$
$= 2(10.53)$
$= 21.06$

<u>Checking for accuracy</u>

Oxygen (O2) balance :

$$b = 10.00 + \frac{0.53}{2} + 2.37 + \frac{21.06}{2} = 23.16$$

Hence, the value of 'b' matches with each other in both calculations.

There fore, the final equation can be written as

$$10.53\,CH_4 + 23.16\,O_2 + 87.1\,N_2$$
$$\rightarrow 10.0\,CO_2 + 0.53\,CO + 2.37\,O_2 + 21.06\,H_2O + 87.1\,N_2$$

Dividing through by 10.53 yields the combustion equation per kmol of fuel.

$$CH_4 + 2.2\,O_2 + 8.27\,N_2$$
$$\rightarrow 0.95\,CO_2 + 0.05\,CO + 2H_2O$$
$$+ 0.225\,O_2 + 8.27\,N_2$$

The actual air-fuel ratio on a mole basis is

$$(AF)_{\text{actual, mole}} = \frac{2.2 + 8.27}{1}$$

$$= 10.47 \text{ kmol air/kmol fuel}$$

$$(AF)_{\text{actual, mass}} = (AF)_{\text{actual, mole}} \frac{M_{air}}{M_{fuel}}$$

$$= (10.47)\frac{28.97}{16.0}$$

$$= 18.97 \text{ kg air/kg fuel}$$

The theoretical air-fuel ratio is found by writing the combustion equation for theoretical air.

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

$$(AF)_{theo, mass} = \frac{(2 + 7.52)(28.97)}{16}$$

$$= 17.23 \text{ kg air/kg fuel}$$

The equivalence ratio, ϕ, is :

$$\phi = \frac{(AF)_{theo, mass}}{(AF)_{actual, mass}}$$

$$= \frac{17.23}{18.97}$$

Since $\phi = \frac{1}{\text{Percent theoretical air}}$

$\Rightarrow$ Percent theoretical air

$$= \frac{1}{\phi} = \frac{18.97}{17.23} = 110\%$$