Thermodynamics – MECH32102

Solution to Tutorial Questions

Chemical Reactions

Q1

Problem Statement

Is the air–fuel ratio expressed on a mole basis identical to the air–fuel ratio expressed on a mass basis?

Solution

No. Because the molar mass of the fuel and the molar mass of the air, in general, are different.

Q2

Problem Statement

A certain natural gas has the following volumetric analysis: 65 percent CH_4, 8 percent H_2, 18 percent N_2, 3 percent O_2, and 6 percent CO_2. This gas is now burned completely with the stoichiometric amount of dry air with moist air that enters the combustion chamber at 25°C, 1 atm, and 85 percent relative humidity. What is the air–fuel ratio for this combustion process?

Solution

The composition of a certain natural gas is given. The gas is burned with stoichiometric amount of moist air. The AF ratio is to be determined.

Assumptions

1. Combustion is complete. **2** The combustion products contain CO_2, H_2O, and N_2 only.

Properties

The molar masses of C, H_2, N_2, O_2, and air are 12 kg/kmol, 2 kg/kmol, 28 kg/kmol, 32 kg/kmol, and 29 kg/kmol, respectively (Table A-1).

Analysis

The fuel is burned completely with the stoichiometric amount of air, and thus the products will contain only H_2O, CO_2 and N_2, but no free O_2. The moisture in the air does not react with anything; it simply shows up as additional H_2O in the products. Therefore, we can simply balance the combustion equation using dry air, and then add the moisture to both sides of the equation.

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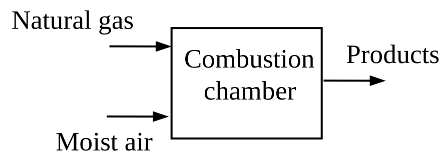
Considering 1 kmol of fuel, the combustion equation can be written as

$$(0.65CH_4 + 0.08H_2 + 0.18N_2 + 0.03O_2 + 0.06CO_2) + a_{th}(O_2 + 3.76N_2) \longrightarrow xCO_2 + yH_2O + zN_2$$

The unknown coefficients in the above equation are determined from mass balances,

$$C: 0.65 + 0.06 = x \longrightarrow x = 0.71$$
$$H: 0.65 \times 4 + 0.08 \times 2 = 2y \longrightarrow y = 1.38$$
$$O_2: 0.03 + 0.06 + a_{th} = x + y/2 \longrightarrow a_{th} = 1.31$$
$$N_2: 0.18 + 3.76a_{th} = z \longrightarrow z = 5.106$$



Thus,

$$(0.65CH_4 + 0.08H_2 + 0.18N_2 + 0.03O_2 + 0.06CO_2) + 1.31(O_2 + 3.76N_2)$$
$$\longrightarrow 0.71CO_2 + 1.38H_2O + 51.06N_2$$

Next we determine the amount of moisture that accompanies $4.76a_{th}$ = (4.76)(1.31) = 6.24 kmol of dry air. The partial pressure of the moisture in the air is

$$P_{v,\text{in}} = \phi_{\text{air}} P_{\text{sat @ 25°C}} = (0.85)(3.1698 \text{ kPa}) = 2.694 \text{ kPa}$$

Assuming ideal gas behavior, the number of moles of the moisture in the air ($N_{v,\text{ in}}$) is determined to be

$$N_{v,\text{in}} = \left(\frac{P_{v,\text{in}}}{P_{\text{total}}}\right) N_{\text{total}} = \left(\frac{2.694 \text{ kPa}}{101.325 \text{ kPa}}\right)(6.24 + N_{v,\text{in}}) \longrightarrow N_{v,\text{air}} = 0.1703 \text{ kmol}$$

The balanced combustion equation is obtained by substituting the coefficients determined earlier and adding 0.1703 kmol of H_2O to both sides of the equation,

$$(0.65CH_4 + 0.08H_2 + 0.18N_2 + 0.03O_2 + 0.06CO_2) + 1.31(O_2 + 3.76N_2) + 0.1703H_2O$$
$$\longrightarrow 0.71CO_2 + 1.550H_2O + 51.06N_2$$

The air-fuel ratio for the this reaction is determined by taking the ratio of the mass of the air to the mass of the fuel,

$$m_{\text{air}} = (1.31 \times 4.76 \text{ kmol})(29 \text{ kg/kmol}) + (0.1703 \text{ kmol} \times 18 \text{ kg/kmol}) = 183.9 \text{ kg}$$
$$m_{\text{fuel}} = (0.65 \times 16 + 0.08 \times 2 + 0.18 \times 28 + 0.03 \times 32 + 0.06 \times 44) \text{kg} = 19.20 \text{ kg}$$

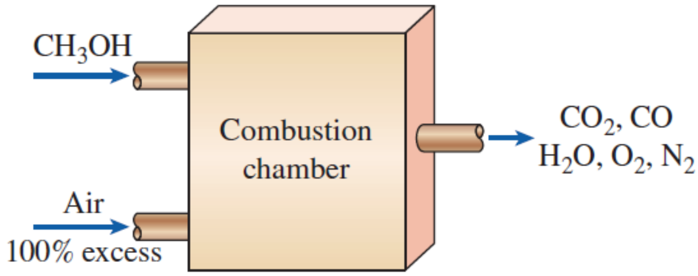
and

$$\text{AF}_{\text{th}} = \frac{m_{\text{air,th}}}{m_{\text{fuel}}} = \frac{183.9 \text{ kg}}{19.20 \text{ kg}} = \mathbf{9.58 \text{ kg air / kg fuel}}$$

Q3

Problem Statement

Methyl alcohol (CH_3OH) is burned with 100 percent excess air. During the combustion process, 60 percent of the carbon in the fuel is converted to CO_2 and 40 percent is converted to CO. Write the balanced reaction equation and determine the air–fuel ratio.



Solution

Methyl alcohol is burned with 100% excess air. The combustion is incomplete. The balanced chemical reaction is to be written and the air-fuel ratio is to be determined.

Assumptions

1. Combustion is incomplete. **2.** The combustion products contain CO_2, CO, H_2O, O_2, and N_2 only.

Properties The molar masses of C, H_2, O_2, N_2 and air are 12 kg/kmol, 2 kg/kmol, 32 kg/kmol, 28 kg/kmol, and 29 kg/kmol, respectively (Table A-1).

Analysis The balanced reaction equation for stoichiometric air is

$$CH_3OH + a_{th}\left[O_2 + 3.76N_2\right] \longrightarrow CO_2 + 2\ H_2O + a_{th} \times 3.76\ N_2$$

The stoichiometric coefficient a_{th} is determined from an O_2 balance:

$$0.5 + a_{th} = 1 + 1 \longrightarrow a_{th} = 1.5$$

Solution continued on next page...

Substituting,

$$CH_3OH + 1.5[O_2 + 3.76N_2] \longrightarrow CO_2 + 2\ H_2O + 1.5 \times 3.76\ N_2$$

The reaction with 100% excess air and incomplete combustion can be written as

$$CH_3OH + 2 \times 1.5[O_2 + 3.76N_2] \longrightarrow 0.60\ CO_2 + 0.40\ CO + 2\ H_2O + x\ O_2 + 2 \times 1.5 \times 3.76\ N_2$$

The coefficient for O_2 is determined from a mass balance,

O_2 balance:

$$0.5 + 2 \times 1.5 = 0.6 + 0.2 + 1 + x \longrightarrow x = 1.7$$

Substituting,

$$CH_3OH + 3[O_2 + 3.76N_2] \longrightarrow 0.6\ CO_2 + 0.4\ CO + 2\ H_2O + 1.7\ O_2 + 11.28\ N_2$$

The air-fuel mass ratio is

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{(3 \times 4.76 \times 29)\ \text{kg}}{(1 \times 32)\ \text{kg}} = \frac{414.1\ \text{kg}}{32\ \text{kg}} = \mathbf{12.94\ kg\ air\ /\ kg\ fuel}$$

Q4

Problem Statement

Determine the enthalpy of combustion of methane (CH_4) at 25°C and 1 atm, using the enthalpy of formation data from Table A–26. Assume that the water in the products is in the liquid form. Compare your result to the value listed in Table A–27.

Answer: –890,330 kJ/kmol

Solution

The enthalpy of combustion of methane at a 25°C and 1 atm is to be determined using the data from Table A-26 and to be compared to the value listed in Table A-27.

Assumptions The water in the products is in the liquid phase.

Analysis The stoichiometric equation for this reaction is

$$\mathrm{CH_4} + 2[\mathrm{O_2} + 3.76\mathrm{N_2}] \longrightarrow \mathrm{CO_2} + 2\mathrm{H_2O}(\ell) + 7.52\mathrm{N_2}$$

Both the reactants and the products are at the standard reference state of 25°C and 1 atm. Also, N_2 and O_2 are stable elements, and thus their enthalpy of formation is zero. Then the enthalpy of combustion of CH_4 becomes

$$h_C = H_P - H_R = \sum N_P \bar{h}^\circ_{f,P} - \sum N_R \bar{h}^\circ_{f,R} = \left(N\bar{h}^\circ_f\right)_{\mathrm{CO_2}} + \left(N\bar{h}^\circ_f\right)_{\mathrm{H_2O}} - \left(N\bar{h}^\circ_f\right)_{\mathrm{CH_4}}$$

Using $\bar{h}^o_f$ values from Table A-26,

$$\begin{aligned} h_C &= (1\text{ kmol})(-393{,}520\text{ kJ/kmol}) + (2\text{ kmol})(-285{,}830\text{ kJ/kmol}) \\ &\quad -(1\text{ kmol})(-74{,}850\text{ kJ/kmol}) \\ &= \mathbf{-890{,}330\ kJ}\,(\text{per kmol CH}_4) \end{aligned}$$

The listed value in Table A-27 is -890,868 kJ/kmol, which is almost identical to the calculated value. Since the water in the products is assumed to be in the liquid phase, this h_c value corresponds to the higher heating value of CH_4.

Q5

Problem Statement

A constant-volume tank contains a mixture of 120 g of methane (CH_4) gas and 600 g of O_2 at 25°C and 200 kPa. The contents of the tank are now ignited, and the methane gas burns completely. If the final temperature is 1200 K, determine (*a*) the final pressure in the tank and (*b*) the heat transfer during this process.

Solution

A mixture of methane and oxygen contained in a tank is burned at constant volume. The final pressure in the tank and the heat transfer during this process are to be determined.

Assumptions

1. Air and combustion gases are ideal gases. **2.** Combustion is complete.

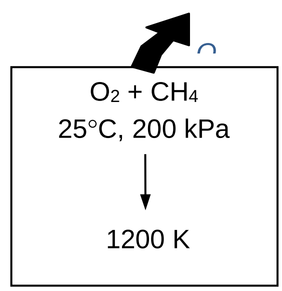
Properties

The molar masses of CH_4 and O_2 are 16 kg/kmol and 32 kg/kmol, respectively (Table A-1).

Analysis (*a*) The combustion is assumed to be complete, and thus all the carbon in the methane burns to CO_2 and all of the hydrogen to H_2O. The number of moles of CH_4 and O_2 in the tank are

$$N_{CH_4} = \frac{m_{CH_4}}{M_{CH_4}} = \frac{0.12 \text{ kg}}{16 \text{ kg/kmol}} = 7.5 \times 10^{-3} \text{ kmol} = 7.5 \text{ mol}$$

$$N_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{0.6 \text{ kg}}{32 \text{ kg/kmol}} = 18.75 \times 10^{-3} \text{ kmol} = 18.75 \text{ mol}$$



Then the combustion equation can be written as

$$7.5CH_4 + 18.75O_2 \longrightarrow 7.5CO_2 + 15H_2O + 3.75O_2$$

At 1200 K, water exists in the gas phase. Assuming both the reactants and the products to be ideal gases, the final pressure in the tank is determined to be

$$\left.\begin{array}{l} P_R V = N_R R_u T_R \\ P_P V = N_P R_u T_P \end{array}\right\} P_P = P_R \left(\frac{N_P}{N_R}\right)\left(\frac{T_P}{T_R}\right)$$

Solution continued on next page...

Substituting,

$$P_P = (200 \text{ kPa})\left(\frac{26.25 \text{ mol}}{26.25 \text{ mol}}\right)\left(\frac{1200 \text{ K}}{298 \text{ K}}\right) = \mathbf{805 \text{ kPa}}$$

which is relatively low. Therefore, the ideal gas assumption utilized earlier is appropriate.

(*b*) The heat transfer for this constant volume combustion process is determined from the energy balance $E_{in} - E_{out} = \Delta E_{system}$ applied on the combustion chamber with $W = 0$. It reduces to

$$-Q_{out} = \sum N_P \left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{V}\right)_P - \sum N_R \left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{V}\right)_R$$

Since both the reactants and products are assumed to be ideal gases, all the internal energy and enthalpies depend on temperature only, and the $P\bar{V}$ terms in this equation can be replaced by R_uT. It yields

$$-Q_{out} = \sum N_P \left(\bar{h}_f^\circ + \bar{h}_{1200\text{ K}} - \bar{h}_{298\text{ K}} - R_uT\right)_P - \sum N_R \left(\bar{h}_f^\circ - R_uT\right)_R$$

since the reactants are at the standard reference temperature of 25°C. From the tables,

Substance	$\bar{h}_f^\circ$ kJ/kmol	$\bar{h}_{298\text{ K}}$ kJ/kmol	$\bar{h}_{1200\text{ K}}$ kJ/kmol
CH_4	74,850	---	---
O_2	0	8682	38,447
H_2O (*g*)	241,820	9904	44,380
CO_2	393,520	9364	53,848

Thus,

$$\begin{aligned} -Q_{out} &= (7.5)(-393{,}520 + 53{,}848 - 9364 - 8.314 \times 1200) \\ &\quad + (15)(-241{,}820 + 44{,}380 - 9904 - 8.314 \times 1200) \\ &\quad + (3.75)(0 + 38{,}447 - 8682 - 8.314 \times 1200) \\ &\quad - (7.5)(-74{,}850 - 8.314 \times 298) - (18.75)(-8.314 \times 298) \\ &= -5{,}251{,}791 \text{ J} = -5252 \text{ kJ} \end{aligned}$$

Thus $Q_{out} = \mathbf{5252 \text{ kJ}}$ of heat is transferred from the combustion chamber as 120 g of CH_4 burned in this combustion chamber.