

## CHAPTER 3

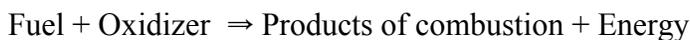
### FUELS AND COMBUSTION

#### 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<sub>m</sub>.

Molecule	Molecular Weight
C	12
N <sub>2</sub>	28
O <sub>2</sub>	32
S	32
H <sub>2</sub>	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, CH<sub>4</sub>, 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:

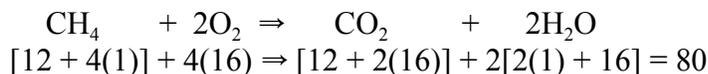


Because atoms are neither created nor destroyed, Equation (3.1) states that methane (consisting of one atom of carbon and four atoms of hydrogen) reacts with four atoms of oxygen to yield carbon dioxide and water products with the same number of atoms of each *element* as in the reactants. This is the 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 CO<sub>2</sub> 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 CO<sub>2</sub> in the products.

There are 44 mass units of CO<sub>2</sub> in the 80 mass units of products for a *mass*

*fraction* of CO<sub>2</sub> 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 CO<sub>2</sub> 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  $m_{\text{water}}$  is the mass of liquid water in the combustion products, and  $h_{\text{fg}}$  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  $\text{O}_2$  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  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . 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

<b>Fuel</b>	<b>Type of Furnace or Burners</b>	<b>Excess Air, % by Weight</b>
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

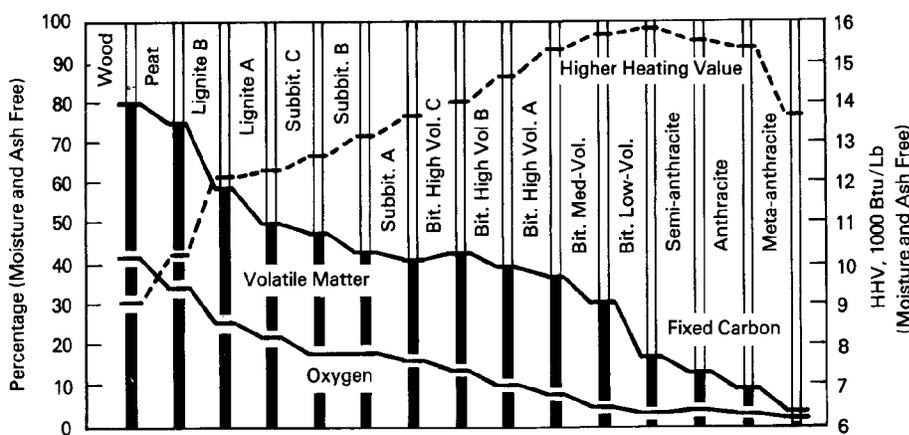
Calculations by Parr formulas

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

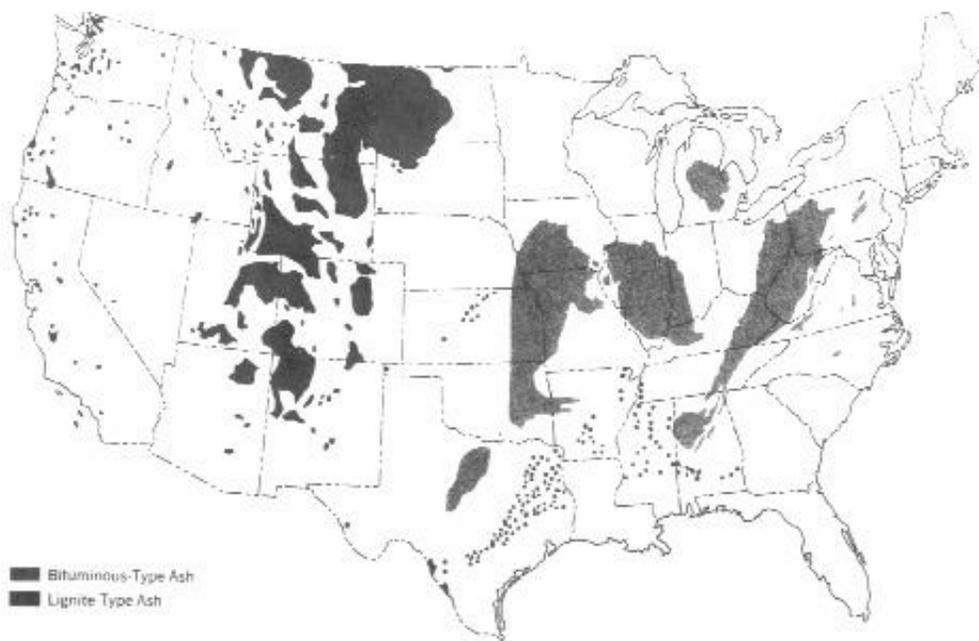


FIGURE 3.2 Coal fields of the United States. (Courtesy of Babcock and Wilcox.)

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% H<sub>2</sub>, 4.87% O<sub>2</sub>, 0.57% N<sub>2</sub>, 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	Ash (wt, %)	VM (wt, %)	FC (wt, %)	Ultimate Analysis, Dry, wt, %					Heating Value (Btu/lb)
						C	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	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

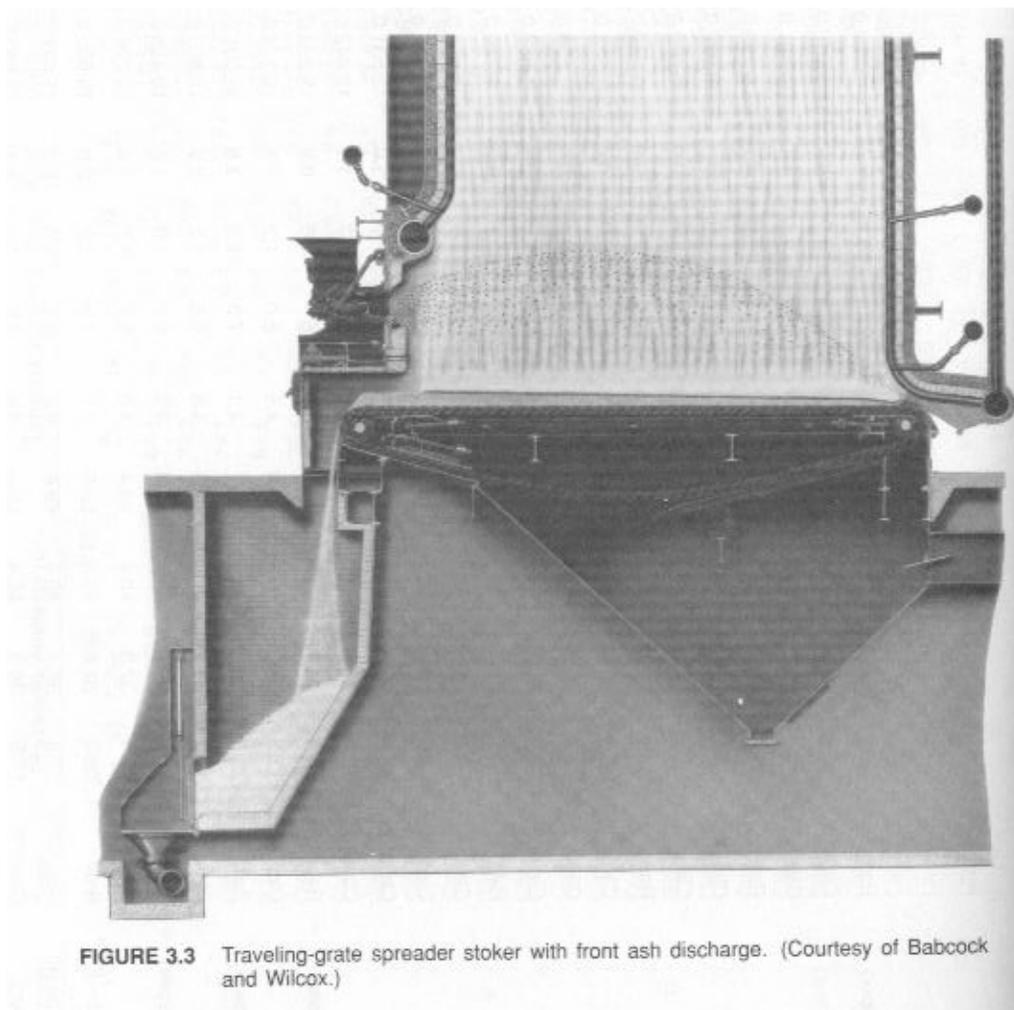
(continued on next page)

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 <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	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 <sub>2</sub>	Hydrogen	—	—	1.82	—	—
CH <sub>4</sub>	Methane	83.40	84.00	93.33	90.00	84.10
C <sub>2</sub> H <sub>4</sub>	Ethylene	—	—	0.25	—	—
C <sub>2</sub> H <sub>6</sub>	Ethane	15.80	14.80	—	5.00	6.70
CO	Carbon monoxide	—	—	0.45	—	—
CO <sub>2</sub>	Carbon dioxide	—	0.70	0.22	—	0.80
N <sub>2</sub>	Nitrogen	0.80	0.50	3.40	5.00	8.40
O <sub>2</sub>	Oxygen	—	—	0.35	—	—
H <sub>2</sub> S	Hydrogen sulfide	—	—	0.18	—	—
<i>Ultimate, % by weight</i>						
S	Sulfur	—	—	0.34	—	—
H <sub>2</sub>	Hydrogen	23.53	23.30	23.20	22.68	20.85
C	Carbon	75.25	74.72	69.12	69.26	64.84
N <sub>2</sub>	Nitrogen	1.22	0.76	5.76	8.06	12.90
O <sub>2</sub>	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 <sup>3</sup> @ 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 (CH<sub>4</sub>), 0-16% ethane (C<sub>2</sub>H<sub>6</sub>), 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/ft<sup>3</sup> on a volume basis and 22,000 Btu/lb<sub>m</sub> 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  $\text{CO}_2$  molecules and 3  $\text{H}_2\text{O}$  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 <sub>2</sub>	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 <sub>2</sub>	C	N <sub>2</sub>	O <sub>2</sub>	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 H<sub>2</sub>, 0.02 S, and 0.02 O<sub>2</sub> 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 <sub>2</sub>	$0.09 \times 0.9 =$	0.081	8	0.648
S	$0.02 \times 0.9 =$	0.018	1.0	0.018
O <sub>2</sub>	$0.02 \times 0.9 =$	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 CO<sub>2</sub> 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 CO<sub>2</sub> to C in the reaction  $C + O_2 \rightarrow CO_2$ . The CO<sub>2</sub>/C mass ratio is the ratio of the molecular weights of CO<sub>2</sub> 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 <sub>wfg</sub>	mf <sub>dfg</sub>	Moles <i>j</i> / kg Fuel	x <sub>wfg</sub>	x <sub>dfg</sub>
CO <sub>2</sub>	2.871	0.1836	0.1931	2.871/44 = 0.0653	0.1226	0.1332
H <sub>2</sub> O	0.769	0.0492	—	0.769/18 = 0.0427	0.0801	—
SO <sub>2</sub>	0.036	0.0023	0.0024	0.036/64 = 0.00056	0.0011	0.0012
O <sub>2</sub>	0.684	0.0437	0.0460	0.684/32 = 0.0214	0.0402	0.0437
N <sub>2</sub>	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 (H<sub>2</sub>O 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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{SO}_2$  present goes into solution in the liquid. The remaining combustion gases measured are  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ , and  $\text{N}_2$ . 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	$\text{CO}_2$
	$\text{N}_2$
	$\text{O}_2$
	$\text{CO}$
	$\text{H}_2\text{O}$
	$\text{SO}_2$
	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 CO<sub>2</sub> 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% CO<sub>2</sub>, 0.5% CO, and 3.2% O<sub>2</sub>. 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.

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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% CO<sub>2</sub>, 3% O<sub>2</sub>, 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.

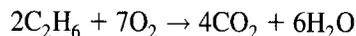
TABLE 3.8 Spreadsheet Solution to Example 3.8

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

COMPONENT OF FUEL	$x_i$	MW <sub>i</sub>	MASS $i$ / MOLE FUEL	$m_f i_i$	CARBON FACTOR	MASS C / MASS FUEL	OXYGEN FACTOR	MASS O <sub>2</sub> / MASS FUEL
CH <sub>4</sub>	0.841	16	13.456	0.7406	0.75	0.555421	4	2.962245
C <sub>2</sub> H <sub>4</sub>	0	28	0	0	0.85714	0	3.42857	0
C <sub>2</sub> H <sub>6</sub>	0.067	30	2.01	0.1106	0.8	0.088498	3.73333	0.412988
H <sub>2</sub>	0	2	0	0	0	0	8	0
CO	0	28	0	0	0.42857	0	0.57143	0
N <sub>2</sub>	0.084	28	2.352	0.1294	0	0	0	0
CO <sub>2</sub>	0.008	44	0.352	0.0194	0.27273	0.005283	0	0
O <sub>2</sub>	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 <sub>j</sub>	MASS $j$ / MOLE dfg	$m_f j_j$	CARBON FACTOR	MASS C / MASS dfg		
CO <sub>2</sub>	0.09	44	3.96	0.134	0.27273	0.036536		
O <sub>2</sub>	0.03	32	0.96	0.0325	0	0		
CO	0.005	28	0.14	0.0047	0.42857	0.00203		
N <sub>2</sub>	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.