

Chapter 15

CHEMICAL REACTIONS

In the preceding chapters we limited our consideration to nonreacting systems—systems whose chemical composition remains unchanged during a process. This was the case even with mixing processes during which a homogeneous mixture is formed from two or more fluids without the occurrence of any chemical reactions. In this chapter, we specifically deal with systems whose chemical composition changes during a process, that is, systems that involve *chemical reactions*.

When dealing with nonreacting systems, we need to consider only the *sensible internal energy* (associated with temperature and pressure changes) and the *latent internal energy* (associated with phase changes). When dealing with reacting systems, however, we also need to consider the *chemical internal energy*, which is the energy associated with the destruction and formation of chemical bonds between the atoms. The energy balance relations developed for nonreacting systems are equally applicable to reacting systems, but the energy terms in the latter case should include the chemical energy of the system.

In this chapter we focus on a particular type of chemical reaction, known as *combustion*, because of its importance in engineering. But the reader should keep in mind, however, that the principles developed are equally applicable to other chemical reactions.

We start this chapter with a general discussion of fuels and combustion. Then we apply the mass and energy balances to reacting systems. In this regard we discuss the adiabatic flame temperature, which is the highest temperature a reacting mixture can attain. Finally, we examine the second-law aspects of chemical reactions.

Objectives

The objectives of Chapter 15 are to:

- Give an overview of fuels and combustion.
- Apply the conservation of mass to reacting systems to determine balanced reaction equations.
- Define the parameters used in combustion analysis, such as air–fuel ratio, percent theoretical air, and dew-point temperature.
- Apply energy balances to reacting systems for both steady-flow control volumes and fixed mass systems.
- Calculate the enthalpy of reaction, enthalpy of combustion, and the heating values of fuels.
- Determine the adiabatic flame temperature for reacting mixtures.
- Evaluate the entropy change of reacting systems.
- Analyze reacting systems from the second-law perspective.

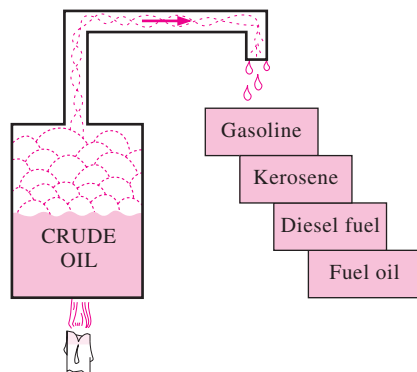


FIGURE 15–1

Most liquid hydrocarbon fuels are obtained from crude oil by distillation.

15–1 ■ FUELS AND COMBUSTION

Any material that can be burned to release thermal energy is called a **fuel**. Most familiar fuels consist primarily of hydrogen and carbon. They are called **hydrocarbon fuels** and are denoted by the general formula C_nH_m . Hydrocarbon fuels exist in all phases, some examples being coal, gasoline, and natural gas.

The main constituent of coal is carbon. Coal also contains varying amounts of oxygen, hydrogen, nitrogen, sulfur, 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. Most liquid hydrocarbon fuels are a mixture of numerous hydrocarbons and are obtained from crude oil by distillation (Fig. 15–1). The most volatile hydrocarbons vaporize first, forming what we know as gasoline. The less volatile fuels obtained during distillation are kerosene, diesel fuel, and fuel oil. The composition of a particular fuel depends on the source of the crude oil as well as on the refinery.

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. The 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.

Natural gas is produced from gas wells or oil wells rich in natural gas. It is composed mainly of methane, but it also contains small amounts of ethane, propane, hydrogen, helium, carbon dioxide, nitrogen, hydrogen sulfate, and water vapor. On vehicles, it 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°C as LNG (liquefied natural gas). Over a million vehicles in the world, mostly buses, run on natural gas. Liquefied petroleum gas (LPG) is a byproduct of natural gas processing or the crude oil refining. It consists mainly of propane and thus LPG is usually referred to as propane. However, it also contains varying amounts of butane, propylene, and butylenes. Propane is commonly used in fleet vehicles, taxis, school buses, and private cars. Ethanol is obtained from corn, grains, and organic waste. Methanol is produced mostly from natural gas, but it can also be obtained from coal and biomass. Both alcohols are commonly used as additives in oxygenated gasoline and reformulated fuels to reduce air pollution.

Vehicles are a major source of air pollutants such as nitric oxides, carbon monoxide, and hydrocarbons, as well as the greenhouse gas carbon dioxide, and thus there is a growing shift in the transportation industry from the traditional petroleum-based fuels such as gasoline and diesel fuel to the cleaner burning *alternative fuels* friendlier to the environment such as natural gas, alcohols (ethanol and methanol), liquefied petroleum gas (LPG), and hydrogen. The use of electric and hybrid cars is also on the rise. A comparison of some alternative fuels for transportation to gasoline is given in Table 15–1. Note that the energy contents of alternative fuels per unit volume are lower than that of gasoline or diesel fuel, and thus the driving range of a

TABLE 15–1

A comparison of some alternative fuels to the traditional petroleum-based fuels used in transportation

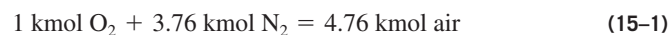
Fuel	Energy content kJ/L	Gasoline equivalence,* L/L-gasoline
Gasoline	31,850	1
Light diesel	33,170	0.96
Heavy diesel	35,800	0.89
LPG (Liquefied petroleum gas, primarily propane)	23,410	1.36
Ethanol (or ethyl alcohol)	29,420	1.08
Methanol (or methyl alcohol)	18,210	1.75
CNG (Compressed natural gas, primarily methane, at 200 atm)	8,080	3.94
LNG (Liquefied natural gas, primarily methane)	20,490	1.55

*Amount of fuel whose energy content is equal to the energy content of 1-L gasoline.

vehicle on a full tank is lower when running on an alternative fuel. Also, when comparing cost, a realistic measure is the cost per unit energy rather than cost per unit volume. For example, methanol at a unit cost of \$1.20/L may appear cheaper than gasoline at \$1.80/L, but this is not the case since the cost of 10,000 kJ of energy is \$0.57 for gasoline and \$0.66 for methanol.

A chemical reaction during which a fuel is oxidized and a large quantity of energy is released is called **combustion** (Fig. 15–2). The oxidizer most often used in combustion processes is air, for obvious reasons—it is free and readily available. Pure oxygen O_2 is used as an oxidizer only in some specialized applications, such as cutting and welding, where air cannot be used. Therefore, a few words about the composition of air are in order.

On a mole or a volume basis, dry air is composed of 20.9 percent oxygen, 78.1 percent nitrogen, 0.9 percent argon, and small amounts of carbon dioxide, helium, neon, and hydrogen. In the analysis of combustion processes, the argon in the air is treated as nitrogen, and the gases that exist in trace amounts are disregarded. Then dry air can be approximated as 21 percent oxygen and 79 percent nitrogen by mole numbers. Therefore, each mole of oxygen entering a combustion chamber is accompanied by $0.79/0.21 = 3.76$ mol of nitrogen (Fig. 15–3). That is,



During combustion, nitrogen behaves as an inert gas and does not react with other elements, other than forming a very small amount of nitric oxides. However, even then the presence of nitrogen greatly affects the outcome of a combustion process since nitrogen usually enters a combustion chamber in large quantities at low temperatures and exits at considerably higher temperatures, absorbing a large proportion of the chemical energy released during combustion. Throughout this chapter, nitrogen is assumed to remain perfectly

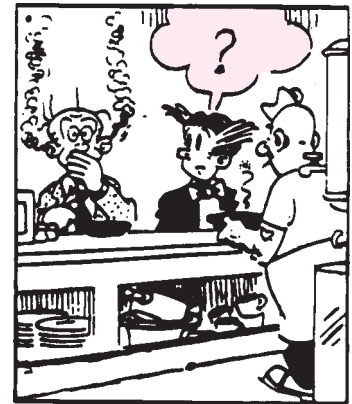


FIGURE 15–2

Combustion is a chemical reaction during which a fuel is oxidized and a large quantity of energy is released.

© Reprinted with special permission of King Features Syndicate.

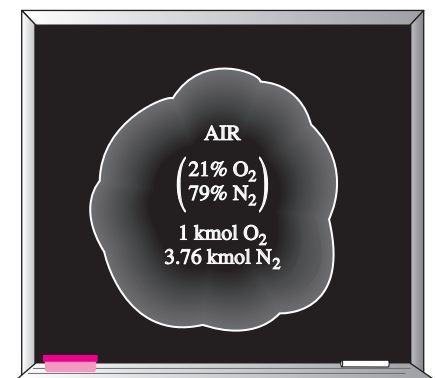


FIGURE 15–3

Each kmol of O_2 in air is accompanied by 3.76 kmol of N_2 .

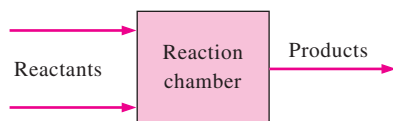


FIGURE 15-4

In a steady-flow combustion process, the components that enter the reaction chamber are called reactants and the components that exit are called products.

inert. Keep in mind, however, that at very high temperatures, such as those encountered in internal combustion engines, a small fraction of nitrogen reacts with oxygen, forming hazardous gases such as nitric oxide.

Air that enters a combustion chamber normally contains some water vapor (or moisture), which also deserves consideration. For most combustion processes, the moisture in the air and the H_2O that forms during combustion can also be treated as an inert gas, like nitrogen. At very high temperatures, however, some water vapor dissociates into H_2 and O_2 as well as into H , O , and OH . When the combustion gases are cooled below the dew-point temperature of the water vapor, some moisture condenses. It is important to be able to predict the dew-point temperature since the water droplets often combine with the sulfur dioxide that may be present in the combustion gases, forming sulfuric acid, which is highly corrosive.

During a combustion process, the components that exist before the reaction are called **reactants** and the components that exist after the reaction are called **products** (Fig. 15-4). Consider, for example, the combustion of 1 kmol of carbon with 1 kmol of pure oxygen, forming carbon dioxide,



Here C and O_2 are the reactants since they exist before combustion, and CO_2 is the product since it exists after combustion. Note that a reactant does not have to react chemically in the combustion chamber. For example, if carbon is burned with air instead of pure oxygen, both sides of the combustion equation will include N_2 . That is, the N_2 will appear both as a reactant and as a product.

We should also mention that bringing a fuel into intimate contact with oxygen is not sufficient to start a combustion process. (Thank goodness it is not. Otherwise, the whole world would be on fire now.) The fuel must be brought above its **ignition temperature** to start the combustion. The minimum ignition temperatures of various substances in atmospheric air are approximately 260°C for gasoline, 400°C for carbon, 580°C for hydrogen, 610°C for carbon monoxide, and 630°C for methane. Moreover, the proportions of the fuel and air must be in the proper range for combustion to begin. For example, natural gas does not burn in air in concentrations less than 5 percent or greater than about 15 percent.

As you may recall from your chemistry courses, chemical 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* (Fig. 15-5). That is, the total mass of each element on the right-hand side of the reaction equation (the products) must be equal to the total mass of that element on the left-hand side (the reactants) even though the elements exist in different chemical compounds in the reactants and products. Also, the total number of atoms of each element is conserved during a chemical reaction since the total number of atoms is equal to the total mass of the element divided by its atomic mass.

For example, both sides of Eq. 15-2 contain 12 kg of carbon and 32 kg of oxygen, even though the carbon and the oxygen exist as elements in the reactants and as a compound in the product. Also, the total mass of reactants is equal to the total mass of products, each being 44 kg. (It is common practice to round the molar masses to the nearest integer if great accuracy is

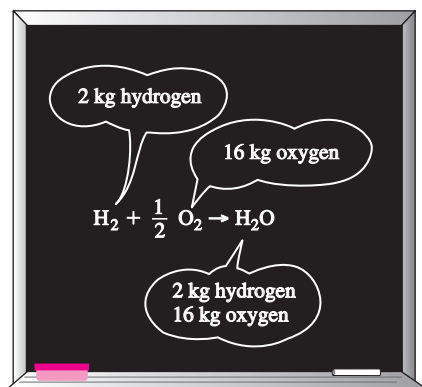


FIGURE 15-5

The mass (and number of atoms) of each element is conserved during a chemical reaction.

not required.) However, notice that the total mole number of the reactants (2 kmol) is not equal to the total mole number of the products (1 kmol). That is, *the total number of moles is not conserved during a chemical reaction.*

A frequently used quantity in the analysis of combustion processes to quantify the amounts of fuel and air is the **air–fuel ratio** AF. It 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 (Fig. 15–6). That is,

$$AF = \frac{m_{\text{air}}}{m_{\text{fuel}}} \quad (15-3)$$

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 air–fuel ratio can also be expressed on a mole basis as the ratio of the mole numbers of air to the mole numbers of fuel. But we will use the former definition. The reciprocal of air–fuel ratio is called the **fuel–air ratio**.

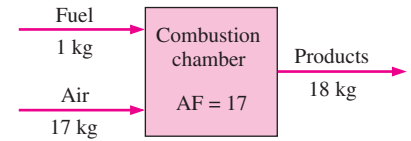


FIGURE 15–6

The air–fuel ratio (AF) represents the amount of air used per unit mass of fuel during a combustion process.

EXAMPLE 15–1 Balancing the Combustion Equation

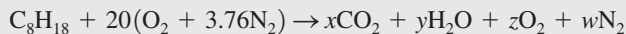
One kmol of octane (C_8H_{18}) is burned with air that contains 20 kmol of O_2 , as shown in Fig. 15–7. Assuming the products contain only CO_2 , H_2O , O_2 , and N_2 , determine the mole number of each gas in the products and the air–fuel ratio for this combustion process.

Solution The amount of fuel and the amount of oxygen in the air are given. The amount of the products and the AF are to be determined.

Assumptions The combustion products contain CO_2 , H_2O , O_2 , and N_2 only.

Properties The molar mass of air is $M_{\text{air}} = 28.97 \text{ kg/kmol} \cong 29.0 \text{ kg/kmol}$ (Table A–1).

Analysis The chemical equation for this combustion process can be written as



where the terms in the parentheses represent the composition of dry air that contains 1 kmol of O_2 and x , y , z , and w represent the unknown mole numbers of the gases in the products. These unknowns are determined by applying the mass balance to each of the elements—that is, by requiring that the total mass or mole number of each element in the reactants be equal to that in the products:

$$\begin{aligned} \text{C:} & & 8 &= x & \rightarrow & x = \mathbf{8} \\ \text{H:} & & 18 &= 2y & \rightarrow & y = \mathbf{9} \\ \text{O:} & & 20 \times 2 &= 2x + y + 2z & \rightarrow & z = \mathbf{7.5} \\ \text{N}_2: & & (20)(3.76) &= w & \rightarrow & w = \mathbf{75.2} \end{aligned}$$

Substituting yields



Note that the coefficient 20 in the balanced equation above represents the number of moles of *oxygen*, not the number of moles of air. The latter is obtained by adding $20 \times 3.76 = 75.2$ moles of nitrogen to the 20 moles of

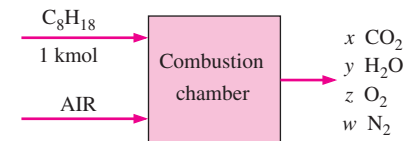


FIGURE 15–7

Schematic for Example 15–1.

oxygen, giving a total of 95.2 moles of air. The air–fuel ratio (AF) is determined from Eq. 15–3 by taking the ratio of the mass of the air and the mass of the fuel,

$$\begin{aligned} \text{AF} &= \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{(NM)_{\text{air}}}{(NM)_{\text{C}} + (NM)_{\text{H}_2}} \\ &= \frac{(20 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(8 \text{ kmol})(12 \text{ kg/kmol}) + (9 \text{ kmol})(2 \text{ kg/kmol})} \\ &= \mathbf{24.2 \text{ kg air/kg fuel}} \end{aligned}$$

That is, 24.2 kg of air is used to burn each kilogram of fuel during this combustion process.

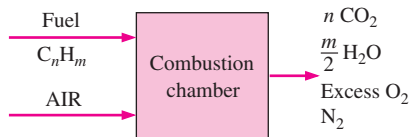


FIGURE 15–8

A combustion process is complete if all the combustible components of the fuel are burned to completion.

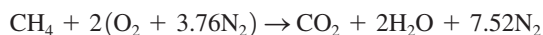
15–2 ■ THEORETICAL AND ACTUAL COMBUSTION PROCESSES

It is often instructive to study the combustion of a fuel by assuming that the combustion is complete. 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 . That is, all the combustible components of a fuel are burned to completion during a complete combustion process (Fig. 15–8). Conversely, the combustion process is **incomplete** if the combustion products contain any unburned fuel or components such as C, H_2 , CO, or OH.

Insufficient oxygen is an obvious reason for incomplete combustion, but it is not the only one. Incomplete combustion occurs even when more oxygen is present in the combustion chamber than is needed for complete combustion. This may be attributed to insufficient mixing in the combustion chamber during the limited time that the fuel and the oxygen are in contact. Another cause of incomplete combustion is *dissociation*, which becomes important at high temperatures.

Oxygen has a much greater tendency to combine with hydrogen than it does with carbon. Therefore, the hydrogen in the fuel normally burns to completion, forming H_2O , even when there is less oxygen than needed for complete combustion. Some of the carbon, however, ends up as CO or just as plain C particles (soot) in the products.

The minimum amount of air needed for the complete combustion of a fuel is called the **stoichiometric** or **theoretical air**. Thus, when a fuel is completely burned with theoretical air, no uncombined oxygen is present in the product gases. The theoretical air is also referred to as the *chemically correct amount of air*, or *100 percent theoretical air*. A combustion process with less than the theoretical air is bound to be incomplete. The ideal combustion process during which a fuel is burned completely with theoretical air is called the **stoichiometric** or **theoretical combustion** of that fuel (Fig. 15–9). For example, the theoretical combustion of methane is



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

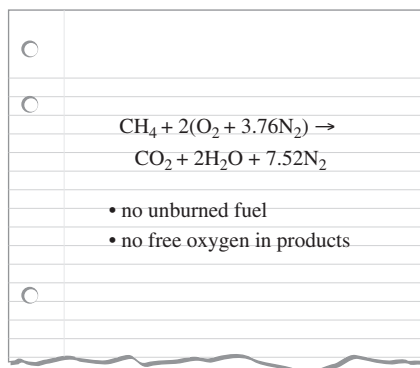


FIGURE 15–9

The complete combustion process with no oxygen in the products is called theoretical combustion.

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 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**. For example, 50 percent excess air is equivalent to 150 percent theoretical air, and 200 percent excess air is equivalent to 300 percent theoretical air. Of course, the stoichiometric air can be expressed as 0 percent excess air or 100 percent theoretical 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 percent theoretical air is equivalent to 10 percent deficiency of air. The amount of air used in combustion processes is also expressed in terms of the **equivalence ratio**, which is the ratio of the actual fuel–air ratio to the stoichiometric fuel–air ratio.

Predicting the composition of the products is relatively easy when the combustion process is assumed to be complete and the exact amounts of the fuel and air used are known. All one needs to do in this case is simply apply the mass balance to each element that appears in the combustion equation, without needing to take any measurements. Things are not so simple, however, when one is dealing with actual combustion processes. For one thing, actual combustion processes are hardly ever complete, even in the presence of excess air. Therefore, it is impossible to predict the composition of the products on the basis of the mass balance alone. Then the only alternative we have is to measure the amount of each component in the products directly.

A commonly used device to analyze the composition of combustion gases is the **Orsat gas analyzer**. In this device, a sample of the combustion gases is collected and cooled to room temperature and pressure, at which point its volume is measured. The sample is then brought into contact with a chemical that absorbs the CO_2 . The remaining gases are returned to the room temperature and pressure, and the new volume they occupy is measured. The ratio of the reduction in volume to the original volume is the volume fraction of the CO_2 , which is equivalent to the mole fraction if ideal-gas behavior is assumed (Fig. 15–10). The volume fractions of the other gases are determined by repeating this procedure. In Orsat analysis the gas sample is collected over water and is maintained saturated at all times. Therefore, the vapor pressure of water remains constant during the entire test. For this reason the presence of water vapor in the test chamber is ignored and data are reported on a dry basis. However, the amount of H_2O formed during combustion is easily determined by balancing the combustion equation.

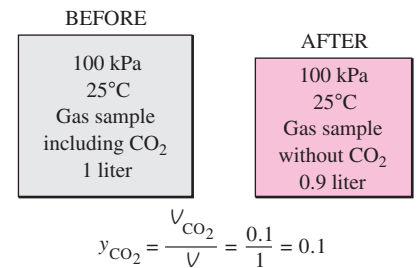


FIGURE 15–10

Determining the mole fraction of the CO_2 in combustion gases by using the Orsat gas analyzer.

EXAMPLE 15–2 Dew-Point Temperature of Combustion Products

Ethane (C_2H_6) is burned with 20 percent excess air during a combustion process, as shown in Fig. 15–11. Assuming complete combustion and a total pressure of 100 kPa, determine (a) the air–fuel ratio and (b) the dew-point temperature of the products.

Solution The fuel is burned completely with excess air. The AF and the dew point of the products are to be determined.

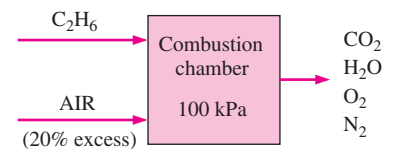


FIGURE 15–11

Schematic for Example 15–2.

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,

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

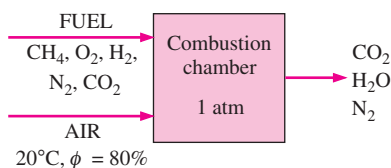


FIGURE 15–12
Schematic for Example 15–3.

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.

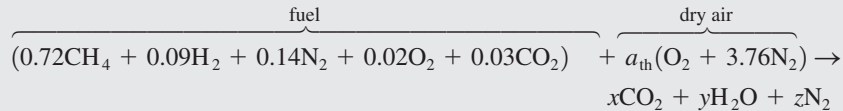
Solution A gaseous fuel is burned with the stoichiometric amount of moist air. The dew point temperature of the products is to be determined.

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

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

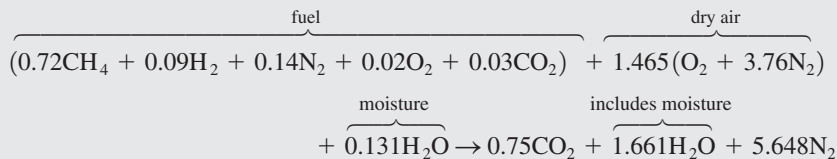
Assuming ideal-gas behavior, the number of moles of the moisture in the air is

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

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

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

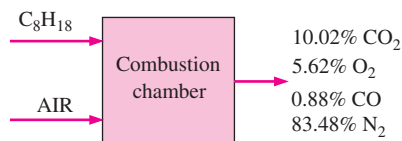


FIGURE 15-13

Schematic for Example 15-4.

Thus,

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

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.

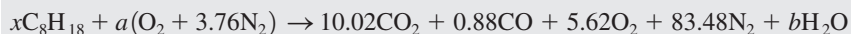
Solution Combustion products whose composition is given are cooled to 25°C. The AF, the percent theoretical air used, and the fraction of water vapor that condenses are to be determined.

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,

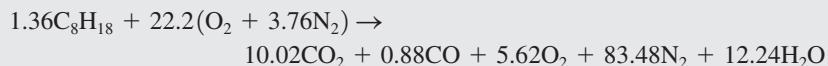
$$\text{N}_2: \quad 3.76a = 83.48 \quad \rightarrow \quad a = 22.20$$

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

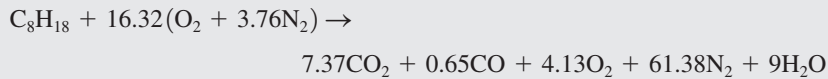
$$\text{H}: \quad 18x = 2b \quad \rightarrow \quad b = 12.24$$

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

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 .

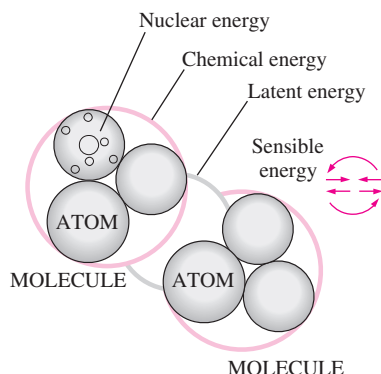


FIGURE 15-14

The microscopic form of energy of a substance consists of sensible, latent, chemical, and nuclear energies.

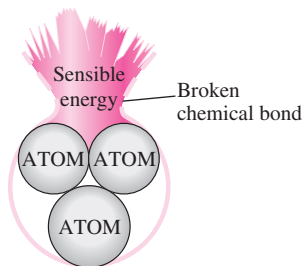


FIGURE 15-15

When the existing chemical bonds are destroyed and new ones are formed during a combustion process, usually a large amount of sensible energy is absorbed or released.

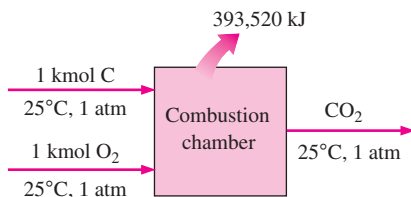


FIGURE 15-16

The formation of CO_2 during a steady-flow combustion process at 25°C and 1 atm.

15-3 ■ ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

We mentioned in Chap. 2 that the molecules of a system possess energy in various forms such as *sensible* and *latent energy* (associated with a change of state), *chemical energy* (associated with the molecular structure), and *nuclear energy* (associated with the atomic structure), as illustrated in Fig. 15-14. In this text we do not intend to deal with nuclear energy. We also ignored chemical energy until now since the systems considered in previous chapters involved no changes in their chemical structure, and thus no changes in chemical energy. Consequently, all we needed to deal with were the sensible and latent energies.

During a chemical reaction, some chemical bonds that bind the atoms into molecules are broken, and new ones are formed. The chemical energy associated with these bonds, in general, is different for the reactants and the products. Therefore, a process that involves chemical reactions involves changes in chemical energies, which must be accounted for in an energy balance (Fig. 15-15). Assuming the atoms of each reactant remain intact (no nuclear reactions) and disregarding any changes in kinetic and potential energies, the energy change of a system during a chemical reaction is due to a change in state and a change in chemical composition. That is,

$$\Delta E_{\text{sys}} = \Delta E_{\text{state}} + \Delta E_{\text{chem}} \quad (15-4)$$

Therefore, when the products formed during a chemical reaction exit the reaction chamber at the inlet state of the reactants, we have $\Delta E_{\text{state}} = 0$ and the energy change of the system in this case is due to the changes in its chemical composition only.

In thermodynamics we are concerned with the *changes* in the energy of a system during a process, and not the energy values at the particular states. Therefore, we can choose any state as the reference state and assign a value of zero to the internal energy or enthalpy of a substance at that state. When a process involves no changes in chemical composition, the reference state chosen has no effect on the results. When the process involves chemical reactions, however, the composition of the system at the end of a process is no longer the same as that at the beginning of the process. In this case it becomes necessary to have a common reference state for all substances. The chosen reference state is 25°C (77°F) and 1 atm, which is known as the **standard reference state**. Property values at the standard reference state are indicated by a superscript ($^\circ$) (such as h° and u°).

When analyzing reacting systems, we must use property values relative to the standard reference state. However, it is not necessary to prepare a new set of property tables for this purpose. We can use the existing tables by subtracting the property values at the standard reference state from the values at the specified state. The ideal-gas enthalpy of N_2 at 500 K relative to the standard reference state, for example, is $\bar{h}_{500\text{K}} - \bar{h}^\circ = 14,581 - 8669 = 5912$ kJ/kmol.

Consider the formation of CO_2 from its elements, carbon and oxygen, during a steady-flow combustion process (Fig. 15-16). Both the carbon and the oxygen enter the combustion chamber at 25°C and 1 atm. The CO_2 formed during this process also leaves the combustion chamber at 25°C and 1 atm. The combustion of carbon is an *exothermic reaction* (a reaction dur-

ing which chemical energy is released in the form of heat). Therefore, some heat is transferred from the combustion chamber to the surroundings during this process, which is 393,520 kJ/kmol CO₂ formed. (When one is dealing with chemical reactions, it is more convenient to work with quantities per unit mole than per unit time, even for steady-flow processes.)

The process described above involves no work interactions. Therefore, from the steady-flow energy balance relation, the heat transfer during this process must be equal to the difference between the enthalpy of the products and the enthalpy of the reactants. That is,

$$Q = H_{\text{prod}} - H_{\text{react}} = -393,520 \text{ kJ/kmol} \quad (15-5)$$

Since both the reactants and the products are at the same state, the enthalpy change during this process is solely due to the changes in the chemical composition of the system. This enthalpy change is different for different reactions, and it is very desirable to have a property to represent the changes in chemical energy during a reaction. This property is the **enthalpy of reaction** h_R , which is defined as *the difference between the enthalpy of the products at a specified state and the enthalpy of the reactants at the same state for a complete reaction*.

For combustion processes, the enthalpy of reaction is usually referred to as the **enthalpy of combustion** h_C , which represents the amount of heat released during a steady-flow combustion process when 1 kmol (or 1 kg) of fuel is burned completely at a specified temperature and pressure (Fig. 15–17). It is expressed as

$$h_R = h_C = H_{\text{prod}} - H_{\text{react}} \quad (15-6)$$

which is $-393,520 \text{ kJ/kmol}$ for carbon at the standard reference state. The enthalpy of combustion of a particular fuel is different at different temperatures and pressures.

The enthalpy of combustion is obviously a very useful property for analyzing the combustion processes of fuels. However, there are so many different fuels and fuel mixtures that it is not practical to list h_C values for all possible cases. Besides, the enthalpy of combustion is not of much use when the combustion is incomplete. Therefore a more practical approach would be to have a more fundamental property to represent the chemical energy of an element or a compound at some reference state. This property is the **enthalpy of formation** \bar{h}_f , which can be viewed as *the enthalpy of a substance at a specified state due to its chemical composition*.

To establish a starting point, we assign the enthalpy of formation of all stable elements (such as O₂, N₂, H₂, and C) a value of zero at the standard reference state of 25°C and 1 atm. That is, $\bar{h}_f = 0$ for all stable elements. (This is no different from assigning the internal energy of saturated liquid water a value of zero at 0.01°C.) Perhaps we should clarify what we mean by *stable*. The stable form of an element is simply the chemically stable form of that element at 25°C and 1 atm. Nitrogen, for example, exists in diatomic form (N₂) at 25°C and 1 atm. Therefore, the stable form of nitrogen at the standard reference state is diatomic nitrogen N₂, not monatomic nitrogen N. If an element exists in more than one stable form at 25°C and 1 atm, one of the forms should be specified as the stable form. For carbon, for example, the stable form is assumed to be graphite, not diamond.

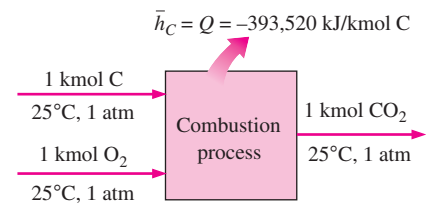


FIGURE 15–17

The enthalpy of combustion represents the amount of energy released as a fuel is burned during a steady-flow process at a specified state.

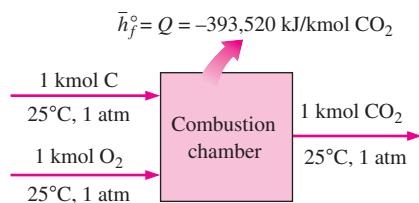


FIGURE 15–18

The enthalpy of formation of a compound represents the amount of energy absorbed or released as the component is formed from its stable elements during a steady-flow process at a specified state.

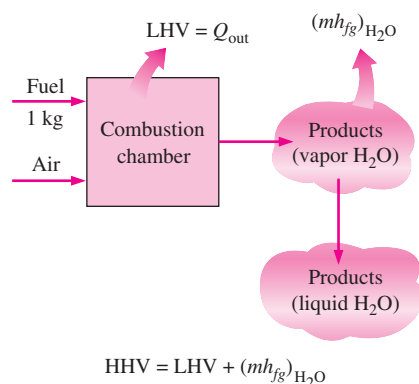


FIGURE 15–19

The higher heating value of a fuel is equal to the sum of the lower heating value of the fuel and the latent heat of vaporization of the H_2O in the products.

Now reconsider the formation of CO_2 (a compound) from its elements C and O_2 at 25°C and 1 atm during a steady-flow process. The enthalpy change during this process was determined to be $-393,520$ kJ/kmol. However, $H_{\text{react}} = 0$ since both reactants are elements at the standard reference state, and the products consist of 1 kmol of CO_2 at the same state. Therefore, the enthalpy of formation of CO_2 at the standard reference state is $-393,520$ kJ/kmol (Fig. 15–18). That is,

$$\bar{h}_{f,\text{CO}_2}^o = -393,520 \text{ kJ/kmol}$$

The negative sign is due to the fact that the enthalpy of 1 kmol of CO_2 at 25°C and 1 atm is 393,520 kJ less than the enthalpy of 1 kmol of C and 1 kmol of O_2 at the same state. In other words, 393,520 kJ of chemical energy is released (leaving the system as heat) when C and O_2 combine to form 1 kmol of CO_2 . Therefore, a negative enthalpy of formation for a compound indicates that heat is released during the formation of that compound from its stable elements. A positive value indicates heat is absorbed.

You will notice that two h_f^o values are given for H_2O in Table A–26, one for liquid water and the other for water vapor. This is because both phases of H_2O are encountered at 25°C , and the effect of pressure on the enthalpy of formation is small. (Note that under equilibrium conditions, water exists only as a liquid at 25°C and 1 atm.) The difference between the two enthalpies of formation is equal to the h_{fg} of water at 25°C , which is 2441.7 kJ/kg or 44,000 kJ/kmol.

Another term commonly used in conjunction with the combustion of fuels is the **heating value** of the fuel, which is defined as the amount of heat released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants. In other words, the heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel. That is,

$$\text{Heating value} = |h_c| \quad (\text{kJ/kg fuel})$$

The heating value depends on the *phase* of the H_2O in the products. The heating value is called the **higher heating value** (HHV) when the H_2O in the products is in the liquid form, and it is called the **lower heating value** (LHV) when the H_2O in the products is in the vapor form (Fig. 15–19). The two heating values are related by

$$\text{HHV} = \text{LHV} + (mh_{fg})_{\text{H}_2\text{O}} \quad (\text{kJ/kg fuel}) \quad (15-7)$$

where m is the mass of H_2O in the products per unit mass of fuel and h_{fg} is the enthalpy of vaporization of water at the specified temperature. Higher and lower heating values of common fuels are given in Table A–27.

The heating value or enthalpy of combustion of a fuel can be determined from a knowledge of the enthalpy of formation for the compounds involved. This is illustrated with the following example.

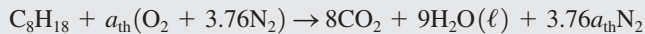
EXAMPLE 15–5 Evaluation of the Enthalpy of Combustion

Determine the enthalpy of combustion of liquid octane (C_8H_{18}) at 25°C and 1 atm, using enthalpy-of-formation data from Table A–26. Assume the water in the products is in the liquid form.

Solution The enthalpy of combustion of a fuel is to be determined using enthalpy of formation data.

Properties The enthalpy of formation at 25°C and 1 atm is $-393,520$ kJ/kmol for CO_2 , $-285,830$ kJ/kmol for $\text{H}_2\text{O}(\ell)$, and $-249,950$ kJ/kmol for $\text{C}_8\text{H}_{18}(\ell)$ (Table A-26).

Analysis The combustion of C_8H_{18} is illustrated in Fig. 15–20. The stoichiometric equation for this reaction is



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 C_8H_{18} becomes (Eq. 15–6)

$$\begin{aligned} \bar{h}_C &= H_{\text{prod}} - H_{\text{react}} \\ &= \sum N_p \bar{h}_{f,p}^\circ - \sum N_r \bar{h}_{f,r}^\circ = (N\bar{h}_f^\circ)_{\text{CO}_2} + (N\bar{h}_f^\circ)_{\text{H}_2\text{O}} - (N\bar{h}_f^\circ)_{\text{C}_8\text{H}_{18}} \end{aligned}$$

Substituting,

$$\begin{aligned} \bar{h}_C &= (8 \text{ kmol})(-393,520 \text{ kJ/kmol}) + (9 \text{ kmol})(-285,830 \text{ kJ/kmol}) \\ &\quad - (1 \text{ kmol})(-249,950 \text{ kJ/kmol}) \\ &= \mathbf{-5,471,000 \text{ kJ/kmol C}_8\text{H}_{18} = -47,891 \text{ kJ/kg C}_8\text{H}_{18}} \end{aligned}$$

which is practically identical to the listed value of 47,890 kJ/kg in Table A-27. Since the water in the products is assumed to be in the liquid phase, this h_C value corresponds to the HHV of liquid C_8H_{18} .

Discussion It can be shown that the result for gaseous octane is $-5,512,200$ kJ/kmol or $-48,255$ kJ/kg.

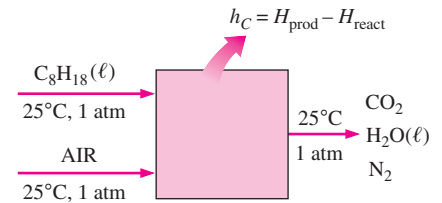


FIGURE 15–20

Schematic for Example 15–5.

When the exact composition of the fuel is known, the *enthalpy of combustion* of that fuel can be determined using enthalpy of formation data as shown above. However, for fuels that exhibit considerable variations in composition depending on the source, such as coal, natural gas, and fuel oil, it is more practical to determine their enthalpy of combustion experimentally by burning them directly in a bomb calorimeter at constant volume or in a steady-flow device.

15–4 ■ FIRST-LAW ANALYSIS OF REACTING SYSTEMS

The energy balance (or the first-law) relations developed in Chaps. 4 and 5 are applicable to both reacting and nonreacting systems. However, chemically reacting systems involve changes in their chemical energy, and thus it is more convenient to rewrite the energy balance relations so that the changes in chemical energies are explicitly expressed. We do this first for steady-flow systems and then for closed systems.

Steady-Flow Systems

Before writing the energy balance relation, we need to express the enthalpy of a component in a form suitable for use for reacting systems. That is, we need to express the enthalpy such that it is relative to the standard reference

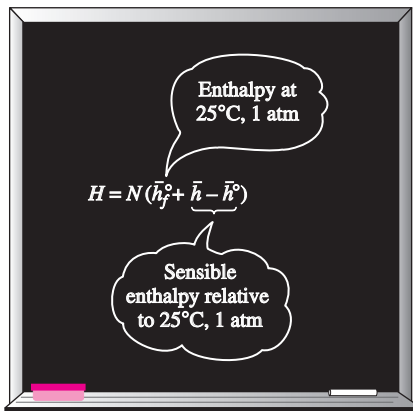


FIGURE 15-21

The enthalpy of a chemical component at a specified state is the sum of the enthalpy of the component at 25°C, 1 atm (h_f°), and the sensible enthalpy of the component relative to 25°C, 1 atm.

state and the chemical energy term appears explicitly. When expressed properly, the enthalpy term should reduce to the enthalpy of formation \bar{h}_f° at the standard reference state. With this in mind, we express the enthalpy of a component on a unit mole basis as (Fig. 15–21)

$$\text{Enthalpy} = \bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ) \quad (\text{kJ/kmol})$$

where the term in the parentheses represents the sensible enthalpy relative to the standard reference state, which is the difference between \bar{h} (the sensible enthalpy at the specified state) and \bar{h}° (the sensible enthalpy at the standard reference state of 25°C and 1 atm). This definition enables us to use enthalpy values from tables regardless of the reference state used in their construction.

When the changes in kinetic and potential energies are negligible, the steady-flow energy balance relation $\dot{E}_{\text{in}} = \dot{E}_{\text{out}}$ can be expressed for a *chemically reacting steady-flow system* more explicitly as

$$\underbrace{\dot{Q}_{\text{in}} + \dot{W}_{\text{in}} + \sum \dot{n}_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r}_{\text{Rate of net energy transfer in by heat, work, and mass}} = \underbrace{\dot{Q}_{\text{out}} + \dot{W}_{\text{out}} + \sum \dot{n}_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p}_{\text{Rate of net energy transfer out by heat, work, and mass}} \quad (15-8)$$

where \dot{n}_p and \dot{n}_r represent the molal flow rates of the product p and the reactant r , respectively.

In combustion analysis, it is more convenient to work with quantities expressed *per mole of fuel*. Such a relation is obtained by dividing each term of the equation above by the molal flow rate of the fuel, yielding

$$\underbrace{Q_{\text{in}} + W_{\text{in}} + \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r}_{\text{Energy transfer in per mole of fuel by heat, work, and mass}} = \underbrace{Q_{\text{out}} + W_{\text{out}} + \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p}_{\text{Energy transfer out per mole of fuel by heat, work, and mass}} \quad (15-9)$$

where N_r and N_p represent the number of moles of the reactant r and the product p , respectively, per mole of fuel. Note that $N_r = 1$ for the fuel, and the other N_r and N_p values can be picked directly from the balanced combustion equation. Taking heat transfer *to* the system and work done *by* the system to be *positive* quantities, the energy balance relation just discussed can be expressed more compactly as

$$Q - W = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r \quad (15-10)$$

or as

$$Q - W = H_{\text{prod}} - H_{\text{react}} \quad (\text{kJ/kmol fuel}) \quad (15-11)$$

where

$$H_{\text{prod}} = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p \quad (\text{kJ/kmol fuel})$$

$$H_{\text{react}} = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r \quad (\text{kJ/kmol fuel})$$

If the enthalpy of combustion \bar{h}_c° for a particular reaction is available, the steady-flow energy equation per mole of fuel can be expressed as

$$Q - W = \bar{h}_c^\circ + \sum N_p(\bar{h} - \bar{h}^\circ)_p - \sum N_r(\bar{h} - \bar{h}^\circ)_r \quad (\text{kJ/kmol}) \quad (15-12)$$

The energy balance relations above are sometimes written without the work term since most steady-flow combustion processes do not involve any work interactions.

A combustion chamber normally involves heat output but no heat input. Then the energy balance for a *typical steady-flow combustion process* becomes

$$Q_{\text{out}} = \underbrace{\sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)}_{\text{Energy in by mass per mole of fuel}, r} - \underbrace{\sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)}_{\text{Energy out by mass per mole of fuel}, p} \quad (15-13)$$

It expresses that the heat output during a combustion process is simply the difference between the energy of the reactants entering and the energy of the products leaving the combustion chamber.

Closed Systems

The general closed-system energy balance relation $E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$ can be expressed for a stationary *chemically reacting closed system* as

$$(Q_{\text{in}} - Q_{\text{out}}) + (W_{\text{in}} - W_{\text{out}}) = U_{\text{prod}} - U_{\text{react}} \quad (\text{kJ/kmol fuel}) \quad (15-14)$$

where U_{prod} represents the internal energy of the products and U_{react} represents the internal energy of the reactants. To avoid using another property—the *internal energy of formation* \bar{u}_f° —we utilize the definition of enthalpy ($\bar{u} = \bar{h} - P\bar{v}$ or $\bar{u}_f^\circ + \bar{u} - \bar{u}^\circ = \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v}$) and express the above equation as (Fig. 15–22)

$$Q - W = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_p - \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_r \quad (15-15)$$

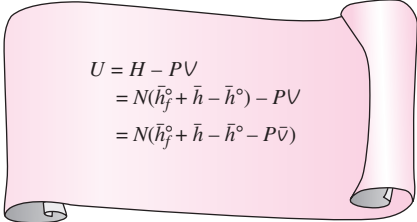
where we have taken heat transfer *to* the system and work done *by* the system to be *positive* quantities. The $P\bar{v}$ terms are negligible for solids and liquids, and can be replaced by $R_u T$ for gases that behave as an ideal gas. Also, if desired, the $\bar{h} - P\bar{v}$ terms in Eq. 15–15 can be replaced by \bar{u} .

The work term in Eq. 15–15 represents all forms of work, including the boundary work. It was shown in Chap. 4 that $\Delta U + W_b = \Delta H$ for nonreacting closed systems undergoing a quasi-equilibrium $P = \text{constant}$ expansion or compression process. This is also the case for chemically reacting systems.

There are several important considerations in the analysis of reacting systems. For example, we need to know whether the fuel is a solid, a liquid, or a gas since the enthalpy of formation h_f° of a fuel depends on the phase of the fuel. We also need to know the state of the fuel when it enters the combustion chamber in order to determine its enthalpy. For entropy calculations it is especially important to know if the fuel and air enter the combustion chamber premixed or separately. When the combustion products are cooled to low temperatures, we need to consider the possibility of condensation of some of the water vapor in the product gases.

EXAMPLE 15–6 First-Law Analysis of Steady-Flow Combustion

Liquid propane (C_3H_8) enters a combustion chamber at 25°C at a rate of 0.05 kg/min where it is mixed and burned with 50 percent excess air that enters the combustion chamber at 7°C , as shown in Fig. 15–23. An analysis of the combustion gases reveals that all the hydrogen in the fuel burns to H_2O but only 90 percent of the carbon burns to CO_2 , with the remaining 10 percent forming CO . If the exit temperature of the combustion gases is



$$\begin{aligned} U &= H - PV \\ &= N(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ) - PV \\ &= N(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v}) \end{aligned}$$

FIGURE 15–22

An expression for the internal energy of a chemical component in terms of the enthalpy.

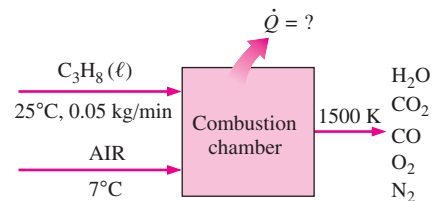


FIGURE 15–23

Schematic for Example 15–6.

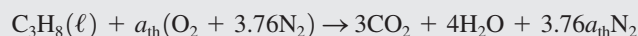
1500 K, determine (a) the mass flow rate of air and (b) the rate of heat transfer from the combustion chamber.

Solution Liquid propane is burned steadily with excess air. The mass flow rate of air and the rate of heat transfer are to be determined.

Assumptions **1** Steady operating conditions exist. **2** Air and the combustion gases are ideal gases. **3** Kinetic and potential energies are negligible.

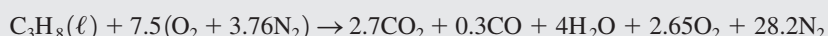
Analysis We note that all the hydrogen in the fuel burns to H₂O but 10 percent of the carbon burns incompletely and forms CO. Also, the fuel is burned with excess air and thus there is some free O₂ in the product gases.

The theoretical amount of air is determined from the stoichiometric reaction to be



O₂ balance: $a_{\text{th}} = 3 + 2 = 5$

Then the balanced equation for the actual combustion process with 50 percent excess air and some CO in the products becomes



(a) The air–fuel ratio for this combustion process is

$$\begin{aligned} \text{AF} &= \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{(7.5 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(3 \text{ kmol})(12 \text{ kg/kmol}) + (4 \text{ kmol})(2 \text{ kg/kmol})} \\ &= 25.53 \text{ kg air/kg fuel} \end{aligned}$$

Thus,

$$\begin{aligned} \dot{m}_{\text{air}} &= (\text{AF})(\dot{m}_{\text{fuel}}) \\ &= (25.53 \text{ kg air/kg fuel})(0.05 \text{ kg fuel/min}) \\ &= \mathbf{1.18 \text{ kg air/min}} \end{aligned}$$

(b) The heat transfer for this steady-flow combustion process is determined from the steady-flow energy balance $E_{\text{out}} = E_{\text{in}}$ applied on the combustion chamber per unit mole of the fuel,

$$Q_{\text{out}} + \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r$$

or

$$Q_{\text{out}} = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r - \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p$$

Assuming the air and the combustion products to be ideal gases, we have $h = h(T)$, and we form the following minitable using data from the property tables:

Substance	\bar{h}_f° kJ/kmol	$\bar{h}_{280 \text{ K}}$ kJ/kmol	$\bar{h}_{298 \text{ K}}$ kJ/kmol	$\bar{h}_{1500 \text{ K}}$ kJ/kmol
C ₃ H ₈ (ℓ)	−118,910	—	—	—
O ₂	0	8150	8682	49,292
N ₂	0	8141	8669	47,073
H ₂ O(g)	−241,820	—	9904	57,999
CO ₂	−393,520	—	9364	71,078
CO	−110,530	—	8669	47,517

The \bar{h}_f° of liquid propane is obtained by subtracting the \bar{h}_{fg} of propane at 25°C from the \bar{h}_f° of gas propane. Substituting gives

$$\begin{aligned} Q_{\text{out}} &= (1 \text{ kmol C}_3\text{H}_8)[(-118,910 + h_{298} - h_{298}) \text{ kJ/kmol C}_3\text{H}_8] \\ &\quad + (7.5 \text{ kmol O}_2)[(0 + 8150 - 8682) \text{ kJ/kmol O}_2] \\ &\quad + (28.2 \text{ kmol N}_2)[(0 + 8141 - 8669) \text{ kJ/kmol N}_2] \\ &\quad - (2.7 \text{ kmol CO}_2)[(-393,520 + 71,078 - 9364) \text{ kJ/kmol CO}_2] \\ &\quad - (0.3 \text{ kmol CO})[(-110,530 + 47,517 - 8669) \text{ kJ/kmol CO}] \\ &\quad - (4 \text{ kmol H}_2\text{O})[(-241,820 + 57,999 - 9904) \text{ kJ/kmol H}_2\text{O}] \\ &\quad - (2.65 \text{ kmol O}_2)[(0 + 49,292 - 8682) \text{ kJ/kmol O}_2] \\ &\quad - (28.2 \text{ kmol N}_2)[(0 + 47,073 - 8669) \text{ kJ/kmol N}_2] \\ &= 363,880 \text{ kJ/kmol of C}_3\text{H}_8 \end{aligned}$$

Thus 363,880 kJ of heat is transferred from the combustion chamber for each kmol (44 kg) of propane. This corresponds to $363,880/44 = 8270$ kJ of heat loss per kilogram of propane. Then the rate of heat transfer for a mass flow rate of 0.05 kg/min for the propane becomes

$$\dot{Q}_{\text{out}} = \dot{m}q_{\text{out}} = (0.05 \text{ kg/min})(8270 \text{ kJ/kg}) = 413.5 \text{ kJ/min} = \mathbf{6.89 \text{ kW}}$$

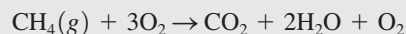
EXAMPLE 15–7 First-Law Analysis of Combustion in a Bomb

The constant-volume tank shown in Fig. 15–24 contains 1 lbmol of methane (CH_4) gas and 3 lbmol of O_2 at 77°F and 1 atm. The contents of the tank are ignited, and the methane gas burns completely. If the final temperature is 1800 R, determine (a) the final pressure in the tank and (b) the heat transfer during this process.

Solution Methane is burned in a rigid tank. The final pressure in the tank and the heat transfer are 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, the air, and the combustion gases are ideal gases. **3** Kinetic and potential energies are negligible. **4** There are no work interactions involved.

Analysis The balanced combustion equation is



(a) At 1800 R, water exists in the gas phase. Using the ideal-gas relation for both the reactants and the products, the final pressure in the tank is determined to be

$$\left. \begin{aligned} P_{\text{react}}V &= N_{\text{react}}R_uT_{\text{react}} \\ P_{\text{prod}}V &= N_{\text{prod}}R_uT_{\text{prod}} \end{aligned} \right\} P_{\text{prod}} = P_{\text{react}} \left(\frac{N_{\text{prod}}}{N_{\text{react}}} \right) \left(\frac{T_{\text{prod}}}{T_{\text{react}}} \right)$$

Substituting, we get

$$P_{\text{prod}} = (1 \text{ atm}) \left(\frac{4 \text{ lbmol}}{4 \text{ lbmol}} \right) \left(\frac{1800 \text{ R}}{537 \text{ R}} \right) = \mathbf{3.35 \text{ atm}}$$

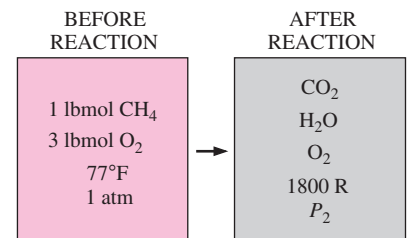


FIGURE 15–24

Schematic for Example 15–7.

(b) Noting that the process involves no work interactions, the heat transfer during this constant-volume combustion process can be determined from the energy balance $E_{in} - E_{out} = \Delta E_{system}$ applied to the tank,

$$-Q_{out} = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_p - \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_r$$

Since both the reactants and the 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 $R_u T$. It yields

$$Q_{out} = \sum N_r(\bar{h}_f^\circ - R_u T)_r - \sum N_p(\bar{h}_f^\circ + \bar{h}_{1800\text{ R}} - \bar{h}_{537\text{ R}} - R_u T)_p$$

since the reactants are at the standard reference temperature of 537 R. From \bar{h}_f° and ideal-gas tables in the Appendix,

Substance	\bar{h}_f° Btu/lbmol	$\bar{h}_{537\text{ R}}$ Btu/lbmol	$\bar{h}_{1800\text{ R}}$ Btu/lbmol
CH ₄	-32,210	—	—
O ₂	0	3725.1	13,485.8
CO ₂	-169,300	4027.5	18,391.5
H ₂ O(g)	-104,040	4258.0	15,433.0

Substituting, we have

$$\begin{aligned} Q_{out} &= (1 \text{ lbmol CH}_4)[(-32,210 - 1.986 \times 537) \text{ Btu/lbmol CH}_4] \\ &\quad + (3 \text{ lbmol O}_2)[(0 - 1.986 \times 537) \text{ Btu/lbmol O}_2] \\ &\quad - (1 \text{ lbmol CO}_2)[(-169,300 + 18,391.5 - 4027.5 - 1.986 \times 1800) \\ &\quad \quad \text{Btu/lbmol CO}_2] \\ &\quad - (2 \text{ lbmol H}_2\text{O})[(-104,040 + 15,433.0 - 4258.0 - 1.986 \times 1800) \\ &\quad \quad \text{Btu/lbmol H}_2\text{O}] \\ &\quad - (1 \text{ lbmol O}_2)[(0 + 13,485.8 - 3725.1 - 1.986 \times 1800) \text{ Btu/lbmol O}_2] \\ &= \mathbf{308,730 \text{ Btu/lbmol CH}_4} \end{aligned}$$

Discussion On a mass basis, the heat transfer from the tank would be $308,730/16 = 19,300$ Btu/lbm of methane.

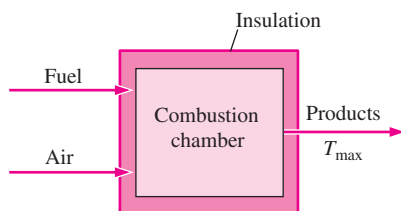


FIGURE 15–25

The temperature of a combustion chamber becomes maximum when combustion is complete and no heat is lost to the surroundings ($Q = 0$).

15–5 ■ ADIABATIC FLAME TEMPERATURE

In the absence of any work interactions and any changes in kinetic or potential energies, the chemical energy released during a combustion process either is lost as heat to the surroundings or is used internally to raise the temperature of the combustion products. The smaller the heat loss, the larger the temperature rise. In the limiting case of no heat loss to the surroundings ($Q = 0$), the temperature of the products reaches a maximum, which is called the **adiabatic flame** or **adiabatic combustion temperature** of the reaction (Fig. 15–25).

The adiabatic flame temperature of a steady-flow combustion process is determined from Eq. 15–11 by setting $Q = 0$ and $W = 0$. It yields

$$H_{\text{prod}} = H_{\text{react}} \quad (15-16)$$

or

$$\sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r \quad (15-17)$$

Once the reactants and their states are specified, the enthalpy of the reactants H_{react} can be easily determined. The calculation of the enthalpy of the products H_{prod} is not so straightforward, however, because the temperature of the products is not known prior to the calculations. Therefore, the determination of the adiabatic flame temperature requires the use of an iterative technique unless equations for the sensible enthalpy changes of the combustion products are available. A temperature is assumed for the product gases, and the H_{prod} is determined for this temperature. If it is not equal to H_{react} , calculations are repeated with another temperature. The adiabatic flame temperature is then determined from these two results by interpolation. When the oxidant is air, the product gases mostly consist of N_2 , and a good first guess for the adiabatic flame temperature is obtained by treating the entire product gases as N_2 .

In combustion chambers, the highest temperature to which a material can be exposed is limited by metallurgical considerations. Therefore, the adiabatic flame temperature is an important consideration in the design of combustion chambers, gas turbines, and nozzles. The maximum temperatures that occur in these devices are considerably lower than the adiabatic flame temperature, however, since the combustion is usually incomplete, some heat loss takes place, and some combustion gases dissociate at high temperatures (Fig. 15–26). The maximum temperature in a combustion chamber can be controlled by adjusting the amount of excess air, which serves as a coolant.

Note that the adiabatic flame temperature of a fuel is not unique. Its value depends on (1) the state of the reactants, (2) the degree of completion of the reaction, and (3) the amount of air used. For a specified fuel at a specified state burned with air at a specified state, *the adiabatic flame temperature attains its maximum value when complete combustion occurs with the theoretical amount of air.*

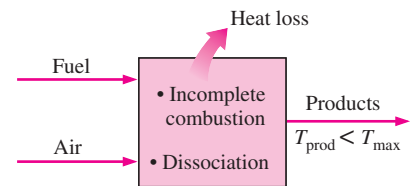


FIGURE 15–26

The maximum temperature encountered in a combustion chamber is lower than the theoretical adiabatic flame temperature.

EXAMPLE 15–8 Adiabatic Flame Temperature in Steady Combustion

Liquid octane (C_8H_{18}) enters the combustion chamber of a gas turbine steadily at 1 atm and 25°C , and it is burned with air that enters the combustion chamber at the same state, as shown in Fig. 15–27. Determine the adiabatic flame temperature for (a) complete combustion with 100 percent theoretical air, (b) complete combustion with 400 percent theoretical air, and (c) incomplete combustion (some CO in the products) with 90 percent theoretical air.

Solution Liquid octane is burned steadily. The adiabatic flame temperature is to be determined for different cases.

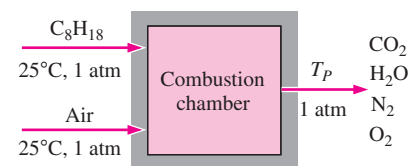


FIGURE 15–27

Schematic for Example 15–8.

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 $T_{\text{prod}} = 2395 \text{ K}$.

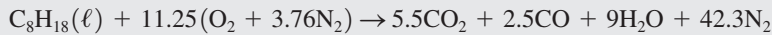
(b) The balanced equation for the complete combustion process with 400 percent theoretical air is



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.*

15-6 ■ ENTROPY CHANGE OF REACTING SYSTEMS

So far we have analyzed combustion processes from the conservation of mass and the conservation of energy points of view. The thermodynamic analysis of a process is not complete, however, without the examination of the second-law aspects. Of particular interest are the exergy and exergy destruction, both of which are related to entropy.

The entropy balance relations developed in Chap. 7 are equally applicable to both reacting and nonreacting systems provided that the entropies of individual constituents are evaluated properly using a common basis. The **entropy balance** for *any system* (including reacting systems) undergoing *any process* can be expressed as

$$\underbrace{S_{\text{in}} - S_{\text{out}}}_{\text{Net entropy transfer by heat and mass}} + \underbrace{S_{\text{gen}}}_{\text{Entropy generation}} = \underbrace{\Delta S_{\text{system}}}_{\text{Change in entropy}} \quad (\text{kJ/K}) \quad (15-18)$$

Using quantities per unit mole of fuel and taking the positive direction of heat transfer to be *to* the system, the entropy balance relation can be expressed more explicitly for a *closed* or *steady-flow* reacting system as (Fig. 15-28)

$$\sum \frac{Q_k}{T_k} + S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}} \quad (\text{kJ/K}) \quad (15-19)$$

where T_k is temperature at the boundary where Q_k crosses it. For an *adiabatic process* ($Q = 0$), the entropy transfer term drops out and Eq. 15-19 reduces to

$$S_{\text{gen,adiabatic}} = S_{\text{prod}} - S_{\text{react}} \geq 0 \quad (15-20)$$

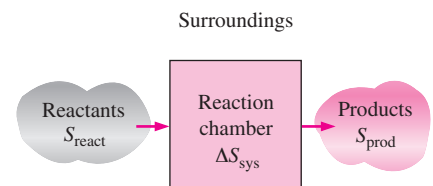


FIGURE 15-28

The entropy change associated with a chemical relation.

The *total* entropy generated during a process can be determined by applying the entropy balance to an *extended system* that includes the system itself and its immediate surroundings where external irreversibilities might be occurring. When evaluating the entropy transfer between an extended system and the surroundings, the boundary temperature of the extended system is simply taken to be the *environment temperature*, as explained in Chap. 7.

The determination of the entropy change associated with a chemical reaction seems to be straightforward, except for one thing: The entropy relations for the reactants and the products involve the *entropies* of the components, *not entropy changes*, which was the case for nonreacting systems. Thus we are faced with the problem of finding a common base for the entropy of all substances, as we did with enthalpy. The search for such a common base led to the establishment of the **third law of thermodynamics** in the early part of this century. The third law was expressed in Chap. 7 as follows: *The entropy of a pure crystalline substance at absolute zero temperature is zero.*

Therefore, the third law of thermodynamics provides an absolute base for the entropy values for all substances. Entropy values relative to this base are called the **absolute entropy**. The \bar{s}° values listed in Tables A–18 through A–25 for various gases such as N_2 , O_2 , CO , CO_2 , H_2 , H_2O , OH , and O are the *ideal-gas absolute entropy values* at the specified temperature and *at a pressure of 1 atm*. The absolute entropy values for various fuels are listed in Table A–26 together with the \bar{h}_f° values at the standard reference state of 25°C and 1 atm.

Equation 15–20 is a general relation for the entropy change of a reacting system. It requires the determination of the entropy of each individual component of the reactants and the products, which in general is not very easy to do. The entropy calculations can be simplified somewhat if the gaseous components of the reactants and the products are approximated as ideal gases. However, entropy calculations are never as easy as enthalpy or internal energy calculations, since entropy is a function of both temperature and pressure even for ideal gases.

When evaluating the entropy of a component of an ideal-gas mixture, we should use the temperature and the partial pressure of the component. Note that the temperature of a component is the same as the temperature of the mixture, and the partial pressure of a component is equal to the mixture pressure multiplied by the mole fraction of the component.

Absolute entropy values at pressures other than $P_0 = 1$ atm for any temperature T can be obtained from the ideal-gas entropy change relation written for an imaginary isothermal process between states (T, P_0) and (T, P) , as illustrated in Fig. 15–29:

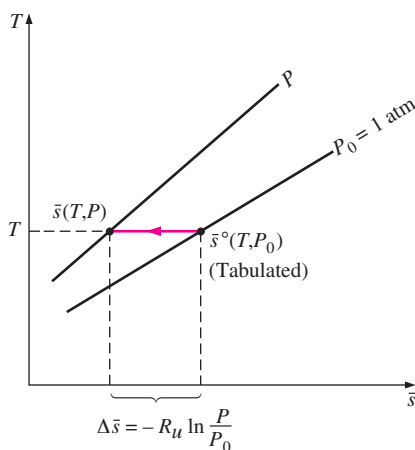


FIGURE 15–29

At a specified temperature, the absolute entropy of an ideal gas at pressures other than $P_0 = 1$ atm can be determined by subtracting $R_u \ln(P/P_0)$ from the tabulated value at 1 atm.

$$\bar{s}(T, P) = \bar{s}^\circ(T, P_0) - R_u \ln \frac{P}{P_0} \quad (15-21)$$

For the component i of an ideal-gas mixture, this relation can be written as

$$\bar{s}_i(T, P_i) = \bar{s}_i^\circ(T, P_0) - R_u \ln \frac{y_i P_m}{P_0} \quad (\text{kJ/kmol} \cdot \text{K}) \quad (15-22)$$

where $P_0 = 1$ atm, P_i is the partial pressure, y_i is the mole fraction of the component, and P_m is the total pressure of the mixture.

If a gas mixture is at a relatively high pressure or low temperature, the deviation from the ideal-gas behavior should be accounted for by incorporating more accurate equations of state or the generalized entropy charts.

15-7 ■ SECOND-LAW ANALYSIS OF REACTING SYSTEMS

Once the total entropy change or the entropy generation is evaluated, the **exergy destroyed** $X_{\text{destroyed}}$ associated with a chemical reaction can be determined from

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} \quad (\text{kJ}) \quad (15-23)$$

where T_0 is the thermodynamic temperature of the surroundings.

When analyzing reacting systems, we are more concerned with the changes in the exergy of reacting systems than with the values of exergy at various states (Fig. 15-30). Recall from Chap. 8 that the **reversible work** W_{rev} represents the maximum work that can be done during a process. In the absence of any changes in kinetic and potential energies, the reversible work relation for a steady-flow combustion process that involves heat transfer with only the surroundings at T_0 can be obtained by replacing the enthalpy terms by $\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ$, yielding

$$W_{\text{rev}} = \sum N_r (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0 \bar{s})_r - \sum N_p (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0 \bar{s})_p \quad (15-24)$$

An interesting situation arises when both the reactants and the products are at the temperature of the surroundings T_0 . In that case, $\bar{h} - T_0 \bar{s} = (\bar{h} - T_0 \bar{s})_{T_0} = \bar{g}_0$, which is, by definition, the **Gibbs function** of a unit mole of a substance at temperature T_0 . The W_{rev} relation in this case can be written as

$$W_{\text{rev}} = \sum N_r \bar{g}_{0,r} - \sum N_p \bar{g}_{0,p} \quad (15-25)$$

or

$$W_{\text{rev}} = \sum N_r (\bar{g}_f^\circ + \bar{g}_{T_0} - \bar{g}^\circ)_r - \sum N_p (\bar{g}_f^\circ + \bar{g}_{T_0} - \bar{g}^\circ)_p \quad (15-26)$$

where \bar{g}_f° is the Gibbs function of formation ($\bar{g}_f^\circ = 0$ for stable elements like N_2 and O_2 at the standard reference state of 25°C and 1 atm, just like the enthalpy of formation) and $\bar{g}_{T_0} - \bar{g}^\circ$ represents the value of the sensible Gibbs function of a substance at temperature T_0 relative to the standard reference state.

For the very special case of $T_{\text{react}} = T_{\text{prod}} = T_0 = 25^\circ\text{C}$ (i.e., the reactants, the products, and the surroundings are at 25°C) and the partial pressure $P_i = 1$ atm for each component of the reactants and the products, Eq. 15-26 reduces to

$$W_{\text{rev}} = \sum N_r \bar{g}_{f,r}^\circ - \sum n_p \bar{g}_{f,p}^\circ \quad (\text{kJ}) \quad (15-27)$$

We can conclude from the above equation that the $-\bar{g}_f^\circ$ value (the negative of the Gibbs function of formation at 25°C and 1 atm) of a compound represents the *reversible work* associated with the formation of that compound from its stable elements at 25°C and 1 atm in an environment at 25°C and 1 atm (Fig. 15-31). The \bar{g}_f° values of several substances are listed in Table A-26.

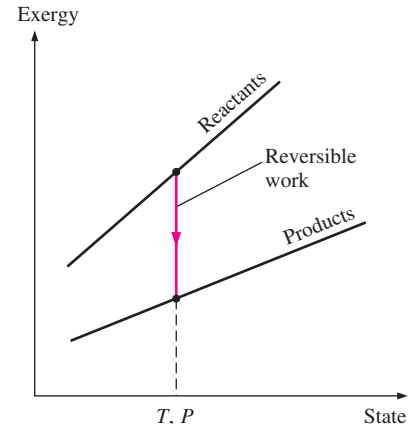


FIGURE 15-30

The difference between the exergy of the reactants and of the products during a chemical reaction is the reversible work associated with that reaction.

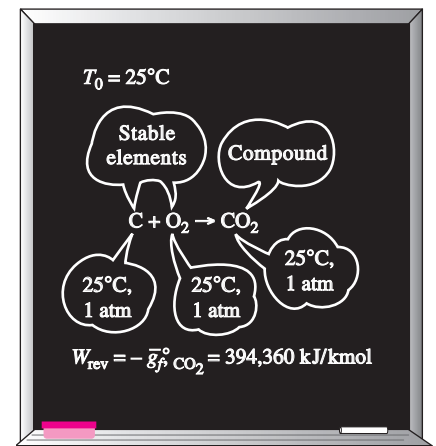


FIGURE 15-31

The negative of the Gibbs function of formation of a compound at 25°C , 1 atm represents the reversible work associated with the formation of that compound from its stable elements at 25°C , 1 atm in an environment that is at 25°C , 1 atm.

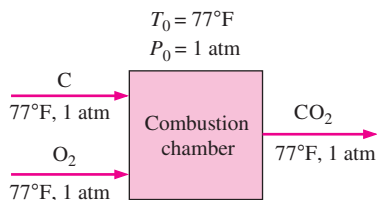


FIGURE 15-32

Schematic for Example 15-9.

EXAMPLE 15-9 Reversible Work Associated with a Combustion Process

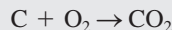
One lbmol of carbon at 77°F and 1 atm is burned steadily with 1 lbmol of oxygen at the same state as shown in Fig. 15-32. The CO₂ formed during the process is then brought to 77°F and 1 atm, the conditions of the surroundings. Assuming the combustion is complete, determine the reversible work for this process.

Solution Carbon is burned steadily with pure oxygen. The reversible work associated with this process is to be determined.

Assumptions 1 Combustion is complete. 2 Steady-flow conditions exist during combustion. 3 Oxygen and the combustion gases are ideal gases. 4 Changes in kinetic and potential energies are negligible.

Properties The Gibbs function of formation at 77°F and 1 atm is 0 for C and O₂, and -169,680 Btu/lbmol for CO₂. The enthalpy of formation is 0 for C and O₂, and -169,300 Btu/lbmol for CO₂. The absolute entropy is 1.36 Btu/lbmol · R for C, 49.00 Btu/lbmol · R for O₂, and 51.07 Btu/lbmol · R for CO₂ (Table A-26E).

Analysis The combustion equation is



The C, O₂, and CO₂ are at 77°F and 1 atm, which is the standard reference state and also the state of the surroundings. Therefore, the reversible work in this case is simply the difference between the Gibbs function of formation of the reactants and that of the products (Eq. 15-27):

$$\begin{aligned} W_{\text{rev}} &= \sum N_r \bar{g}_{f,r}^{\circ} - \sum N_p \bar{g}_{f,p}^{\circ} \\ &= N_{\text{C}} \bar{g}_{f,\text{C}}^{\circ} + N_{\text{O}_2} \bar{g}_{f,\text{O}_2}^{\circ} - N_{\text{CO}_2} \bar{g}_{f,\text{CO}_2}^{\circ} \\ &= (-1 \text{ lbmol})(-169,680 \text{ Btu/lbmol}) \\ &= \mathbf{169,680 \text{ Btu}} \end{aligned}$$

since the \bar{g}_f° of stable elements at 77°F and 1 atm is zero. Therefore, 169,680 Btu of work could be done as 1 lbmol of C is burned with 1 lbmol of O₂ at 77°F and 1 atm in an environment at the same state. The reversible work in this case represents the exergy of the reactants since the product (the CO₂) is at the state of the surroundings.

Discussion We could also determine the reversible work without involving the Gibbs function by using Eq. 15-24:

$$\begin{aligned} W_{\text{rev}} &= \sum N_r (\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ} - T_0 \bar{s})_r - \sum N_p (\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ} - T_0 \bar{s})_p \\ &= \sum N_r (\bar{h}_f^{\circ} - T_0 \bar{s})_r - \sum N_p (\bar{h}_f^{\circ} - T_0 \bar{s})_p \\ &= N_{\text{C}} (\bar{h}_f^{\circ} - T_0 \bar{s}^{\circ})_{\text{C}} + N_{\text{O}_2} (\bar{h}_f^{\circ} - T_0 \bar{s}^{\circ})_{\text{O}_2} - N_{\text{CO}_2} (\bar{h}_f^{\circ} - T_0 \bar{s}^{\circ})_{\text{CO}_2} \end{aligned}$$

Substituting the enthalpy of formation and absolute entropy values, we obtain

$$\begin{aligned} W_{\text{rev}} &= (1 \text{ lbmol C})[0 - (537 \text{ R})(1.36 \text{ Btu/lbmol} \cdot \text{R})] \\ &\quad + (1 \text{ lbmol O}_2)[0 - (537 \text{ R})(49.00 \text{ Btu/lbmol} \cdot \text{R})] \\ &\quad - (1 \text{ lbmol CO}_2)[-169,300 \text{ Btu/lbmol} - (537 \text{ R})(51.07 \text{ Btu/lbmol} \cdot \text{R})] \\ &= \mathbf{169,680 \text{ Btu}} \end{aligned}$$

which is identical to the result obtained before.

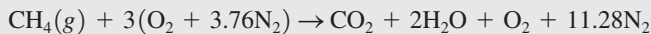
EXAMPLE 15–10 Second-Law Analysis of Adiabatic Combustion

Methane (CH_4) gas enters a steady-flow adiabatic combustion chamber at 25°C and 1 atm. It is burned with 50 percent excess air that also enters at 25°C and 1 atm, as shown in Fig. 15–33. Assuming complete combustion, determine (a) the temperature of the products, (b) the entropy generation, and (c) the reversible work and exergy destruction. Assume that $T_0 = 298\text{ K}$ and the products leave the combustion chamber at 1 atm pressure.

Solution Methane is burned with excess air in a steady-flow combustion chamber. The product temperature, entropy generated, reversible work, and exergy destroyed are to be determined.

Assumptions 1 Steady-flow conditions exist during combustion. 2 Air and the combustion gases are ideal gases. 3 Changes in kinetic and potential energies are negligible. 4 The combustion chamber is adiabatic and thus there is no heat transfer. 5 Combustion is complete.

Analysis (a) The balanced equation for the complete combustion process with 50 percent excess air is



Under steady-flow conditions, the adiabatic flame temperature is determined from $H_{\text{prod}} = H_{\text{react}}$, which reduces to

$$\sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p = \sum N_r \bar{h}_{f,r}^\circ = (N\bar{h}_f^\circ)_{\text{CH}_4}$$

since all the reactants are at the standard reference state and $\bar{h}_f^\circ = 0$ for O_2 and N_2 . Assuming ideal-gas behavior for air and for the products, the \bar{h}_f° and h values of various components at 298 K can be listed as

Substance	\bar{h}_f° kJ/kmol	$\bar{h}_{298\text{ K}}$ kJ/kmol
$\text{CH}_4(g)$	-74,850	—
O_2	0	8682
N_2	0	8669
$\text{H}_2\text{O}(g)$	-241,820	9904
CO_2	-393,520	9364

Substituting, we have

$$\begin{aligned} & (1 \text{ kmol CO}_2)[(-393,520 + \bar{h}_{\text{CO}_2} - 9364) \text{ kJ/kmol CO}_2] \\ & + (2 \text{ kmol H}_2\text{O})[(-241,820 + \bar{h}_{\text{H}_2\text{O}} - 9904) \text{ kJ/kmol H}_2\text{O}] \\ & + (11.28 \text{ kmol N}_2)[(0 + \bar{h}_{\text{N}_2} - 8669) \text{ kJ/kmol N}_2] \\ & + (1 \text{ kmol O}_2)[(0 + \bar{h}_{\text{O}_2} - 8682) \text{ kJ/kmol O}_2] \\ & = (1 \text{ kmol CH}_4)(-74,850 \text{ kJ/kmol CH}_4) \end{aligned}$$

which yields

$$\bar{h}_{\text{CO}_2} + 2\bar{h}_{\text{H}_2\text{O}} + \bar{h}_{\text{O}_2} + 11.28\bar{h}_{\text{N}_2} = 937,950 \text{ kJ}$$

By trial and error, the temperature of the products is found to be

$$T_{\text{prod}} = \mathbf{1789 \text{ K}}$$

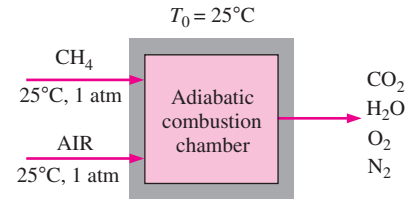


FIGURE 15–33

Schematic for Example 15–10.

(b) Noting that combustion is adiabatic, the entropy generation during this process is determined from Eq. 15–20:

$$S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}} = \sum N_p \bar{s}_p - \sum N_r \bar{s}_r$$

The CH_4 is at 25°C and 1 atm, and thus its absolute entropy is $\bar{s}_{\text{CH}_4} = 186.16 \text{ kJ/kmol} \cdot \text{K}$ (Table A–26). The entropy values listed in the ideal-gas tables are for 1 atm pressure. Both the air and the product gases are at a total pressure of 1 atm, but the entropies are to be calculated at the partial pressure of the components, which is equal to $P_i = y_i P_{\text{total}}$, where y_i is the mole fraction of component i . From Eq. 15–22:

$$S_i = N_i \bar{s}_i(T, P_i) = N_i [\bar{s}_i^\circ(T, P_0) - R_u \ln y_i P_m]$$

The entropy calculations can be represented in tabular form as follows:

	N_i	y_i	$\bar{s}_i^\circ(T, 1 \text{ atm})$	$-R_u \ln y_i P_m$	$N_i \bar{s}_i$
CH_4	1	1.00	186.16	—	186.16
O_2	3	0.21	205.04	12.98	654.06
N_2	11.28	0.79	191.61	1.96	2183.47
$S_{\text{react}} = 3023.69$					
CO_2	1	0.0654	302.517	22.674	325.19
H_2O	2	0.1309	258.957	16.905	551.72
O_2	1	0.0654	264.471	22.674	287.15
N_2	11.28	0.7382	247.977	2.524	2825.65
$S_{\text{prod}} = 3989.71$					

Thus,

$$\begin{aligned} S_{\text{gen}} &= S_{\text{prod}} - S_{\text{react}} = (3989.71 - 3023.69) \text{ kJ/kmol} \cdot \text{K CH}_4 \\ &= \mathbf{966.0 \text{ kJ/kmol} \cdot \text{K}} \end{aligned}$$

(c) The exergy destruction or irreversibility associated with this process is determined from Eq. 15–23,

$$\begin{aligned} X_{\text{destroyed}} &= T_0 S_{\text{gen}} = (298 \text{ K})(966.0 \text{ kJ/kmol} \cdot \text{K}) \\ &= \mathbf{288 \text{ MJ/kmol CH}_4} \end{aligned}$$

That is, 288 MJ of work potential is wasted during this combustion process for each kmol of methane burned. This example shows that even complete combustion processes are highly irreversible.

This process involves no actual work. Therefore, the reversible work and exergy destroyed are identical:

$$W_{\text{rev}} = \mathbf{288 \text{ MJ/kmol CH}_4}$$

That is, 288 MJ of work could be done during this process but is not. Instead, the entire work potential is wasted.

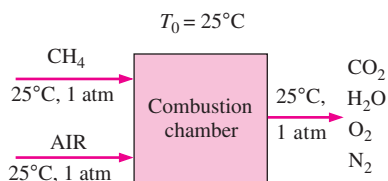


FIGURE 15–34

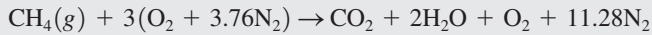
Schematic for Example 15–11.

EXAMPLE 15–11 Second-Law Analysis of Isothermal Combustion

Methane (CH_4) gas enters a steady-flow combustion chamber at 25°C and 1 atm and is burned with 50 percent excess air, which also enters at 25°C and 1 atm, as shown in Fig. 15–34. After combustion, the products are allowed to cool to 25°C . Assuming complete combustion, determine

(a) the heat transfer per kmol of CH_4 , (b) the entropy generation, and (c) the reversible work and exergy destruction. Assume that $T_0 = 298 \text{ K}$ and the products leave the combustion chamber at 1 atm pressure.

Solution This is the same combustion process we discussed in Example 15–10, except that the combustion products are brought to the state of the surroundings by transferring heat from them. Thus the combustion equation remains the same:



At 25°C , part of the water will condense. The amount of water vapor that remains in the products is determined from (see Example 15–3)

$$\frac{N_v}{N_{\text{gas}}} = \frac{P_v}{P_{\text{total}}} = \frac{3.1698 \text{ kPa}}{101.325 \text{ kPa}} = 0.03128$$

and

$$N_v = \left(\frac{P_v}{P_{\text{total}}} \right) N_{\text{gas}} = (0.03128)(13.28 + N_v) \rightarrow N_v = 0.43 \text{ kmol}$$

Therefore, 1.57 kmol of the H_2O formed is in the liquid form, which is removed at 25°C and 1 atm. When one is evaluating the partial pressures of the components in the product gases, the only water molecules that need to be considered are those that are in the vapor phase. As before, all the gaseous reactants and products are treated as ideal gases.

(a) Heat transfer during this steady-flow combustion process is determined from the steady-flow energy balance $E_{\text{out}} = E_{\text{in}}$ on the combustion chamber,

$$Q_{\text{out}} + \sum N_p \bar{h}_{f,p}^\circ = \sum N_r \bar{h}_{f,r}^\circ$$

since all the reactants and products are at the standard reference of 25°C and the enthalpy of ideal gases depends on temperature only. Solving for Q_{out} and substituting the \bar{h}_f° values, we have

$$\begin{aligned} Q_{\text{out}} &= (1 \text{ kmol CH}_4)(-74,850 \text{ kJ/kmol CH}_4) \\ &\quad - (1 \text{ kmol CO}_2)(-393,520 \text{ kJ/kmol CO}_2) \\ &\quad - [0.43 \text{ kmol H}_2\text{O}(g)][-241,820 \text{ kJ/kmol H}_2\text{O}(g)] \\ &\quad - [1.57 \text{ kmol H}_2\text{O}(\ell)][-285.830 \text{ kJ/kmol H}_2\text{O}(\ell)] \\ &= \mathbf{871,400 \text{ kJ/kmol CH}_4} \end{aligned}$$

(b) The entropy of the reactants was evaluated in Example 15–10 and was determined to be $S_{\text{react}} = 3023.69 \text{ kJ/kmol} \cdot \text{K CH}_4$. By following a similar approach, the entropy of the products is determined to be

	N_i	y_i	$\bar{s}_i^\circ(T, 1 \text{ atm})$	$-R_u \ln y_i P_m$	$N_i \bar{s}_i$
$\text{H}_2\text{O}(\ell)$	1.57	1.0000	69.92	—	109.77
H_2O	0.43	0.0314	188.83	28.77	93.57
CO_2	1	0.0729	213.80	21.77	235.57
O_2	1	0.0729	205.04	21.77	226.81
N_2	11.28	0.8228	191.61	1.62	2179.63
$S_{\text{prod}} =$					2845.35

Then the total entropy generation during this process is determined from an entropy balance applied on an *extended system* that includes the immediate surroundings of the combustion chamber

$$\begin{aligned} S_{\text{gen}} &= S_{\text{prod}} - S_{\text{react}} + \frac{Q_{\text{out}}}{T_{\text{surr}}} \\ &= (2845.35 - 3023.69) \text{ kJ/kmol} + \frac{871,400 \text{ kJ/kmol}}{298 \text{ K}} \\ &= \mathbf{2746 \text{ kJ/kmol} \cdot \text{K CH}_4} \end{aligned}$$

(c) The exergy destruction and reversible work associated with this process are determined from

$$\begin{aligned} X_{\text{destroyed}} &= T_0 S_{\text{gen}} = (298 \text{ K})(2746 \text{ kJ/kmol} \cdot \text{K}) \\ &= \mathbf{818 \text{ MJ/kmol CH}_4} \end{aligned}$$

and

$$W_{\text{rev}} = X_{\text{destroyed}} = \mathbf{818 \text{ MJ/kmol CH}_4}$$

since this process involves no actual work. Therefore, 818 MJ of work could be done during this process but is not. Instead, the entire work potential is wasted. The reversible work in this case represents the exergy of the reactants before the reaction starts since the products are in equilibrium with the surroundings, that is, they are at the dead state.

Discussion Note that, for simplicity, we calculated the entropy of the product gases before they actually entered the atmosphere and mixed with the atmospheric gases. A more complete analysis would consider the composition of the atmosphere and the mixing of the product gases with the gases in the atmosphere, forming a homogeneous mixture. There is additional entropy generation during this mixing process, and thus additional wasted work potential.

TOPIC OF SPECIAL INTEREST*

Fuel Cells

Fuels like methane are commonly burned to provide thermal energy at high temperatures for use in heat engines. However, a comparison of the reversible works obtained in the last two examples reveals that the exergy of the reactants (818 MJ/kmol CH₄) decreases by 288 MJ/kmol as a result of the irreversible adiabatic combustion process alone. That is, the exergy of the hot combustion gases at the end of the adiabatic combustion process is 818 – 288 = 530 MJ/kmol CH₄. In other words, the work potential of the hot combustion gases is about 65 percent of the work potential of the reactants. It seems that when methane is burned, 35 percent of the work potential is lost before we even start using the thermal energy (Fig. 15–35).

Thus, the second law of thermodynamics suggests that there should be a better way of converting the chemical energy to work. The better way is, of course, the less irreversible way, the best being the reversible case. In chemi-

*This section can be skipped without a loss in continuity.

cal reactions, the irreversibility is due to uncontrolled electron exchange between the reacting components. The electron exchange can be controlled by replacing the combustion chamber by electrolytic cells, like car batteries. (This is analogous to replacing unrestrained expansion of a gas in mechanical systems by restrained expansion.) In the electrolytic cells, the electrons are exchanged through conductor wires connected to a load, and the chemical energy is directly converted to electric energy. The energy conversion devices that work on this principle are called **fuel cells**. Fuel cells are not heat engines, and thus their efficiencies are not limited by the Carnot efficiency. They convert chemical energy to electric energy essentially in an isothermal manner.

A fuel cell functions like a battery, except that it produces its own electricity by combining a fuel with oxygen in a cell electrochemically without combustion, and discards the waste heat. A fuel cell consists of two electrodes separated by an electrolyte such as a solid oxide, phosphoric acid, or molten carbonate. The electric power generated by a single fuel cell is usually too small to be of any practical use. Therefore, fuel cells are usually stacked in practical applications. This modularity gives the fuel cells considerable flexibility in applications: The same design can be used to generate a small amount of power for a remote switching station or a large amount of power to supply electricity to an entire town. Therefore, fuel cells are termed the “microchip of the energy industry.”

The operation of a hydrogen–oxygen fuel cell is illustrated in Fig. 15–36. Hydrogen is ionized at the surface of the anode, and hydrogen ions flow through the electrolyte to the cathode. There is a potential difference between the anode and the cathode, and free electrons flow from the anode to the cathode through an external circuit (such as a motor or a generator). Hydrogen ions combine with oxygen and the free electrons at the surface of the cathode, forming water. Therefore, the fuel cell operates like an electrolysis system working in reverse. In steady operation, hydrogen and oxygen continuously enter the fuel cell as reactants, and water leaves as the product. Therefore, the exhaust of the fuel cell is drinkable quality water.

The fuel cell was invented by William Groves in 1839, but it did not receive serious attention until the 1960s, when they were used to produce electricity and water for the Gemini and Apollo spacecraft during their missions to the moon. Today they are used for the same purpose in the space shuttle missions. Despite the irreversible effects such as internal resistance to electron flow, fuel cells have a great potential for much higher conversion efficiencies. Currently fuel cells are available commercially, but they are competitive only in some niche markets because of their higher cost. Fuel cells produce high-quality electric power efficiently and quietly while generating low emissions using a variety of fuels such as hydrogen, natural gas, propane, and biogas. Recently many fuel cells have been installed to generate electricity. For example, a remote police station in Central Park in New York City is powered by a 200-kW phosphoric acid fuel cell that has an efficiency of 40 percent with negligible emissions (it emits 1 ppm NO_x and 5 ppm CO).

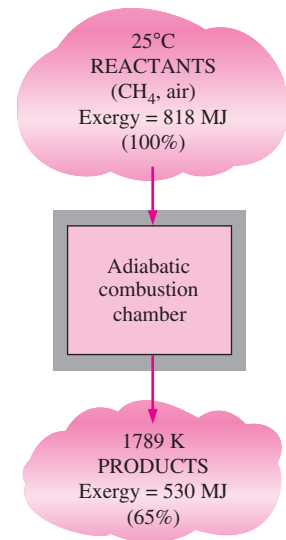


FIGURE 15–35

The availability of methane decreases by 35 percent as a result of irreversible combustion process.

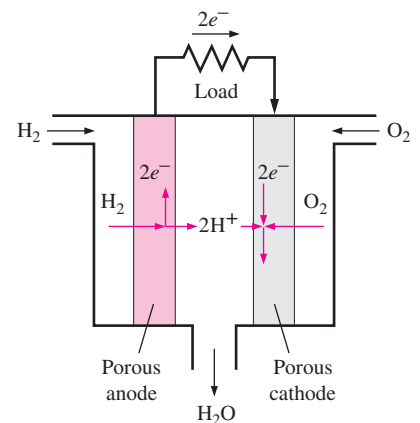


FIGURE 15–36

The operation of a hydrogen–oxygen fuel cell.

Hybrid power systems (HPS) that combine high-temperature fuel cells and gas turbines have the potential for very high efficiency in converting natural gas (or even coal) to electricity. Also, some car manufacturers are planning to introduce cars powered by fuel-cell engines, thus more than doubling the efficiency from less than 30 percent for the gasoline engines to up to 60 percent for fuel cells. In 1999, DaimlerChrysler unveiled its hydrogen fuel-cell powered car called NECAR IV that has a refueling range of 280 miles and can carry 4 passengers at 90 mph. Some research programs to develop such hybrid systems with an efficiency of at least 70 percent by 2010 are under way.

SUMMARY

Any material that can be burned to release energy is called a *fuel*, and a chemical reaction during which a fuel is oxidized and a large quantity of energy is released is called *combustion*. The oxidizer most often used in combustion processes is air. The dry air can be approximated as 21 percent oxygen and 79 percent nitrogen by mole numbers. Therefore,

$$1 \text{ kmol O}_2 + 3.76 \text{ kmol N}_2 = 4.76 \text{ kmol air}$$

During a combustion process, the components that exist before the reaction are called *reactants* and the components that exist after the reaction are called *products*. Chemical equations are balanced on the basis of the *conservation of mass principle*, which states that the total mass of each element is conserved during a chemical reaction. The ratio of the mass of air to the mass of fuel during a combustion process is called the *air–fuel ratio* AF:

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

where $m_{\text{air}} = (NM)_{\text{air}}$ and $m_{\text{fuel}} = \sum(N_i M_i)_{\text{fuel}}$.

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 . The minimum amount of air needed for the complete combustion of a fuel is called the *stoichiometric* or *theoretical air*. The theoretical air is also referred to as the chemically correct amount of air or 100 percent theoretical air. The ideal combustion process during which a fuel is burned completely with theoretical air is called the *stoichiometric* or *theoretical combustion* of that fuel. The air in excess of the stoichiometric amount is called the *excess air*. The amount of excess air is usually expressed in terms of the stoichiometric air as *percent excess air* or *percent theoretical air*.

During a chemical reaction, some chemical bonds are broken and others are formed. Therefore, a process that involves chemical reactions involves changes in chemical energies. Because of the changed composition, it is necessary to have a

standard reference state for all substances, which is chosen to be 25°C (77°F) and 1 atm.

The difference between the enthalpy of the products at a specified state and the enthalpy of the reactants at the same state for a complete reaction is called the *enthalpy of reaction* h_R . For combustion processes, the enthalpy of reaction is usually referred to as the *enthalpy of combustion* h_C , which represents the amount of heat released during a steady-flow combustion process when 1 kmol (or 1 kg) of fuel is burned completely at a specified temperature and pressure. The enthalpy of a substance at a specified state due to its chemical composition is called the *enthalpy of formation* \bar{h}_f . The enthalpy of formation of all stable elements is assigned a value of zero at the standard reference state of 25°C and 1 atm. The *heating value* of a fuel is defined as the amount of heat released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants. The heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel,

$$\text{Heating value} = |h_C| \quad (\text{kJ/kg fuel})$$

Taking heat transfer *to* the system and work done *by* the system to be positive quantities, the conservation of energy relation for chemically reacting steady-flow systems can be expressed per unit mole of fuel as

$$Q - W = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p - \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r$$

where the superscript $^\circ$ represents properties at the standard reference state of 25°C and 1 atm. For a closed system, it becomes

$$Q - W = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_p - \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_r$$

The $P\bar{v}$ terms are negligible for solids and liquids and can be replaced by $R_u T$ for gases that behave as ideal gases.

In the absence of any heat loss to the surroundings ($Q = 0$), the temperature of the products will reach a maximum, which is called the *adiabatic flame temperature* of the reaction. The adiabatic flame temperature of a steady-flow combustion process is determined from $H_{\text{prod}} = H_{\text{react}}$ or

$$\sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r$$

Taking the positive direction of heat transfer to be *to* the system, the entropy balance relation can be expressed for a *closed system* or *steady-flow combustion chamber* as

$$\sum \frac{Q_k}{T_k} + S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}}$$

For an *adiabatic process* it reduces to

$$S_{\text{gen,adiabatic}} = S_{\text{prod}} - S_{\text{react}} \geq 0$$

The *third law of thermodynamics* states that the entropy of a pure crystalline substance at absolute zero temperature is zero. The third law provides a common base for the entropy of all substances, and the entropy values relative to this base are called the *absolute entropy*. The ideal-gas tables list the absolute entropy values over a wide range of temperatures but at a fixed pressure of $P_0 = 1$ atm. Absolute entropy values at other pressures P for any temperature T are determined from

$$\bar{s}(T, P) = \bar{s}^\circ(T, P_0) - R_u \ln \frac{P}{P_0}$$

For component i of an ideal-gas mixture, this relation can be written as

$$\bar{s}_i(T, P_i) = \bar{s}_i^\circ(T, P_0) - R_u \ln \frac{y_i P_m}{P_0}$$

where P_i is the partial pressure, y_i is the mole fraction of the component, and P_m is the total pressure of the mixture in atmospheres.

The *exergy destruction* and the *reversible work* associated with a chemical reaction are determined from

$$X_{\text{destroyed}} = W_{\text{rev}} - W_{\text{act}} = T_0 S_{\text{gen}}$$

and

$$W_{\text{rev}} = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0 \bar{s})_r - \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0 \bar{s})_p$$

When both the reactants and the products are at the temperature of the surroundings T_0 , the reversible work can be expressed in terms of the Gibbs functions as

$$W_{\text{rev}} = \sum N_r(\bar{g}_f^\circ + \bar{g}_{T_0} - \bar{g}^\circ)_r - \sum N_p(\bar{g}_f^\circ + \bar{g}_{T_0} - \bar{g}^\circ)_p$$



REFERENCES AND SUGGESTED READINGS

1. S. W. Angrist. *Direct Energy Conversion*. 4th ed. Boston: Allyn and Bacon, 1982.
2. W. Z. Black and J. G. Hartley. *Thermodynamics*. New York: Harper & Row, 1985.
3. I. Glassman. *Combustion*. New York: Academic Press, 1977.
4. R. Strehlow. *Fundamentals of Combustion*. Scranton, PA: International Textbook Co., 1968.
5. K. Wark and D. E. Richards. *Thermodynamics*. 6th ed. New York: McGraw-Hill, 1999.

PROBLEMS*

Fuels and Combustion

15-1C What are the approximate chemical compositions of gasoline, diesel fuel, and natural gas?

*Problems designated by a “C” are concept questions, and students are encouraged to answer them all. Problems designated by an “E” are in English units, and the SI users can ignore them. Problems with a CD-EES icon  are solved using EES, and complete solutions together with parametric studies are included on the enclosed DVD. Problems with a computer-EES icon  are comprehensive in nature, and are intended to be solved with a computer, preferably using the EES software that accompanies this text.

15-2C How does the presence of N_2 in air affect the outcome of a combustion process?

15-3C How does the presence of moisture in air affect the outcome of a combustion process?

15-4C What does the dew-point temperature of the product gases represent? How is it determined?

15-5C Is the number of atoms of each element conserved during a chemical reaction? How about the total number of moles?

15-6C What is the air–fuel ratio? How is it related to the fuel–air ratio?

15-7C Is the air–fuel ratio expressed on a mole basis identical to the air–fuel ratio expressed on a mass basis?

Theoretical and Actual Combustion Processes

15-8C What are the causes of incomplete combustion?

15-9C Which is more likely to be found in the products of an incomplete combustion of a hydrocarbon fuel, CO or OH? Why?

15-10C What does 100 percent theoretical air represent?

15-11C Are complete combustion and theoretical combustion identical? If not, how do they differ?

15-12C Consider a fuel that is burned with (a) 130 percent theoretical air and (b) 70 percent excess air. In which case is the fuel burned with more air?

15-13 Methane (CH_4) is burned with stoichiometric amount of air during a combustion process. Assuming complete combustion, determine the air–fuel and fuel–air ratios.

15-14 Propane (C_3H_8) is burned with 75 percent excess air during a combustion process. Assuming complete combustion, determine the air–fuel ratio. *Answer: 27.5 kg air/kg fuel*

15-15 Acetylene (C_2H_2) is burned with stoichiometric amount of air during a combustion process. Assuming complete combustion, determine the air–fuel ratio on a mass and on a mole basis.

15-16 One kmol of ethane (C_2H_6) is burned with an unknown amount of air during a combustion process. An analysis of the combustion products reveals that the combustion is complete, and there are 3 kmol of free O_2 in the products. Determine (a) the air–fuel ratio and (b) the percentage of theoretical air used during this process.

15-17E Ethylene (C_2H_4) is burned with 200 percent theoretical air during a combustion process. Assuming complete combustion and a total pressure of 14.5 psia, determine (a) the air–fuel ratio and (b) the dew-point temperature of the products. *Answers: (a) 29.6 lbm air/lbm fuel, (b) 101°F*

15-18 Propylene (C_3H_6) is burned with 50 percent excess air during a combustion process. Assuming complete combustion and a total pressure of 105 kPa, determine (a) the air–fuel ratio and (b) the temperature at which the water vapor in the products will start condensing.

15-19 Propyl alcohol ($\text{C}_3\text{H}_7\text{OH}$) is burned with 50 percent excess air. Write the balanced reaction equation for complete combustion and determine the air-to-fuel ratio.

Answer: 15.5 kg air/kg fuel

15-20 Butane (C_4H_{10}) is burned in 200 percent theoretical air. For complete combustion, how many kmol of water must be sprayed into the combustion chamber per kmol of fuel if

the products of combustion are to have a dew-point temperature of 60°C when the product pressure is 100 kPa?

15-21 A fuel mixture of 20 percent by mass methane (CH_4) and 80 percent by mass ethanol ($\text{C}_2\text{H}_6\text{O}$), is burned completely with theoretical air. If the total flow rate of the fuel is 31 kg/s, determine the required flow rate of air. *Answer: 330 kg/s*

15-22 Octane (C_8H_{18}) is burned with 250 percent theoretical air, which enters the combustion chamber at 25°C. Assuming complete combustion and a total pressure of 1 atm, determine (a) the air–fuel ratio and (b) the dew-point temperature of the products.

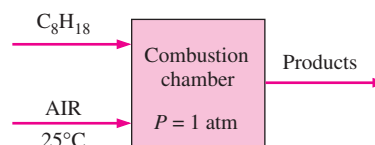


FIGURE P15-22

15-23 Gasoline (assumed C_8H_{18}) is burned steadily with air in a jet engine. If the air–fuel ratio is 18 kg air/kg fuel, determine the percentage of theoretical air used during this process.

15-24 In a combustion chamber, ethane (C_2H_6) is burned at a rate of 8 kg/h with air that enters the combustion chamber at a rate of 176 kg/h. Determine the percentage of excess air used during this process. *Answer: 37 percent*

15-25 One kilogram of butane (C_4H_{10}) is burned with 25 kg of air that is at 30°C and 90 kPa. Assuming that the combustion is complete and the pressure of the products is 90 kPa, determine (a) the percentage of theoretical air used and (b) the dew-point temperature of the products.

15-26E One lbm of butane (C_4H_{10}) is burned with 25 lbm of air that is at 90°F and 14.7 psia. Assuming that the combustion is complete and the pressure of the products is 14.7 psia, determine (a) the percentage of theoretical air used and (b) the dew-point temperature of the products. *Answers: (a) 161 percent, (b) 113°F*


15-27 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. What is the air–fuel ratio for this combustion process?

15-28 Repeat Prob. 15-27 by replacing the dry air by moist air that enters the combustion chamber at 25°C, 1 atm, and 85 percent relative humidity.

15-29 A gaseous fuel with a volumetric analysis of 60 percent CH_4 , 30 percent H_2 , and 10 percent N_2 is burned to completion with 130 percent theoretical air. Determine (a) the

air–fuel ratio and (b) the fraction of water vapor that would condense if the product gases were cooled to 20°C at 1 atm.

Answers: (a) 18.6 kg air/kg fuel, (b) 88 percent

15–30  Reconsider Prob. 15–29. Using EES (or other) software, study the effects of varying the percentages of CH₄, H₂, and N₂ making up the fuel and the product gas temperature in the range 5 to 150°C.

15–31 A certain coal has the following analysis on a mass basis: 82 percent C, 5 percent H₂O, 2 percent H₂, 1 percent O₂, and 10 percent ash. The coal is burned with 50 percent excess air. Determine the air–fuel ratio. *Answer: 15.1 kg air/kg coal*

15–32 Octane (C₈H₁₈) is burned with dry air. The volumetric analysis of the products on a dry basis is 9.21 percent CO₂, 0.61 percent CO, 7.06 percent O₂, and 83.12 percent N₂. Determine (a) the air–fuel ratio and (b) the percentage of theoretical air used.

15–33 Carbon (C) is burned with dry air. The volumetric analysis of the products is 10.06 percent CO₂, 0.42 percent CO, 10.69 percent O₂, and 78.83 percent N₂. Determine (a) the air–fuel ratio and (b) the percentage of theoretical air used.

15–34 Methane (CH₄) is burned with dry air. The volumetric analysis of the products on a dry basis is 5.20 percent CO₂, 0.33 percent CO, 11.24 percent O₂, and 83.23 percent N₂. Determine (a) the air–fuel ratio and (b) the percentage of theoretical air used. *Answers: (a) 34.5 kg air/kg fuel, (b) 200 percent*

Enthalpy of Formation and Enthalpy of Combustion

15–35C What is enthalpy of combustion? How does it differ from the enthalpy of reaction?

15–36C What is enthalpy of formation? How does it differ from the enthalpy of combustion?

15–37C What are the higher and the lower heating values of a fuel? How do they differ? How is the heating value of a fuel related to the enthalpy of combustion of that fuel?


15–38C When are the enthalpy of formation and the enthalpy of combustion identical?

15–39C Does the enthalpy of formation of a substance change with temperature?

15–40C The \bar{h}_f° of N₂ is listed as zero. Does this mean that N₂ contains no chemical energy at the standard reference state?

15–41C Which contains more chemical energy, 1 kmol of H₂ or 1 kmol of H₂O?

15–42 Determine the enthalpy of combustion of methane (CH₄) 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*

15–43  Reconsider Prob. 15–42. Using EES (or other) software, study the effect of temperature on the enthalpy of combustion. Plot the enthalpy of combustion as a function of temperature over the range 25 to 600°C.

15–44 Repeat Prob. 15–42 for gaseous ethane (C₂H₆).

15–45 Repeat Prob. 15–42 for liquid octane (C₈H₁₈).

First-Law Analysis of Reacting Systems

15–46C Derive an energy balance relation for a reacting closed system undergoing a quasi-equilibrium constant pressure expansion or compression process.

15–47C Consider a complete combustion process during which both the reactants and the products are maintained at the same state. Combustion is achieved with (a) 100 percent theoretical air, (b) 200 percent theoretical air, and (c) the chemically correct amount of pure oxygen. For which case will the amount of heat transfer be the highest? Explain.

15–48C Consider a complete combustion process during which the reactants enter the combustion chamber at 20°C and the products leave at 700°C. Combustion is achieved with (a) 100 percent theoretical air, (b) 200 percent theoretical air, and (c) the chemically correct amount of pure oxygen. For which case will the amount of heat transfer be the lowest? Explain.

15–49 Methane (CH₄) is burned completely with the stoichiometric amount of air during a steady-flow combustion process. If both the reactants and the products are maintained at 25°C and 1 atm and the water in the products exists in the liquid form, determine the heat transfer from the combustion chamber during this process. What would your answer be if combustion were achieved with 100 percent excess air?

Answer: 890,330 kJ/kmol

15–50 Hydrogen (H₂) is burned completely with the stoichiometric amount of air during a steady-flow combustion process. If both the reactants and the products are maintained at 25°C and 1 atm and the water in the products exists in the liquid form, determine the heat transfer from the combustion chamber during this process. What would your answer be if combustion were achieved with 50 percent excess air?

15–51 Liquid propane (C₃H₈) enters a combustion chamber at 25°C at a rate of 1.2 kg/min where it is mixed and burned with 150 percent excess air that enters the combustion chamber at 12°C. If the combustion is complete and the exit

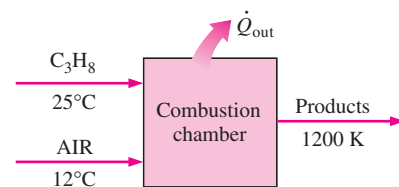


FIGURE P15–51

temperature of the combustion gases is 1200 K, determine (a) the mass flow rate of air and (b) the rate of heat transfer from the combustion chamber. *Answers: (a) 47.1 kg/min, (b) 5194 kJ/min*

15-52E Liquid propane (C_3H_8) enters a combustion chamber at 77°F at a rate of 0.75 lbm/min where it is mixed and burned with 150 percent excess air that enters the combustion chamber at 40°F. If the combustion is complete and the exit temperature of the combustion gases is 1800 R, determine (a) the mass flow rate of air and (b) the rate of heat transfer from the combustion chamber. *Answers: (a) 29.4 lbm/min, (b) 4479 Btu/min*


15-53 Acetylene gas (C_2H_2) is burned completely with 20 percent excess air during a steady-flow combustion process. The fuel and air enter the combustion chamber at 25°C, and the products leave at 1500 K. Determine (a) the air-fuel ratio and (b) the heat transfer for this process.


15-54E Liquid octane (C_8H_{18}) at 77°F is burned completely during a steady-flow combustion process with 180 percent theoretical air that enters the combustion chamber at 77°F. If the products leave at 2500 R, determine (a) the air-fuel ratio and (b) the heat transfer from the combustion chamber during this process.

15-55 Benzene gas (C_6H_6) at 25°C is burned during a steady-flow combustion process with 95 percent theoretical air that enters the combustion chamber at 25°C. All the hydrogen in the fuel burns to H_2O , but part of the carbon burns to CO. If the products leave at 1000 K, determine (a) the mole fraction of the CO in the products and (b) the heat transfer from the combustion chamber during this process. *Answers: (a) 2.1 percent, (b) 2,112,800 kJ/kmol C_6H_6*

15-56 Diesel fuel ($C_{12}H_{26}$) at 25°C is burned in a steady-flow combustion chamber with 20 percent excess air that also enters at 25°C. The products leave the combustion chamber at 500 K. Assuming combustion is complete, determine the required mass flow rate of the diesel fuel to supply heat at a rate of 2000 kJ/s. *Answer: 49.5 g/s*

15-57E Diesel fuel ($C_{12}H_{26}$) at 77°F is burned in a steady-flow combustion chamber with 20 percent excess air that also enters at 77°F. The products leave the combustion chamber at 800 R. Assuming combustion is complete, determine the required mass flow rate of the diesel fuel to supply heat at a rate of 1800 Btu/s. *Answer: 0.1 lbm/s*

15-58  Octane gas (C_8H_{18}) at 25°C is burned steadily with 30 percent excess air at 25°C, 1 atm, and 60 percent relative humidity. Assuming combustion is complete and the products leave the combustion chamber at 600 K, determine the heat transfer for this process per unit mass of octane.

15-59  Reconsider Prob. 15-58. Using EES (or other) software, investigate the effect of the amount

of excess air on the heat transfer for the combustion process. Let the excess air vary from 0 to 200 percent. Plot the heat transfer against excess air, and discuss the results.

15-60 Ethane gas (C_2H_6) at 25°C is burned in a steady-flow combustion chamber at a rate of 5 kg/h with the stoichiometric amount of air, which is preheated to 500 K before entering the combustion chamber. An analysis of the combustion gases reveals that all the hydrogen in the fuel burns to H_2O but only 95 percent of the carbon burns to CO_2 , the remaining 5 percent forming CO. If the products leave the combustion chamber at 800 K, determine the rate of heat transfer from the combustion chamber. *Answer: 200,170 kJ/h*

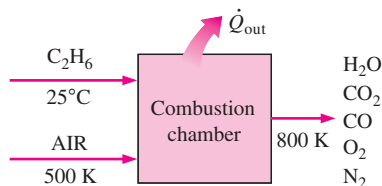




FIGURE P15-60

15-61  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.

15-62  Reconsider Prob. 15-61. Using EES (or other) software, investigate the effect of the final temperature on the final pressure and the heat transfer for the combustion process. Let the final temperature vary from 500 to 1500 K. Plot the final pressure and heat transfer against the final temperature, and discuss the results.

15-63 A closed combustion chamber is designed so that it maintains a constant pressure of 300 kPa during a combustion process. The combustion chamber has an initial volume of 0.5 m³ and contains a stoichiometric mixture of octane (C_8H_{18}) gas and air at 25°C. The mixture is now ignited, and the product gases are observed to be at 1000 K at the end of the combustion process. Assuming complete combustion, and treating both the reactants and the products as ideal gases, determine the heat transfer from the combustion chamber during this process. *Answer: 3610 kJ*

15-64 A constant-volume tank contains a mixture of 1 kmol of benzene (C_6H_6) gas and 30 percent excess air at 25°C and 1 atm. The contents of the tank are now ignited, and all the hydrogen in the fuel burns to H_2O but only 92 percent of the carbon burns to CO_2 , the remaining 8 percent forming CO. If the final temperature in the tank is 1000 K, determine the heat transfer from the combustion chamber during this process.

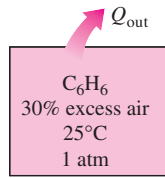


FIGURE P15-64

15-65E A constant-volume tank contains a mixture of 1 lbmol of benzene (C_6H_6) gas and 30 percent excess air at $77^\circ F$ and 1 atm. The contents of the tank are now ignited, and all the hydrogen in the fuel burns to H_2O but only 92 percent of the carbon burns to CO_2 , the remaining 8 percent forming CO. If the final temperature in the tank is 1800 R, determine the heat transfer from the combustion chamber during this process. *Answer: 946,870 Btu*


15-66 To supply heated air to a house, a high-efficiency gas furnace burns gaseous propane (C_3H_8) with a combustion efficiency of 96 percent. Both the fuel and 140 percent theoretical air are supplied to the combustion chamber at $25^\circ C$ and 100 kPa, and the combustion is complete. Because this is a high-efficiency furnace, the product gases are cooled to $25^\circ C$ and 100 kPa before leaving the furnace. To maintain the house at the desired temperature, a heat transfer rate of 31,650 kJ/h is required from the furnace. Determine the volume of water condensed from the product gases per day. *Answer: 8.7 L/day*

15-67 Liquid ethyl alcohol ($C_2H_5OH(\ell)$) at $25^\circ C$ is burned in a steady-flow combustion chamber with 40 percent excess air that also enters at $25^\circ C$. The products leave the combustion chamber at 600 K. Assuming combustion is complete, determine the required volume flow rate of the liquid ethyl alcohol, to supply heat at a rate of 2000 kJ/s. At $25^\circ C$ the density of liquid ethyl alcohol is 790 kg/m^3 , the specific heat at a constant pressure is $114.08 \text{ kJ/kmol} \cdot K$, and the enthalpy of vaporization is $42,340 \text{ kJ/kmol}$. *Answer: 6.81 L/min*

Adiabatic Flame Temperature

15-68C A fuel is completely burned first with the stoichiometric amount of air and then with the stoichiometric amount of pure oxygen. For which case will the adiabatic flame temperature be higher?

15-69C A fuel at $25^\circ C$ is burned in a well-insulated steady-flow combustion chamber with air that is also at $25^\circ C$. Under what conditions will the adiabatic flame temperature of the combustion process be a maximum?

15-70  Hydrogen (H_2) at $7^\circ C$ is burned with 20 percent excess air that is also at $7^\circ C$ during an adiabatic steady-flow combustion process. Assuming complete combustion, determine the exit temperature of the product gases. *Answer: 2251.4 K*

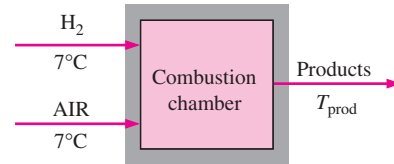



FIGURE P15-70


15-71  Reconsider Prob. 15-70. Using EES (or other) software, modify this problem to include the fuels butane, ethane, methane, and propane as well as H_2 ; to include the effects of inlet air and fuel temperatures; and the percent theoretical air supplied. Select a range of input parameters and discuss the results for your choices.

15-72E Hydrogen (H_2) at $40^\circ F$ is burned with 20 percent excess air that is also at $40^\circ F$ during an adiabatic steady-flow combustion process. Assuming complete combustion, find the exit temperature of the product gases.

15-73 Acetylene gas (C_2H_2) at $25^\circ C$ is burned during a steady-flow combustion process with 30 percent excess air at $27^\circ C$. It is observed that 75,000 kJ of heat is being lost from the combustion chamber to the surroundings per kmol of acetylene. Assuming combustion is complete, determine the exit temperature of the product gases. *Answer: 2301 K*

15-74 An adiabatic constant-volume tank contains a mixture of 1 kmol of hydrogen (H_2) gas and the stoichiometric amount of air at $25^\circ C$ and 1 atm. The contents of the tank are now ignited. Assuming complete combustion, determine the final temperature in the tank.

15-75 Octane gas (C_8H_{18}) at $25^\circ C$ is burned steadily with 30 percent excess air at $25^\circ C$, 1 atm, and 60 percent relative humidity. Assuming combustion is complete and adiabatic, calculate the exit temperature of the product gases.

15-76  Reconsider Prob. 15-75. Using EES (or other) software, investigate the effect of the relative humidity on the exit temperature of the product gases. Plot the exit temperature of the product gases as a function of relative humidity for $0 < \phi < 100$ percent.

Entropy Change and Second-Law Analysis of Reacting Systems

15-77C Express the increase of entropy principle for chemically reacting systems.

15-78C How are the absolute entropy values of ideal gases at pressures different from 1 atm determined?

15-79C What does the Gibbs function of formation g_f° of a compound represent?

15-80 One kmol of H_2 at $25^\circ C$ and 1 atm is burned steadily with 0.5 kmol of O_2 at the same state. The H_2O formed during the process is then brought to $25^\circ C$ and 1 atm, the conditions

of the surroundings. Assuming combustion is complete, determine the reversible work and exergy destruction for this process.

15-81 Ethylene (C_2H_4) gas enters an adiabatic combustion chamber at $25^\circ C$ and 1 atm and is burned with 20 percent excess air that enters at $25^\circ C$ and 1 atm. The combustion is complete, and the products leave the combustion chamber at 1 atm pressure. Assuming $T_0 = 25^\circ C$, determine (a) the temperature of the products, (b) the entropy generation, and (c) the exergy destruction. *Answers: (a) 2269.6 K, (b) 1311.3 kJ/kmol \cdot K, (c) 390,760 kJ/kmol*

15-82 Liquid octane (C_8H_{18}) enters a steady-flow combustion chamber at $25^\circ C$ and 1 atm at a rate of 0.25 kg/min. It is burned with 50 percent excess air that also enters at $25^\circ C$ and 1 atm. After combustion, the products are allowed to cool to $25^\circ C$. Assuming complete combustion and that all the H_2O in the products is in liquid form, determine (a) the heat transfer rate from the combustion chamber, (b) the entropy generation rate, and (c) the exergy destruction rate. Assume that $T_0 = 298$ K and the products leave the combustion chamber at 1 atm pressure.

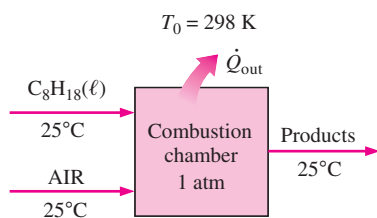



FIGURE P15-82


15-83 Acetylene gas (C_2H_2) is burned completely with 20 percent excess air during a steady-flow combustion process. The fuel and the air enter the combustion chamber separately at $25^\circ C$ and 1 atm, and heat is being lost from the combustion chamber to the surroundings at $25^\circ C$ at a rate of 300,000 kJ/kmol C_2H_2 . The combustion products leave the combustion chamber at 1 atm pressure. Determine (a) the temperature of the products, (b) the total entropy change per kmol of C_2H_2 , and (c) the exergy destruction during this process.

15-84 A steady-flow combustion chamber is supplied with CO gas at $37^\circ C$ and 110 kPa at a rate of 0.4 m^3/min and air at $25^\circ C$ and 110 kPa at a rate of 1.5 kg/min. Heat is transferred to a medium at 800 K, and the combustion products leave the combustion chamber at 900 K. Assuming the combustion is complete and $T_0 = 25^\circ C$, determine (a) the rate of heat transfer from the combustion chamber and (b) the rate of exergy destruction. *Answers: (a) 3567 kJ/min, (b) 1610 kJ/min*

15-85E Benzene gas (C_6H_6) at 1 atm and $77^\circ F$ is burned during a steady-flow combustion process with 95 percent

theoretical air that enters the combustion chamber at $77^\circ F$ and 1 atm. All the hydrogen in the fuel burns to H_2O , but part of the carbon burns to CO. Heat is lost to the surroundings at $77^\circ F$, and the products leave the combustion chamber at 1 atm and 1500 R. Determine (a) the heat transfer from the combustion chamber and (b) the exergy destruction.

15-86  Liquid propane (C_3H_8) enters a steady-flow combustion chamber at $25^\circ C$ and 1 atm at a rate of 0.4 kg/min where it is mixed and burned with 150 percent excess air that enters the combustion chamber at $12^\circ C$. If the combustion products leave at 1200 K and 1 atm, determine (a) the mass flow rate of air, (b) the rate of heat transfer from the combustion chamber, and (c) the rate of entropy generation during this process. Assume $T_0 = 25^\circ C$. *Answers: (a) 15.7 kg/min, (b) 1732 kJ/min, (c) 34.2 kJ/min \cdot K*

15-87  Reconsider Prob. 15-86. Using EES (or other) software, study the effect of varying the surroundings temperature from 0 to $38^\circ C$ on the rate of exergy destruction, and plot it as a function of surroundings temperature.

Review Problems

15-88 A 1-g sample of a certain fuel is burned in a bomb calorimeter that contains 2 kg of water in the presence of 100 g of air in the reaction chamber. If the water temperature rises by $2.5^\circ C$ when equilibrium is established, determine the heating value of the fuel, in kJ/kg.

15-89E Hydrogen (H_2) is burned with 100 percent excess air that enters the combustion chamber at $90^\circ F$, 14.5 psia, and 60 percent relative humidity. Assuming complete combustion, determine (a) the air-fuel ratio and (b) the volume flow rate of air required to burn the hydrogen at a rate of 25 lbm/h.

15-90 A gaseous fuel with 80 percent CH_4 , 15 percent N_2 , and 5 percent O_2 (on a mole basis) is burned to completion with 120 percent theoretical air that enters the combustion chamber at $30^\circ C$, 100 kPa, and 60 percent relative humidity. Determine (a) the air-fuel ratio and (b) the volume flow rate of air required to burn fuel at a rate of 2 kg/min.

15-91 A gaseous fuel with 80 percent CH_4 , 15 percent N_2 , and 5 percent O_2 (on a mole basis) is burned with dry air that enters the combustion chamber at $25^\circ C$ and 100 kPa. The volumetric analysis of the products on a dry basis is 3.36 percent CO_2 , 0.09 percent CO, 14.91 percent O_2 , and 81.64 percent N_2 . Determine (a) the air-fuel ratio, (b) the percent theoretical

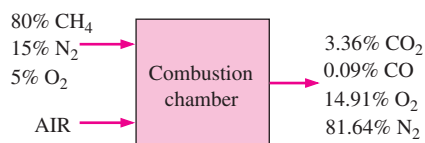


FIGURE P15-91

air used, and (c) the volume flow rate of air used to burn fuel at a rate of 1.4 kg/min.

15-92 A steady-flow combustion chamber is supplied with CO gas at 37°C and 110 kPa at a rate of 0.4 m³/min and air at 25°C and 110 kPa at a rate of 1.5 kg/min. The combustion products leave the combustion chamber at 900 K. Assuming combustion is complete, determine the rate of heat transfer from the combustion chamber.

15-93 Methane gas (CH₄) at 25°C is burned steadily with dry air that enters the combustion chamber at 17°C. The volumetric analysis of the products on a dry basis is 5.20 percent CO₂, 0.33 percent CO, 11.24 percent O₂, and 83.23 percent N₂. Determine (a) the percentage of theoretical air used and (b) the heat transfer from the combustion chamber per kmol of CH₄ if the combustion products leave at 700 K.

15-94 A 6-m³ rigid tank initially contains a mixture of 1 kmol of hydrogen (H₂) gas and the stoichiometric amount of air at 25°C. The contents of the tank are ignited, and all the hydrogen in the fuel burns to H₂O. If the combustion products are cooled to 25°C, determine (a) the fraction of the H₂O that condenses and (b) the heat transfer from the combustion chamber during this process.

15-95 Propane gas (C₃H₈) enters a steady-flow combustion chamber at 1 atm and 25°C and is burned with air that enters the combustion chamber at the same state. Determine the adiabatic flame temperature for (a) complete combustion with 100 percent theoretical air, (b) complete combustion with 300 percent theoretical air, and (c) incomplete combustion (some CO in the products) with 95 percent theoretical air.

15-96 Determine the highest possible temperature that can be obtained when liquid gasoline (assumed C₈H₁₈) at 25°C is burned steadily with air at 25°C and 1 atm. What would your answer be if pure oxygen at 25°C were used to burn the fuel instead of air?


15-97E Determine the work potential of 1 lbmol of diesel fuel (C₁₂H₂₆) at 77°F and 1 atm in an environment at the same state. *Answer: 3,375,000 Btu*

15-98 Liquid octane (C₈H₁₈) enters a steady-flow combustion chamber at 25°C and 8 atm at a rate of 0.8 kg/min. It is burned with 200 percent excess air that is compressed and preheated to 500 K and 8 atm before entering the combustion chamber. After combustion, the products enter an adiabatic turbine at 1300 K and 8 atm and leave at 950 K and 2 atm. Assuming complete combustion and $T_0 = 25^\circ\text{C}$, determine (a) the heat transfer rate from the combustion chamber, (b) the power output of the turbine, and (c) the reversible work and exergy destruction for the entire process. *Answers: (a) 770 kJ/min, (b) 263 kW, (c) 514 kW, 251 kW*

15-99 The combustion of a fuel usually results in an increase in pressure when the volume is held constant, or an increase in volume when the pressure is held constant,

because of the increase in the number of moles and the temperature. The increase in pressure or volume will be maximum when the combustion is complete and when it occurs adiabatically with the theoretical amount of air.

Consider the combustion of methyl alcohol vapor (CH₃OH(g)) with the stoichiometric amount of air in an 0.8-L combustion chamber. Initially, the mixture is at 25°C and 98 kPa. Determine (a) the maximum pressure that can occur in the combustion chamber if the combustion takes place at constant volume and (b) the maximum volume of the combustion chamber if the combustion occurs at constant pressure.

15-100  Reconsider Prob. 15-99. Using EES (or other) software, investigate the effect of the initial volume of the combustion chamber over the range 0.1 to 2.0 liters on the results. Plot the maximum pressure of the chamber for constant volume combustion or the maximum volume of the chamber for constant pressure combustion as functions of the initial volume.

15-101 Repeat Prob. 15-99 using methane (CH₄(g)) as the fuel instead of methyl alcohol.

15-102 A mixture of 40 percent by volume methane (CH₄) and 60 percent by volume propane (C₃H₈), is burned completely with theoretical air and leaves the combustion chamber at 100°C. The products have a pressure of 100 kPa and are cooled at constant pressure to 39°C. Sketch the T - s diagram for the water vapor that does not condense, if any. How much of the water formed during the combustion process will be condensed, in kmol H₂O/kmol fuel? *Answer: 1.96*

15-103 Liquid propane (C₃H₈(ℓ)) enters a combustion chamber at 25°C and 1 atm at a rate of 0.4 kg/min where it is mixed and burned with 150 percent excess air that enters the combustion chamber at 25°C. The heat transfer from the combustion process is 53 kW. Write the balanced combustion equation and determine (a) the mass flow rate of air; (b) the average molar mass (molecular weight) of the product gases; (c) the average specific heat at constant pressure of the product gases; and (d) the temperature of the products of combustion. *Answers: (a) 15.63 kg/min, (b) 28.63 kg/kmol, (c) 36.06 kJ/kmol · K, (d) 1282 K*

15-104 A gaseous fuel mixture of 30 percent propane (C₃H₈), and 70 percent butane (C₄H₁₀), on a volume basis is burned in air such that the air-fuel ratio is 20 kg air/kg fuel when the combustion process is complete. Determine (a) the moles of nitrogen in the air supplied to the combustion process, in kmol/kmol fuel; (b) the moles of water formed in the combustion process, in kmol/kmol fuel; and (c) the moles of oxygen in the product gases. *Answers: (a) 29.41, (b) 4.7, (c) 1.77*

15-105 A liquid-gas fuel mixture consists of 90 percent octane (C₈H₁₈), and 10 percent alcohol (C₂H₅OH), by moles. This fuel is burned with 200 percent theoretical dry air. Write the balanced reaction equation for complete combustion of

this fuel mixture. Determine (a) the theoretical air–fuel ratio for this reaction; (b) the product–fuel ratio for this reaction; (c) the air-flow rate for a fuel mixture flow rate of 5 kg/s; and (d) the lower heating value of the fuel mixture with 200 percent theoretical air at 25°C. *Answers: (a) 14.83 kg air/kg fuel, (b) 30.54 kg product/kg fuel, (c) 148.3 kg/s, (d) 43,672 kJ/kg fuel*

15–106 The furnace of a particular power plant can be considered to consist of two chambers: an adiabatic combustion chamber where the fuel is burned completely and adiabatically, and a heat exchanger where heat is transferred to a Carnot heat engine isothermally. The combustion gases in the heat exchanger are well-mixed so that the heat exchanger is at a uniform temperature at all times that is equal to the temperature of the exiting product gases, T_p . The work output of the Carnot heat engine can be expressed as

$$W = Q\eta_C = Q\left(1 - \frac{T_0}{T_p}\right)$$

where Q is the magnitude of the heat transfer to the heat engine and T_0 is the temperature of the environment. The work output of the Carnot engine will be zero either when $T_p = T_{af}$ (which means the product gases will enter and exit the heat exchanger at the adiabatic flame temperature T_{af} , and thus $Q = 0$) or when $T_p = T_0$ (which means the temperature

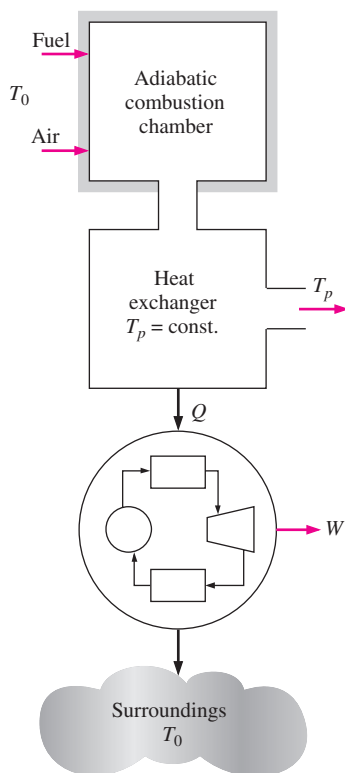


FIGURE P15–106

of the product gases in the heat exchanger will be T_0 , and thus $\eta_C = 0$), and will reach a maximum somewhere in between. Treating the combustion products as ideal gases with constant specific heats and assuming no change in their composition in the heat exchanger, show that the work output of the Carnot heat engine will be maximum when

$$T_p = \sqrt{T_{af}T_0}$$

Also, show that the maximum work output of the Carnot engine in this case becomes

$$W_{\max} = CT_{af}\left(1 - \sqrt{\frac{T_0}{T_{af}}}\right)^2$$

where C is a constant whose value depends on the composition of the product gases and their specific heats.

15–107 The furnace of a particular power plant can be considered to consist of two chambers: an adiabatic combustion chamber where the fuel is burned completely and adiabatically and a counterflow heat exchanger where heat is transferred to a reversible heat engine. The mass flow rate of the working fluid of the heat engine is such that the working fluid is heated from T_0 (the temperature of the environment) to T_{af} (the adiabatic flame temperature) while the combustion products are cooled from T_{af} to T_0 . Treating the combustion products as ideal gases with constant specific heats and assuming no change in their composition in the heat exchanger, show that the work output of this reversible heat engine is

$$W = CT_0\left(\frac{T_{af}}{T_0} - 1 - \ln \frac{T_{af}}{T_0}\right)$$

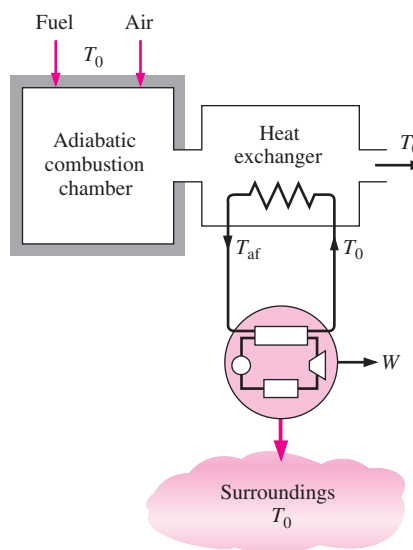



FIGURE P15–107


where C is a constant whose value depends on the composition of the product gases and their specific heats.


Also, show that the *effective flame temperature* T_e of this furnace is


$$T_e = \frac{T_{af} - T_0}{\ln(T_{af}/T_0)}$$


That is, the work output of the reversible engine would be the same if the furnace above is considered to be an isothermal furnace at a constant temperature T_e .


15-108  Using EES (or other) software, determine the effect of the amount of air on the adiabatic flame temperature of liquid octane (C_8H_{18}). Assume both the air and the octane are initially at $25^\circ C$. Determine the adiabatic flame temperature for 75, 90, 100, 120, 150, 200, 300, 500, and 800 percent theoretical air. Assume the hydrogen in the fuel always burns H_2O and the carbon CO_2 , except when there is a deficiency of air. In the latter case, assume that part of the carbon forms CO . Plot the adiabatic flame temperature against the percent theoretical air, and discuss the results.


15-109  Using EES (or other) software, write a general program to determine the heat transfer during the complete combustion of a hydrocarbon fuel (C_nH_m) at $25^\circ C$ in a steady-flow combustion chamber when the percent of excess air and the temperatures of air and the products are specified. As a sample case, determine the heat transfer per unit mass of fuel as liquid propane (C_3H_8) is burned steadily with 50 percent excess air at $25^\circ C$ and the combustion products leave the combustion chamber at 1800 K.


15-110  Using EES (or other) software, write a general program to determine the adiabatic flame temperature during the complete combustion of a hydrocarbon fuel (C_nH_m) at $25^\circ C$ in a steady-flow combustion chamber when the percent of excess air and its temperature are specified. As a sample case, determine the adiabatic flame temperature of liquid propane (C_3H_8) as it is burned steadily with 50 percent excess air at $25^\circ C$.


15-111  Using EES (or other) software, determine the adiabatic flame temperature of the fuels $CH_4(g)$, $C_2H_2(g)$, $CH_3OH(g)$, $C_3H_8(g)$, $C_8H_{18}(l)$. Assume both the fuel and the air enter the steady-flow combustion chamber at $25^\circ C$.


15-112  Using EES (or other) software, determine the minimum percent of excess air that needs to be used for the fuels $CH_4(g)$, $C_2H_2(g)$, $CH_3OH(g)$, $C_3H_8(g)$, $C_8H_{18}(l)$ if the adiabatic flame temperature is not to exceed 1500 K. Assume both the fuel and the air enter the steady-flow combustion chamber at $25^\circ C$.

15-113  Using EES (or other) software, repeat Prob. 15-112 for adiabatic flame temperatures of (a) 1200 K, (b) 1750 K, and (c) 2000 K.

15-114  Using EES (or other) software, determine the adiabatic flame temperature of $CH_4(g)$ when both the fuel and the air enter the combustion chamber at $25^\circ C$ for the cases of 0, 20, 40, 60, 80, 100, 200, 500, and 1000 percent excess air.

15-115  Using EES (or other) software, determine the rate of heat transfer for the fuels $CH_4(g)$, $C_2H_2(g)$, $CH_3OH(g)$, $C_3H_8(g)$, and $C_8H_{18}(l)$ when they are burned completely in a steady-flow combustion chamber with the theoretical amount of air. Assume the reactants enter the combustion chamber at 298 K and the products leave at 1200 K.

15-116  Using EES (or other) software, repeat Prob. 15-115 for (a) 50, (b) 100, and (c) 200 percent excess air.

15-117  Using EES (or other) software, determine the fuel among $CH_4(g)$, $C_2H_2(g)$, $C_2H_6(g)$, $C_3H_8(g)$, $C_8H_{18}(l)$ that gives the highest temperature when burned completely in an adiabatic constant-volume chamber with the theoretical amount of air. Assume the reactants are at the standard reference state.

Fundamentals of Engineering (FE) Exam Problems

15-118 A fuel is burned with 90 percent theoretical air. This is equivalent to

- (a) 10% excess air
(b) 90% excess air
(c) 10% deficiency of air
(d) 90% deficiency of air
(e) stoichiometric amount of air

15-119 Propane (C_3H_8) is burned with 150 percent theoretical air. The air–fuel mass ratio for this combustion process is

- (a) 5.3
(b) 10.5
(c) 15.7
(d) 23.4
(e) 39.3

15-120 One kmol of methane (CH_4) is burned with an unknown amount of air during a combustion process. If the combustion is complete and there are 2 kmol of free O_2 in the products, the air–fuel mass ratio is

- (a) 34.3
(b) 17.2
(c) 19.0
(d) 14.9
(e) 12.1

15-121 A fuel is burned steadily in a combustion chamber. The combustion temperature will be the highest except when

- (a) the fuel is preheated.
(b) the fuel is burned with a deficiency of air.
(c) the air is dry.
(d) the combustion chamber is well insulated.
(e) the combustion is complete.

15-122 An equimolar mixture of carbon dioxide and water vapor at 1 atm and $60^\circ C$ enter a dehumidifying section where the entire water vapor is condensed and removed from the mixture, and the carbon dioxide leaves at 1 atm and $60^\circ C$.

The entropy change of carbon dioxide in the dehumidifying section is

- (a) $-2.8 \text{ kJ/kg} \cdot \text{K}$ (b) $-0.13 \text{ kJ/kg} \cdot \text{K}$
 (c) 0 (d) $0.13 \text{ kJ/kg} \cdot \text{K}$
 (e) $2.8 \text{ kJ/kg} \cdot \text{K}$

15-123 Methane (CH_4) is burned completely with 80 percent excess air during a steady-flow combustion process. If both the reactants and the products are maintained at 25°C and 1 atm and the water in the products exists in the liquid form, the heat transfer from the combustion chamber per unit mass of methane is

- (a) 890 MJ/kg (b) 802 MJ/kg (c) 75 MJ/kg
 (d) 56 MJ/kg (e) 50 MJ/kg

15-124 The higher heating value of a hydrocarbon fuel C_nH_m with $m = 8$ is given to be 1560 MJ/kmol of fuel. Then its lower heating value is

- (a) 1384 MJ/kmol (b) 1208 MJ/kmol
 (c) 1402 MJ/kmol (d) 1514 MJ/kmol
 (e) 1551 MJ/kmol

15-125 Acetylene gas (C_2H_2) is burned completely during a steady-flow combustion process. The fuel and the air enter the combustion chamber at 25°C , and the products leave at 1500 K. If the enthalpy of the products relative to the standard reference state is -404 MJ/kmol of fuel, the heat transfer from the combustion chamber is

- (a) 177 MJ/kmol (b) 227 MJ/kmol (c) 404 MJ/kmol
 (d) 631 MJ/kmol (e) 751 MJ/kmol

15-126 Benzene gas (C_6H_6) is burned with 90 percent theoretical air during a steady-flow combustion process. The mole fraction of the CO in the products is

- (a) 1.6% (b) 4.4% (c) 2.5%
 (d) 10% (e) 16.7%

15-127 A fuel is burned during a steady-flow combustion process. Heat is lost to the surroundings at 300 K at a rate of 1120 kW. The entropy of the reactants entering per unit time is 17 kW/K and that of the products is 15 kW/K. The total rate of exergy destruction during this combustion process is

- (a) 520 kW (b) 600 kW (c) 1120 kW
 (d) 340 kW (e) 739 kW

Design and Essay Problems

15-128 Design a combustion process suitable for use in a gas-turbine engine. Discuss possible fuel selections for the several applications of the engine.

15-129 Constant-volume vessels that contain flammable mixtures of hydrocarbon vapors and air at low pressures are

frequently used. Although the ignition of such mixtures is very unlikely as there is no source of ignition in the tank, the Safety and Design Codes require that the tank withstand four times the pressure that may occur should an explosion take place in the tank. For operating gauge pressures under 25 kPa, determine the pressure for which these vessels must be designed in order to meet the requirements of the codes for (a) acetylene $\text{C}_2\text{H}_2(g)$, (b) propane $\text{C}_3\text{H}_8(g)$, and (c) *n*-octane $\text{C}_8\text{H}_{18}(g)$. Justify any assumptions that you make.

15-130 The safe disposal of hazardous waste material is a major environmental concern for industrialized societies and creates challenging problems for engineers. The disposal methods commonly used include landfilling, burying in the ground, recycling, and incineration or burning. Incineration is frequently used as a practical means for the disposal of combustible waste such as organic materials. The EPA regulations require that the waste material be burned almost completely above a specified temperature without polluting the environment. Maintaining the temperature above a certain level, typically about 1100°C , necessitates the use of a fuel when the combustion of the waste material alone is not sufficient to obtain the minimum specified temperature.

A certain industrial process generates a liquid solution of ethanol and water as the waste product at a rate of 10 kg/s. The mass fraction of ethanol in the solution is 0.2. This solution is to be burned using methane (CH_4) in a steady-flow combustion chamber. Propose a combustion process that will accomplish this task with a minimal amount of methane. State your assumptions.

15-131 Obtain the following information about a power plant that is closest to your town: the net power output; the type and amount of fuel; the power consumed by the pumps, fans, and other auxiliary equipment; stack gas losses; and the rate of heat rejection at the condenser. Using these data, determine the rate of heat loss from the pipes and other components, and calculate the thermal efficiency of the plant.

15-132 What is oxygenated fuel? How would the heating value of oxygenated fuels compare to those of comparable hydrocarbon fuels on a unit-mass basis? Why is the use of oxygenated fuels mandated in some major cities in winter months?

15-133 A promising method of power generation by direct energy conversion is through the use of magnetohydrodynamic (MHD) generators. Write an essay on the current status of MHD generators. Explain their operation principles and how they differ from conventional power plants. Discuss the problems that need to be overcome before MHD generators can become economical.