

Thermodynamics in the News...

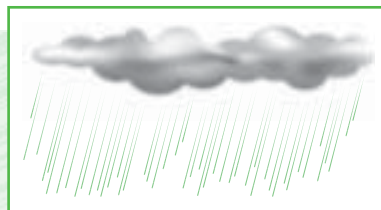
Airborne Soot Adds to Weather Woes, Some Say

According to a new study, the weather in northern Africa, India, China, and the southern United States is being affected by soot from cooking fires and diesel engines. Like global warming associated with carbon dioxide, researchers believe that soot may contribute significantly to climate change.

Widespread use of fuels such as coal, cow dung, crop residue, and wood in developing countries produces vast amounts of unburned black carbon, or soot. Diesel engine exhaust also contains soot. The sooty carbon particles are thought to increase the absorption of sunlight in the upper atmosphere, causing hotter upper air and less sunlight to reach the ground. With uneven warming, the air becomes unstable and more clouds form. Computer models of weather

patterns indicate that this leads to heavy rainfall and flooding in some areas, while dry conditions and dust storms occur in other areas.

Soot is turning out to be more significant than previously thought, experts say. Based on the computer models, soot seems to have as much of an effect on climate as carbon dioxide, although the atmospheric mechanisms are different. Industrialized nations produce the most carbon dioxide, whereas developing nations tend to emit more soot into the atmosphere. These new findings suggest that curbing both sources of atmospheric emission might be needed to address climate change concerns.



EXAMPLE 13.2 Using a Dry Product Analysis

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 a molar and a mass basis, (b) the percent theoretical air, (c) the dew point temperature of the products, in $^\circ\text{C}$, if the mixture were cooled at 1 atm.

SOLUTION

Known: Methane is burned with dry air. The molar analysis of the products on a dry basis is provided.

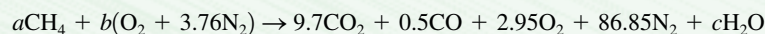
Find: Determine (a) the air–fuel ratio on both a molar and a mass basis, (b) the percent theoretical air, and (c) the dew point temperature of the products, in $^\circ\text{C}$, if cooled at 1 atm.

Assumptions:

- Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen, which is inert.
- The products form an ideal gas mixture.

Analysis:

- ① (a) The solution is conveniently conducted on the basis of 100 kmol of dry products. The chemical equation then reads

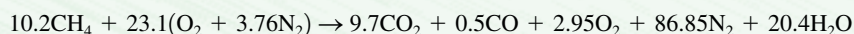


In addition to the assumed 100 kmol of dry products, water must be included as a product.

Applying conservation of mass to carbon, hydrogen, and oxygen, respectively

$$\begin{aligned} \text{C:} & & 9.7 + 0.5 &= a \\ \text{H:} & & 2c &= 4a \\ \text{O:} & (9.7)(2) + 0.5 + 2(2.95) + c &= 2b \end{aligned}$$

- ② Solving this set of equations gives $a = 10.2$, $b = 23.1$, $c = 20.4$. The balanced chemical equation is



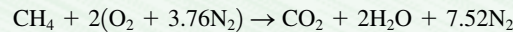
On a molar basis, the air–fuel ratio is

$$\overline{AF} = \frac{23.1(4.76)}{10.2} = 10.78 \frac{\text{kmol (air)}}{\text{kmol (fuel)}}$$

On a mass basis

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

(b) The balanced chemical equation for the *complete combustion* of methane with the *theoretical amount* of air is



The theoretical air–fuel ratio on a molar basis is

$$(\overline{AF})_{\text{theo}} = \frac{2(4.76)}{1} = 9.52 \frac{\text{kmol (air)}}{\text{kmol (fuel)}}$$

The percent theoretical air is then found from

$$\begin{aligned} \% \text{ theoretical air} &= \frac{(\overline{AF})}{(\overline{AF})_{\text{theo}}} \\ &= \frac{10.78 \text{ kmol (air)/kmol (fuel)}}{9.52 \text{ kmol (air)/kmol (fuel)}} = 1.13 \text{ (113\%)} \end{aligned}$$

3 (c) To determine the dew point temperature requires the partial pressure of the water vapor p_v . The partial pressure p_v is found from $p_v = y_v p$, where y_v is the mole fraction of the water vapor in the combustion products and p is 1 atm.

Referring to the balanced chemical equation of part (a), the mole fraction of the water vapor is

$$y_v = \frac{20.4}{100 + 20.4} = 0.169$$

Thus, $p_v = 0.169 \text{ atm} = 0.1712 \text{ bar}$. Interpolating in Table A-2, $T = 57^\circ\text{C}$.

1 The solution could be obtained on the basis of any assumed amount of dry products—for example, 1 lbmol. With some other assumed amount, the values of the coefficients of the balanced chemical equation would differ from those obtained in the solution, but the air–fuel ratio, the value for the percent of theoretical air, and the dew point temperature would be unchanged.

2 The three unknown coefficients, a , b , and c , are evaluated here by application of conservation of mass to carbon, hydrogen, and oxygen. As a check, note that the nitrogen also balances

$$\text{N: } b(3.76) = 86.85$$

This confirms the accuracy of both the given product analysis and the calculations conducted to determine the unknown coefficients.

3 If the products of combustion were cooled at constant pressure below the dew point temperature of 134°F , some condensation of the water vapor would occur.

In Example 13.3, a fuel mixture having a known molar analysis is burned with air, giving products with a known dry analysis.

EXAMPLE 13.3 Burning Natural Gas with Excess Air

A natural gas has the following molar analysis: CH₄, 80.62%; C₂H₆, 5.41%; C₃H₈, 1.87%; C₄H₁₀, 1.60%; N₂, 10.50%. The gas is burned with dry air, giving products having a molar analysis on a dry basis: CO₂, 7.8%; CO, 0.2%; O₂, 7%; N₂, 85%. (a) Determine the air–fuel ratio on a molar basis. (b) Assuming ideal gas behavior for the fuel mixture, determine the amount of products in kmol that would be formed from 100 m³ of fuel mixture at 300 K and 1 bar. (c) Determine the percent of theoretical air.

SOLUTION

Known: A natural gas with a specified molar analysis burns with dry air giving products having a known molar analysis on a dry basis.

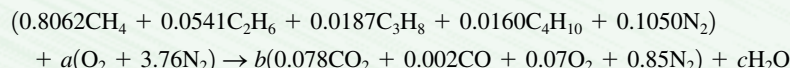
Find: Determine the air–fuel ratio on a molar basis, the amount of products in kmol that would be formed from 100 m³ of natural gas at 300 K and 1 bar, and the percent of theoretical air.

Assumptions:

1. Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen, which is inert.
2. The fuel mixture can be modeled as an ideal gas.

Analysis:

(a) The solution can be conducted on the basis of an assumed amount of fuel mixture or on the basis of an assumed amount of dry products. Let us illustrate the first procedure, basing the solution on 1 kmol of fuel mixture. The chemical equation then takes the form



The products consist of b kmol of dry products and c kmol of water vapor, each per kmol of fuel mixture.

Applying conservation of mass to carbon

$$b(0.078 + 0.002) = 0.8062 + 2(0.0541) + 3(0.0187) + 4(0.0160)$$

Solving gives $b = 12.931$. Conservation of mass for hydrogen results in

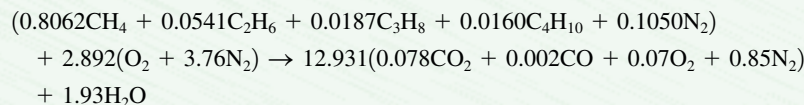
$$2c = 4(0.8062) + 6(0.0541) + 8(0.0187) + 10(0.0160)$$

which gives $c = 1.93$. The unknown coefficient a can be found from either an oxygen balance or a nitrogen balance. Applying conservation of mass to oxygen

$$12.931[2(0.078) + 0.002 + 2(0.07)] + 1.93 = 2a$$

- ① giving $a = 2.892$.

The balanced chemical equation is then



The air–fuel ratio on a molar basis is

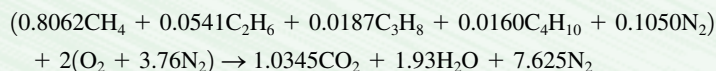
$$\overline{AF} = \frac{(2.892)(4.76)}{1} = 13.77 \frac{\text{kmol (air)}}{\text{kmol (fuel)}}$$

(b) By inspection of the chemical reaction equation, the total amount of products is $b + c = 12.931 + 1.93 = 14.861$ kmol of products per kmol of fuel. The amount of fuel in kmol, n_F , present in 100 m³ of fuel mixture at 300 K and 1 bar can be determined from the ideal gas equation of state as

$$\begin{aligned} n_F &= \frac{pV}{RT} \\ &= \frac{(10^5 \text{ N/m}^2)(100 \text{ m}^3)}{(8314 \text{ N} \cdot \text{m/kmol} \cdot \text{K})(300 \text{ K})} = 4.01 \text{ kmol (fuel)} \end{aligned}$$

Accordingly, the amount of product mixture that would be formed from 100 m³ of fuel mixture is (14.861)(4.01) = 59.59 kmol of product gas.

(c) The balanced chemical equation for the *complete combustion* of the fuel mixture with the *theoretical amount* of air is



The theoretical air–fuel ratio on a molar basis is

$$(\overline{AF})_{\text{theo}} = \frac{2(4.76)}{1} = 9.52 \frac{\text{kmol (air)}}{\text{kmol (fuel)}}$$

The percent theoretical air is then

$$\% \text{ theoretical air} = \frac{13.77 \text{ kmol (air)/kmol (fuel)}}{9.52 \text{ kmol (air)/kmol (fuel)}} = 1.45 \text{ (145\%)}$$

1 A check on both the accuracy of the given molar analyses and the calculations conducted to determine the unknown coefficients is obtained by applying conservation of mass to nitrogen. The amount of nitrogen in the reactants is

$$0.105 + (3.76)(2.892) = 10.98 \text{ kmol/kmol of fuel}$$

The amount of nitrogen in the products is (0.85)(12.931) = 10.99 kmol/kmol of fuel. The difference can be attributed to round-off.

13.2 Conservation of Energy—Reacting Systems

The objective of the present section is to illustrate the application of the conservation of energy principle to reacting systems. The forms of the conservation of energy principle introduced previously remain valid whether or not a chemical reaction occurs within the system. However, the methods used for evaluating the properties of reacting systems differ somewhat from the practices used to this point.

► 13.2.1 Evaluating Enthalpy for Reacting Systems

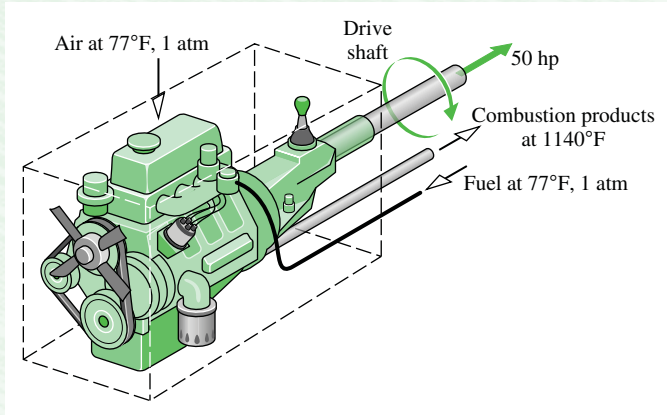
In each of the tables of thermodynamic properties used thus far, values for the specific internal energy, enthalpy, and entropy are given relative to some arbitrary datum state where the enthalpy (or alternatively the internal energy) and entropy are set to zero. This approach is satisfactory for evaluations involving *differences* in property values between states of the same composition, for then arbitrary datums cancel. However, when a chemical reaction occurs, reactants disappear and products are formed, so differences cannot be calculated for all substances involved. For reacting systems, it is necessary to evaluate h , u , and s in such a way that there are no subsequent ambiguities or inconsistencies in evaluating properties. In this section, we will consider how this is accomplished for h and u . The case of entropy is handled differently and is taken up in Sec. 13.5.

An enthalpy datum for the study of reacting systems can be established by assigning arbitrarily a value of zero to the enthalpy of the *stable elements* at a state called the *standard reference state* and defined by $T_{\text{ref}} = 298.15 \text{ K (25°C)}$ and $p_{\text{ref}} = 1 \text{ atm}$. Note that only *stable* elements are assigned a value of zero enthalpy at the standard state. The term *stable* simply means that the particular element is in a chemically stable form. For

standard reference state

Liquid Octane
 Mass flow rate=0.0018 kg/s
 theoretical air
 Entrance: T=25C, P=1 atm,
 Exit: T=890 C,
 W=37kw
 Q=?

Schematic and Given Data:

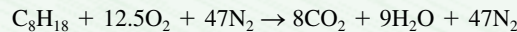


Assumptions:

1. The control volume identified by a dashed line on the accompanying figure operates at steady state.
2. Kinetic and potential energy effects can be ignored.
3. The combustion air and the products of combustion each form ideal gas mixtures.
4. Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen. The nitrogen is inert and combustion is complete.

◀ Figure E13.4

Analysis: The balanced chemical equation for complete combustion with the theoretical amount of air is obtained from the solution to Example 13.1 as



The energy rate balance reduces, with assumptions 1–3, to give

$$\begin{aligned} \frac{\dot{Q}_{\text{cv}}}{\dot{n}_{\text{F}}} &= \frac{\dot{W}_{\text{cv}}}{\dot{n}_{\text{F}}} + \bar{h}_{\text{P}} - \bar{h}_{\text{R}} \\ &= \frac{\dot{W}_{\text{cv}}}{\dot{n}_{\text{F}}} + \{8[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{CO}_2} + 9[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{H}_2\text{O}(\text{g})} + 47[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{N}_2}\} \\ &\quad - \{[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{C}_8\text{H}_{18}(\text{l})} + 12.5[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{O}_2} + 47[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{N}_2}\} \end{aligned}$$

where each coefficient is the same as the corresponding term of the balanced chemical equation and Eq. 13.9 has been used to evaluate enthalpy terms. The enthalpy of formation terms for oxygen and nitrogen are zero, and $\Delta\bar{h} = 0$ for each of the reactants, because the fuel and combustion air enter at 25°C.

With the enthalpy of formation for $\text{C}_8\text{H}_{18}(\text{l})$ from Table A-25

$$\bar{h}_{\text{R}} = (\bar{h}_f^\circ)_{\text{C}_8\text{H}_{18}(\text{l})} = -249,910 \text{ kJ/kmol (fuel)}$$

With enthalpy of formation values for CO_2 and $\text{H}_2\text{O}(\text{g})$ from Table A-25, and enthalpy values for N_2 , H_2O , and CO_2 from Table A-23

$$\begin{aligned} \bar{h}_{\text{P}} &= 8[-393,520 + (36,876 - 9364)] + 9[-241,820 + (31,429 - 9,904)] \\ &\quad + 47[26,568 - 8,669] \\ &= -4,069,466 \text{ kJ/kmol} \end{aligned}$$

Using the molecular weight of the fuel from Table A-1, the molar flow rate of the fuel is

$$\dot{n}_{\text{F}} = \frac{1.8 \times 10^{-3} \text{ kg (fuel)/s}}{114.22 \text{ lb(fuel)/kmol(fuel)}} = 1.58 \times 10^{-5} \text{ kmol(fuel)/s}$$

Inserting values into the expression for the rate of heat transfer

$$\begin{aligned} \dot{Q}_{\text{cv}} &= \dot{W}_{\text{cv}} + \dot{n}_{\text{F}}(\bar{h}_{\text{P}} - \bar{h}_{\text{R}}) \\ &= 37 \text{ kW} + \left[1.58 \times 10^{-5} \frac{\text{kmol (fuel)}}{\text{s}} \right] [-4,069,466 - (-249,910)] \left(\frac{\text{kJ}}{\text{kmol (fuel)}} \right) \left(\frac{1 \text{ kW}}{1 \text{ kJ/s}} \right) \\ &= -23.3 \text{ kW} \end{aligned}$$

where T_P and T_R denote the temperature of the products and reactants, respectively. With expressions of the form of Eq. 13.13 for each of the reactants and products, Eq. 13.17a can be written alternatively as

$$\begin{aligned} Q - W &= \sum_P n(\bar{h}_f^\circ + \Delta\bar{h} - \bar{R}T_P) - \sum_R n(\bar{h}_f^\circ + \Delta\bar{h} - \bar{R}T_R) \\ &= \sum_P n(\bar{h}_f^\circ + \Delta\bar{h}) - \sum_R n(\bar{h}_f^\circ + \Delta\bar{h}) - \bar{R}T_P \sum_P n + \bar{R}T_R \sum_R n \quad (13.17b) \end{aligned}$$

The enthalpy of formation terms are obtained from Table A-25. The $\Delta\bar{h}$ terms are evaluated as discussed above.

The foregoing concepts are illustrated in Example 13.6, where a gaseous mixture burns in a closed, rigid container.

EXAMPLE 13.6 Analyzing Combustion at Constant Volume

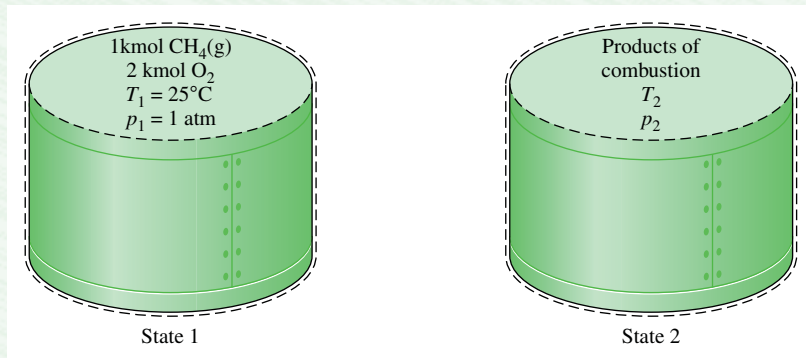
A mixture of 1 kmol of gaseous methane and 2 kmol of oxygen initially at 25°C and 1 atm burns completely in a closed, rigid container. Heat transfer occurs until the products are cooled to 900 K. If the reactants and products each form ideal gas mixtures, determine (a) the amount of heat transfer, in kJ, and (b) the final pressure, in atm.

SOLUTION

Known: A mixture of gaseous methane and oxygen, initially at 25°C and 1 atm, burns completely within a closed rigid container. The products are cooled to 900 K.

Find: Determine the amount of heat transfer, in kJ, and the final pressure of the combustion products, in atm.

Schematic and Given Data:

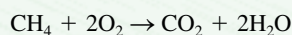


◀ Figure E13.6

Assumptions:

1. The contents of the closed, rigid container are taken as the system.
2. Kinetic and potential energy effects are absent, and $W = 0$.
3. Combustion is complete.
4. The initial mixture and the products of combustion each form ideal gas mixtures.
5. The initial and final states are equilibrium states.

Analysis: The chemical reaction equation for the complete combustion of methane with oxygen is



(a) With assumptions 2 and 3, the closed system energy balance takes the form

$$U_P - U_R = Q - \dot{W}^0$$

or

$$Q = U_P - U_R = (1\bar{u}_{\text{CO}_2} + 2\bar{u}_{\text{H}_2\text{O}(\text{g})}) - (1\bar{u}_{\text{CH}_4(\text{g})} + 2\bar{u}_{\text{O}_2})$$

Each coefficient in this equation is the same as the corresponding term of the balanced chemical equation.

Since each reactant and product behaves as an ideal gas, the respective specific internal energies can be evaluated as $\bar{u} = \bar{h} - RT$. The energy balance then becomes

$$Q = [1(\bar{h}_{\text{CO}_2} - \bar{R}T_2) + 2(\bar{h}_{\text{H}_2\text{O}(\text{g})} - \bar{R}T_2)] - [1(\bar{h}_{\text{CH}_4(\text{g})} - \bar{R}T_1) + 2(\bar{h}_{\text{O}_2} - \bar{R}T_1)]$$

where T_1 and T_2 denote, respectively, the initial and final temperatures. Collecting like terms

$$Q = (\bar{h}_{\text{CO}_2} + 2\bar{h}_{\text{H}_2\text{O}(\text{g})} - \bar{h}_{\text{CH}_4(\text{g})} - 2\bar{h}_{\text{O}_2}) + 3\bar{R}(T_1 - T_2)$$

The specific enthalpies are evaluated in terms of the respective enthalpies of formation to give

$$Q = [(\bar{h}_f^\circ + \Delta\bar{h})_{\text{CO}_2} + 2(\bar{h}_f^\circ + \Delta\bar{h})_{\text{H}_2\text{O}(\text{g})} - (\bar{h}_f^\circ + \Delta\bar{h})_{\text{CH}_4(\text{g})} - 2(\bar{h}_f^\circ + \Delta\bar{h})_{\text{O}_2}] + 3\bar{R}(T_1 - T_2)$$

Since the methane and oxygen are initially at 25°C, $\Delta\bar{h} = 0$ for each of these reactants. Also, $\bar{h}_f^\circ = 0$ for oxygen.

With enthalpy of formation values for CO_2 , $\text{H}_2\text{O}(\text{g})$, and $\text{CH}_4(\text{g})$ from Table A-25 and enthalpy values for H_2O and CO_2 from Table A-23

$$\begin{aligned} Q &= [-393,520 + (37,405 - 9364)] + 2[-241,820 + (31,828 - 9904)] \\ &\quad - (-74,850) + 3(8.314)(298 - 900) \\ &= -745,436 \text{ kJ} \end{aligned}$$

(b) By assumption 3, the initial mixture and the products of combustion each form ideal gas mixtures. Thus, for the reactants

$$p_1V = n_R\bar{R}T_1$$

where n_R is the total number of moles of reactants and p_1 is the initial pressure. Similarly, for the products

$$p_2V = n_P\bar{R}T_2$$

where n_P is the total number of moles of products and p_2 is the final pressure.

Since $n_R = n_P = 3$ and volume is constant, these equations combine to give

$$p_2 = \frac{T_2}{T_1}p_1 = \left(\frac{900 \text{ K}}{298 \text{ K}}\right)(1 \text{ atm}) = 3.02 \text{ atm}$$

► 13.2.3 Enthalpy of Combustion and Heating Values

Although the enthalpy of formation concept underlies the formulations of the energy balances for reactive systems presented thus far, the enthalpy of formation of fuels is not always tabulated. ► **for example. . .** fuel oil and coal are normally composed of several individual chemical substances, the relative amounts of which may vary considerably, depending on the source. Owing to the wide variation in composition that these fuels can exhibit, we do not find their enthalpies of formation listed in Tables A-25 or similar compilations of thermophysical data. ◀ In many cases of practical interest, however, the *enthalpy of combustion*, which is accessible experimentally, can be used to conduct an energy analysis when enthalpy of formation data are lacking.

Ethan, 20% excess air
 $P=100$ kPa
 AFR=?
 dew point temperature=?

Assumptions 1 Combustion is complete. 2 Combustion gases are ideal gases.

Analysis The combustion products contain CO_2 , H_2O , N_2 , and some excess O_2 only. Then the combustion equation can be written as



where a_{th} is the stoichiometric coefficient for air. We have automatically accounted for the 20 percent excess air by using the factor $1.2a_{\text{th}}$ instead of a_{th} for air. The stoichiometric amount of oxygen ($a_{\text{th}}\text{O}_2$) is used to oxidize the fuel, and the remaining excess amount ($0.2a_{\text{th}}\text{O}_2$) appears in the products as unused oxygen. Notice that the coefficient of N_2 is the same on both sides of the equation, and that we wrote the C and H balances directly since they are so obvious. The coefficient a_{th} is determined from the O_2 balance to be

$$\text{O}_2: \quad 1.2a_{\text{th}} = 2 + 1.5 + 0.2a_{\text{th}} \rightarrow a_{\text{th}} = 3.5$$

Substituting,



(a) The air–fuel ratio is determined from Eq. 15–3 by taking the ratio of the mass of the air to the mass of the fuel,

$$\begin{aligned} \text{AF} &= \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{(4.2 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(2 \text{ kmol})(12 \text{ kg/kmol}) + (3 \text{ kmol})(2 \text{ kg/kmol})} \\ &= \mathbf{19.3 \text{ kg air/kg fuel}} \end{aligned}$$

That is, 19.3 kg of air is supplied for each kilogram of fuel during this combustion process.

(b) The dew-point temperature of the products is the temperature at which the water vapor in the products starts to condense as the products are cooled at constant pressure. Recall from Chap. 14 that the dew-point temperature of a gas–vapor mixture is the saturation temperature of the water vapor corresponding to its partial pressure. Therefore, we need to determine the partial pressure of the water vapor P_v in the products first. Assuming ideal-gas behavior for the combustion gases, we have

$$P_v = \left(\frac{N_v}{N_{\text{prod}}} \right) (P_{\text{prod}}) = \left(\frac{3 \text{ kmol}}{21.49 \text{ kmol}} \right) (100 \text{ kPa}) = 13.96 \text{ kPa}$$

Thus,

$$T_{\text{dp}} = T_{\text{sat @ } 13.96 \text{ kPa}} = \mathbf{52.3^\circ\text{C}} \quad (\text{Table A-5})$$

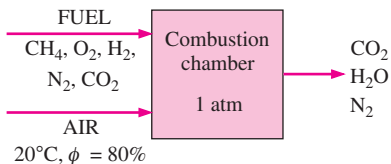


FIGURE 15–12
 Schematic for Example 15–3.

EXAMPLE 15–3 Combustion of a Gaseous Fuel with Moist Air

A certain natural gas has the following volumetric analysis: 72 percent CH_4 , 9 percent H_2 , 14 percent N_2 , 2 percent O_2 , and 3 percent CO_2 . This gas is now burned with the stoichiometric amount of air that enters the combustion chamber at 20°C , 1 atm, and 80 percent relative humidity, as shown in Fig. 15–12. Assuming complete combustion and a total pressure of 1 atm, determine the dew-point temperature of the products.

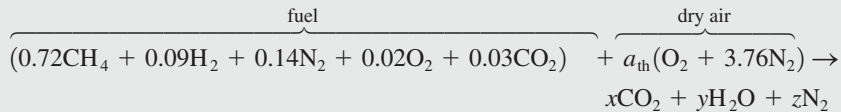
Solution A gaseous fuel is burned with the stoichiometric amount of moist air. The dew point temperature of the products is to be determined.

Assumptions **1** The fuel is burned completely and thus all the carbon in the fuel burns to CO_2 and all the hydrogen to H_2O . **2** The fuel is burned with the stoichiometric amount of air and thus there is no free O_2 in the product gases. **3** Combustion gases are ideal gases.

Properties The saturation pressure of water at 20°C is 2.3392 kPa (Table A-4).

Analysis We note that the moisture in the air does not react with anything; it simply shows up as additional H_2O in the products. Therefore, for simplicity, we balance the combustion equation by using dry air and then add the moisture later to both sides of the equation.

Considering 1 kmol of fuel,



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

$$\text{C:} \quad 0.72 + 0.03 = x \quad \rightarrow \quad x = 0.75$$

$$\text{H:} \quad 0.72 \times 4 + 0.09 \times 2 = 2y \quad \rightarrow \quad y = 1.53$$

$$\text{O}_2: \quad 0.02 + 0.03 + a_{\text{th}} = x + \frac{y}{2} \quad \rightarrow \quad a_{\text{th}} = 1.465$$

$$\text{N}_2: \quad 0.14 + 3.76a_{\text{th}} = z \quad \rightarrow \quad z = 5.648$$

Next we determine the amount of moisture that accompanies $4.76a_{\text{th}} = (4.76)(1.465) = 6.97$ kmol of dry air. The partial pressure of the moisture in the air is

$$P_{v,\text{air}} = \phi_{\text{air}} P_{\text{sat @ } 20^\circ\text{C}} = (0.80)(2.3392 \text{ kPa}) = 1.871 \text{ kPa}$$

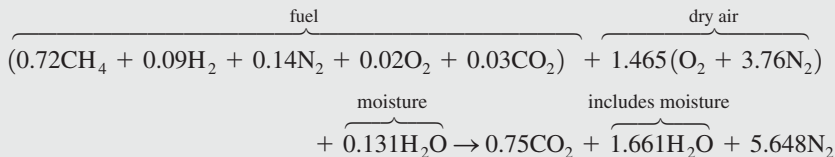
Assuming ideal-gas behavior, the number of moles of the moisture in the air is

$$N_{v,\text{air}} = \left(\frac{P_{v,\text{air}}}{P_{\text{total}}} \right) N_{\text{total}} = \left(\frac{1.871 \text{ kPa}}{101.325 \text{ kPa}} \right) (6.97 + N_{v,\text{air}})$$

which yields

$$N_{v,\text{air}} = 0.131 \text{ kmol}$$

The balanced combustion equation is obtained by substituting the coefficients determined earlier and adding 0.131 kmol of H_2O to both sides of the equation:



The dew-point temperature of the products is the temperature at which the water vapor in the products starts to condense as the products are cooled. Again, assuming ideal-gas behavior, the partial pressure of the water vapor in the combustion gases is

$$P_{v,\text{prod}} = \left(\frac{N_{v,\text{prod}}}{N_{\text{prod}}} \right) P_{\text{prod}} = \left(\frac{1.661 \text{ kmol}}{8.059 \text{ kmol}} \right) (101.325 \text{ kPa}) = 20.88 \text{ kPa}$$

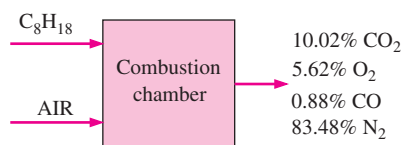


FIGURE 15-13

Schematic for Example 15-4.

Thus,

$$T_{dp} = T_{sat @ 20.88 \text{ kPa}} = 60.9^\circ\text{C}$$

Discussion If the combustion process were achieved with dry air instead of moist air, the products would contain less moisture, and the dew-point temperature in this case would be 59.5°C.

EXAMPLE 15-4 Reverse Combustion Analysis

Octane (C_8H_{18}) is burned with dry air. The volumetric analysis of the products on a dry basis is (Fig. 15-13)

CO_2 :	10.02 percent
O_2 :	5.62 percent
CO :	0.88 percent
N_2 :	83.48 percent

Determine (a) the air–fuel ratio, (b) the percentage of theoretical air used, and (c) the amount of H_2O that condenses as the products are cooled to 25°C at 100 kPa.

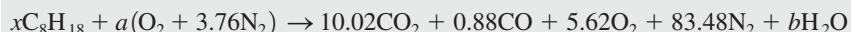
Solution Combustion products whose composition is given are cooled to 25°C. The AF, the percent theoretical air used, and the fraction of water vapor that condenses are to be determined.

Assumptions Combustion gases are ideal gases.

Properties The saturation pressure of water at 25°C is 3.1698 kPa (Table A-4).

Analysis Note that we know the relative composition of the products, but we do not know how much fuel or air is used during the combustion process. However, they can be determined from mass balances. The H_2O in the combustion gases will start condensing when the temperature drops to the dew-point temperature.

For ideal gases, the volume fractions are equivalent to the mole fractions. Considering 100 kmol of dry products for convenience, the combustion equation can be written as



The unknown coefficients x , a , and b are determined from mass balances,

$$\text{N}_2: \quad 3.76a = 83.48 \quad \rightarrow \quad a = 22.20$$

$$\text{C}: \quad 8x = 10.02 + 0.88 \quad \rightarrow \quad x = 1.36$$

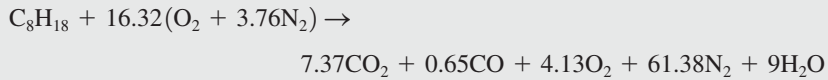
$$\text{H}: \quad 18x = 2b \quad \rightarrow \quad b = 12.24$$

$$\text{O}_2: \quad a = 10.02 + 0.44 + 5.62 + \frac{b}{2} \quad \rightarrow \quad 22.20 = 22.20$$

The O_2 balance is not necessary, but it can be used to check the values obtained from the other mass balances, as we did previously. Substituting, we get



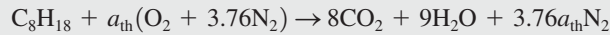
The combustion equation for 1 kmol of fuel is obtained by dividing the above equation by 1.36,



(a) The air–fuel ratio is determined by taking the ratio of the mass of the air to the mass of the fuel (Eq. 15–3),

$$\begin{aligned} \text{AF} &= \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{(16.32 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(8 \text{ kmol})(12 \text{ kg/kmol}) + (9 \text{ kmol})(2 \text{ kg/kmol})} \\ &= \mathbf{19.76 \text{ kg air/kg fuel}} \end{aligned}$$

(b) To find the percentage of theoretical air used, we need to know the theoretical amount of air, which is determined from the theoretical combustion equation of the fuel,



$$\text{O}_2: \quad a_{\text{th}} = 8 + 4.5 \rightarrow a_{\text{th}} = 12.5$$

Then,

$$\begin{aligned} \text{Percentage of theoretical air} &= \frac{m_{\text{air,act}}}{m_{\text{air,th}}} = \frac{N_{\text{air,act}}}{N_{\text{air,th}}} \\ &= \frac{(16.32)(4.76) \text{ kmol}}{(12.50)(4.76) \text{ kmol}} \\ &= \mathbf{131\%} \end{aligned}$$

That is, 31 percent excess air was used during this combustion process. Notice that some carbon formed carbon monoxide even though there was considerably more oxygen than needed for complete combustion.

(c) For each kmol of fuel burned, $7.37 + 0.65 + 4.13 + 61.38 + 9 = 82.53$ kmol of products are formed, including 9 kmol of H_2O . Assuming that the dew-point temperature of the products is above 25°C , some of the water vapor will condense as the products are cooled to 25°C . If N_w kmol of H_2O condenses, there will be $(9 - N_w)$ kmol of water vapor left in the products. The mole number of the products in the gas phase will also decrease to $82.53 - N_w$ as a result. By treating the product gases (including the remaining water vapor) as ideal gases, N_w is determined by equating the mole fraction of the water vapor to its pressure fraction,

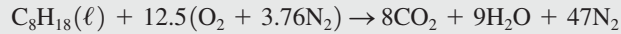
$$\begin{aligned} \frac{N_v}{N_{\text{prod,gas}}} &= \frac{P_v}{P_{\text{prod}}} \\ \frac{9 - N_w}{82.53 - N_w} &= \frac{3.1698 \text{ kPa}}{100 \text{ kPa}} \\ N_w &= \mathbf{6.59 \text{ kmol}} \end{aligned}$$

Therefore, the majority of the water vapor in the products (73 percent of it) condenses as the product gases are cooled to 25°C .

Adiabatic flame temperature of liquid octane with
 a) no excess air
 b) 300% excess air
 c) incomplete combustion (production of CO) with 90% of theoretical air

Assumptions 1 This is a steady-flow combustion process. 2 The combustion chamber is adiabatic. 3 There are no work interactions. 4 Air and the combustion gases are ideal gases. 5 Changes in kinetic and potential energies are negligible.

Analysis (a) The balanced equation for the combustion process with the theoretical amount of air is



The adiabatic flame temperature relation $H_{\text{prod}} = H_{\text{react}}$ in this case reduces to

$$\sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p = \sum N_r \bar{h}_{f,r}^\circ = (N\bar{h}_f^\circ)_{\text{C}_8\text{H}_{18}}$$

since all the reactants are at the standard reference state and $\bar{h}_f^\circ = 0$ for O_2 and N_2 . The \bar{h}_f° and h values of various components at 298 K are

Substance	\bar{h}_f° kJ/kmol	$\bar{h}_{298\text{ K}}$ kJ/kmol
$\text{C}_8\text{H}_{18}(\ell)$	-249,950	—
O_2	0	8682
N_2	0	8669
$\text{H}_2\text{O}(\text{g})$	-241,820	9904
CO_2	-393,520	9364

Substituting, we have

$$\begin{aligned} & (8 \text{ kmol CO}_2)[(-393,520 + \bar{h}_{\text{CO}_2} - 9364) \text{ kJ/kmol CO}_2] \\ & + (9 \text{ kmol H}_2\text{O})[(-241,820 + \bar{h}_{\text{H}_2\text{O}} - 9904) \text{ kJ/kmol H}_2\text{O}] \\ & + (47 \text{ kmol N}_2)[(0 + \bar{h}_{\text{N}_2} - 8669) \text{ kJ/kmol N}_2] \\ & = (1 \text{ kmol C}_8\text{H}_{18})(-249,950 \text{ kJ/kmol C}_8\text{H}_{18}) \end{aligned}$$

which yields

$$8\bar{h}_{\text{CO}_2} + 9\bar{h}_{\text{H}_2\text{O}} + 47\bar{h}_{\text{N}_2} = 5,646,081 \text{ kJ}$$

It appears that we have one equation with three unknowns. Actually we have only one unknown—the temperature of the products T_{prod} —since $h = h(T)$ for ideal gases. Therefore, we have to use an equation solver such as EES or a trial-and-error approach to determine the temperature of the products.

A first guess is obtained by dividing the right-hand side of the equation by the total number of moles, which yields $5,646,081/(8 + 9 + 47) = 88,220$ kJ/kmol. This enthalpy value corresponds to about 2650 K for N_2 , 2100 K for H_2O , and 1800 K for CO_2 . Noting that the majority of the moles are N_2 , we see that T_{prod} should be close to 2650 K, but somewhat under it. Therefore, a good first guess is 2400 K. At this temperature,

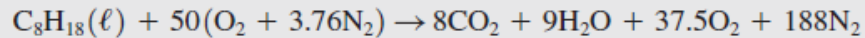
$$\begin{aligned} 8\bar{h}_{\text{CO}_2} + 9\bar{h}_{\text{H}_2\text{O}} + 47\bar{h}_{\text{N}_2} &= 8 \times 125,152 + 9 \times 103,508 + 47 \times 79,320 \\ &= 5,660,828 \text{ kJ} \end{aligned}$$

This value is higher than 5,646,081 kJ. Therefore, the actual temperature is slightly under 2400 K. Next we choose 2350 K. It yields

$$8 \times 122,091 + 9 \times 100,846 + 47 \times 77,496 = 5,526,654$$

which is lower than 5,646,081 kJ. Therefore, the actual temperature of the products is between 2350 and 2400 K. By interpolation, it is found to be $T_{\text{prod}} = 2395 \text{ K}$.

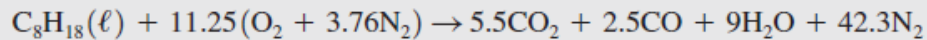
(b) The balanced equation for the complete combustion process with 400 percent theoretical air is



By following the procedure used in (a), the adiabatic flame temperature in this case is determined to be $T_{\text{prod}} = 962 \text{ K}$.

Notice that the temperature of the products decreases significantly as a result of using excess air.

(c) The balanced equation for the incomplete combustion process with 90 percent theoretical air is



Following the procedure used in (a), we find the adiabatic flame temperature in this case to be $T_{\text{prod}} = 2236 \text{ K}$.

Discussion Notice that the adiabatic flame temperature decreases as a result of incomplete combustion or using excess air. Also, *the maximum adiabatic flame temperature is achieved when complete combustion occurs with the theoretical amount of air.*