

CHAPTER 3

FUELS AND COMBUSTION

3.1 Introduction to Combustion

Combustion Basics

The last chapter set forth the basics of the Rankine cycle and the principles of operation of steam cycles of modern steam power plants. An important aspect of power generation involves the supply of heat to the working fluid, which in the case of steam power usually means turning liquid water into superheated steam. This heat comes from an *energy source*. With the exception of nuclear and solar power and a few other exotic sources, most power plants are driven by a chemical reaction called *combustion*, which usually involves sources that are compounds of hydrogen and carbon. Process industries, businesses, homes, and transportation systems have vast heat requirements that are also satisfied by combustion reactions. The subject matter of this chapter therefore has wide applicability to a variety of heating processes.

Combustion is the conversion of a substance called a *fuel* into chemical compounds known as *products of combustion* by combination with an *oxidizer*. The combustion process is an *exothermic* chemical reaction, i.e., a reaction that releases energy as it occurs. Thus combustion may be represented symbolically by:



Here the fuel and the oxidizer are *reactants*, i.e., the substances present before the reaction takes place. This relation indicates that the reactants produce combustion products and energy. Either the chemical energy released is transferred to the surroundings as it is produced, or it remains in the combustion products in the form of elevated internal energy (temperature), or some combination thereof.

Fuels are evaluated, in part, based on the amount of energy or heat that they release per unit mass or per mole during combustion of the fuel. Such a quantity is known as the fuel's *heat of reaction* or *heating value*.

Heats of reaction may be measured in a calorimeter, a device in which chemical energy release is determined by transferring the released heat to a surrounding fluid. The amount of heat transferred to the fluid in returning the products of combustion to their initial temperature yields the heat of reaction.

In combustion processes the oxidizer is usually air but could be pure oxygen, an oxygen mixture, or a substance involving some other oxidizing element such as fluorine. Here we will limit our attention to combustion of a fuel with air or pure oxygen.

Chemical fuels exist in gaseous, liquid, or solid form. Natural gas, gasoline, and coal, perhaps the most widely used examples of these three forms, are each a complex mixture of reacting and inert compounds. We will consider each more closely later in the chapter. First let's review some important fundamentals of mixtures of gases, such as those involved in combustion reactions.

Mass and Mole Fractions

The amount of a substance present in a sample may be indicated by its mass or by the number of moles of the substance. A *mole* is defined as the mass of a substance equal to its molecular mass or molecular weight. A few molecular weights commonly used in combustion analysis are tabulated below. For most combustion calculations, it is sufficiently accurate to use integer molecular weights. The error incurred may easily be evaluated for a given reaction and should usually not be of concern. Thus a gram-mole of water is 18 grams, a kg-mole of nitrogen is 28 kg, and a pound-mole of sulfur is 32 lb_m.

| Molecule | Molecular Weight |
|----------------|------------------|
| C | 12 |
| N ₂ | 28 |
| O ₂ | 32 |
| S | 32 |
| H ₂ | 2 |

The composition of a mixture may be given as a list of the fractions of each of the substances present. Thus we define the *mass fraction*, of a component i , mf_i , as the ratio of the mass of the component, m_i , to the mass of the mixture, m :

$$mf_i = m_i/m$$

It is evident that the sum of the mass fractions of all the components must be 1. Thus

$$mf_1 + mf_2 + \dots = 1$$

Analogous to the mass fraction, we define the *mole fraction* of component i , x_i , as the ratio of the number of moles of i , n_i , to the total number of moles in the mixture, n :

$$x_i = n_i/n$$

The total number of moles, n , is the sum of the number of moles of all the components of the mixture:

$$n = n_1 + n_2 + \dots$$

It follows that the sum of all the mole fractions of the mixture must also equal 1.

$$x_1 + x_2 + \dots = 1$$

The mass of component i in a mixture is the product of the number of moles of i and its molecular weight, M_i . The mass of the mixture is therefore the sum, $m = n_1M_1 + n_2M_2 + \dots$, over all components of the mixture. Substituting $x_i n$ for n_i , the total mass becomes

$$m = (x_1M_1 + x_2M_2 + \dots)n$$

But the average molecular weight of the mixture is the ratio of the total mass to the total number of moles. Thus the average molecular weight is

$$M = m/n = x_1M_1 + x_2M_2 + \dots$$

EXAMPLE 3.1

Express the mass fraction of component 1 of a mixture in terms of: (a) the number of moles of the three components of the mixture, n_1 , n_2 , and n_3 , and (b) the mole fractions of the three components. (c) If the mole fractions of carbon dioxide and nitrogen in a three component gas containing water vapor are 0.07 and 0.38, respectively, what are the mass fractions of the three components?

Solution

(a) Because the mass of i can be written as $m_i = n_iM_i$, the mass fraction of component i can be written as:

$$\text{mf}_i = n_iM_i / (n_1M_1 + n_2M_2 + \dots) \quad [\text{dl}]$$

For the first of the three components, $i = 1$, this becomes:

$$\text{mf}_1 = n_1M_1 / (n_1M_1 + n_2M_2 + n_3M_3)$$

Similarly, for $i = 2$ and $i = 3$:

$$\text{mf}_2 = n_2M_2 / (n_1M_1 + n_2M_2 + n_3M_3)$$

$$\text{mf}_3 = n_3M_3 / (n_1M_1 + n_2M_2 + n_3M_3)$$

(b) Substituting $n_1 = x_1 n$, $n_2 = x_2 n$, etc. in the earlier equations and simplifying, we obtain for the mass fractions:

$$\text{mf}_1 = x_1 M_1 / (x_1 M_1 + x_2 M_2 + x_3 M_3)$$

$$\text{mf}_2 = x_2 M_2 / (x_1 M_1 + x_2 M_2 + x_3 M_3)$$

$$\text{mf}_3 = x_3 M_3 / (x_1 M_1 + x_2 M_2 + x_3 M_3)$$

(c) Identifying the subscripts 1, 2, and 3 with carbon dioxide, nitrogen, and water vapor, respectively, we have $x_1 = 0.07$, $x_2 = 0.38$ and $x_3 = 1 - 0.07 - 0.038 = 0.55$. Then:

$$\text{mf}_1 = (0.07)(44) / [(0.07)(44) + (0.38)(28) + (0.55)(18)]$$

$$= (0.07)(44) / (23.62) = 0.1304$$

$$\text{mf}_2 = (0.38)(28) / (23.62) = 0.4505$$

$$\text{mf}_3 = (0.55)(18) / (23.62) = 0.4191$$

As a check we sum the mass fractions: $0.1304 + 0.4505 + 0.4191 = 1.0000$.

For a mixture of gases at a given temperature and pressure, the ideal gas law shows that $pV_i = n_i \mathcal{R}T$ holds for any component, and $pV = n \mathcal{R}T$ for the mixture as a whole. Forming the ratio of the two equations we observe that the mole fractions have the same values as the volume fraction:

$$x_i = V_i / V = n_i / n \quad [\text{dl}]$$

Similarly, for a given volume of a mixture of gases at a given temperature, $p_i V = n_i \mathcal{R}T$ for each component and $pV = n \mathcal{R}T$ for the mixture. The ratio of the two equations shows that the *partial pressure* of any component i is the product of the mole fraction of i and the pressure of the mixture:

$$p_i = p n_i / n = p x_i$$

EXAMPLE 3.2

What is the partial pressure of water vapor in Example 3.1 if the mixture pressure is two atmospheres?

Solution

The mole fraction of water vapor in the mixture of Example 3.1 is 0.55. The partial pressure of the water vapor is therefore $(0.55)(2) = 1.1$ atm.

Characterizing Air for Combustion Calculations

Air is a mixture of about 21% oxygen, 78% nitrogen, and 1% other constituents by volume. For combustion calculations it is usually satisfactory to represent air as a 21% oxygen, 79% nitrogen mixture, by volume. Thus for every 21 moles of oxygen that react when air oxidizes a fuel, there are also 79 moles of nitrogen involved. Therefore, $79/21 = 3.76$ moles of nitrogen are present for every mole of oxygen in the air.

At room temperature both oxygen and nitrogen exist as diatomic molecules, O_2 and N_2 , respectively. It is usually assumed that the nitrogen in the air is nonreacting at combustion temperatures; that is, there are as many moles of pure nitrogen in the products as there were in the reactants. At very high temperatures small amounts of nitrogen react with oxygen to form oxides of nitrogen, usually termed NO_x . These small quantities are important in pollution analysis because of the major role of even small traces of NO_x in the formation of smog. However, since these NO_x levels are insignificant in energy analysis applications, nitrogen is treated as inert here.

The molecular weight of a compound or mixture is the mass of 1 mole of the substance. The average molecular weight, M , of a mixture, as seen earlier, is the linear combination of the products of the mole fractions of the components and their respective molecular weights. Thus the molecular weight for air, M_{air} , is given by the sum of the products of the molecular weights of oxygen and nitrogen and their respective mole fractions in air. Expressed in words:

$$M_{air} = \text{Mass of air/Mole of air} = (\text{Moles of } N_2/\text{Mole of air})(\text{Mass of } N_2/\text{Mole of } N_2) \\ + (\text{Moles of } O_2/\text{Mole of air})(\text{Mass of } O_2/\text{Mole of } O_2)$$

or

$$M_{air} = 0.79 M_{nitrogen} + 0.21 M_{oxygen} \\ = 0.79(28) + 0.21(32) = 28.84$$

The mass fractions of oxygen and nitrogen in air are then

$$mf_{oxygen} = (0.21)(32)/28.84 = 0.233, \text{ or } 23.3\%$$

and

$$mf_{nitrogen} = (0.79)(28)/28.84 = 0.767, \text{ or } 76.7\%$$

3.2 Combustion Chemistry of a Simple Fuel

Methane, CH₄, is a common fuel that is a major constituent of most natural gases. Consider the complete combustion of methane in pure oxygen. The chemical reaction equation for the complete combustion of methane in oxygen may be written as:

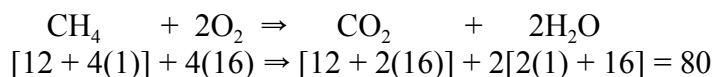


Because atoms are neither created nor destroyed, Equation (3.1) states that methane (consisting of one atom of carbon and four atoms of hydrogen) reacts with four atoms of oxygen to yield carbon dioxide and water products with the same number of atoms of each *element* as in the reactants. This is the basic principle involved in balancing all chemical reaction equations.

Carbon dioxide is the product formed by complete combustion of carbon through the reaction $\text{C} + \text{O}_2 \Rightarrow \text{CO}_2$. Carbon dioxide has only one carbon atom per molecule. Since in Equation (3.1) there is only one carbon atom on the left side of the equation, there can be only one carbon atom and therefore one CO₂ molecule on the right. Similarly, *water is the product of the complete combustion of hydrogen*. It has two atoms of hydrogen per molecule. Because there are four hydrogen atoms in the reactants of Equation (3.1), there must be four in the products, implying that two molecules of water formed. These observations require four atoms of oxygen on the right, which implies the presence of two molecules (four atoms) of oxygen on the left.

The coefficients in chemical equations such as Equation (3.1) may be interpreted as the number of moles of the substance required for the reaction to occur as written. Thus another way of interpreting Equation (3.1) is that one mole of methane reacts with two moles of oxygen to form one mole of carbon dioxide and two moles of water. While not evident in this case, it is not necessary that there be the same number of moles of products as reactants. It will be seen in numerous other cases that a different number of moles of products is produced from a given number of moles of reactants.

Thus although the numbers of atoms of each element must be conserved during a reaction, the total number of moles need not. Because the number of atoms of each element cannot change, it follows that the mass of each element and the total mass must be conserved during the reaction. Thus, using the atomic weights (masses) of each element, the sums of the masses of the reactants and products in Equation (3.1) are both 80:



Other observations may be made with respect to Equation (3.1). There are 2 moles of water in the 3 moles of combustion products, and therefore a *mole fraction* of water in the combustion products of $x_{\text{water}} = 2/3 = 0.667$. Similarly, $x_{\text{Carbon dioxide}} = 1/3 = 0.333$ moles of CO₂ in the products.

There are 44 mass units of CO₂ in the 80 mass units of products for a *mass*

fraction of CO₂ in the products,

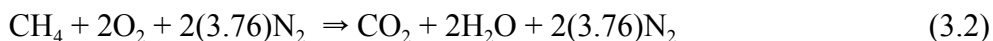
$$\text{mf}_{\text{carbon dioxide}} = 44/80 = 0.55$$

Likewise, the mass fraction of water in the products is $2(18)/80 = 0.45$.

We also observe that there are 12 mass units of carbon in the products and therefore a carbon mass fraction of $12/80 = 0.15$. Note that because the mass of any element and the total mass are conserved in a chemical reaction, the mass fraction of any element is also conserved in the reaction. Thus the mass fraction of carbon in the reactants is 0.15, as in the products.

Combustion in Air

Let us now consider the *complete combustion* of methane in air. The same combustion products are expected as with combustion in oxygen; the only additional reactant present is nitrogen, and it is considered inert. Moreover, because we know that in air every mole of oxygen is accompanied by 3.76 moles of nitrogen, the reaction equation can be written as



It is seen that the reaction equation for combustion in air may be obtained from the combustion equation for the reaction in oxygen by adding the appropriate number of moles of nitrogen to both sides of the equation.

Note that both Equations (3.1) and (3.2) describe reactions of one mole of methane fuel. Because the same amount of fuel is present in both cases, both reactions release the same amount of energy. We can therefore compare combustion reactions in air and in oxygen. It will be seen that the presence of nitrogen acts to dilute the reaction, both chemically and thermally. With air as oxidizer, there are 2 moles of water vapor per 10.52 moles of combustion products, compared with 2 moles of water per 3 moles of products for combustion in oxygen. Similarly, with air, there is a mass fraction of CO₂ of 0.1514 and a carbon mass fraction of 0.0413 in the combustion products, compared with 0.55 and 0.15, respectively, for combustion in oxygen.

The diluting energetic effect of nitrogen when combustion is in air may be reasoned as follows: The same amount of energy is released in both reactions, because the same amount of fuel is completely consumed. However, the nonreacting nitrogen molecules in the air have heat capacity. This added heat capacity of the additional nitrogen molecules absorbs much of the energy released, resulting in a lower internal energy per unit mass of products and hence a lower temperature of the products. Thus the energy released by the reaction is shared by a greater mass of combustion products when the combustion is in air.

Often, products of combustion are released to the atmosphere through a chimney, stack, or flue. These are therefore sometimes referred to as *flue gases*. The flue gas composition may be stated in terms of *wet flue gas* (wfg) or *dry flue gas* (dfg), because

under some circumstances the water vapor in the gas condenses and then escapes as a liquid rather than remaining as a gaseous component of the flue gas. When liquid water is present in combustion products, the combustion product gaseous mass fractions may be taken with respect to the mass of flue gas products, with the product water present or omitted. Thus, for Equation (3.2), the mass of dry combustion products is 254.56. Hence the mass fraction of carbon dioxide is $44/254.56 = 0.1728$ with respect to dry flue gas, and $44/290.56 = 0.1514$ with respect to wet flue gas.

In combustion discussions reference is frequently made to higher and lower heating values. The term *higher heating value*, HHV, refers to a heating value measurement in which the product water vapor is allowed to condense. As a consequence, the heat of vaporization of the water is released and becomes part of the heating value. The *lower heating value*, LHV, corresponds to a heating value in which the water remains a vapor and does not yield its heat of vaporization. Thus the energy difference between the two values is due to the heat of vaporization of water, and

$$\text{HHV} = \text{LHV} + (m_{\text{water}}/m_{\text{fuel}})h_{\text{fg}} \quad [\text{Btu/lb}_m \mid \text{kJ/kg}]$$

where m_{water} is the mass of liquid water in the combustion products, and h_{fg} is the latent heat of vaporization of water.

Air-Fuel Ratio

It is important to know how much oxygen or air must be supplied for complete combustion of a given quantity of fuel. This information is required in sizing fans and ducts that supply oxidizer to combustion chambers or burners and for numerous other design purposes. The mass *air-fuel ratio*, A/F, or oxygen-fuel ratio, O/F, for complete combustion may be determined by calculating the masses of oxidizer and fuel from the appropriate reaction equation. Let's return to Equation (3.2):



The A/F for methane is $[(2)(32) + (2)(3.76)(28)]/(12 + 4) = 17.16$ and the O/F is $2(32)/(12 + 4) = 4$. Thus 4 kg of O_2 or 17.16 kg of air must be supplied for each kilogram of methane completely consumed.

Of course it is possible, within limits, to supply an arbitrary amount of air to a burner to burn the fuel. The terms *stoichiometric* or *theoretical* are applied to the situation just described, in which just enough oxidizer is supplied to completely convert the fuel to CO_2 and H_2O . Thus the stoichiometric O/F and A/F ratios for methane are 4.0 and 17.16, respectively. If less than the theoretical amount of air is supplied, the products will contain unburned fuel. Regardless of the magnitude of A/F, when unburned fuel remains in the products (including carbon, carbon monoxide, or hydrogen), combustion is said to be *incomplete*. Because air is virtually free and fuel is expensive, it is usually important to burn all of the fuel by using more air than the theoretical air-fuel ratio indicates is needed. Thus most burners operate with *excess air*.

The actual air-fuel ratio used in a combustor is frequently stated as a percentage of the theoretical air-fuel ratio

$$\% \text{ theoretical air} = 100(A/F)_{\text{actual}} / (A/F)_{\text{theor}} \quad (3.3)$$

Thus, for methane, 120% of theoretical air implies an actual mass air-fuel ratio of $(120/100)(17.16) = 20.59$.

Excess air is defined as the difference between the actual and the theoretical air supplied. Accordingly, the *percentage of excess air* is

$$\% \text{ excess air} = 100[(A/F)_{\text{actual}} - (A/F)_{\text{theor}}] / (A/F)_{\text{theor}} \quad (3.4)$$

Thus, for methane, 120% of theoretical air implies

$$\% \text{ excess air} = (100)(20.59 - 17.16) / 17.16 = 20\%.$$

Note also that combining Equations (3.4) and (3.3) yields the following general result:

$$\% \text{ excess air} = \% \text{ theoretical air} - 100\% \quad (3.5)$$

Again, the excess air percentage is $120\% - 100\% = 20\%$. Table 3.1 shows examples of ranges of excess air used with certain fuels and combustion systems.

The air/fuel parameters just discussed emphasize the amount of air supplied to burn *a given amount of fuel* relative to the theoretical requirement. An alternate approach considers *a given amount of air* and indicates the mass of fuel supplied, the fuel-air ratio, F/A , which is the inverse of the air-fuel ratio. A measure of how much fuel is actually supplied, called the *equivalence ratio*, is the ratio of the actual fuel-air ratio to the theoretical fuel-air ratio:

$$\begin{aligned} \Phi &= (F/A)_{\text{actual}} / (F/A)_{\text{theor}} = (A/F)_{\text{theor}} / (A/F)_{\text{actual}} \\ &= 100 / (\% \text{ theoretical air}) \end{aligned}$$

Thus 100% theoretical air corresponds to an equivalence ratio of 1, and 20% excess air to $\Phi = 100/120 = 0.833$. When the equivalence ratio is less than 1, the mixture is called *lean*; when greater than 1, it is called *rich*.

This section has dealt with the application of combustion chemistry or stoichiometry applied to methane gas. Other fuels for which a reaction equation such as Equation (3.1) or (3.2) is available may be treated in a similar way. Before considering more complex combustion problems, it is appropriate to investigate the nature and description of the various types of fossil fuels.

TABLE 3.1 Usual Amount of Excess Air Supplied to Fuel-Burning Equipment

| Fuel | Type of Furnace or Burners | Excess Air, % by Weight |
|--------------------------------------|-----------------------------------------------------------------|--------------------------------|
| Pulverized coal | Completely water-cooled furnace for slag-tap or dry-ash-removal | 15–20 |
| | Partially water-cooled furnace for dry-ash-removal | 15–40 |
| Crushed coal | Cyclone furnace—pressure or suction | 10–15 |
| Coal | Spreader stoker | 30–60 |
| | Water-cooled vibrating grate stoker | 30–60 |
| | Chain-grate and traveling-grate stokers | 15–50 |
| | Underfeed stoker | 20–50 |
| Fuel oil | Oil burners, register type | 5–10 |
| | Multifuel burners and flat-flame | 10–20 |
| Acid sludge | Cone and flat-flame-type burners, steam-atomized | 10–15 |
| Natural, coke-oven, and refinery gas | Register-type burners | 5–10 |
| | Multifuel burners | 7–12 |
| Blast-furnace gas | Intertube nozzle-type burners | 15–18 |
| Wood | Dutch oven (10–23% through grates) and Hoff-type | 20–25 |
| Bagasse | All furnaces | 25–35 |
| Black liquor | Recovery furnaces for kraft and soda-pulping processes | 5–7 |

Courtesy of Babcock and Wilcox Co.

3.3 Fossil Fuel Characteristics

Most chemical fuels are found in nature in the form of crude oil, natural gas, and coal. These fuels are called fossil fuels because they are believed to have been formed by the decay of vegetable and animal matter over many thousands of years under conditions of high pressure and temperature and with a deficiency or absence of oxygen. Other fuels such as gasoline, syngas (synthetic gas), and coke may be derived from fossil fuels by some form of industrial or chemical processing. These derived fuels are also called fossil fuels.

Coal

Coal is an abundant solid fuel found in many locations around the world in a variety of forms. The American Society for Testing Materials, ASTM, has established a ranking system (ref. 3) that classifies coals as anthracite (I), bituminous (II), subbituminous (III), and lignite (IV), according to their physical characteristics. Table 3.2 lists

TABLE 3.2 Seventeen Selected U.S. Coals Arranged in Order of ASTM Classification

| No. | Coal Rank | | County and State | Coal Analysis, Bed Moisture Bases | | | | | | Rank | Rank |
|-----|-----------|-------|--------------------|-----------------------------------|------|------|------|------|--------|------|--------|
| | Class | Group | | M | VM | FC | A | S | Btu | FC | Btu |
| 1 | I | 1 | Schuylkill, Pa. | 4.5 | 1.7 | 84.1 | 9.7 | 0.77 | 12,745 | 99.2 | 14,280 |
| 2 | I | 2 | Lackawanna, Pa. | 2.5 | 6.2 | 79.4 | 11.9 | 0.60 | 12,925 | 94.1 | 14,880 |
| 3 | I | 3 | Montgomery, Va. | 2.0 | 10.6 | 67.2 | 20.2 | 0.62 | 11,925 | 88.7 | 15,340 |
| 4 | II | 1 | McDowell, W.Va. | 1.0 | 16.6 | 77.3 | 5.1 | 0.74 | 14,715 | 82.8 | 15,600 |
| 5 | II | 1 | Cambria, Pa. | 1.3 | 17.5 | 70.9 | 10.3 | 1.68 | 13,800 | 81.3 | 15,595 |
| 6 | II | 2 | Somerset, Pa. | 1.5 | 20.8 | 67.5 | 10.2 | 1.68 | 13,720 | 77.5 | 15,485 |
| 7 | II | 2 | Indiana, Pa. | 1.5 | 23.4 | 64.9 | 10.2 | 2.20 | 13,800 | 74.5 | 15,580 |
| 8 | II | 3 | Westmoreland, Pa. | 1.5 | 30.7 | 56.6 | 11.2 | 1.82 | 13,325 | 65.8 | 15,230 |
| 9 | II | 3 | Pike, Ky. | 2.5 | 36.7 | 57.5 | 3.8 | 0.70 | 14,480 | 61.3 | 15,040 |
| 10 | II | 3 | Belmont, Ohio | 3.6 | 40.0 | 47.3 | 9.1 | 4.00 | 12,850 | 55.4 | 14,380 |
| 11 | II | 4 | Williamson, Ill. | 5.8 | 36.2 | 46.3 | 11.7 | 2.70 | 11,910 | 57.3 | 13,710 |
| 12 | II | 4 | Emory, Utah | 5.2 | 38.2 | 50.2 | 6.4 | 0.90 | 12,600 | 57.3 | 13,560 |
| 13 | II | 5 | Vermilion, Ill. | 12.2 | 38.8 | 40.0 | 9.0 | 3.20 | 11,340 | 51.8 | 12,630 |
| 14 | III | 1 | Musselshell, Mont. | 14.1 | 32.2 | 46.7 | 7.0 | 0.43 | 11,140 | 59.0 | 12,075 |
| 15 | III | 2 | Sheridan, Wyo. | 25.0 | 30.5 | 40.8 | 3.7 | 0.30 | 9,345 | 57.5 | 9,745 |
| 16 | III | 3 | Campbell, Wyo. | 31.0 | 31.4 | 32.8 | 4.8 | 0.55 | 8,320 | 51.5 | 8,790 |
| 17 | IV | 1 | Mercer, N.D. | 37.0 | 26.6 | 32.2 | 4.2 | 0.40 | 7,255 | 55.2 | 7,610 |

Data on Coal (Bed Moisture Basis)

M = equilibrium moisture, %; VM = volatile matter, %

FC = fixed carbon, %; A = ash, %; S = sulfur, %

Btu = Btu per lb, high heating value

Courtesy of Babcock and Wilcox Co.

Rank FC = dry, mineral-matter-free fixed carbon, %

Rank Btu = moist, mineral-matter-free Btu per lb

Calculations by Parr formulas

seventeen of the many United States coals according to this class ranking.

Coal is formed over long periods of time, in a progression shown from left to right in Figure 3.1. The bars on the ordinate show the division of the combustibles between fixed carbon and volatile matter in the fuels. "Fixed carbon" and "volatile matter" indicate roughly how much of the fuel burns as a solid and as a thermally generated gas, respectively. It is seen that the volatile matter and oxygen contained in the fuels decrease with increasing age.

Peat is a moist fuel, at the geologically young end of the scale, that has a relatively low heating value. It is not considered a coal but, nevertheless, follows the patterns of characteristics shown in the figure. Peat is regarded as an early stage or precursor of coal. At the other extreme, anthracite is a geologically old, very hard, shiny coal with high carbon content and high heating value. Bituminous is much more abundant than anthracite, has a slightly lower carbon content, but also has a high heating value. Subbituminous coal, lignite, and peat have successively poorer heating values and higher volatile matter than bituminous.

Coal is a highly inhomogeneous material, of widely varying composition, found in seams (layers) of varying thickness at varying depths below the earth's surface. The wide geographic distribution of coal in the United States is shown in Figure 3.2.

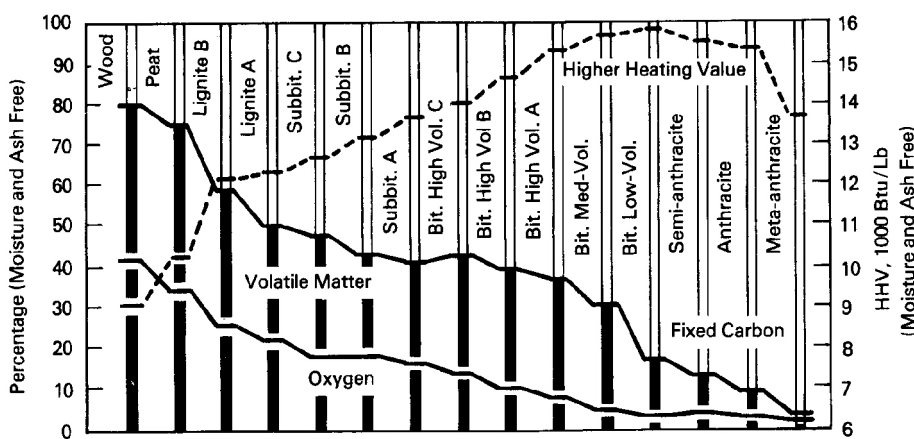


FIGURE 3.1 Progressive stages of the transformation of vegetal matter into coal. (Reproduced with permission from Combustion/Fossil Power Systems, ©1981, Combustion Engineering, Inc.)

According to reference 1, the average seam in the United States is about 5.5 ft. thick. The largest known seam is 425 ft. thick and is found in Manchuria.

Coal Analyses

It is often difficult to obtain representative samples of coal because of composition variations from location to location even within a given seam. As a result there are limits on the accuracy and adequacy of coal analyses in assessing coal behavior in a given application. Before discussing the nature of these analyses, it is important to establish the *basis* on which they are conducted.

Coal contains varying amounts of loosely held moisture and noncombustible materials or mineral matter (ash), which are of little or no use. The *basis* of an analysis helps to specify the conditions under which the coal is tested. The coal sample may be freshly taken from the mine, the *as-mined basis*. It may have resided in a coal pile for months, and be analyzed just before burning, the *as-fired basis*. It may be examined immediately after transport from the mine, the *as-received basis*. Exposure to rain or dry periods, weathering, and separation and loss of noncombustible mineral matter through abrasion and the shifting of loads during transport and storage may cause the same load of coal to have changing mineral matter and moisture content over time. It is therefore important to specify the basis for any test that is conducted. Published tabulations of coal properties are frequently presented on a *dry, ash-free*, or *dry and ash-free basis*, that is, in the absence of water and/or noncombustible mineral matter.

Coal ranking and analysis of combustion processes rely on two types of analysis of coal composition: the *proximate analysis* and the *ultimate analysis*. The *proximate analysis* starts with a representative sample of coal. The sample is first weighed, then raised to a temperature high enough to drive off water, and then reweighed. The weight

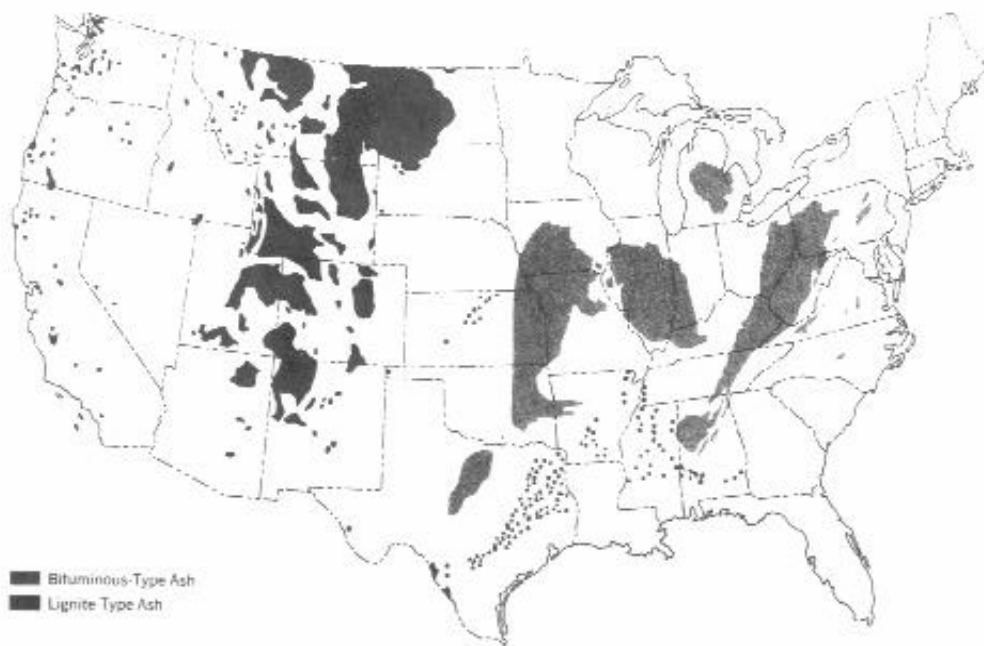


FIGURE 3.2 Coal fields of the United States. (Courtesy of Babcock and Wilcox.)

loss divided by the initial weight gives the coal *moisture* content, M . The remaining material is then heated at a much higher temperature, in the absence of oxygen, for a time long enough to drive off gases. The resulting weight-loss fraction gives the *volatile matter* content, VM , of the coal. The remainder of the sample is then burned in air until only noncombustibles remain. The weight loss gives the *fixed carbon*, FC , and the remaining material is identified as non-combustible mineral matter or *ash*, A .

The proximate analysis may be reported as percentages (or fractions) of the four quantities moisture, ash, volatile matter, and fixed carbon, as in Table 3.2, or without ash and moisture and with the FC and VM normalized to 100%. Sulfur, as a fraction of the coal mass, is sometimes reported with the proximate analysis. The proximate analysis, while providing very limited information, can be performed with limited laboratory resources.

A more sophisticated and useful analysis is the *ultimate analysis*, a chemical analysis that provides the elemental mass fractions of carbon, hydrogen, nitrogen, oxygen, and sulfur, usually on a dry, ash-free basis. The ash content of the coal and heating value are sometimes provided also.

Data from a dry, ash-free analysis can be converted to another basis by using the basis adjustment factor, $1 - A - M$, as follows. The mass of coal is the mass of ultimate or proximate analysis components plus the masses of water (moisture) and ash:

$$m = m_{comp} + m_{ash} + m_{moist} \quad [\text{lb}_m \mid \text{kg}]$$

Dividing through by the total mass m and rearranging, we get the following as the ratio of the mass of components to the total mass:

$$m_{comp} / m = 1 - A - M \quad [dl]$$

where A is the ash fraction and M is the moisture fraction of the total coal mass. A component of a coal analysis may be converted from the dry, ash-free basis to some other basis by forming the product of the component fraction and the basis adjustment factor. Thus an equation for the wet and ashy volatile matter fraction in the proximate analysis may be determined from the dry, ash-free proximate analysis by using

$$\begin{aligned} VM_{as-fired} &= (\text{Mass of combustibles/Total mass})VM_{dry,ashfree} \\ &= (1 - A - M) VM_{dry,ash-free} \end{aligned} \quad (3.6)$$

where A and M are, respectively, the ash and moisture fractions for the as-fired coal. Here the as-fired (wet, ashy) mass fraction of volatile matter is the product of the dry, ash-free mass fraction and the basis adjustment factor. Fixed carbon, heating values, and components of the ultimate analysis may be dealt with in a similar way.

Table 3.3 gives proximate and ultimate analyses for a number of United States coals on a dry basis. Another extensive tabulation of the characteristics of American and world coals is given in Appendix E.

EXAMPLE 3.3

If the as-fired moisture fraction for Schuylkill, Pa. anthracite culm characterized in Table 3.3 is 4.5%, determine the as-fired proximate and ultimate analysis and heating value of the coal. (*Culm* is the fine coal refuse remaining from anthracite mining.)

Solution

The FC, VM, and ash contents are given in Table 3.3. Because ash is already present in the analysis, the appropriate adjustment factor is $1 - A - M = 1 - 0.0 - 0.045 = 0.955$.

Using Equation (3.6) and the data from Table 3.3, we get

$$\begin{aligned} VM_{as-fired} &= (0.955)(8.3) = 7.927 \\ FC_{as-fired} &= (0.955)(32.6) = 31.133 \\ A_{as-fired} &= (0.955)(59.1) = 56.411 \\ M_{as-fired} &= \underline{4.500} \\ \text{Check Sum} &= 99.971 \\ \text{Heating value}_{as-fired} &= (0.955)(4918) = 4697 \text{ Btu/lb}_m \end{aligned}$$

Similarly, the as-fired ultimate analysis is 32% C, 1.15% H₂, 4.87% O₂, 0.57% N₂, 0.48% S, 56.44% ash, and 4.5% moisture, with a checksum of 100.01.

TABLE 3.3 Proximate and Ultimate Analyses of United States Coals

| County and State | Geological Name | Type | Proximate Analysis (Dry) | | | | Ultimate Analysis, Dry, wt, % | | | | | Heating Value (Btu/lb) |
|--------------------------|--------------------------------------------------------|---------|--------------------------|------------|------------|------|-------------------------------|----------------|----------------|-----|----------|------------------------|
| | | | Ash (wt, %) | VM (wt, %) | FC (wt, %) | C | H ₂ | O ₂ | N ₂ | S | | |
| Schuylkill, Pa. | Anthracite culm | Raw | 59.1 | 8.3 | 32.6 | 33.5 | 1.2 | 5.1 | 0.6 | 0.5 | 4,918.0 | |
| | | Clean 1 | 10.6 | 11.1 | 78.3 | 79.9 | 2.7 | 5.0 | 0.9 | 0.9 | 12,733.0 | |
| | | Clean 2 | 27.7 | 16.2 | 56.0 | 61.6 | 2.6 | 5.8 | 0.9 | 1.4 | 10,135.0 | |
| Freestone, Tex. | Big brown lignite | Raw | 18.4 | 45.5 | 36.1 | 63.2 | 4.8 | 11.3 | 1.2 | 1.1 | 9,954.0 | |
| | | Clean 1 | 9.1 | 47.1 | 43.8 | 64.8 | 4.7 | 19.1 | 1.2 | 1.0 | 11,369.0 | |
| | | Clean 2 | 9.6 | 45.3 | 45.1 | 63.8 | 4.7 | 20.1 | 1.0 | 0.9 | 11,222.0 | |
| | | Clean 3 | 14.0 | 44.3 | 41.7 | 66.3 | 4.9 | 12.7 | 1.2 | 0.9 | 10,687.0 | |
| Indiana, Pa. | Freeport (upper) | Clean 4 | 10.2 | 45.8 | 44.0 | 61.9 | 4.3 | 21.5 | 1.1 | 0.9 | 11,159.0 | |
| | | Raw | 31.7 | 22.3 | 46.0 | 57.1 | 3.5 | 4.0 | 1.7 | 1.9 | 10,239.0 | |
| | | Clean 1 | 16.4 | 26.2 | 57.3 | 71.7 | 4.3 | 4.2 | 1.9 | 1.4 | 12,846.0 | |
| | | Clean 2 | 20.4 | 26.4 | 53.2 | 67.6 | 4.1 | 5.2 | 0.8 | 1.8 | 12,193.0 | |
| Clearfield, Pa. | Freeport (upper) Freeport (lower) 50% of each | Raw | 12.3 | 24.8 | 62.9 | 76.3 | 4.5 | 3.4 | 1.8 | 1.7 | 13,559.0 | |
| | | Clean 1 | 6.5 | 27.6 | 65.9 | 82.2 | 4.9 | 4.0 | 1.6 | 0.9 | 14,541.0 | |
| | | Clean 2 | 7.0 | 26.3 | 66.7 | 81.4 | 4.7 | 4.8 | 1.4 | 0.7 | 14,476.0 | |
| | | Clean 3 | 9.2 | 26.5 | 64.3 | 78.9 | 4.7 | 4.8 | 1.7 | 0.7 | 14,187.0 | |
| Indiana, Pa. | Freeport (upper) Kittanning (lower) 20% F, 80% K | Clean 4 | 8.9 | 26.3 | 64.7 | 79.2 | 4.7 | 5.1 | 1.3 | 0.7 | 14,168.0 | |
| | | Raw | 33.6 | 19.4 | 47.0 | 54.3 | 3.3 | 3.8 | 1.2 | 3.8 | 9,780.0 | |
| | | Clean 1 | 12.6 | 22.1 | 65.3 | 75.5 | 4.4 | 4.0 | 1.6 | 1.9 | 13,563.0 | |
| | | Clean 2 | 17.0 | 22.0 | 61.0 | 71.8 | 4.2 | 3.2 | 1.1 | 2.7 | 12,814.0 | |
| British Columbia, Canada | Hat Creek A zone | Raw | 40.8 | 31.9 | 27.3 | 32.7 | 2.8 | 22.3 | 0.6 | 0.8 | 6,642.0 | |
| | | Clean 1 | 20.3 | 39.0 | 40.8 | 53.2 | 3.9 | 20.8 | 1.0 | 0.9 | 9,496.0 | |

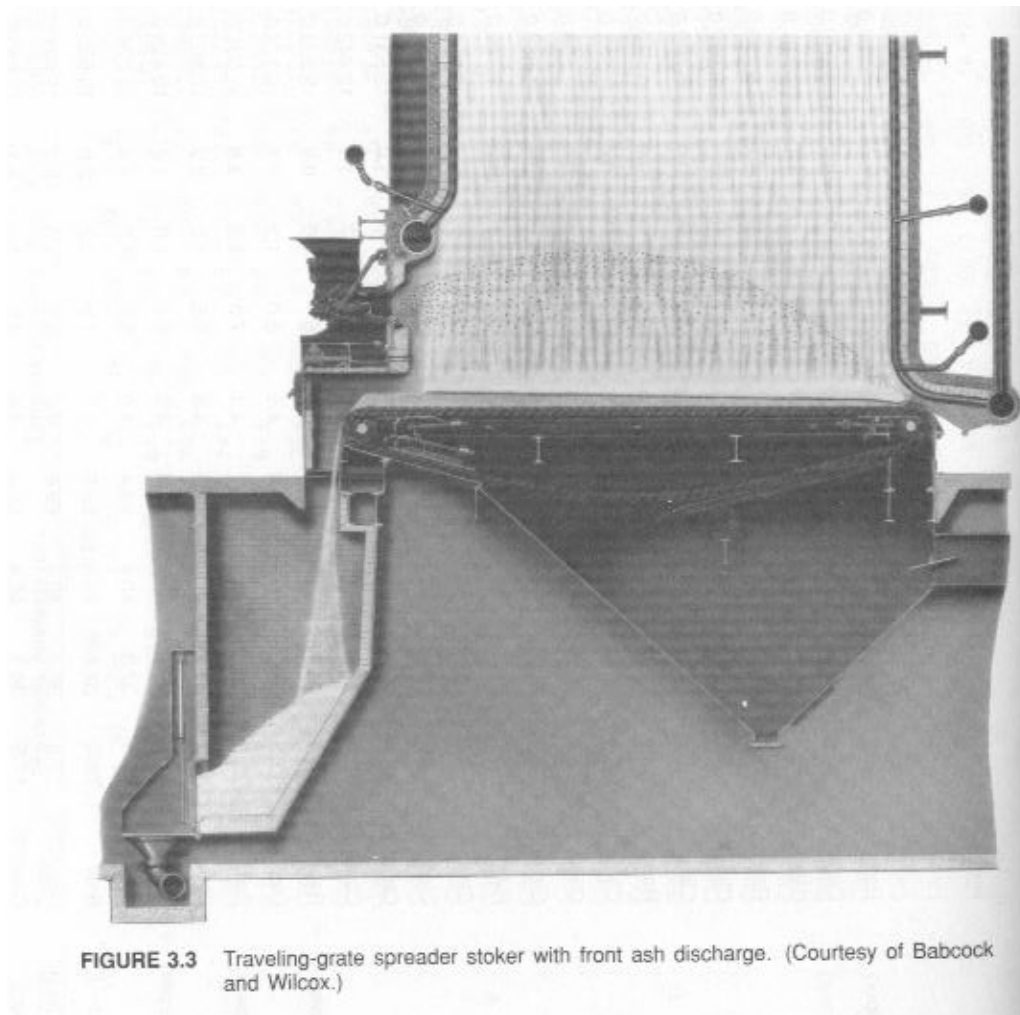
(continued on next page)

TABLE 3.3 (continued)

| County and State | Geological Name | Type | Proximate Analysis (Dry) | | | | Ultimate Analysis, Dry, wt, % | | | | | Heating Value (Btu/lb) |
|---------------------|--------------------|---------|--------------------------|------------|------------|------|-------------------------------|----------------|----------------|-----|----------|------------------------|
| | | | Ash (wt, %) | VM (wt, %) | FC (wt, %) | C | H ₂ | O ₂ | N ₂ | S | | |
| Nova Scotia, Canada | Hub seam | Raw | 23.4 | 30.8 | 45.8 | 61.1 | 4.1 | 6.1 | 1.3 | 4.0 | 10,994.0 | |
| | | Clean 1 | 2.1 | 40.5 | 57.4 | 79.3 | 5.4 | 9.9 | 1.5 | 1.7 | 14,564.0 | |
| | | Clean 2 | 6.5 | 37.7 | 55.7 | 74.7 | 5.0 | 8.5 | 1.5 | 3.8 | 13,770.0 | |
| Perry, Ill. | Illinois no. 6 | Raw | 18.5 | 36.7 | 44.7 | 61.6 | 4.2 | 9.7 | 1.3 | 4.6 | 11,345.0 | |
| | | Clean 1 | 11.1 | 40.8 | 48.1 | 70.5 | 4.8 | 9.1 | 1.4 | 3.1 | 12,627.0 | |
| | | Clean 2 | 8.6 | 41.9 | 49.5 | 72.4 | 5.1 | 9.8 | 1.2 | 2.9 | 13,023.0 | |
| | | Clean 3 | 10.5 | 39.5 | 50.0 | 71.1 | 4.8 | 9.1 | 1.4 | 3.1 | 12,818.0 | |
| | | Clean 4 | 9.5 | 39.7 | 50.8 | 70.6 | 6.2 | 9.5 | 1.3 | 3.0 | 12,865.0 | |
| Muhlenberg, Ky. | Kentucky no. 9 | Clean 5 | 8.8 | 40.4 | 50.8 | 72.3 | 5.0 | 9.5 | 1.4 | 3.0 | 13,025.0 | |
| | | Raw | 16.1 | 36.3 | 47.5 | 64.8 | 4.5 | 9.2 | 1.5 | 3.9 | 11,952.0 | |
| | | Clean 1 | 6.3 | 43.2 | 50.6 | 73.5 | 5.1 | 10.5 | 1.8 | 2.8 | 13,536.0 | |
| | | Clean 2 | 7.3 | 42.6 | 50.1 | 72.4 | 5.0 | 10.4 | 1.8 | 3.0 | 13,446.0 | |
| | | Clean 3 | 8.7 | 39.3 | 52.0 | 71.0 | 5.0 | 10.5 | 1.6 | 3.2 | 13,107.0 | |
| Union, Ky. | Kentucky no. 11 | Clean 4 | 7.9 | 40.7 | 51.3 | 72.4 | 5.0 | 10.0 | 1.6 | 2.9 | 13,260.0 | |
| | | Raw | 39.3 | 29.9 | 30.8 | 45.9 | 3.2 | 6.3 | 1.3 | 4.0 | 8,117.0 | |
| | | Clean 1 | 6.8 | 41.7 | 51.5 | 72.7 | 5.0 | 10.4 | 1.9 | 3.2 | 13,254.0 | |
| | | Clean 2 | 9.0 | 40.8 | 50.2 | 70.8 | 4.9 | 10.0 | 1.9 | 3.4 | 12,856.0 | |
| | | Clean 3 | 7.9 | 42.0 | 50.1 | 71.4 | 4.9 | 10.8 | 1.9 | 3.1 | 13,085.0 | |
| Cambria, Pa. | Kittanning (lower) | Raw | 24.8 | 17.2 | 58.0 | 65.9 | 3.6 | 3.1 | 1.2 | 1.4 | 11,510.0 | |
| | | Clean 1 | 9.7 | 19.1 | 71.2 | 80.5 | 4.3 | 2.7 | 1.8 | 1.0 | 14,238.0 | |
| | | Clean 2 | 10.0 | 18.8 | 71.2 | 79.9 | 4.2 | 3.5 | 1.5 | 0.9 | 14,069.0 | |
| | | Clean 3 | 5.8 | 19.9 | 74.3 | 84.7 | 4.5 | 2.5 | 1.7 | 0.8 | 14,820.0 | |
| | | Clean 4 | 7.8 | 19.4 | 72.8 | 81.9 | 4.3 | 3.6 | 1.6 | 0.8 | 14,467.0 | |

| | | | | | | | | | | | |
|-----------------|--------------------|---------|------|------|------|------|-----|------|-----|-----|----------|
| Nicholas, W.Va. | Kittanning (upper) | Raw | 15.2 | 32.3 | 52.5 | 70.2 | 4.6 | 7.6 | 1.4 | 1.2 | 12,704.0 |
| | | Clean 1 | 6.3 | 36.5 | 57.2 | 79.1 | 5.0 | 6.5 | 2.0 | 1.2 | 14,240.0 |
| | | Clean 2 | 5.4 | 37.2 | 57.4 | 80.0 | 5.1 | 6.2 | 2.1 | 1.2 | 14,401.0 |
| Belmont, Ohio | Pittsburgh | Raw | 33.0 | 32.4 | 34.6 | 51.5 | 3.7 | 6.3 | 1.0 | 4.5 | 9,493.0 |
| | | Clean 1 | 6.2 | 43.2 | 50.6 | 75.5 | 5.3 | 8.3 | 1.3 | 3.4 | 13,922.0 |
| | | Clean 2 | 6.7 | 43.4 | 49.9 | 74.7 | 5.3 | 8.2 | 1.2 | 3.9 | 13,820.0 |
| Big Horn, Mon. | Robinson | Raw | 10.6 | 37.4 | 52.0 | 64.5 | 4.0 | 19.0 | 1.0 | 0.9 | 11,280.0 |
| | | Clean 1 | 6.3 | 37.7 | 56.0 | 65.9 | 4.2 | 22.3 | 0.9 | 0.4 | 11,981.0 |
| | | Clean 2 | 6.7 | 37.6 | 55.7 | 65.7 | 4.3 | 22.5 | 0.4 | 0.4 | 11,833.0 |
| | | Clean 3 | 8.2 | 37.8 | 54.0 | 65.8 | 4.3 | 20.3 | 1.0 | 0.4 | 11,868.0 |
| Greene, Pa. | Sewickley | Raw | 33.6 | 29.1 | 37.2 | 54.5 | 3.8 | 5.6 | 1.1 | 1.3 | 9,786.0 |
| | | Clean 1 | 7.6 | 36.3 | 56.1 | 78.7 | 5.2 | 5.9 | 1.7 | 0.9 | 14,021.0 |
| | | Clean 2 | 8.7 | 37.0 | 54.3 | 77.3 | 5.1 | 6.3 | 1.7 | 0.9 | 13,805.0 |
| | | Clean 3 | 10.4 | 35.8 | 53.8 | 74.8 | 4.9 | 7.2 | 1.6 | 1.0 | 13,531.0 |
| | | Clean 4 | 10.9 | 35.9 | 53.2 | 74.8 | 5.0 | 6.6 | 1.7 | 1.1 | 13,442.0 |
| Kanawha, W.Va. | Stockton-Lewiston | Raw | 40.4 | 24.2 | 35.4 | 48.0 | 3.3 | 6.7 | 1.0 | 0.6 | 8,294.0 |
| | | Clean 1 | 17.5 | 31.9 | 50.6 | 68.0 | 4.5 | 8.0 | 1.3 | 0.7 | 12,174.0 |
| Belmont, Ohio | Washington (lower) | Raw | 23.8 | 34.1 | 42.1 | 59.1 | 4.1 | 7.9 | 1.3 | 3.8 | 11,001.0 |
| | | Clean 1 | 12.1 | 39.2 | 48.7 | 69.5 | 4.8 | 9.5 | 1.2 | 2.9 | 12,807.0 |
| Belmont, Ohio | Washington (upper) | Raw | 27.1 | 31.8 | 41.1 | 57.3 | 4.0 | 9.0 | 1.0 | 1.6 | 10,423.0 |
| | | Clean 1 | 22.3 | 37.3 | 40.4 | 63.4 | 4.3 | 8.2 | 1.3 | 1.4 | 11,276.0 |
| Belmont, Ohio | 20% Washington (l) | Raw | 25.6 | 32.6 | 41.8 | 58.6 | 4.1 | 7.9 | 1.2 | 2.6 | 10,606.0 |
| | | Clean 1 | 17.6 | 36.7 | 45.7 | 65.6 | 4.6 | 8.5 | 1.5 | 2.3 | 11,881.0 |
| | | Clean 2 | 17.5 | 36.1 | 46.4 | 66.0 | 4.6 | 8.6 | 1.1 | 2.1 | 11,910.0 |
| Belmont, Ohio | Waynesburg | Raw | 27.7 | 32.7 | 39.6 | 56.0 | 3.9 | 7.0 | 1.2 | 4.1 | 10,315.0 |

Adapted From: Coal Quality Information Book EPRI CS-5421, December 1987



As a solid fuel, coal may be burned in a number of ways. Starting with the smallest of installations, coal may be burned in a furnace, in chunk form on a stationary or moving grate. Air is usually supplied from below with combustion gases passing upward and ash falling through a stationary grate or dropping off the end of a moving grate into an ash pit. A wide variety of solid fuels can be burned in this way.

Though all furnaces were onced fired manually, today many are fired by or with the assistance of mechanical devices called stokers. Figure 3.3 shows a spreader stoker, which scatters coal in a uniform pattern in the furnace, the finer particles burning in suspension in the rising combustion air stream while the heavier particles drop to the grate as they burn. The particles that reach the grate burn rapidly in a thin layer, and the remaining ash drops off the end into the ash pit. This type of combustion system has been in use for over fifty years for hot water heating and steam generation.

In large installations, coal is crushed to a particular size, and sometimes pulverized to powder immediately before firing, to provide greater surface exposure to the

TABLE 3.4 Selected Samples of Natural Gas from United States Fields

| Source of Gas: | | Pa. | So. Calif. | Ohio | La. | Okla. |
|-------------------------------------------|------------------|--------|------------|--------|--------|--------|
| Analyses | | | | | | |
| <i>Constituents, % by volume</i> | | | | | | |
| H ₂ | Hydrogen | — | — | 1.82 | — | — |
| CH ₄ | Methane | 83.40 | 84.00 | 93.33 | 90.00 | 84.10 |
| C ₂ H ₄ | Ethylene | — | — | 0.25 | — | — |
| C ₂ H ₆ | Ethane | 15.80 | 14.80 | — | 5.00 | 6.70 |
| CO | Carbon monoxide | — | — | 0.45 | — | — |
| CO ₂ | Carbon dioxide | — | 0.70 | 0.22 | — | 0.80 |
| N ₂ | Nitrogen | 0.80 | 0.50 | 3.40 | 5.00 | 8.40 |
| O ₂ | Oxygen | — | — | 0.35 | — | — |
| H ₂ S | Hydrogen sulfide | — | — | 0.18 | — | — |
| <i>Ultimate, % by weight</i> | | | | | | |
| S | Sulfur | — | — | 0.34 | — | — |
| H ₂ | Hydrogen | 23.53 | 23.30 | 23.20 | 22.68 | 20.85 |
| C | Carbon | 75.25 | 74.72 | 69.12 | 69.26 | 64.84 |
| N ₂ | Nitrogen | 1.22 | 0.76 | 5.76 | 8.06 | 12.90 |
| O ₂ | Oxygen | — | 1.22 | 1.58 | — | 1.41 |
| Specific gravity (relative to air) | | 0.636 | 0.636 | 0.567 | 0.600 | 0.630 |
| Higher heating value | | | | | | |
| Btu/ft ³ @ 60° F and 30 in. Hg | | 1,129 | 1,116 | 964 | 1,002 | 974 |
| Btu/lb of fuel | | 23,170 | 22,904 | 22,077 | 21,824 | 20,160 |

Courtesy of Babcock and Wilcox Co.

oxidizer and to ensure rapid removal of combustion gases. Because of the wide variation in the characteristics of coals, specialized types of combustion systems tailored to a specific coal or range of coal characteristics are used.

Natural Gas

Natural gas is a mixture of hydrocarbons and nitrogen, with other gases appearing in small quantities. Table 3.4 shows the composition of samples of natural gases found in several regions of the United States. For these samples, it is seen that the gases contain 83-94% methane (CH₄), 0-16% ethane (C₂H₆), 0.5-8.4% nitrogen and small quantities of other components, by volume. The ultimate analysis shows that the gases contain about 65-75% carbon, 20-24% hydrogen, 0.75-13% nitrogen, and small amounts of oxygen and sulfur in some cases. The higher heating values are in the neighborhood of 1000 Btu/ft³ on a volume basis and 22,000 Btu/lb_m on a mass basis. In regions where it is abundant, natural gas is frequently the fuel of choice because of its low sulfur and ash content and ease of use.

EXAMPLE 3.4

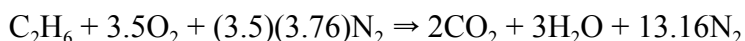
Determine the molecular weight and stoichiometric mole and mass air-fuel ratios for the Oklahoma gas mole composition given in Table 3.4.

Solution

Equation (3.2),



shows that there are $2 + 2(3.76) = 9.52$ moles of air required for complete combustion of each mole of methane. Similarly for ethane, the stoichiometric reaction equation is:



where 2 carbon and 6 hydrogen atoms in ethane require 2 CO_2 molecules and 3 H_2O molecules, respectively, in the products. There are then 7 oxygen atoms in the products, which implies 3.5 oxygen molecules in the reactants. This in turn dictates the presence of $(3.5)(3.76) = 13.16$ nitrogen molecules in both the reactants and products. The reaction equation then indicates that $3.5(1 + 3.76) = 16.66$ moles of air are required for complete combustion of one mole of ethane.

In Table 3.5, the molecular weight of the gas mixture, 18.169, is found in the fourth column by summing the products of the mole fractions of the fuel components and the component molecular weights. This is analogous to the earlier determination of the average air molecular weight from the nitrogen and oxygen mixture mole fractions.

The products of the mole fractions of fuel components and the moles of air required per mole of fuel component (as determined earlier and tabulated in the fifth column of Table 3.5) then yield the moles of air required for each combustible per mole of fuel (in the sixth column). Summing these, the number of moles of air required per mole of fuel yields the stoichiometric mole air-fuel ratio, 9.114.

The stoichiometric mass A/F is then given by the mole A/F times the ratio of air molecular weight to fuel molecular weight: $(9.114)(28.9)/18.169 = 14.5$.

Table 3.5 Calculations for Example 3.4

| <i>i</i> | M_i | x_i | $x_i M_i$ | Moles air per mole <i>i</i> | Moles air per mole fuel |
|-----------------|-------|-------|-----------|-----------------------------|------------------------------|
| Methane | 16 | 0.841 | 13.456 | 9.52 | $(0.841)(9.52) = 7.998$ |
| Ethane | 30 | 0.067 | 2.010 | 16.66 | $(0.067)(16.66) = 1.116$ |
| CO ₂ | 44 | 0.008 | 0.351 | 0.0 | |
| Nitrogen | 28 | 0.084 | 2.352 | 0.0 | |
| Totals | | 1.000 | 18.169 | | moles air /mole fuel = 9.114 |

TABLE 3.6 Analyses of Several Liquid Fuels

| Fuel | Mass Fraction of: | | | | | | Heating Value (Btu/lb) |
|----------------|-------------------|----------------|-------|----------------|----------------|--------|---------------------------|
| | S | H ₂ | C | N ₂ | O ₂ | Ash | |
| No. 1 fuel oil | 0.001 | 0.138 | 0.861 | — | Nil | Nil | 19,810 |
| No. 2 fuel oil | 0.003 | 0.125 | 0.872 | 0.0002 | Nil | Nil | 19,430 |
| No. 6 fuel oil | 0.023 | 0.097 | 0.856 | ← 0.02 → | | 0.0012 | 18,300 |
| Gasoline | 0.008 | 0.1476 | 0.849 | — | — | — | 20,750 |

Adapted from reference 1.

Liquid Fuels

Liquid fuels are primarily derived from crude oil through cracking and fractional distillation. *Cracking* is a process by which long-chain hydrocarbons are broken up into smaller molecules. *Fractional distillation* separates high-boiling-point hydrocarbons from those with lower boiling points. Liquid fuels satisfy a wide range of combustion requirements and are particularly attractive for transportation applications because of their compactness and fluidity. Table 3.6 gives representative analyses of some of these liquid fuels. Compositions of liquid and solid fuels, unlike gaseous fuels, are usually stated as mass fractions.

3.4 Combustion Reactions and Analysis

Mechanism of Combustion

Details of the mechanics of combustion depend to a great extent on the fuel and the nature of the combustion system. They are sometimes not well understood and are largely beyond the scope of this book. There are, however, certain fundamentals that are useful in dealing with combustion systems.

The chemical reaction equations presented here do not portray the actual mechanism of combustion; they merely indicate the initial and final chemical compositions of a reaction. In most cases the reactions involve a sequence of steps, leading from the reactants to the products, the nature of which depends on the temperature, pressure, and other conditions of combustion. Fuel molecules, for instance, may undergo *thermal cracking*, producing more numerous and smaller fuel molecules and perhaps breaking the molecules down completely into carbon and hydrogen atoms before oxidation is completed.

In the case of solid fuels, combustion may be governed by the rate at which oxidizer diffuses from the surrounding gases to the surface and by the release of combustible gases near the surface. Combustion of solids may be enhanced by increasing the fuel surface area exposed to the oxidizer by reducing fuel particle size.

The following simple model illustrates the effect.

EXAMPLE 3.5

Show that reduction of the size of spherical particles into smaller spherical particles increases their surface area.

Solution

The ratio of the surface area of the reduced-size particles to the area of the original particles, S_2/S_1 , is given by the square of the radius ratio:

$$\frac{S_2}{S_1} = \left(\frac{N_2}{N_1}\right) \left(\frac{R_2}{R_1}\right)^2$$

where N_1 and N_2 are the numbers of particles of each size. The total volume of the particles is unchanged. Therefore,

$$N_1 \pi R_1^3 = N_2 \pi R_2^3$$

Then

$$\frac{R_2}{R_1} = \left(\frac{N_1}{N_2}\right)^{1/3}$$

and

$$\frac{S_2}{S_1} = \left(\frac{N_2}{N_1}\right)^{1/3} = \frac{R_1}{R_2}$$

Thus the surface area increases as the particle size is reduced.

Example 3.5 is, of course, an idealized example. In reality, the reacting surface area of solid fuels is usually much larger than the spherical surface area implied by their size.

We have seen that, for combustion to occur, molecules of oxidizer must affiliate with fuel molecules, an action enhanced by the three T's of combustion: turbulence, time, and temperature. Chemical reactions take place more rapidly at high temperatures but nevertheless require finite time for completion. It is therefore important that burners be long enough to retain the fuel-air mixture for a sufficiently long time so that combustion is completed before the mixture leaves. *Turbulence*, or *mixing*, enhances the opportunities for contact of oxidizer and fuel molecules and removal of products of combustion.

A flame propagates at a given speed through a flammable mixture. It will propagate upstream in a flow of a combustible mixture if its *flame speed* exceeds the flow velocity. If a fixed flame front is to exist at a fixed location in a duct flow in which the velocity of the combustion gas stream exceeds the propagation speed, some form of *flame stabilization* is required. Otherwise the flame front is swept downstream and flameout occurs. Stabilization may be achieved by using fixed *flameholders* (partial

flow obstructions that create local regions of separated flow in their bases where the flame speed is greater than the local flow velocity) or by directing a portion of the flow upstream to provide a low-speed region where stable combustion may occur.

Each combination of oxidizer and fuel has been seen to have a particular stoichiometric oxidizer-fuel ratio for which the fuel is completely burned with a minimum of oxidizer. It has also been pointed out that it is usually desirable to operate burners at greater than the theoretical air-fuel ratio to assure complete combustion of the fuel and that this is sometimes referred to as a *lean mixture*. Occasionally it may be desirable to have *incomplete combustion*, perhaps to produce a stream of products in which carbon monoxide exists or to assure that all the oxidizer in the mixture is consumed. In that case a burner is operated at less than the stoichiometric air-fuel ratio with what is called a *rich mixture*.

There are limits to the range of air-fuel ratios for which combustion will occur called *limits of flammability*. Here the density of the mixture is important. The limits of flammability around the stoichiometric A/F are reduced at low densities. If combustion is to occur reliably in mixtures at low densities, it is necessary to closely control the air-fuel ratio.

Combustion Analysis of Solid Fuels

In the determination of the air-fuel ratio and flue gas composition for the combustion of solid fuels, it is important to account for the ash and moisture in the fuel in the as-fired condition. In the following analyses, all of the elements of the reactants in the fuel and oxidizer are assumed to be present in the flue gas products except for the ash, which is assumed to fall as a solid or flow as molten slag to the furnace bottom. Nitrogen and oxygen are present in many solid fuels and should be accounted for in predicting the flue gas composition. While both carbon monoxide and oxygen may be present in combustion products at the same time because of imperfect mixing of combustibles and oxygen in some instances, we will assume for prediction of the flue gas composition that perfect mixing occurs such that no carbon monoxide is present when excess air is supplied.

EXAMPLE 3.6

A coal with a dry, ash-free composition of 0.87 C, 0.09 H₂, 0.02 S, and 0.02 O₂ is burned with 25% excess air. The as-fired ash and moisture contents are 6% and 4%, respectively.

- (a) What are the stoichiometric and actual air-fuel ratios?
- (b) What is the flue gas composition?

Solution

- (a) Before performing combustion calculations, it is necessary to convert coal composition data to an as-fired basis. The ratio of as-fired to dry, ash-free

masses is $1 - A - M = 1 - 0.06 - 0.04 = 0.9$. The as-fired composition and oxygen requirements are then

| Component i | | kg i / kg Coal | kg O_2 / kg i | kg O_2 / kg Coal |
|----------------|---------------------|------------------|-------------------|--------------------|
| C | $0.87 \times 0.9 =$ | 0.783 | 2.667 | 2.087 |
| H ₂ | $0.09 \times 0.9 =$ | 0.081 | 8 | 0.648 |
| S | $0.02 \times 0.9 =$ | 0.018 | 1.0 | 0.018 |
| O ₂ | $0.02 \times 0.9 =$ | 0.018 | -1.0 | -0.018 |
| Ash | | 0.06 | | |
| Moisture | | 0.04 | | |
| Checksum | | 1.000 | Total | 2.735 |

The oxygen requirements of each of the combustibles are determined independently and summed to obtain the total oxygen requirement of the coal. Note that the presence of oxygen in the coal reduces the amount of oxygen required from the combustion air.

The theoretical air-fuel ratio follows from division of the required oxygen by the mass fraction of oxygen in air,

$$\frac{2.735 \text{ kg } O_2 / \text{kg coal}}{0.2325 \text{ kg } O_2 / \text{kg air}} = 11.79 \text{ kg air / kg coal}$$

and the actual air-fuel ratio is

$$1.25 \times 11.79 = 14.74 \text{ kg air / kg coal}$$

- (b) The ratios of the masses of the flue gas components j per unit mass of fuel are individually determined from the mass fractions of each component of the coal; they are tabulated in Table 3.7.

The mass of CO₂ in the flue gas per unit mass of coal is the product of the mass fraction of C in the coal and the ratio of the mass of CO₂ to C in the reaction $C + O_2 \rightarrow CO_2$. The CO₂/C mass ratio is the ratio of the molecular weights of CO₂ and C, 44/12. Thus the mass of carbon dioxide, as seen in the second column of Table 3.7, is

$$(0.783)(44/12) = 2.871 \text{ kg } CO_2 / \text{kg coal}$$

Likewise, based on $S + O_2 \rightarrow SO_2$, the mass of sulfur dioxide in the flue gas is given by

$$(0.018)(64/32) = 0.036 \text{ kg } SO_2 / \text{kg coal}$$

The mass of water in the flue gas is the sum of the mass fractions of the moisture in the coal and the water vapor created by the combustion of

TABLE 3.7 Flue Gas Composition

| <i>j</i> | kg <i>j</i> per kg Fuel | mf _{wfg} | mf _{dfg} | Moles <i>j</i> / kg Fuel | x _{wfg} | x _{dfg} |
|------------------|-------------------------|-------------------|-------------------|--------------------------|------------------|------------------|
| CO ₂ | 2.871 | 0.1836 | 0.1931 | 2.871/44 = 0.0653 | 0.1226 | 0.1332 |
| H ₂ O | 0.769 | 0.0492 | — | 0.769/18 = 0.0427 | 0.0801 | — |
| SO ₂ | 0.036 | 0.0023 | 0.0024 | 0.036/64 = 0.00056 | 0.0011 | 0.0012 |
| O ₂ | 0.684 | 0.0437 | 0.0460 | 0.684/32 = 0.0214 | 0.0402 | 0.0437 |
| N ₂ | 11.280 | 0.7212 | 0.7585 | 11.28/28 = 0.4028 | 0.7561 | 0.8219 |
| | 15.640 | 1.0000 | 1.0000 | | 1.0001 | 1.0000 |

kg-moles of wfg/kg coal = 0.53276
kg-moles dfg/kg coal = 0.49006 (H₂O omitted)

hydrogen. Thus,

$$\begin{aligned}
 m_{\text{water}} &= \text{mf}_{\text{moist,coal}} + \text{mf}_{\text{hydr}} \left(\frac{M_{\text{water}}}{M_{\text{hydr}}} \right) \\
 &= 0.04 + (0.081) \left(\frac{18}{2} \right) = 0.769 \text{ kg water/kg coal}
 \end{aligned}$$

The mass of excess oxygen in the flue gas is obtained by multiplying the excess air–fuel ratio, $(0.25)(11.79) = (14.74 - 11.79)$, and the mass fraction of oxygen in air:

$$m_{\text{oxygen}} = (14.74 - 11.79)(0.233) = 0.684$$

The mass of nitrogen in the flue gas is proportional to the actual air–fuel ratio and the mass fraction of nitrogen in air. The mass fraction of nitrogen in air, in turn, is proportional to the mole fraction of nitrogen in air and the molecular weight ratio of nitrogen to air. Thus

$$m_{\text{nitrogen}} = \frac{14.74(0.79)(28)}{28.9} = 11.28 \text{ kg nitrogen/kg coal}$$

The total mass of wet flue gas (wfg) per unit mass of fuel is then

$$2.871 + 0.769 + 0.036 + 0.684 + 11.28 = 15.64$$

Omitting the water vapor component, the total mass of dry flue gas (dfg) is

$$2.871 + 0.036 + 0.684 + 11.28 = 14.871$$

Dividing the masses of each component *j* by the total mass of flue gas (fg) yields the component mass fractions shown in columns 3 and 4:

$$\text{mf}_j = (\text{kg } j / \text{kg fg}) = (\text{kg } j / \text{kg coal}) / (\text{kg fg} / \text{kg coal})$$

For example, the mass fraction of CO_2 on a wet flue gas basis is $2.871 / 15.64 = 0.1836$, as shown in column 3 of Table 3.7. Similarly, the mass fraction of CO_2 in the flue gas on a dry basis is $2.871 / 14.871 = 0.1931$, as shown in column 4.

Moles of each flue gas component per mass of fuel are then obtained by dividing the mass of j per kg of coal by the molecular weight of j as shown in the table. The sum of these for all flue gas components is the total number of kg-moles of flue gas per kg of fuel. The mole fractions in Table 3.7 may then be obtained by dividing the number of moles of each component by the total number of moles. For example, the moles of CO_2 per kg of coal is $2.871 / 44 = 0.0653$, and the mole fraction of carbon dioxide in the wet flue gas is $0.06536 / 0.53276 = 0.1226$. Omitting the water component of the flue gas, the mole fraction of carbon dioxide in the dry flue gas is $0.06536 / 0.49006 = 0.1332$.

Flue Gas Analysis

A device known as an Orsat analyzer is sometimes used to determine the chemical composition of combustion gas. The analyzer collects gas samples over liquid water and therefore condenses the water vapor. Any SO_2 present goes into solution in the liquid. The remaining combustion gases measured are CO_2 , CO , O_2 , and N_2 . The analyzer determines mole fractions of the first three, and the nitrogen mole fraction is obtained by subtracting the sum of the measured mole fractions from 1:

$$x_{\text{N}_2} = 1 - x_{\text{CO}_2} - x_{\text{CO}} - x_{\text{O}_2}$$

The model and terminology used in flue gas analysis is shown in the following:

| Reactants | Products |
|-------------------------|----------------------|
| Oxidizer and fuel | CO_2 |
| | N_2 |
| | O_2 |
| | CO |
| | H_2O |
| | SO_2 |
| | Bottom ash |
| Fly ash | |

}

Dry
Orsat
products

}

Wet
flue
gases

}

Solid products

Assuming that all of the carbon in the fuel is burned and becomes part of the flue gas and that there is no leakage from the system, the actual air-fuel ratio may be determined from the Orsat analysis and the ultimate analysis of the fuel. The

calculation of the air–fuel ratio makes use of the fact that all of the nitrogen and carbon in the reactants (fuel and combustion air) arrive in the combustion gas products. Thus the nitrogen-to-carbon mole ratio $(N_2/C)_{\text{mole}}$ (and the mass ratio) in the dry flue gas is equal to that in the reactants. Using the results of the Orsat analysis, the mole nitrogen-to-carbon ratio becomes

$$(N_2/C)_{\text{mole}} = \left(\frac{x_{N_2}}{x_{CO_2} + x_{CO}} \right)_{\text{dfg}}$$

where the sum of the mole fractions of CO and CO₂ is the mole fraction of carbon in the flue gas. The mass ratio of nitrogen to carbon in the flue gas is then obtained by multiplying by 28/12. Then the total mass of nitrogen per unit mass of fuel in both reactants and products is the product of the flue gas nitrogen–carbon mass ratio and the coal carbon mass fraction.

The mass of nitrogen supplied by the combustion air is the total mass of nitrogen less the mass of nitrogen from the fuel. Thus the mass of nitrogen supplied by combustion air per unit mass of fuel is given by

$$\left(\frac{28}{12} \right) \left(\frac{\text{Moles } N_2 \text{ in flue gas}}{\text{Mole C in flue gas}} \right) \left(\frac{\text{Mass C}}{\text{Mass of fuel}} \right) - \frac{\text{Mass } N_2 \text{ in fuel}}{\text{Mass of fuel}}$$

or

$$\left(\frac{28}{12} \right) \left(\frac{x_{N_2}}{x_{CO_2} + x_{CO}} \right) C_f - (N_2)_f$$

where the mass fractions of carbon and nitrogen in the fuel are given by C_f and $(N_2)_f$, respectively. Then the mass air–fuel ratio is obtained by dividing by the mass fraction of nitrogen in air:

$$A/F = \frac{(28/12)[x_{N_2}/(x_{CO_2} + x_{CO})]C_f - (N_2)_f}{0.766}$$

Similarly, the air–fuel ratio may be obtained using the flue gas mass fractions, rather than mole fractions, from

$$A/F = \frac{(\text{mf}_{N_2}/\text{mf}_C)C_f - (N_2)_f}{0.766}$$

EXAMPLE 3.7

The Orsat analysis of the stack gases for the fuel burned in Example 3.6 is 13% CO₂, 0.5% CO, and 3.2% O₂. What is the actual air–fuel ratio and the percentage of excess air?

Solution

The mole fraction of nitrogen in the flue gas is $1 - 0.13 - 0.005 - 0.032 = 0.833$.

The nitrogen–carbon mole ratio is then $0.833/(0.13 + 0.005) = 6.17$. Using $C_f = 0.783$ and $(N_2)_f = 0$ from the fuel as-fired analysis, the air–fuel ratio is

$$(A/F)_{\text{actual}} = \frac{(6.17)(28/12)(0.783) - 0}{0.766} = 14.7$$

From the solution of Exercise 3.6, the theoretical air–fuel ratio is 11.79. The percentage of excess air is therefore

$$\% \text{ excess air} = (100) \left(\frac{14.7 - 11.79}{11.79} \right) = 24.8\%$$

Thus, despite firing with 24.8% excess air, because of imperfect mixing the flue gas contains 0.5% carbon monoxide. Combustion is therefore incomplete.

While the analyses of solid and liquid fuels are customarily given in terms of mass fractions of their chemical elements, the composition of gaseous fuels is usually presented as volume fractions or mole fractions of the constituents. Natural gases, for instance, are mixtures of hydrocarbons and other compounds, as seen at the top of Table 3.4. The elemental or ultimate analysis of the fuel given in the table may be determined from the compound mole fractions by summing the masses of each element in the compounds of the mixture. The following example illustrates this and the way in which the air–fuel ratio and molecular weight of the product flue gas may be obtained when an Orsat analysis is available.

EXAMPLE 3.8

Determine the carbon component of the ultimate analysis, the theoretical mass and mole air–fuel ratios, and the molecular weight of the Oklahoma natural gas cited in Table 3.4. Determine the true air–fuel ratio and percentage of excess air if the flue gas Orsat analysis is 9% CO₂, 3% O₂, and 0.5% CO. Determine also the mass of wet combustion products per unit mass of natural gas consumed.

Solution

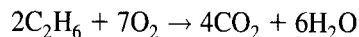
Table 3.8 presents the details of the solution in spreadsheet format. (The spreadsheet is included on the accompanying diskette for closer examination of the calculations and to enable rapid solution of similar problems for other fuels and flue gas analyses.) The mole composition of the fuel is tabulated in the first tier of computations and converted to mass fractions by multiplying by the compound molecular masses. The sum of the masses of the components per mole of fuel is the average molecular mass of the fuel. The mass fraction of methane, for example, is $mf_i = 13.456/18.17 = 0.7405$. The carbon factors for each of the compounds are obtained by dividing the mass of atoms of carbon of each compound by its molecular mass. For example, for methane and ethane the carbon factors are $12/16 = 0.75$ and $24/30 = 0.8$, respectively. The masses of carbon per mass of fuel are then the products of the carbon factor and the mass fraction of the compound in the fuel. For methane this is $(0.75)(0.7405) = 0.5554$. The carbon mass fractions of each of the components are then summed to obtain the carbon component of the ultimate analysis of the fuel, the mass fraction of carbon in the fuel, 0.6492.

TABLE 3.8 Spreadsheet Solution to Example 3.8

ANALYSIS OF COMBUSTION OF GASEOUS FUEL
 FUEL: Oklahoma natural gas, Sample 5, Table 3-4

| COMPONENT OF FUEL | x_i | MW _i | MASS i / MOLE FUEL | $m_f i$ | CARBON FACTOR | MASS C / MASS FUEL | OXYGEN FACTOR | MASS O ₂ / MASS FUEL |
|-------------------------------|-------|-----------------|----------------------|---------|---------------|--------------------|---------------|---------------------------------|
| CH ₄ | 0.841 | 16 | 13.456 | 0.7406 | 0.75 | 0.555421 | 4 | 2.962245 |
| C ₂ H ₄ | 0 | 28 | 0 | 0 | 0.85714 | 0 | 3.42857 | 0 |
| C ₂ H ₆ | 0.067 | 30 | 2.01 | 0.1106 | 0.8 | 0.088498 | 3.73333 | 0.412988 |
| H ₂ | 0 | 2 | 0 | 0 | 0 | 0 | 8 | 0 |
| CO | 0 | 28 | 0 | 0 | 0.42857 | 0 | 0.57143 | 0 |
| N ₂ | 0.084 | 28 | 2.352 | 0.1294 | 0 | 0 | 0 | 0 |
| CO ₂ | 0.008 | 44 | 0.352 | 0.0194 | 0.27273 | 0.005283 | 0 | 0 |
| O ₂ | 0 | 32 | 0 | 0 | 0 | 0 | -1 | 0 |
| 1 MW FUEL= | | | 18.17 | 1 | | 0.6492 | | 3.375234 |
| THEORETICAL A/F | | | 14.55 | | | | | |
| THEORETICAL MOLE A/F= | | | 9.15 | | | | | |
| ORSAT ANALYSIS | | | | | | | | |
| COMPONENT | x_j | MW _j | MASS j / MOLE dfg | $m_f j$ | CARBON FACTOR | MASS C / MASS dfg | | |
| CO ₂ | 0.09 | 44 | 3.96 | 0.134 | 0.27273 | 0.036536 | | |
| O ₂ | 0.03 | 32 | 0.96 | 0.0325 | 0 | 0 | | |
| CO | 0.005 | 28 | 0.14 | 0.0047 | 0.42857 | 0.00203 | | |
| N ₂ | 0.875 | 28 | 24.5 | 0.8288 | 0 | 0 | | |
| 1 MW dfg | | | 29.56 | 1 | | 0.038566 | | |

The oxygen requirement for complete combustion of the fuel is obtained by summing the oxygen requirements of each of the components. For example, the reaction equation for combustion of ethane,



gives the mass of oxygen per unit mass of ethane:

$$\frac{(7)(32)}{(2)(24 + 6)} = 3.733$$

The oxygen required for combustion of ethane per unit mass of fuel is then the product of the oxygen factor and the ethane mass fraction:

$$(3.733)(0.1106) = 0.4129$$

The total oxygen requirement per unit mass of fuel is obtained by summing the contributions of each of the components, which in this case is 3.375. The stoichiometric air-fuel ratio is then $3.375/0.2325 = 14.5$. The mole A/F is then obtained using the

molecular weights of air and fuel:

$$\frac{(14.5)(18.17)}{28.9} = 9.15$$

In the second tier of computations in the table, the Orsat analysis is given and the mole fractions are converted to mass fractions. The mass fraction of carbon in the flue gas is calculated from the Orsat mass fractions in the same way as the earlier fuel carbon computation. The nitrogen-to-carbon mass ratio may then be determined as $0.8288/0.03857 = 21.49$. So the air-fuel ratio is

$$\frac{(21.49)(0.6492) - 0.1294}{0.766} = 18.1$$

The total flue gas products per mass of fuel consumed, including water vapor, may then be determined from the mass of air and fuel by applying the conservation of mass to products and reactants to obtain $1 + A/F = 1 + 18.1 = 19.1$.

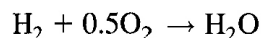
3.5 Combustion Analysis Using the JANAF Tables

The JANAF Tables are often used to analyze flows of chemical reactants within control volumes, such as combustion chambers and furnaces, where it is desirable to account for the variation of gas properties with temperature. The tables are based on representation of the enthalpy of a component of a gas as the sum of an enthalpy of formation of the gas at a reference state and a temperature-dependent sensible enthalpy difference relative to the reference.

Heats of Formation

The *heat of formation* of a compound is the energy transfer necessary to create the compound from its constituent elements while both the product and the reactants are maintained at a standard temperature and pressure. The heat of formation of a compound created in a steady flow through a control volume is known as an *enthalpy of formation*. This is as opposed to a formation reaction that occurs in a closed system. Only steady-flow reaction is considered here.

Consider the formation reaction for water, in which a mole of hydrogen reacts with a half mole of oxygen to form a mole of water vapor:



A given amount of energy must be supplied or removed in order to bring molecules such as hydrogen and oxygen together to form a stable compound such as water. In this case, and in all combustion reactions, the reaction is *exothermic*, so heat is released rather than absorbed.

Table 3.9 gives enthalpies of formation, h_f , for a variety of combustion-related substances relative to a reference of 298.15K (536.7° R) temperature and 1 bar pressure.

TABLE 3.9 Heats of Formation for 1-Bar and 298.15K Standard State

| Substance | State | Molecular Weight | Heats of Formation | | | |
|------------------|-------|------------------|--------------------|-----------|---------------------|-------------|
| | | | kJ/g-mole | kJ/kg | Btu/lb _m | Btu/lb-mole |
| H ₂ | Gas | 2.01588 | 0 | 0.0 | 0 | 0 |
| H ₂ O | Liq | 18.01528 | -285.83 | -15,866.0 | -6,821.14 | -122,885 |
| | Gas | 18.01528 | -241.826 | -13,423.4 | -5,771.02 | -103,966 |
| O ₂ | Gas | 31.9988 | 0 | 0.0 | 0 | 0 |
| N ₂ | Gas | 28.0134 | 0 | 0.0 | 0 | 0 |
| NO | Gas | 30.0061 | 90.291 | 3,009.1 | 1,293.675 | 38,818.14 |
| NO ₂ | Gas | 46.0055 | 33.1 | 719.5 | 309.3204 | 14,230.44 |
| NO ₃ | Gas | 62.0049 | 71.13 | 1,147.2 | 493.1923 | 30,580.39 |
| C | Sol | 12.011 | 0 | 0.0 | 0 | 0 |
| CO | Gas | 28.0104 | -110.53 | -3,946.0 | -1,696.49 | -47,519.3 |
| CO ₂ | Gas | 44.0098 | -393.522 | -8,941.7 | -3,844.23 | -169,184 |
| CH ₄ | Gas | 16.04276 | -74.873 | -4,667.1 | -2,006.49 | -32,189.6 |
| S | Sol | 32.06 | 0 | 0.0 | 0 | 0 |
| SO ₂ | Gas | 64.0588 | -296.842 | -4,633.9 | -1,992.22 | -127,619 |

Adapted from reference 4.

(Note: The reference conditions of the 1985 JANAF Thermochemical tables used differ slightly from those of preceding editions.) Heats of formation are usually determined based on statistical thermodynamics and spectroscopic measurements.

By definition, heats of formation are zero for all elements in the standard state. Hence, from the steady-flow First Law of Thermodynamics, the heat transferred in a formation reaction of a compound created from elements in the standard state is the heat of formation for the compound, as in the hydrogen-to-water example just mentioned.

Heat Transfer in a Chemically Reacting Flow

Consider now the combustion problem in which fuel and oxidizer flow into a control volume and combustion products flow out. The steady-flow First Law of Thermodynamics applied to the control volume may be written as

$$Q = H_p - H_r + W_s \quad [\text{Btu} \mid \text{kJ}] \quad (3.7)$$

where Q is heat flow into the control volume, W_s is the shaft work delivered by the control volume, and the enthalpies, H , include chemical as well as thermal energy. The subscripts r and p refer to the reactants entering and products leaving the control volume, respectively. The enthalpy H_p is the sum of the enthalpies of all product streams *leaving* the control volume. A similar statement applies to H_r for the *entering* reactant streams.

The individual enthalpies may each be written as the product of the number of moles of the component in the reaction equation and its respective enthalpy per mole of the component. For example, for k products:

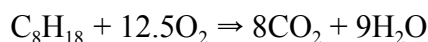
$$H_p = n_1 h_1 + n_2 h_2 + \dots + n_k h_k \quad [\text{Btu} \mid \text{kJ}] \quad (3.8)$$

where the n 's are the stoichiometric coefficients of the chemical equation for the combustion reaction, and the enthalpies are on a per-mole bases.

EXAMPLE 3.9

Write an equation for the enthalpy of the products of complete combustion of octane in oxygen.

Solution The balanced equation for the complete combustion of octane is



The mole coefficients, 8 and 9, of the products are stoichiometric coefficients that yield

$$H_p = 8h(\text{CO}_2) + 9h(\text{H}_2\text{O}) \quad [\text{Btu} \mid \text{kJ}]$$

per mole of octane consumed.

The enthalpy of any component of the reactants or products may be written as the sum of (1) its enthalpy of formation at the standard temperature, T_o , and standard pressure, and (2) its enthalpy difference between the actual state and the standard state of the components. Thus, for each component:

$$h(T) = h_f(T_o) + [h(T) - h(T_o)] \quad [\text{Btu} / \text{mole} \mid \text{kJ} / \text{mole}] \quad (3.9)$$

where it is assumed that the sensible gas enthalpy difference is independent of pressure. *Sensible enthalpies* (those that depend on temperature but do not involve reactions or phase change) relative to the standard reference state are given in Appendix D.

Thus, returning to the formation reaction for the combustion of hydrogen in oxygen at the standard state to produce water, as discussed in the preceding section, we see that the steady-flow First Law of Thermodynamics becomes

$$Q = (1)h_{f, \text{H}_2\text{O}} - (1)h_{f, \text{H}_2} - (0.5)h_{f, \text{O}_2} = -103,996 - 0 - 0 = -103,996 \text{ Btu/lb-mole}$$

with water in the vapor phase as the product of combustion of one mole of H_2 . Here the sensible enthalpy differences are zero, because both the products and the reactants are at the standard state. Note that because the stoichiometric coefficients of both

hydrogen and water are the same in this reaction, the resulting heat transfer may be interpreted as either per mole of water formed or per mole of hydrogen consumed.

If, instead, liquid water is the combustion product, the heat transfer is given by

$$Q = -122,885 - 0 - 0 = -122,885 \text{ Btu/lb-mole}$$

of H_2O . The difference between the two cases, $18,919 \text{ Btu/lb-mole H}_2\text{O}$, is equivalent to $18,935/18 = 1,051.9 \text{ Btu/lb}_m$ of water, the enthalpy of vaporization of water. This result compares with the enthalpy or latent heat of vaporization of water at 77°F , 1050.1 Btu/lb_m , given in the steam tables.

With either liquid or gaseous water as the product, the heat transfer term for the control volume is negative, indicating, in accordance with the usual sign convention, that the heat flows from the control volume to the surroundings. The two calculations above illustrate the fact that the heat transfer in a formation reaction at the standard state is the heat of formation of the compound created.

EXAMPLE 3.10

What is the enthalpy of water vapor at 1800°R and 1 bar? What is the heat transfer in the formation reaction of water from hydrogen and oxygen if the products are at 1800°R and the reactants are (a) at the standard state, and (b) at 900°R ?

Solution

The heat of formation of water vapor at the standard state of 298.15K . (536.7°R) and one bar is $-103,966 \text{ Btu/lb-mole}$. The enthalpy of water vapor at 1800°R is the sum of the heat of formation at the standard state and the sensible enthalpy difference of water vapor between 536.7°R and 1800°R . Thus:

$$H_p = -103,966 + 11,185 = -92,781 \text{ Btu/lb-mole of water.}$$

(a) In this case, the reactants, oxygen and hydrogen, have zero enthalpies because they are in the standard state and, as elements, their heats of formation are zero. Thus the heat transferred is $-92,781 \text{ Btu/lb-mole}$, or 5154.5 Btu/lb_m of water.

(b) For reactants at 900°R , Appendix D gives $h_{\text{H}_2}(900) - h_{\text{H}_2}(536.7) = 2530 \text{ Btu/mole}$ of H_2 and $h_{\text{O}_2}(900) - h_{\text{O}_2}(536.7) = 2617 \text{ Btu/mole}$ of O_2 . The enthalpy of the reactants is then $H_r = (1.0)(2530) + (0.5)(2617) = 3838.5 \text{ Btu/lb-mole H}_2\text{O}$. The heat transferred is then:

$$Q = H_p - H_r = -92,781 - 3,838.5 = -96,619.5 \text{ Btu/lb-mole of water,}$$

or

$$Q = -96,619.5 / 18 = -5,367.8 \text{ Btu/lb}_m \text{ of water.}$$

Thus more heat must be transferred from the control volume to form water vapor at 1800°R if the reactants are at 900°R than if they are in the 536.7°R standard state.

Combustion Flame Temperature

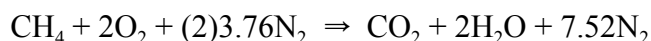
In many combustion problems, the reactants enter the combustor near room temperature and products emerge at an elevated temperature. The temperature of the products flowing from the control volume depends on the energy released in the combustion reaction and heat gain or loss through the boundary of the control volume. The resulting combustion product temperature is sometimes called the *flame temperature*.

EXAMPLE 3.11

Methane and stoichiometric air enter a combustor at the standard state. Using a spreadsheet, calculate the heat transfer as a function of the exit (flame) temperature of the products of complete combustion. Assume the water in the products remains a vapor.

Solution

The reaction equation for complete combustion of methane in air is:



The enthalpy of the products at temperature T and of the reactants at the standard state is

$$H_p = (1)h_{f,\text{CO}_2} + (1)[h_{\text{CO}_2}(T) - h_{\text{CO}_2}(537)] + (2)h_{f,\text{H}_2\text{O}} \\ + (2)[h_{\text{H}_2\text{O}}(T) - h_{\text{H}_2\text{O}}(537)] + (7.52)[h_{\text{N}_2}(T) - h_{\text{N}_2}(537)]$$

$$H_r = h_{f,\text{CH}_4} = -32,189.6 \text{ Btu/lb-mole}$$

of methane, where the heats of formation of elemental nitrogen and oxygen are zero and the heat of formation of water is for the vapor phase. Writing the enthalpy differences as Δh 's and applying the steady-flow First Law of Thermodynamics, we get

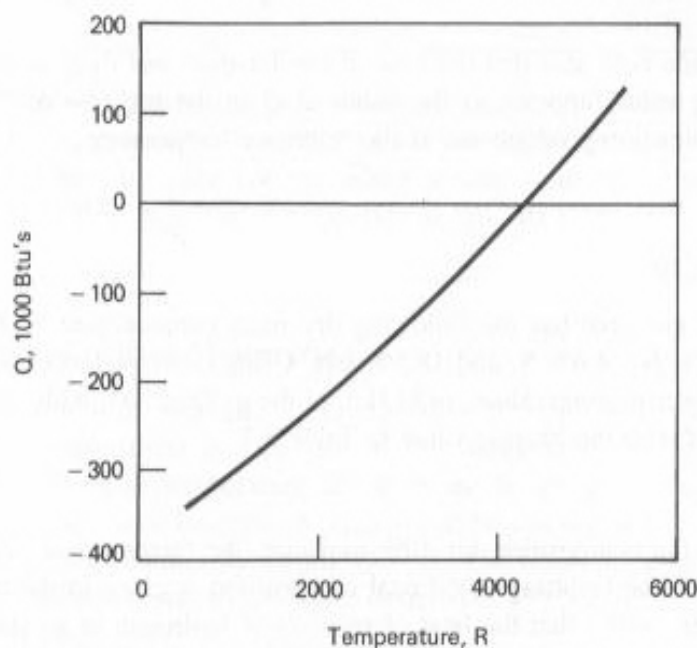
$$Q = H_p - H_r = -169,184 + \Delta h_{\text{CO}_2}(T) + (2)(-103,966) \\ + (2) \Delta h_{\text{H}_2\text{O}}(T) + 7.52 \Delta h_{\text{N}_2}(T) - (-32,189.6) \\ = -344,926.4 + \Delta h_{\text{CO}_2}(T) + (2)\Delta h_{\text{H}_2\text{O}}(T) + 7.52 \Delta h_{\text{N}_2} \text{ Btu/lb-mole}$$

of methane. This function is tabulated in the spreadsheet in Table 3.10 and plotted in Figure 3.4 using values of enthalpies at the temperature T from the the JANAF tables. Negative values of Q indicate that heat must be rejected from the control volume to maintain product effluent temperature below about 4200°R. Beyond 4200°R, the CO_2 ,

TABLE 3.10 Spreadsheet Solution to Example 3.11

Heat Released in Complete Combustion of Methane in Stoichiometric Air with Water Vapor in Products

| T, R | Enthalpy, Btu/lb-mole | | | Q, Btu/lb-mole of methane |
|-------|-----------------------|-----------------|------------------|------------------------------|
| | N ₂ | CO ₂ | H ₂ O | |
| 536.7 | 0 | 0 | 0 | -344926.4 |
| 900 | 2543 | 3573 | 2979 | -316271.9 |
| 1800 | 9234 | 14368 | 11185 | -238751.0 |
| 2700 | 16522 | 26546 | 20715 | -152703.0 |
| 3600 | 24151 | 39338 | 31315 | -61345.0 |
| 3960 | 27259 | 44553 | 35773 | -23842.1 |
| 4140 | 28822 | 47177 | 38040 | -4929.3 |
| 4320 | 30390 | 49809 | 40328 | 14072.8 |
| 4500 | 31963 | 52450 | 42637 | 33159.2 |
| 5400 | 39887 | 65759 | 54443 | 129667.4 |

**FIGURE 3.4** Stoichiometric combustion of methane with water vapor in products.

N_2 , and H_2O outflow carries more energy than is released in the control volume by chemical reaction; hence, heat must flow into the control volume to achieve the resulting high exit temperatures. Thus the final flame temperature clearly depends on the chemical composition of the flow and on the consequent control volume heat transfer.

Heat of Combustion and Heating Value

The *heat of combustion*, or *enthalpy of combustion*, of a fuel is defined as the energy transferred during a steady-flow process in which the fuel is completely burned and where the products are returned to the temperature and pressure of the reactants. It will be seen that the enthalpy of combustion evaluated at the standard state may be determined from the heats of formation. The heat of combustion of hydrogen has, in fact, been determined in a preceding section that examined the formation reaction for water.

The negative of the enthalpy of combustion of a fuel burned in air is usually referred to as the *heating value* of the fuel. When water in the combustion products is condensed, the heat of vaporization of the water adds to the chemical energy released, and the resulting heating value is called the *higher heating value*, HHV. Recall also that the heating value obtained when the product water stays a vapor is called the *lower heating value*, LHV. The difference between HHV and LHV has been illustrated in the previous section for the formation reaction of water resulting from the combustion of hydrogen.

For methane, note also that the heat of combustion, and thus the magnitude of the lower heating value, appears in the value of Q in the top row of table 3.10, since there the combustion products are at the reference temperature.

EXAMPLE 3.12

Illinois no. 6 raw coal has the following dry mass composition: 61.6% C, 4.2% H₂, 9.7% O₂, 1.3% N₂, 4.6% S, and 18.5% ash. Using heats of formation, determine the higher and lower heating values, in kJ / kg, of the as-fired coal with 10% moisture, and compare them with the heating value in Table 3.3.

Solution

To adjust the composition for 10% moisture, the factor $1 - A - M$ becomes $1 - 0 - 0.1 = 0.9$. The resulting moist coal composition is given in the following table.

It was seen earlier that the heat of reaction of hydrogen in its standard state, and thus its heat of combustion, is the heat of formation of its product of combustion. The reaction equation



shows that one mole of hydrogen produces one mole of water. Thus, from Table 3.9, the heat of formation of steam, $-241,826$ kJ per kg-mole of water formed or per kg-mole of hydrogen burned, is also the heat of combustion of hydrogen in the standard state. Thus the hydrogen contributes $241,826/2$ kJ per kg of hydrogen in the coal. The total energy released by the hydrogen in the coal is then $241,826/2$ times the mass fraction of hydrogen in the coal, as shown in the following table. Similar arguments may be made for hydrogen with product water in the liquid phase and the carbon and sulfur components of the coal.

| Element i | Dry mf_i | Wet mf_i | Heat of Combustion | kJ/kg coal |
|-------------|------------|------------|--------------------------|--------------|
| H_2 : | | | | |
| For LHV | 0.042 | 0.0378 | $(241,826)(0.0378)/2 =$ | 4,570.5 (v) |
| For HHV | | | $(285,830)(0.0378)/2$ | 5402.2 (l) |
| C | 0.616 | 0.5544 | $(393,522)(0.5544)/12 =$ | 18,180.7 |
| O_2 | 0.097 | 0.0873 | | |
| N_2 | 0.013 | 0.0117 | | |
| S | 0.046 | 0.0414 | $(296,842)(0.0414)/32 =$ | 384.0 |
| Ash | 0.185 | 0.1665 | | |
| H_2O | _____ | 0.1000 | | |
| | 0.999 | 0.9991 | | 23,135.2 (v) |
| | | | | 23,966.9 (l) |

Thus the lower and higher heating values of the coal are 23,135.2 and 23,966.9 kJ/kg, respectively. Table 3.3 lists a heating value of dry Illinois no. 6 raw coal of 11,345 Btu/lb_m. The corresponding heating value for the wet coal is $(0.9)(11,345) = 10,210.5$ Btu/lb_m. This corresponds to $(10,210.5)/(0.43) = 23,745$ kJ/kg.

Adiabatic Flame Temperature

The results of Example 3.11, tabulated in Figure 3.10, show that for a given air-fuel mixture there is a unique product temperature for which the control volume is adiabatic. This temperature is known as the *adiabatic flame temperature*. It can be determined as in Example 3.11, or it may be calculated from the steady-flow First Law of Thermodynamics by setting $Q = 0$. The resulting First Law equation for the adiabatic flame temperature, designated T^* , becomes:

$$H_p(T^*) = H_r(T_r) \quad [\text{Btu} \mid \text{kJ}] \quad (3.10)$$

where the reactants are at the temperature T_r . The enthalpy terms depend on the individual enthalpies of the components as functions of temperature. Thus a trial-and-error solution is required using data on heat of formation from Table 3.9 and the enthalpy tables in Appendix D. Given a known T_r , the adiabatic flame temperature may also be obtained as the intercept ($Q = 0$) on a graph of Q versus temperature, T , such as Figure 3.4.

Adiabatic Flame Temperature for Solid Fuels

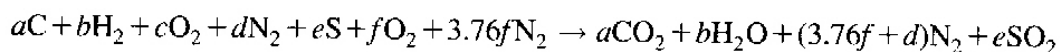
As a final example, we will determine the combustion products, heat of combustion, and adiabatic flame temperature for a solid fuel specified by its ultimate analysis. The solution is presented in a spreadsheet in which enthalpies are tabulated as a function of temperature for the relevant chemical components as given in the JANAF tables.

EXAMPLE 3.13

Consider the combustion of Kanawha, West Virginia, Stockton-Lewiston raw coal with 30% excess air. Determine the heat of combustion, the adiabatic flame temperature with reactants at the reference temperature, the air–fuel ratio, and the wet and dry flue gas compositions.

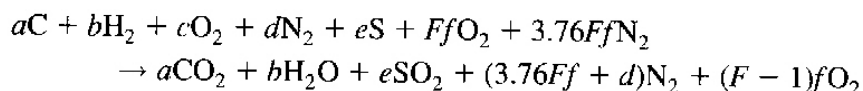
Solution

The *stoichiometric* reaction equation with elements of the ultimate analysis in the reactants may be written with undetermined mole coefficients, as shown below and in the spreadsheet in Table 3.11:



Division of the mass fractions of the coal ultimate analysis by the molecular weight of each component yields the coefficients a , b , c , d , and e per unit mass of fuel. In balancing the equation, it is evident that there must be the same number of moles of CO_2 as of C , because one mole of carbon produces one mole of CO_2 . A similar balancing argument holds for $H_2 - H_2O$ and $S - SO_2$. It is also evident that the sum of the number of atoms of nitrogen in the fuel and in the air must be the number of nitrogen atoms in the flue gas, $3.76f + d$. Balancing the oxygen atoms on both sides of the reaction equation determines the oxygen mole coefficient $f = a + e - c + b/2 = 0.04 + 0.000188 - 0.002094 + 0.0165/2 = 0.046343$.

The *actual reaction equation* for 30% excess air is then obtained from the stoichiometric equation by multiplying the air oxygen and nitrogen terms in the reactants by the actual-to-theoretical air factor F and rebalancing the nitrogen and oxygen atoms in the products, to obtain:



The mole composition x_j of the flue gas is conveniently tabulated on the same spreadsheet lines as the coal analysis. With $F = 1.3$ and using coefficients from the spreadsheet, the reaction equation becomes

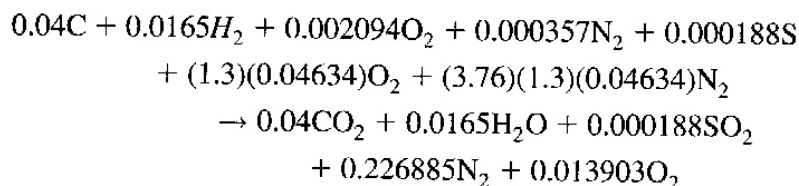
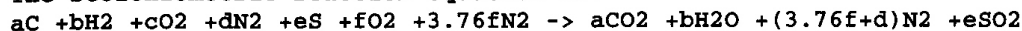


TABLE 3.11 Spreadsheet Solution to Example 3.13

Kanawha, West Virginia Stockton-Lewiston Raw Coal

Theoretical air fraction = 1.3 (F)

The stoichiometric reaction equation is:



| Component | lbs i/ | lb moles i/ | Mole | Component | moles j | wet | dry |
|-----------|----------|-------------|---------|-----------|----------|----------|----------|
| i | dry coal | lb coal | factors | j | /lb coal | xj | xj |
| C | 0.48 | 0.04 | a | CO2 | 0.04 | 0.134465 | 0.142361 |
| H2 | 0.033 | 0.0165 | b | H2O | 0.0165 | 0.055467 | ----- |
| O2 | 0.067 | 0.002094 | c | O2 | 0.013903 | 0.046737 | 0.049482 |
| N2 | 0.01 | 0.000357 | d | N2 | 0.226885 | 0.762701 | 0.80749 |
| S | 0.006 | 0.000188 | e | SO2 | 0.000188 | 0.00063 | 0.000667 |
| Ash | 0.404 | | | | | | |

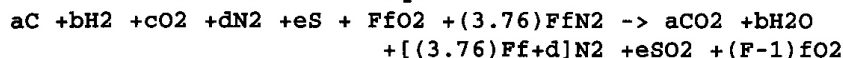
Sum = 1 0.059138 wet total 0.29748 1 1

From oxygen mole balance: dry total 0.28098

$$f = a + e - c + b/2 = 0.046344$$

The stoichiometric air-fuel ratio is $(28.9)(4.76)f = 6.375$ and the actual air fuel ratio is $(28.9)(4.76)Ff = 8.288$

Then the actual reaction equation is:



The steady flow first law gives:

$$Q = H_p - H_r = a[h_f + dh(T)]|CO_2 + b[h_f + dh(T)]|H_2O + e[h_f + dh(T)]|SO_2$$

$$+ [d + 3.76Ff]dh(T)|N_2 + (F-1)fdh(T)|O_2 = 0$$

Heat of Formation, Btu/lb-mole- \rightarrow -169184 -103966 -127619

Flue gas comp.: (F-1)f d+3.76Ff a b e

lb-mole/lb fuel 0.013903 0.226885 0.04 0.0165 0.000188

| TEMPERATURE | | ENTHALPY, BTU/LB-MOLE | | | | | Q |
|-------------|--------|-----------------------|-------|-------|-------|-------|----------------|
| R | K | O2 | N2 | CO2 | H2O | SO2 | Btu/lb of fuel |
| 536.7 | 298.15 | 0 | 0 | 0 | 0 | 0 | -8506.7 |
| 540 | 300 | 23 | 23 | 30 | 27 | 32 | -8499.5 |
| 720 | 400 | 1301 | 1278 | 1722 | 1485 | 1828 | -8104.9 |
| 900 | 500 | 2617 | 2543 | 3573 | 2979 | 3768 | -7700.6 |
| 1080 | 600 | 3977 | 3826 | 5553 | 4518 | 5827 | -7285.6 |
| 1260 | 700 | 5377 | 5135 | 7638 | 6106 | 7980 | -6859.1 |
| 1440 | 800 | 6812 | 6473 | 9811 | 7745 | 10205 | -6421.2 |
| 1620 | 900 | 8278 | 7840 | 12059 | 9438 | 12486 | -5972.5 |
| 1800 | 1000 | 9767 | 9234 | 14368 | 11185 | 14811 | -5513.9 |
| 1980 | 1100 | 11277 | 10652 | 16728 | 12988 | 17171 | -5046.5 |
| 2160 | 1200 | 12803 | 12093 | 19133 | 14845 | 19559 | -4571.1 |
| 2340 | 1300 | 14345 | 13553 | 21574 | 16753 | 21970 | -4088.8 |
| 2520 | 1400 | 15899 | 15030 | 24047 | 18711 | 24401 | -3600.4 |
| 2700 | 1500 | 17466 | 16522 | 26546 | 20715 | 26847 | -3106.6 |
| 2880 | 1600 | 19044 | 18028 | 29069 | 22762 | 29307 | -2608.0 |
| 3060 | 1700 | 20632 | 19544 | 31612 | 24848 | 31780 | -2105.2 |
| 3240 | 1800 | 22230 | 21071 | 34172 | 26971 | 34263 | -1598.7 |
| 3420 | 1900 | 23839 | 22607 | 36748 | 29128 | 36755 | -1088.7 |
| 3600 | 2000 | 25458 | 24151 | 39338 | 31315 | 39257 | -575.8 |
| 3780 | 2100 | 27086 | 25702 | 41940 | 33531 | 41765 | -60.1 |
| 3960 | 2200 | 28725 | 27259 | 44553 | 35773 | 44281 | 457.9 |
| 4140 | 2300 | 30373 | 28822 | 47177 | 38040 | 46803 | 978.3 |

The number of moles of excess O_2 in the flue gas per pound of coal may also be obtained from the excess air-fuel ratio:

$$[(A/F)_{\text{actual}} - (A/F)_{\text{theor}}](0.233)/32 = (8.288 - 6.375)(0.233)/32 = 0.0139$$

The number of moles of flue gas nitrogen is also given by

$$[(A/F)_{\text{actual}}](1 - 0.233)/28 + d = 8.288(0.767)/28 + 0.000357 = 0.227$$

With the actual balanced reaction equation known, the mole coefficients may then be used to write an equation for the enthalpy of the products per unit mass of coal. Because all the reactants are assumed to be elements at the reference temperature, the enthalpy of the reactants is zero. By setting $Q = H_p = 0$, we can solve this First Law equation for the adiabatic flame temperature by trial and error. However, with a spreadsheet, it is convenient to calculate the heat transfer at each temperature-enthalpy data point and determine the adiabatic flame temperature by inspection and, if additional precision is required, by explicit interpolation. The heat transfer equation is shown on the spreadsheet, and the values of the flue gas mole coefficients and heats of formation are shown above the appropriate JANAF enthalpies to which they relate.

It is seen that the adiabatic flame temperature for combustion with 30% excess air is about 2110K, or 3800°R. Note also that the heat of combustion of the coal, 8506.7 Btu/lb_m of coal, may be read from the spreadsheet at the JANAF table reference temperature. This is possible because the heat of reaction is independent of the amount of excess air employed in the reaction.

The spreadsheet for Example 3.13 is easily modified to compute and plot the composition of the flue gas as a function of the percentage of excess air. Figure 3.5 shows that the mole fractions of excess oxygen and of nitrogen increase while the fractions of other products decrease. Excess oxygen measured from a flue gas sample is commonly used as a measure of excess air in adjusting the air-fuel ratio of combustion systems.

3.6 Molecular Vibration, Dissociation, and Ionization

The temperature of a gas is a measure of the random translational kinetic energy of molecules. The simple kinetic theory of the heat capacity of a gas predicts heat capacities that are independent of temperature and determined by the number of degrees of freedom of the molecules. The kinetic theory is usually regarded as applicable at low pressures and moderate and high temperatures, conditions at which collisions between molecules are rare.

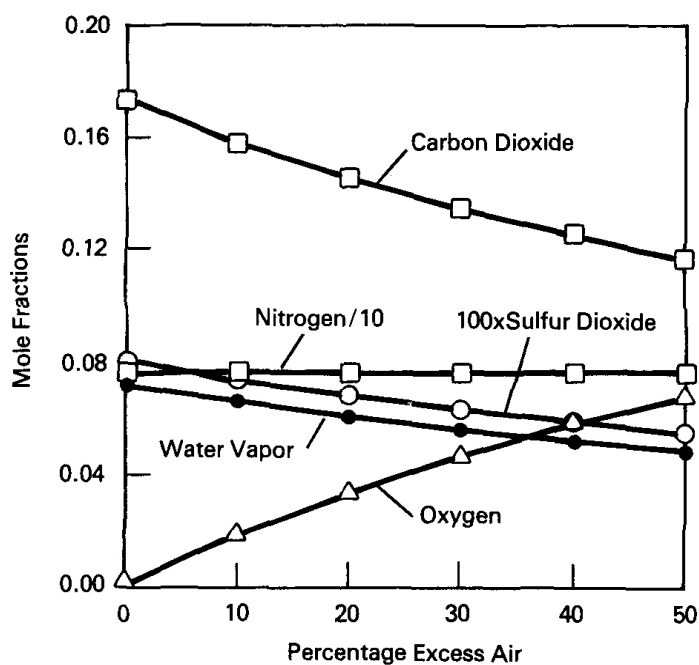


FIGURE 3.5 Wet flue gas composition for Kanawha, W. Va., raw coal.

For monatomic gases, kinetic theory predicts an internal energy per atom of

$$u = 3kT/2$$

and an enthalpy of

$$h = u + pv = 3kT/2 + kT = 5kT/2$$

Here k , the Boltzmann constant, is the ideal-gas constant per molecule, which can be calculated from the universal gas constant, \mathbb{R} , and Avogadro's number of molecules per mole. Thus

$$k = \mathbb{R}/N_0 = 8.32/(6.025 \times 10^{23}) = 1.38 \times 10^{-23} \text{ J/K}$$

From their definitions, Equations (1.14) and (1.15), this leads to $c_v = 3k/2$ and $c_p = 5k/2$ per atom and to a heat capacity ratio of $k = c_p/c_v = 5/3 = 1.667$.

The concept of *equipartition of energy* assumes that the energy of a particle is equally divided among its various degrees of freedom. Each mode of energy storage of a molecule is assigned an energy $kT/2$. The theory then represents the internal energy as $nkT/2$, the enthalpy as $(n+2)kT/2$, and the heat capacity ratio as $k = (n+2)/n$, where n is the number of modes of energy storage, or degrees of freedom, of the molecule. For atoms with three translational and no rotational degrees of freedom, $n = 3$ (an atom is presumed to be a point and to have no rotational kinetic energy

because it has zero radius); and these relations reduce to the findings described in the preceding paragraph.

The simple kinetic theory suggests that a diatomic molecule has five degrees of freedom: three degrees of translational freedom and two modes having significant rotational kinetic energy. For this case we obtain $u = 5kT/2$, $h = 7kT/2$, and $k = 7/5 = 1.4$, in agreement with experiment for oxygen and nitrogen at moderate temperatures and densities.

At higher temperatures, diatomic molecules start to vibrate, adding additional degrees of freedom that reduce the heat capacity ratio k below 1.4. As the temperature increases and the collisions between molecules become more vigorous, molecules not only vibrate but they start to be torn apart, each forming separate atoms, the process known as *dissociation*. The energy required to break the bonds between atoms in molecules is called the dissociation energy. At low temperatures, few molecules have sufficient kinetic energy to provide the energy needed to cause dissociation by collision. At higher temperatures, when more molecules have energies exceeding the dissociation energy, the chemical equilibrium shifts to a composition in which there are more atoms and fewer molecules in the gas. This trend continues as temperature increases.

At still higher temperatures, when particle kinetic energies exceed the ionization energy of the gas, outer electrons are separated from atoms, forming positively charged ions, in a process known as the *ionization*. Particles lose kinetic energy when causing dissociation and ionization. This lost energy is then not reflected in the temperature. Thus, when vibration, dissociation, and ionization occur, the internal energy and enthalpy increase more rapidly than the temperature. Then the simple linear relations just given for u and T are no longer correct. Stated another way, the temperature of a gas rises less rapidly with heat addition when it is at temperature levels where significant vibration, dissociation, or ionization take place. The phenomenon may be thought of as analogous to phase change, in which enthalpy increases with heat addition while temperature does not.

As a result of these phenomena, high flame temperatures determined with ideal gas enthalpies may be overestimated. At temperatures exceeding 2000K (3600°R), flame temperature calculations based on the JANAF gas enthalpies may start to become inaccurate. At these temperature levels, dissociation (and at still higher temperatures, ionization) starts to influence the composition of the gases and hence their thermodynamic properties. The progression of dissociation and ionization with temperature is shown for air at sea level density in Figure 3.6. It is seen that, at this density, little dissociation of nitrogen occurs below about 6000 K. but that oxygen starts to dissociate significantly above 3000 K.. At lower densities, the onset of dissociation occurs at progressively lower temperatures. In Figure 3.6, the number of particles per initial atom of air may be obtained by multiplying the ordinates by 1.993.

Usually, dissociation does not seriously influence combustion calculations when the oxidizer is air, but the high combustion temperatures resulting from use of pure oxygen may be significantly influenced by dissociation. The reader is referred to advanced thermodynamics, physical chemistry, and advanced engineering texts for methods of predicting the effects of dissociation and ionization.

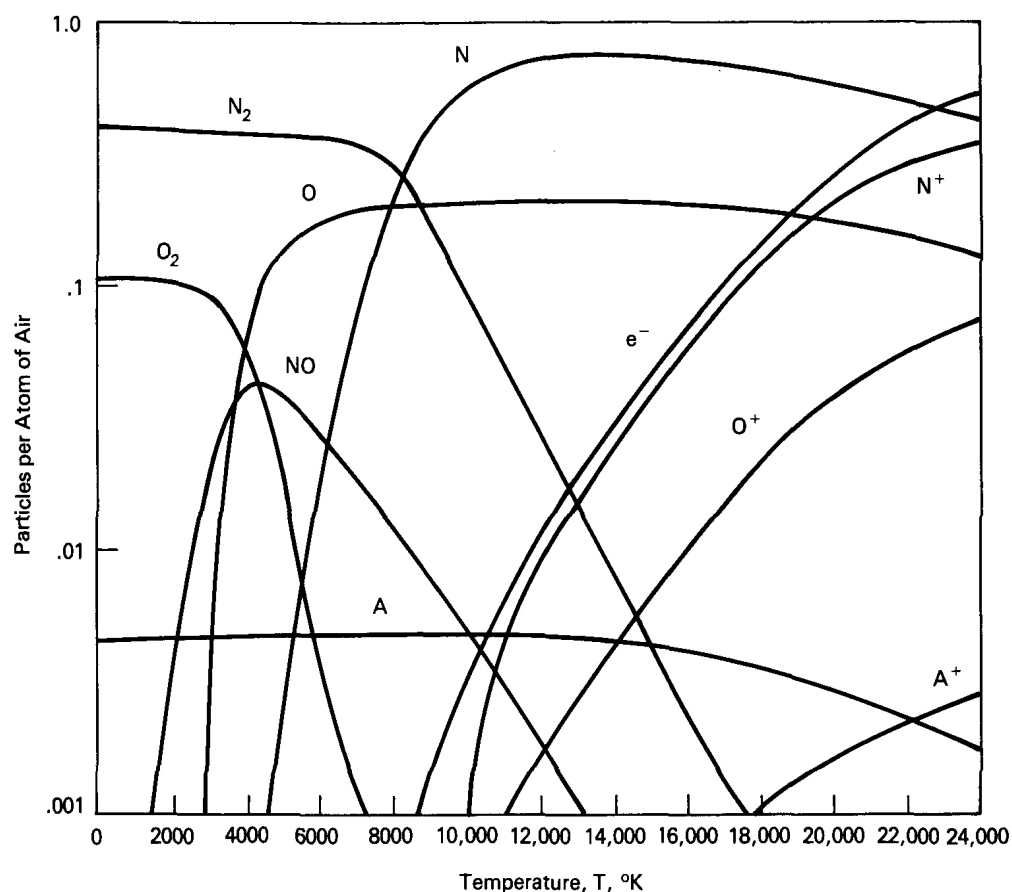


FIGURE 3.6 Equilibrium composition of air to 24,000K. Sea level density. (Source: ref. 15.)

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EXERCISES

- 3.1 Determine the mass fractions of a mixture of six grams of carbon, three grams of sulfur, and one gram of sodium chloride.
- 3.2 Determine the mole fractions of a gas consisting of a mole of oxygen, eight moles of nitrogen, a mole of CO, and two moles of CO₂. Determine also the mass fractions. What is the average molecular weight of the gas?
- 3.3 Write the balanced reaction equation for the complete combustion of sulfur in oxygen. What are the mass and mole fractions of oxygen in the reactants?
- 3.4 Write the balanced reaction equation for the complete combustion of carbon in oxygen. What are the mass and mole fractions of oxygen in the reactants?
- 3.5 Write the balanced reaction equation for the complete combustion of carbon in air. What are the mass and mole fractions of fuel, air, oxygen, and nitrogen in the reactants?

3.6 Write the balanced reaction equation for the complete combustion of ethane, C_2H_6 , in air. What are the mass and mole fractions of fuel, air, oxygen, and nitrogen in the reactants? What are the mass and mole fractions of carbon dioxide and water vapor in the combustion products?

3.7 Write the balanced reaction equation for the complete combustion of propane, C_3H_8 , in air. What are the mass and mole fractions of fuel, air, oxygen, and nitrogen in the reactants? What are the mass and mole fractions of carbon dioxide and water vapor in the combustion products. What are the mass and mole air-fuel ratios?

3.8 Write the balanced reaction equation for the complete combustion of C_8H_{18} in air. What are the mass and mole fractions of fuel, air, oxygen, and nitrogen in the reactants? What are the mass and mole fractions of carbon dioxide and water vapor in the combustion products? What are the mass and mole air-fuel ratios?

3.9 Gasoline, sometimes represented as C_8H_{18} , is burned in 25% excess air mass. What are the mass and mole stoichiometric and actual air-fuel ratios? Determine the mass and mole fractions of the combustion products.

3.10 Determine the lower and higher heating values of methane using the JANAF table of heats the formation.

3.11 Determine the as-fired stoichiometric and actual air-fuel ratios for Greene, Pennsylvania raw coal (Table 3.3) with 5% moisture and the mass and mole flue gas compositions for combustion with 20% excess air.

3.12 Compare the stoichiometric and actual air-fuel ratios and the mole flue gas composition for combustion with 20% excess air for the following raw and clean (process #1) coals (Table 3.3): (a) Freestone, Texas, big brown lignite; (b) Indiana, Pennsylvania, Freeport (upper); (c) British Columbia, Hat Creek (A zone); (d) Perry, Illinois no. 6; (e) Muhlenberg, Kentucky no. 9; (f) Nicholas, West Virginia, Kittanning; (g) Belmont, Ohio, Pittsburgh; (h) Big Horn, Montana, Robinson; (i) Greene, Pennsylvania, Sewickley; (j) Kanawha, West Virginia, Stockton-Lewiston; (k) Belmont, Ohio, Waynesburg.

3.13 If Union, Kentucky no. 11 raw coal has 10% moisture, as mined, determine the as-mined proximate and ultimate analyses for this coal.

3.14 If Big Horn, Montana, Robinson raw coal has 15% moisture, as-mined, what are its as-mined proximate and ultimate analyses?

3.15 Determine the ultimate analyses of the raw coals listed in Exercise 3.12 (a-e) assuming 10% as-mined moisture.

3.16 Write the balanced chemical equation for the combustion of methane in stoichiometric air. Use the table of heats of formation to determine the heats of reaction of methane (in Btu/lb_m and Btu/lb-mole), with products and reactants all at the standard state and product water as liquid. What are the values if the product water is vapor? Would the heat of reaction be different if the combustion were in pure oxygen? Compare your results with tabulated heating values for methane.

3.17 Solve Exercise 3.16 in SI units: kJ/gm-mole and kJ/kg.

3.18 Calculate the heating values, in Btu/lb_m and Btu/lb-mole, for the complete combustion of hydrogen, with product water in liquid and in vapor phases. Compare with tabulated heating values. Repeat the calculations in SI units.

3.19 Determine the heat transferred when ethane is burned (a) in stoichiometric air, and (b) in 100% excess air. In both cases the reactants are in the standard state and products at 1000K. Use a heat of formation of $-36,420$ Btu/lb-mole.

3.20 What is the adiabatic flame temperature for the combustion of ethane in air, ignoring dissociation? Use a heat of formation of $-36,420$ Btu/lb-mole of ethane.

3.21 Compare the adiabatic flame temperatures for the stoichiometric combustion of hydrogen in air and in pure oxygen, ignoring dissociation.

3.22 Determine the adiabatic flame temperature for the stoichiometric combustion in air of Illinois no. 6 coal after the clean #2 process. Determine also its heat of combustion, and compare with the tabulated value.

3.23* Develop a spreadsheet that determines the air-fuel ratio for coal characterized by a dry ultimate analysis, such as given in Table 3.3. Apply it to several of the coals in the table, as assigned by your instructor.

3.24* Develop a spreadsheet that determines the air-fuel ratio for a coal characterized by a dry ultimate analysis, such as given in Table 3.3, and a given moisture content. Apply it to a coal in the table and several different moisture contents, as assigned by your instructor.

3.25* Develop a spreadsheet that determines the mass and mole, wet and dry flue gas compositions for a coal characterized by a dry ultimate analysis, such as given in Table 3.3, and a given percentage of excess air. Apply it to several coals in the table for 20% and 40% excess air.

*Exercise numbers with an asterisk involve computer usage.

- 3.26* Develop a spreadsheet that determines the average molecular weight, and the mass and mole, wet and dry flue gas compositions for a coal characterized by a dry ultimate analysis, such as given in Table 3.3, a given percentage of excess air, and a given moisture content. Apply it to a coal in the table for 10% moisture and 10% and 20% excess air.
- 3.27* Develop a spreadsheet that determines the theoretical air-fuel ratio for a gas characterized by any combination of the components of Table 3.4. Apply it to the gases in the table, as assigned by your instructor.
- 3.28* Develop a spreadsheet that determines the average molecular weight, and the mass and mole, wet and dry flue gas compositions for a gas characterized by any combination of the components of Table 3.4 and a given percentage of excess air. Apply it to several the gases in the table for 20% excess air.
- 3.29 What are the theoretical and actual air-fuel ratios and the wet and dry mole flue gas compositions for 20% excess air for the Oklahoma natural gas in Table 3.4?
- 3.30 What are the theoretical and actual air-fuel ratios and the wet and dry mole flue gas compositions for 15% excess air for the Ohio natural gas in Table 3.4?
- 3.31 An adiabatic gas turbine combustor burns methane at 77°F with air at 400°F. The combustion products emerge from the combustion chamber at 3200°F. What is the air-fuel ratio? What is the equivalent external heat transferred per lb_m of air to produce this temperature rise, assuming a mean heat capacity of 0.24 Btu/ lb_m -R?
- 3.32 An adiabatic gas turbine combustor burns methane at 25°C with air at 250°C. The combustion products emerge from the combustion chamber at 2000K. What is the air-fuel ratio? What is the equivalent external heat transferred per kilogram of air to produce this temperature rise, assuming a mean heat capacity of 1.005 kJ/kg-K?
- 3.33 An adiabatic combustor burns methane with 400% excess air. Both air and methane are initially at 298K. What is the exit temperature?
- 3.34 An adiabatic combustor burns methane with 500% theoretical air. Both air and methane are initially at 77°F. What is the flame temperature?
- 3.35 An adiabatic combustor burns methane in 100% excess oxygen. Both fuel and oxidizer enter at the JANAF tables reference temperature. What is the flame temperature?
- 3.36 Calculate and tabulate the higher and lower heating values of methane, in kJ/kg-mole and in kJ/kg.

- 3.37 Determine the theoretical air-fuel ratio and the air-fuel ratio for 20% excess air for Muhlenberg, Kentucky, raw coal with 10% moisture.
- 3.38 Determine the air-fuel ratio and wet and dry flue gas mole and mass fractions for dry Muhlenberg, Kentucky no. 9 raw coal with 20% excess air.
- 3.39 Solve Exercise 3.38 for the coal having 10% moisture in the as-fired condition.
- 3.40 Solve Exercise 3.38 for 40% excess air.
- 3.41* Set up a spreadsheet to solve Exercises 3.38–3.40 where it is necessary to change only one parameter for each of the latter cases.
- 3.42 Using the compound composition data of Table 3.4, calculate the ultimate (elemental) analysis, and compare with the tabular results for the following natural gases: (a) Pennsylvania, (b) Southern California, (c) Ohio, (d) Louisiana, (e) Oklahoma.
- 3.43* Develop an interactive computer program to solicit and receive ultimate analysis data for an arbitrary coal, arbitrary as-fired ash and moisture fractions, an excess air percentage, and output the appropriate air-fuel ratio and mass and mole, wet and dry flue gas compositions.
- 3.44* Develop an interactive computer program to solicit and receive ultimate analysis data for an arbitrary coal, arbitrary as-fired ash and moisture fractions, and Orsat CO, CO₂, and O₂ data. The program should determine the actual operating air-fuel ratio.
- 3.45* Apply the spreadsheet of Example 3.13 to determine the adiabatic flame temperature, heat of combustion, and wet flue gas composition for stoichiometric combustion of the liquid fuels in Table 3.6.
- 3.46* Develop a well-organized spreadsheet in which the user may enter a coal ultimate analysis for C, H, O, N, and S; dry flue gas mole compositions for CO, CO₂, and O₂; and as-fired moisture and ash mass fractions to determine theoretical and actual air-fuel ratios and percentage of excess air.