chapter

2

Combustion and Thermochemistry

OVERVIEW

In this chapter, we examine several thermodynamic concepts that are important in the study of combustion. We first briefly review basic property relations for ideal gases and ideal-gas mixtures and the first law of thermodynamics. Although these concepts are likely to be familiar to you from a previous study of thermodynamics, we present them here since they are an integral part of our study of combustion. We next focus on thermodynamic topics related specifically to combustion and reacting systems: concepts and definitions related to element conservation; a definition of enthalpy that accounts for chemical bonds; and first-law concepts defining heat of reaction, heating values, etc., and adiabatic flame temperatures. Chemical equilibrium, a second-law concept, is developed and applied to combustion-product mixtures. We emphasize equilibrium because, in many combustion devices, a knowledge of equilibrium states is sufficient to define many performance parameters of the device; for example, the temperature and major species at the outlet of a steady-flow combustor are likely to be governed by equilibrium considerations. Several examples are presented to illustrate these principles.

REVIEW OF PROPERTY RELATIONS

Extensive and Intensive Properties

The numerical value of an **extensive property** depends on the amount (mass or number of moles) of the substance considered. Extensive properties are usually denoted with capital letters; for example, V (m^3) for volume, U (J) for internal

energy, H (J) ($= U + PV$) for enthalpy, etc. An **intensive property**, on the other hand, is expressed per unit mass (or per mole), and its numerical value is independent of the amount of substance present. Mass-based intensive properties are generally denoted with lower-case letters; for example, v (m^3/kg) for specific volume, u (J/kg) for specific internal energy, h (J/kg) ($= u + Pv$) for specific enthalpy, etc. Important exceptions to this lower-case convention are the intensive properties temperature T and pressure P. Molar-based intensive properties are indicated in this book with an overbar, e.g., $\bar{u}$ and $\bar{h}$ (J/kmol). Extensive properties are obtained simply from the corresponding intensive properties by multiplying the property value per unit mass (or mole) by the amount of mass (or number of moles); i.e.,

$$\begin{aligned} V &= mv \,(or\, N\bar{v}) \\ U &= mu \,(\text{or}\, N\bar{u}) \\ H &= mh \,(\text{or}\, N\bar{h}), \text{ etc.} \end{aligned} \tag{2.1}$$

In the following developments, we will use either mass- or molar-based intensive properties, depending on which is most appropriate to a particular situation.

Equation of State

An **equation of state** provides the relationship among the pressure, P, temperature, T, and volume V (or specific volume v) of a substance. For ideal-gas behavior, i.e., a gas that can be modeled by neglecting intermolecular forces and the volume of the molecules, the following equivalent forms of the equation of state apply:

$$PV = NR_uT, \tag{2.2a}$$

$$PV = mRT, \tag{2.2b}$$

$$Pv = RT, \tag{2.2c}$$

or

$$P = \rho RT, \tag{2.2d}$$

where the specific gas constant R is related to the universal gas constant R_u ($= 8315$ J/kmol-K) and the gas molecular weight MW by

$$R = R_u/MW. \tag{2.3}$$

The density ρ in Eqn. 2.2d is the reciprocal of the specific volume ($\rho = 1/v = m/V$). Throughout this book, we assume ideal-gas behavior for all gaseous species and gas mixtures. This assumption is appropriate for nearly all of the systems we wish to consider since the high temperatures associated with combustion generally result in sufficiently low densities for ideal-gas behavior to be a reasonable approximation.

Calorific Equations of State

Expressions relating internal energy (or enthalpy) to pressure and temperature are called **calorific equations of state**, i.e.,

$$u = u(T, v) \tag{2.4a}$$

$$h = h(T, P). \tag{2.4b}$$

The word "calorific" relates to expressing energy in units of calories, which has been superseded by the use of joules in the SI system.

General expressions for a differential change in u or h can be expressed by differentiating Eqns. 2.4a and b:

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \tag{2.5a}$$

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP. \tag{2.5b}$$

In the above, we recognize the partial derivatives with respect to temperature to be the **constant-volume** and **constant-pressure specific heats**, respectively, i.e.,

$$c_v \equiv \left(\frac{\partial u}{\partial T}\right)_v \tag{2.6a}$$

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_P. \tag{2.6b}$$

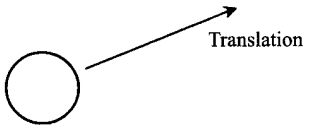
For an ideal gas, the partial derivatives with respect to specific volume, $(\partial u/\partial v)_T$, and pressure, $(\partial h/\partial P)_T$, are zero. Using this knowledge, we integrate Eqn. 2.5, substituting Eqn. 2.6 to provide the following ideal-gas calorific equations of state:

$$u(T) - u_{\text{ref}} = \int_{T_{\text{ref}}}^{T} c_v \, dT \tag{2.7a}$$

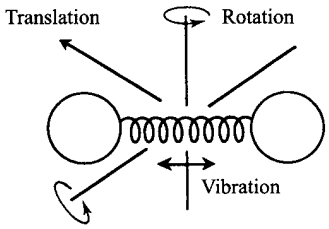
$$h(T) - h_{\text{ref}} = \int_{T_{\text{ref}}}^{T} c_p \, dT. \tag{2.7b}$$

In a subsequent section, we will define an appropriate reference state that accounts for the different bond energies of various compounds.

For both real **and** ideal gases, the specific heats c_v and c_p are generally functions of temperature. This is a consequence of the internal energy of a molecule consisting of three components: translational, vibrational, and rotational; and the fact that, as a consequence of quantum theory, the vibrational and rotational energy storage modes become increasingly active as temperature increases. Figure 2.1 schematically illustrates these three energy storage modes by contrasting a monatomic species, whose internal energy consists solely of translational kinetic energy, and a diatomic molecule, which stores energy in a



(a) **Monatomic species**



(b) **Diatomic species**

Figure 2.1 (a) The internal energy of monatomic species consists only of translational (kinetic) energy, while (b) a diatomic species' internal energy results from translation together with energy from vibration (potential and kinetic) and rotation (kinetic).

vibrating chemical bond, represented as a spring between the two nuclei, and by rotation about two orthogonal axes, as well as possessing kinetic energy from translation. With these simple models (Fig. 2.1), we would expect the specific heats of diatomic molecules to be greater than monatomic species. In general, the more complex the molecule, the greater its molar specific heat. This can be seen clearly in Fig. 2.2, where molar specific heats for a number of combustion product species are shown as functions of temperature. As a group, the triatomics have the greatest specific heats, followed by the diatomics, and, lastly, the monatomics. Note that the triatomic molecules also have a greater temperature dependence than the diatomics, a consequence of the greater number of vibrational and rotational modes that are available to become activated as temperature is increased. In comparison, the monatomic species have nearly constant specific heats over a wide range of temperatures; in fact, the H-atom specific heat is constant ($\bar{c}_p = 20.786$ kJ/kmol-K) from 200 K to 5000 K.

Constant-pressure molar specific heats are tabulated as a function of temperature for various species in Tables A.1 to A.12 in Appendix A. Also provided in Appendix A are the curvefit coefficients, taken from the Chemkin thermodynamic database [1], which were used to generate the tables. These coefficients can be easily used with spreadsheet software to obtain $\bar{c}_p$ values at any temperature within the given temperature range.

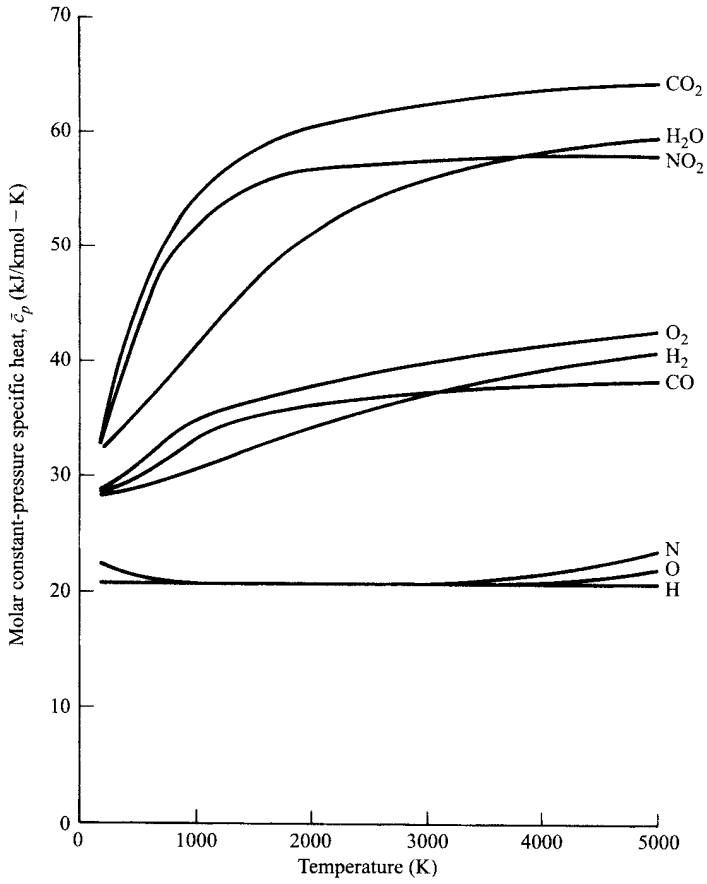


Figure 2.2 Molar constant-pressure specific heats as functions of temperature for monatomic (H, N, and O), diatomic (CO, H_2, and O_2), and triatomic (CO_2, H_2O, and NO_2) species. Values are from Appendix A.

Ideal-Gas Mixtures

Two important and useful concepts used to characterize the composition of a mixture are the constituent mole fractions and mass fractions. Consider a multicomponent mixture of gases composed of N_1 moles of species 1, N_2 moles of species 2, etc. The **mole fraction of species *i***, χ_i, is defined as the fraction of the total number of moles in the system that are species i; i.e.,

$$\chi_i \equiv \frac{N_i}{N_1 + N_2 + \ldots N_i + \ldots} = \frac{N_i}{N_{\text{tot}}}. \tag{2.8}$$

Similarly, the **mass fraction of species *i***, Y_i, is the amount of mass of species i compared with the total mixture mass:

$$Y_i \equiv \frac{m_i}{m_1 + m_2 + \ldots m_i + \ldots} = \frac{m_i}{m_{\text{tot}}}. \tag{2.9}$$

Note that, by definition, the sum of all the constitutent mole (or mass) fractions must be unity, i.e.,

$$\sum_i \chi_i = 1 \tag{2.10a}$$

$$\sum_i Y_i = 1. \tag{2.10b}$$

Mole fractions and mass fractions are readily converted from one to another using the molecular weights of the species of interest and of the mixture:

$$Y_i = \chi_i MW_i / MW_{\text{mix}} \tag{2.11a}$$

$$\chi_i = Y_i MW_{\text{mix}} / MW_i. \tag{2.11b}$$

The **mixture molecular weight**, MW_{mix}, is easily calculated from a knowledge of either the species mole or mass fractions:

$$MW_{\text{mix}} = \sum_i \chi_i MW_i \tag{2.12a}$$

$$MW_{\text{mix}} = \frac{1}{\sum_i (Y_i / MW_i)}. \tag{2.12b}$$

Species mole fractions are also used to determine corresponding species partial pressures. The **partial pressure of the *i*th species**, P_i, is the pressure of the ith species if it were isolated from the mixture at the same temperature and volume as the mixture. For ideal gases, the mixture pressure is the sum of the constituent partial pressures:

$$P = \sum_i P_i. \tag{2.13}$$

The partial pressure can be related to the mixture composition and total pressure as

$$P_i = \chi_i P. \tag{2.14}$$

For ideal-gas mixtures, many **mass- (or molar-) specific mixture properties** are calculated simply as mass (or mole) fraction weighted sums of the individual species-specific properties. For example, mixture enthalpies are calculated as

$$h_{\text{mix}} = \sum_i Y_i h_i \tag{2.15a}$$

$$\bar{h}_{\text{mix}} = \sum_i \chi_i \bar{h}_i. \tag{2.15b}$$

Other frequently used properties that can be treated in this same manner are internal energies, u and $\bar{u}$. Note that, with our ideal-gas assumption, neither the pure-species properties (u_i, $\bar{u}_i$, h_i, $\bar{h}_i$) nor the mixture properties depend on pressure.

The mixture entropy also is calculated as a weighted sum of the constituents:

$$s_{\text{mix}}(T, P) = \sum_i Y_i s_i(T, P_i) \tag{2.16a}$$

$$\bar{s}_{\text{mix}}(T, P) = \sum_i \chi_i \bar{s}_i(T, P_i). \tag{2.16b}$$

In this case, however, the pure-species entropies (s_i and $\bar{s}_i$) depend on the species partial pressures as indicated in Eqn. 2.16. The constituent entropies in Eqn. 2.16 can be evaluated from standard-state ($P_{\text{ref}} \equiv P^o = 1$ atm) values as

$$s_i(T, P_i) = s_i(T, P_{\text{ref}}) - R \ln \frac{P_i}{P_{\text{ref}}} \tag{2.17a}$$

$$\bar{s}_i(T, P) = \bar{s}_i(T, P_{\text{ref}}) = R_u \ln \frac{P_i}{P_{\text{ref}}}. \tag{2.17b}$$

Standard-state molar specific entropies are tabulated in Appendix A for many species of interest to combustion.

Latent Heat of Vaporization

In many combustion processes, a liquid–vapor phase change is important. For example, a liquid fuel droplet must first vaporize before it can burn; and, if cooled sufficiently, water vapor can condense from combustion products. Formally, we define the **latent heat vaporization, h_{fg}**, as the heat required in a constant-pressure process to completely vaporize a unit mass of liquid at a given temperature, i.e.,

$$h_{fg}(T, P) \equiv h_{\text{vapor}}(T, P) - h_{\text{liquid}}(T, P), \tag{2.18}$$

where T and P are the corresponding saturation temperature and pressure, respectively. The latent heat of vaporization is also known as the **enthalpy of vaporization**. Latent heats of vaporization for various fuels at their normal (1 atm) boiling points are tabulated in Table B.1 (Appendix B).

The latent heat of vaporization at a given saturation temperature and pressure is frequently used with the **Clausius–Clapeyron equation** to estimate saturation pressure variation with temperature:

$$\frac{dP_{sat}}{P_{sat}} = \frac{h_{fg}}{R}\frac{dT_{sat}}{T_{sat}^2}. \tag{2.19}$$

This equation assumes that the specific volume of the liquid phase is negligible compared with that of the vapor and that the vapor behaves as an ideal gas. Assuming h_{fg} is constant, Eqn. 2.19 can be integrated from $(P_{sat,1}, T_{sat,1})$ to $(P_{sat,2}, T_{sat,2})$ in order to permit, for example, $P_{sat,2}$ to be estimated from a knowledge of $P_{sat,1}$, $T_{sat,1}$, and $T_{sat,2}$. We will employ this approach in our discussion of droplet evaporation (Chapter 3) and combustion (Chapter 10).

FIRST LAW OF THERMODYNAMICS

First Law—Fixed Mass

Conservation of energy is the fundamental principle embodied in the first law of thermodynamics. For a **fixed mass**, i.e., a **system**, (Fig. 2.3a), energy conservation is expressed for a finite change between two states, 1 and 2, as

$$\underset{\substack{\text{Head added to system in going from state 1 to state 2}}}{{}_1Q_2} - \underset{\substack{\text{Work done by system on surroundings in going from state 1 to state 2}}}{{}_1W_2} = \underset{\substack{\text{Change in total system energy in going from state 1 to state 2}}}{\Delta E_{1-2}} \tag{2.20}$$

Both ${}_1Q_2$ and ${}_1W_2$ are path functions and occur only at the system boundaries; $\Delta E_{1-2} (\equiv E_2 - E_1)$ is the change in the total energy of the system, which is the sum of the internal, kinetic, and potential energies, i.e.,

$$E = m\Big(\underset{\substack{\text{Mass-specific system internal energy}}}{u} + \underset{\substack{\text{Mass-specific system kinetic energy}}}{\tfrac{1}{2}v^2} + \underset{\substack{\text{Mass-specific system potential energy}}}{gz}\Big). \tag{2.21}$$

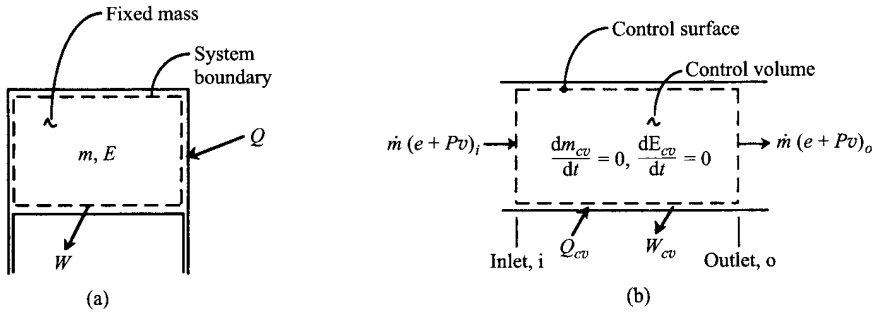


Figure 2.3 (a) Schematic of fixed-mass system with moving boundary above piston. (b) Control volume with fixed boundaries and steady flow.

The system energy is a state variable and, as such, ΔE does not depend on the path taken to execute a change in state. Equation 2.20 can be converted to unit mass basis or expressed to represent an instant in time. These forms are

$$ {}_1q_2 - {}_1w_2 = \Delta e_{1-2} = e_2 - e_1 \tag{2.22} $$

and

$$ \underset{\substack{\text{Instantaneous rate}\\ \text{of heat transferred}\\ \text{into system}}}{\dot{Q}} - \underset{\substack{\text{Instantaneous rate of}\\ \text{work done by system,}\\ \text{or power}}}{\dot{W}} = \underset{\substack{\text{Instantaneous time}\\ \text{rate of change of}\\ \text{system energy}}}{\mathrm{d}E/\mathrm{d}t} \tag{2.23} $$

or

$$ \dot{q} - \dot{w} = \mathrm{d}e/\mathrm{d}t, \tag{2.24} $$

where lower-case letters are used to denote mass-specific quantities, e.g., $e \equiv E/m$.

First Law—Control Volume

We next consider a control volume, illustrated in Fig. 2.3b, in which fluid may flow across the boundaries. The steady-state, steady-flow (SSSF) form of the first law is particularly useful for our purposes and should be reasonably familiar to you from previous studies of thermodynamics [2–4]. Because of its importance, however, we present a brief discussion here. The SSSF first law is expressed as

$$ \underset{\substack{\text{Rate of heat}\\ \text{transferred across}\\ \text{the control surface}\\ \text{from the surroundings,}\\ \text{to the control volume}}}{\dot{Q}_{cv}} - \underset{\substack{\text{Rate of all work}\\ \text{done by the control}\\ \text{volume, including}\\ \text{shaft work, but}\\ \text{excluding flow work}}}{\dot{W}_{cv}} = \underset{\substack{\text{Rate of energy}\\ \text{flowing out of the}\\ \text{control volume}}}{\dot{m}e_o} - \underset{\substack{\text{Rate of energy}\\ \text{flowing into the}\\ \text{control volume}}}{\dot{m}e_i} + \underset{\substack{\text{Net rate of work}\\ \text{associated with}\\ \text{pressure forces}\\ \text{where fluid crosses}\\ \text{the control surface,}\\ \text{flow work}}}{\dot{m}(P_o v_o - P_i v_i)}, \tag{2.25} $$

where the subscripts o and i denote the outlet and inlet, respectively, and $\dot{m}$ is the mass flowrate. Before rewriting Eqn. 2.25 in a more convenient form, it is appropriate to list the principal assumptions embodied in this relation:

1. *The control volume is fixed relative to the coordinate system.* This eliminates any work interactions associated with a moving boundary, as well as eliminating the need to consider changes in the kinetic and potential energies of the control volume itself.
2. *The properties of the fluid at each point within the control volume, or on the control surface, do not vary with time.* This assumption allows us to treat all processes as steady.

3. *Fluid properties are uniform over the inlet and outlet flow areas.* This allows us to use single values, rather than integrating over the area, for the inlet and exit stream properties.
4. *There is only one inlet and one exit stream.* This assumption is invoked to keep the final result in a simple form and can be easily relaxed to allow multiple inlet/exit streams.

The specific energy e of the inlet and outlet streams consists of the specific internal, kinetic, and potential energies, i.e.,

$$\underset{\substack{\text{Total energy}\\ \text{per unit mass}}}{e} = \underset{\substack{\text{Internal energy}\\ \text{per unit mass}}}{u} + \underset{\substack{\text{Kinetic energy}\\ \text{per unit mass}}}{\tfrac{1}{2}v^2} + \underset{\substack{\text{Potential energy}\\ \text{per unit mass}}}{gz}, \tag{2.26}$$

where v and z are the velocity and elevation, respectively, of the stream where it crosses the control surface.

The pressure–specific volume product terms associated with the flow work in Eq. 2.25 can be combined with the specific internal energy of Eqn. 2.26, which we recongize as the useful property, enthalpy:

$$h \equiv u + Pv = u + P/\rho. \tag{2.27}$$

Combining Eqns. 2.25–2.27, and rearranging, yields our final form of energy conservation for a control volume:

$$\dot{Q}_{cv} - \dot{W}_{cv} = \dot{m}\left[(h_o - h_i) + \tfrac{1}{2}(v_o^2 - v_i^2) + g(z_o - z_i)\right]. \tag{2.28}$$

The first law can also be expressed on a mass-specific basis by dividing Eqn. 2.28 by the mass flowrate $\dot{m}$, i.e.,

$$q_{cv} - w_{cv} = h_o - h_i + \tfrac{1}{2}(v_o^2 - v_i^2) + g(z_o - z_i). \tag{2.29}$$

In Chapter 7, we present more complete expressions of energy conservation that are subsequently simplified for our objectives in this book. For the time being, however, Eqn. 2.28 suits our needs.

REACTANT AND PRODUCT MIXTURES

Stoichiometry

The **stoichiometric** quantity of oxidizer is just that amount needed to completely burn a quantity of fuel. If more than a stoichiometric quantity of oxidizer is supplied, the mixture is said to be fuel lean, or just **lean**; while supplying less than the stoichiometric oxidizer results in a fuel-rich, or **rich** mixture. The stoichiometric oxidizer– (or air–) fuel ratio (mass) is determined by writing simple atom balances, assuming that the fuel reacts to form an ideal

set of products. For a hydrocarbon fuel given by C_xH_y, the stoichiometric relation can be expressed as

$$C_xH_y + a(O_2 + 3.76N_2) \rightarrow xCO_2 + (y/2)H_2O + 3.76aN_2, \tag{2.30}$$

where

$$a = x + y/4. \tag{2.31}$$

For simplicity, we assume throughout this book that the simplified composition for air is 21 percent O_2 and 79 percent N_2 (by volume), i.e., that for each mole of O_2 in air, there are 3.76 moles of N_2.

The **stoichiometric air–fuel ratio** can be found as

$$(A/F)_{\text{stoic}} = \left(\frac{m_{\text{air}}}{m_{\text{fuel}}}\right)_{\text{stoic}} = \frac{4.76a}{1}\frac{MW_{\text{air}}}{MW_{\text{fuel}}}, \tag{2.32}$$

where MW_{air} and MW_{fuel} are the molecular weights of the air and fuel, respectively. Table 2.1 shows stoichiometric air–fuel ratios for methane and solid carbon. Also shown is the oxygen–fuel ratio for combusion of H_2 in pure O_2. For all of these systems, we see that there is many times more oxidizer than fuel.

Table 2.1 Some combustion properties of methane, hydrogen, and solid carbon for reactants at 298 K

	Δh_R (kJ/kg$_{\text{fuel}}$)	Δh_R (kJ/kg$_{\text{mix}}$)	$(O/F)_{\text{stoic}}$[a] (kg/kg)	$T_{ad,eq}$ (K)
CH_4 + air	−55,528	−3,066	17.11	2,226
$H_2 + O_2$	−142,919	−15,880	8.0	3,079
C(s) + air	−32,794	−2,645	11.4	2,301

[a] O/F is the oxidizer–fuel ratio, where for combustion with air, the air is the oxidizer not just the oxygen in the air.

The **equivalence ratio, Φ**, is commonly used to indicate quantitatively whether a fuel–oxidizer mixture is rich, lean, or stoichometric. The equivalence ratio is defined as

$$\Phi = \frac{(A/F)_{\text{stoic}}}{(A/F)} = \frac{(F/A)}{(F/A)_{\text{stoic}}} \tag{2.33a}$$

From this definition, we see that for fuel-rich mixtures, $\Phi > 1$, and for fuel-lean mixtures, $\Phi < 1$. For a stoichiometric mixture, Φ equals unity. In many combustion applications, the equivalence ratio is the single most important factor in determining a system's performance. Other parameters frequently used to define relative stoichiometry are **percent stoichiometric air**, which relates to the equivalence ratio as

$$\% \text{ stoichometric air} = \frac{100\%}{\Phi} \tag{2.33b}$$

and **percent excess air**, or

$$\% \text{ excess air} = \frac{(1-\Phi)}{\Phi} \cdot 100\%. \tag{2.33c}$$

Example 2.1

A small, low-emission, stationary gas-turbine engine (see Fig. 2.4) operates at full load (3950 kW) at an equivalence ratio of 0.286 with an air flowrate of 15.9 kg/s. The equivalent composition of the fuel (natural gas) is $C_{1.16}H_{4.32}$. Determine the fuel mass flowrate and the operating air–fuel ratio for the engine.

Solution

Given: $\Phi = 0.286$, $MW_{air} = 28.85$,
$\dot{m}_{air} = 15.9\,\text{kg/s}$, $MW_{fuel} = 1.16(12.01) + 4.32(1.008) = 18.286$
Find: $\dot{m}_{fuel}$ and (A/F).

We will proceed by first finding (A/F) and then $\dot{m}_{fuel}$. The solution requires only the application of definitions expressed in Eqns. 2.32 and 2.33, i.e.,

$$(A/F)_{stoic} = 4.76a \frac{MW_{air}}{MW_{fuel}},$$

where $a = x + y/4 = 1.16 + 4.32/4 = 2.24$. Thus,

$$(A/F)_{stoic} = 4.76\,(2.24)\,\frac{28.85}{18.286} = 16.82,$$

and, from Eqn. 2.33,

$$\boxed{(A/F)} = \frac{(A/F)_{stoic}}{\Phi} = \frac{16.82}{0.286} = \boxed{58.8}$$

Since (A/F) is the ratio of the air flowrate to the fuel flowrate,

$$\boxed{\dot{m}_{fuel}} = \frac{\dot{m}_{air}}{(A/F)} = \frac{15.9\,\text{kg/s}}{58.8} = \boxed{0.270\,\text{kg/s}}$$

Comment

Note that even at full power, a large quantity of excess air is supplied to the engine.

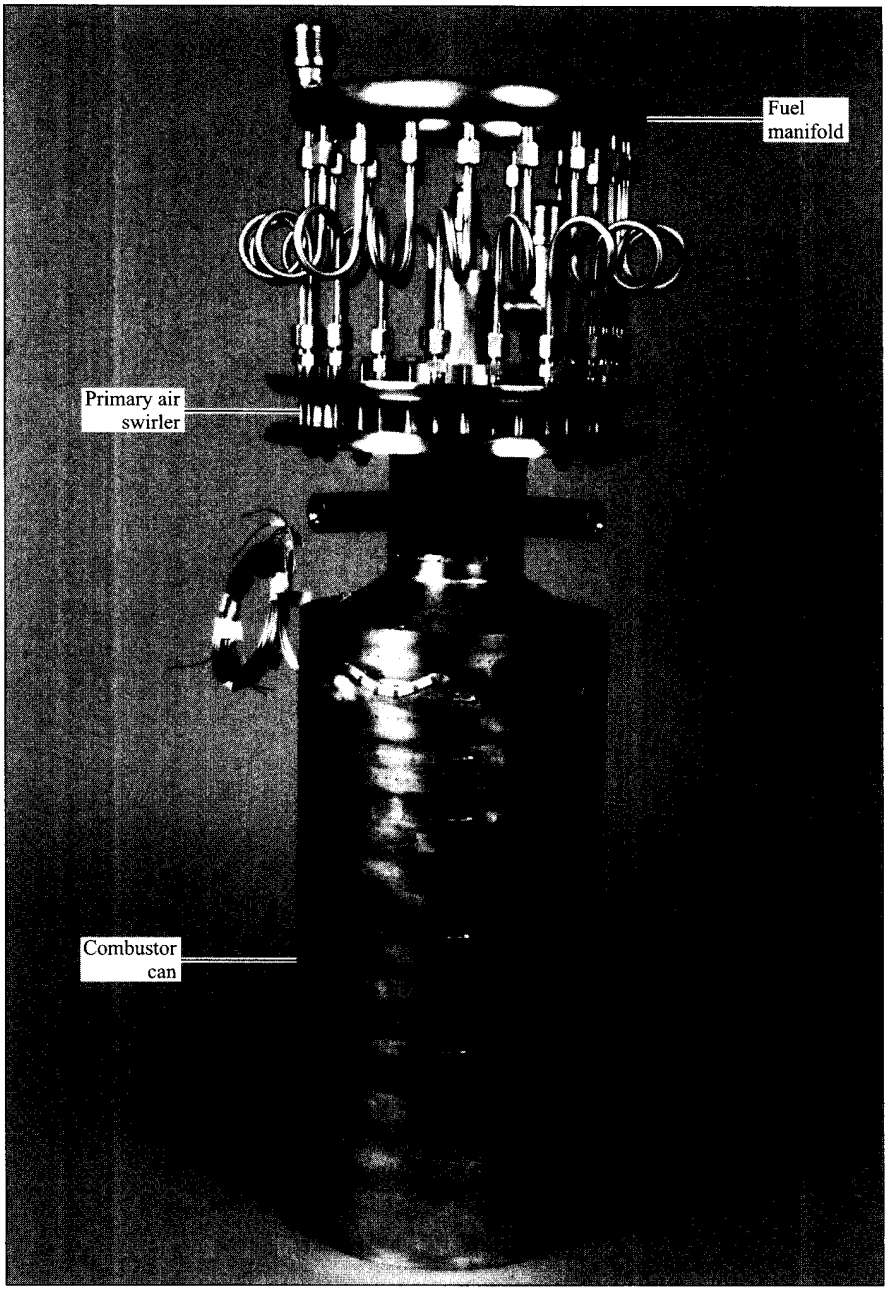
Example 2.2

A natural gas-fired industrial boiler (see Fig. 2.5) operates with an oxygen concentration of 3 mole percent in the flue gases. Determine the operating air–fuel ratio and the equivalence ratio. Treat the natural gas as methane.

Solution

Given: $\chi_{O_2} = 0.03$, $MW_{fuel} = 16.04$,
$MW_{air} = 28.85$.
Find: (A/F) and Φ.

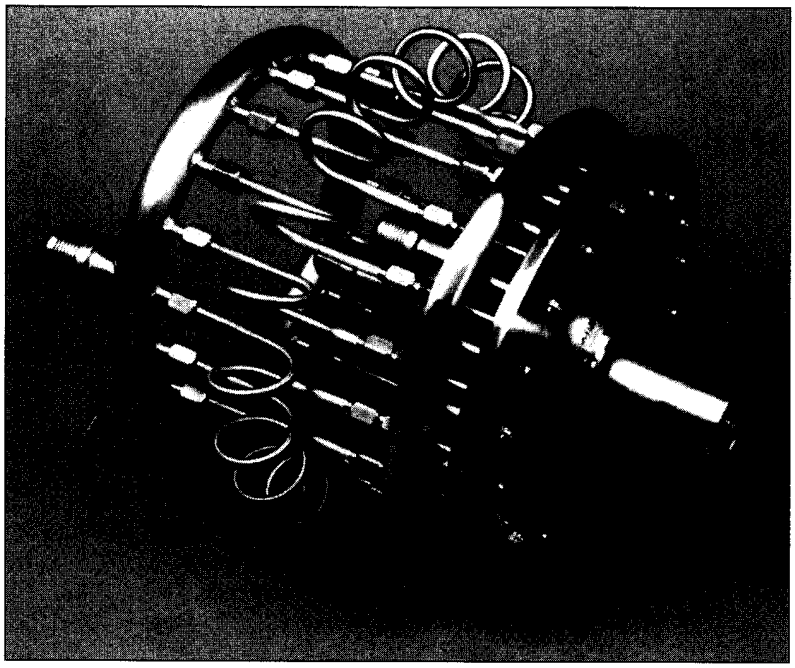
We can use the given O_2 mole fraction to find the air–fuel ratio by writing an overall combustion equation assuming "complete combustion," i.e., no dissociation (all fuel C is found in CO_2 and all fuel H is found in H_2O):



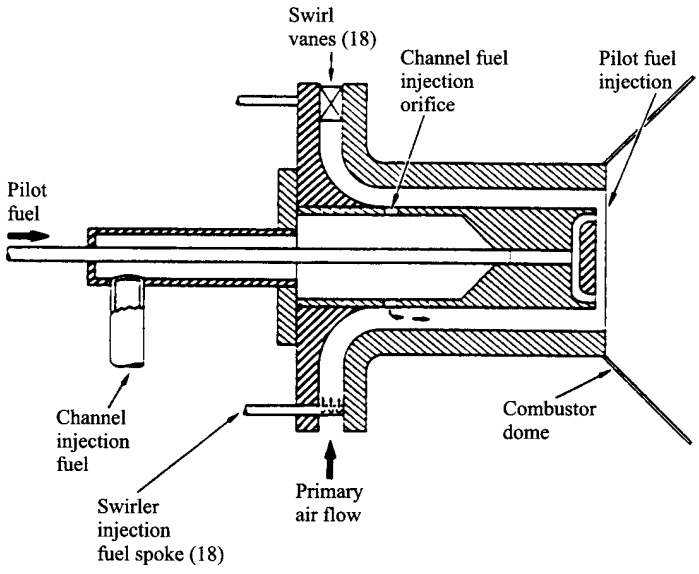
(a)

Figure 2.4 (a) Experimental low-NO_x gas-turbine combustor can and (b)(c) fuel and air mixing system. Eight cans are used in a 3950-kW engine.

SOURCE: Copyright © 1987, Electric Power Research Institute, EPRI AP-5347, NO_x *Reduction for Small Gas Turbine Power Plants;* reprinted with permission.



(b)


Swirl
vanes (18)
Channel fuel
injection
orifice
Pilot fuel
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air flow
Combustor
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(c)

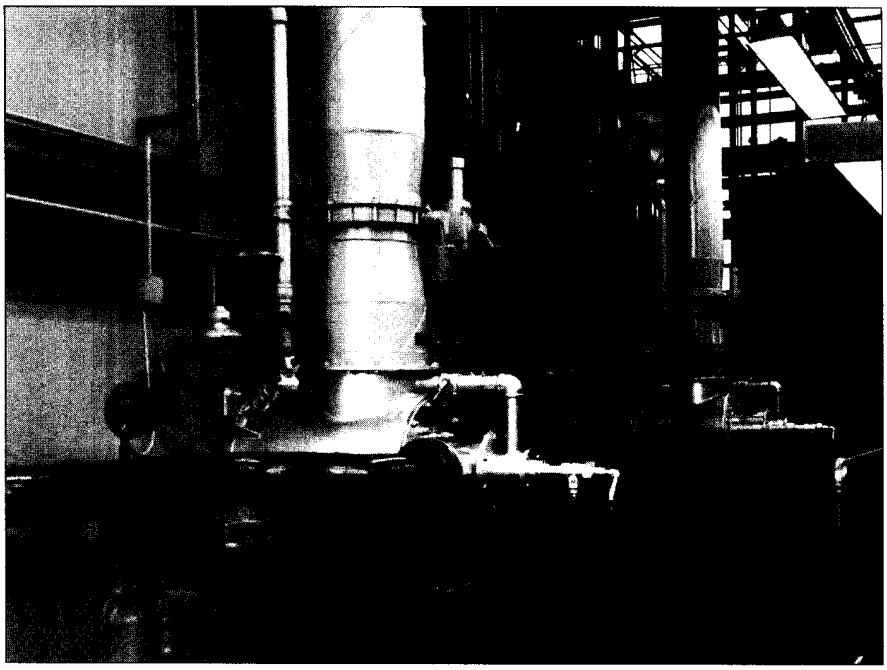

Figure 2.5 Two 10-MW (34 million BTU/hr) natural-gas burners fire into a boiler combustion chamber 3 m deep. Air enters the burners through the large vertical pipes, while the natural gas enters through the horizontal pipe on the left.
SOURCE: Courtesy of North American Manufacturing Co.

$$CH_4 + a(O_2 + 3.76\,N_2) \rightarrow CO_2 + 2H_2O + b\,O_2 + 3.76a\,N_2,$$

where a and b are related from conservation of O atoms,

$$2a = 2 + 2 + 2b$$

or

$$b = a - 2.$$

From the definition of a mole fraction (Eqn. 2.8),

$$\chi_{O_2} = \frac{N_{O_2}}{N_{mix}} = \frac{b}{1 + 2 + b + 3.76a} = \frac{a - 2}{1 + 4.76a}.$$

Substituting the known value of $\chi_{O_2}(= 0.03)$ and then solving for a yields

$$0.03 = \frac{a - 2}{1 + 4.76a}$$

or

$$a = 2.368.$$

The mass air–fuel ratio, in general, is expressed as

$$(A/F) = \frac{N_{\text{air}}}{N_{\text{fuel}}} \frac{MW_{\text{air}}}{MW_{\text{fuel}}},$$

so

$$(A/F) = \frac{4.76a}{1} \frac{MW_{\text{air}}}{MW_{\text{fuel}}}$$

$$\boxed{(A/F)} = \frac{4.76(2.368)(28.85)}{16.04} = \boxed{20.3}$$

To find Φ, we need to determine $(A/F)_{\text{stoic}}$. From Eq. 2.31, $a = 2$; hence,

$$(A/F)_{\text{stoic}} = \frac{4.76(2)28.85}{16.04} = 17.1$$

Applying the definition of Φ (Eqn. 2.33),

$$\boxed{\Phi} = \frac{(A/F)_{\text{stoic}}}{(A/F)} = \frac{17.1}{20.3} = \boxed{0.84}$$

Comment

In the solution, we assumed that the O_2 mole fraction was on a "wet basis," i.e., moles of O_2 per mole of moisture-containing flue gases. Frequently, in the measurement of exhaust species, moisture is removed to prevent condensation in the analyzers; thus, χ_{O_2} can also be reported on a "dry basis" (see Chapter 15).

Absolute (or Standardized) Enthalpy and Enthalpy of Formation

In dealing with chemically reacting systems, the concept of absolute enthalpies is extremely valuable. For any species, we can define an **absolute (or standardized) enthalpy** that is the sum of an enthalpy that takes into account the energy associated with chemical bonds (or lack thereof), the **enthalpy of formation, h_f,** and an enthalpy that is associated only with the temperature, the **sensible enthalpy change, Δh_s.** Thus, we can write the molar absolute enthalpy for species i as

$$\underset{\substack{\text{Absolute enthalpy}\\ \text{at temperature T}}}{\bar{h}_i(T)} = \underset{\substack{\text{Enthalpy of formation}\\ \text{at standard reference}\\ \text{state } (T_{\text{ref}}, P^o)}}{\bar{h}^o_{f,i}(T_{\text{ref}})} + \underset{\substack{\text{Sensible enthalpy}\\ \text{change in going from}\\ T_{\text{ref}} \text{ to } T}}{\Delta\bar{h}_{s,i}(T_{\text{ref}})}, \qquad (2.34)$$

where $\Delta\bar{h}_{s,i} \equiv \bar{h}_i(T) - \bar{h}^o_{f,i}(T_{\text{ref}})$.

To make practical use of Eqn. 2.34, it is necessary to define a **standard reference state.** We employ a standard-state temperature, $T_{\text{ref}} = 25°\text{C}$ (298.15 K), and standard-state pressure, $P_{\text{ref}} = P^o = 1$ atm (101,325 Pa), consistent with the Chemkin [1] and NASA [5] thermodynamic databases. Furthermore, we adopt the convention that enthalpies of formation are zero for the elements in their naturally occurring state at the reference state

temperature and pressure. For example, at 25°C and 1 atm, oxygen exists as diatomic molecules; hence,

$$(\bar{h}^o_{f,O_2})_{298} = 0,$$

where the superscript o is used to denote that the value is for the standard-state pressure.

To form oxygen atoms at the standard state requires the breaking of a rather strong chemical bond. The bond dissociation energy for O_2 at 298 K is 498,390 $kJ/kmol_{O_2}$. Breaking this bond creates two O atoms; thus, the enthalpy of formation for atomic oxygen is half the value of the O_2 bond dissociation energy, i.e.,

$$(\bar{h}^o_{f,O}) = 249{,}195\,kJ/kmol_O.$$

Thus, enthalpies of formation have a clear physical interpretation as the net change in enthalpy associated with breaking the chemical bonds of the standard state elements and forming new bonds to create the compound of interest.

Representing the absolute enthalpy graphically provides a useful way to understand and use this concept. In Fig. 2.6, the absolute enthalpies of atomic oxygen (O) and diatomic oxygen (O_2) are plotted versus temperature starting from absolute zero. At 298.15 K, we see that $\bar{h}_{O_2}$ is zero (by definition of the standard-state reference condition) and the absolute enthalpy of atomic oxygen equals its enthalpy of formation, since the sensible enthalpy at 298.15 K is zero. At the temperature indicated (4000 K), we see the additional sensible enthalpy contribution to the absolute enthalpy. In Appendix A, enthalpies of formation

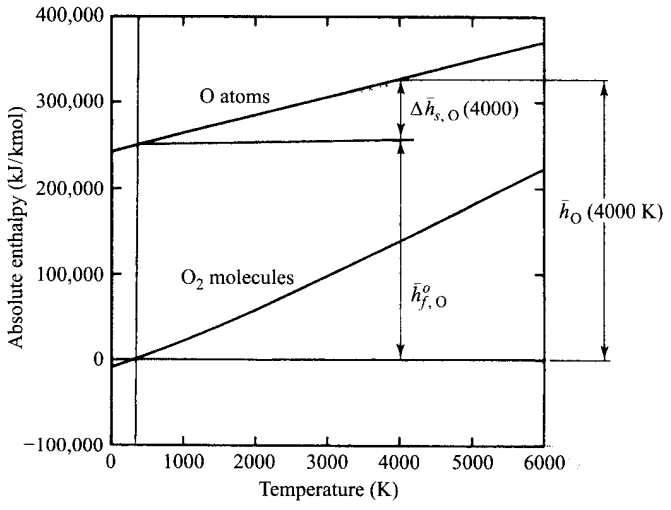

Figure 2.6 Graphical interpretation of absolute enthalpy, heat of formation, and sensible enthalpy.

at the reference state are given, and sensible enthalpies are tabulated as a function of temperature for a number of species of importance in combustion. Enthalpies of formation for reference temperatures other than the standard state 298.15 K are also tabulated.

Example 2.3

A gas stream at 1 atm contains a mixture of CO, CO_2, and N_2 in which the CO mole fraction is 0.10 and the CO_2 mole fraction is 0.20. The gas-stream temperature is 1200 K. Determine the absolute enthalpy of the mixture on both a mole basis (kJ/kmol) and a mass basis (kJ/kg). Also determine the mass fractions of the three component gases.

Solution

Given: $\chi_{CO} = 0.10$, $T = 1200\,\text{K}$,
$\chi_{CO_2} = 0.20$, $P = 1\,\text{atm}$.

Find: $\bar{h}_{mix}$, h_{mix}, Y_{CO}, Y_{CO_2}, and Y_{N_2}.

Finding $\bar{h}_{mix}$ requires the straightforward application of the ideal-gas mixture law, Eqn. 2.15, and, to find χ_{N_2}, the knowledge that $\Sigma\chi_i = 1$ (Eqn. 2.10). Thus,

$$\chi_{N_2} = 1 - \chi_{CO_2} = 0.70$$

and

$$\begin{aligned}\bar{h}_{mix} &= \Sigma\chi_i\bar{h}_i \\ &= \chi_{CO}\left[\bar{h}^o_{f,CO} + (\bar{h}(T) - \bar{h}^o_{f,298})_{CO}\right] \\ &\quad + \chi_{CO_2}\left[\bar{h}^o_{f,CO_2} + (\bar{h}(T) - \bar{h}^o_{f,298})_{CO_2}\right] \\ &\quad + \chi_{N_2}\left[\bar{h}^o_{f,N_2} + (\bar{h}(T) - \bar{h}^o_{f,298})_{N_2}\right].\end{aligned}$$

Substituting values from Appendix A (Table A.1 for CO, Table A.2 for CO_2, and Table A.7 for N_2):

$$\begin{aligned}\bar{h}_{mix} &= 0.10[-110{,}541 + 28{,}440] \\ &\quad + 0.20[-393{,}546 + 44{,}488] \\ &\quad + 0.70[0 + 28{,}118] \\ \boxed{\bar{h}_{mix} &= -58{,}339.1\,\text{kJ/kmol}_{mix}}\end{aligned}$$

To find h_{mix}, we need to determine the molecular weight of the mixture:

$$\begin{aligned}MW_{mix} &= \Sigma\chi_i MW_i \\ &= 0.10(28.01) + 0.20(44.01) + 0.70(28.013) \\ &= 31.212.\end{aligned}$$

Then,

$$\boxed{h_{mix}} = \frac{\bar{h}_{mix}}{MW_{mix}} = \frac{-58{,}339.1}{31.212} = \boxed{-1869.12\,\text{kJ/kg}_{mix}}$$

Since we have previously found MW_{mix}, calculation of the individual mass fractions follows simply from their definitions (Eqn. 2.11):

$$Y_{CO} = 0.10 \frac{28.01}{31.212} = 0.0897$$
$$Y_{CO_2} = 0.20 \frac{44.01}{31.212} = 0.2820$$
$$Y_{N_2} = 0.70 \frac{28.013}{31.212} = 0.6282$$

As a check, we see that $0.0897 + 0.2820 + 0.6282 = 1.000$, as required.

Comment

Both molar and mass units are frequently used in combustion. Because of this, you should be quite comfortable with their interconversions.

Enthalpy of Combustion and Heating Values

Knowing how to express the enthalpy for mixtures of reactants and mixtures of products allows us to define the enthalpy of reaction, or, when dealing specifically with combustion reactions, the enthalpy of combustion. Consider the steady-flow reactor, shown in Fig. 2.7, in which a stoichiometric mixture of reactants enters and products exits, both at standard-state conditions (25°C, 1 atm). The combustion process is assumed to be complete, i.e., all of the fuel carbon is converted to CO_2 and all of the fuel hydrogen is converted to H_2O. For the products to exit at the same temperature as the entering reactants, heat must be removed from the reactor. The amount of heat removed can be related to the reactant and product absolute enthalpies by applying the steady-flow form of the first law (Eqn. 2.29):

$$q_{cv} = h_o - h_i = h_{prod} - h_{reac}. \tag{2.35}$$

The definition of the **enthalpy of reaction**, or the **enthalpy of combustion**, Δh_R (per mass of mixture), is

$$\Delta h_R \equiv q_{cv} = h_{prod} - h_{reac}, \tag{2.36a}$$

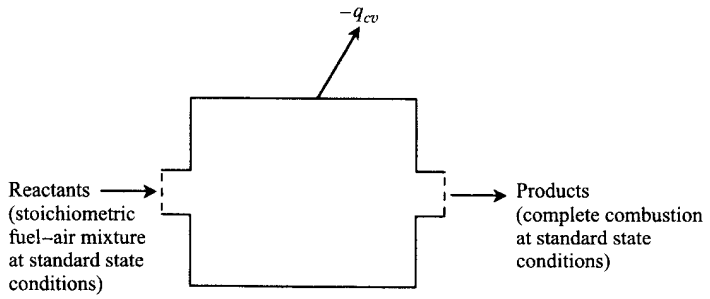

Figure 2.7 Steady-flow reactor used to determine enthalpy of combustion.

or, in terms of extensive properties,

$$\Delta H_R = H_{\text{prod}} - H_{\text{reac}}. \tag{2.36b}$$

The enthalpy of combustion can be illustrated graphically, as shown in Fig. 2.8. Consistent with the heat transfer being negative, the absolute enthalpy of the products lies below that of the reactants. For example, at 25°C and 1 atm, the reactants enthalpy of a stoichiometric mixture of CH_4 and air, where 1 kmol of fuel reacts, is −74,831 kJ. At the same conditions (25°C, 1 atm), the combustion products have an absolute enthalpy of −877,236 kJ. Thus,

$$\Delta H_R = -877{,}236 - (-74{,}831) = -802{,}405\,\text{kJ}.$$

This value can be adjusted to a per-mass-of-fuel basis:

$$\Delta h_R\left(\frac{\text{kJ}}{\text{kg}_{\text{fuel}}}\right) = \Delta H_R / MW_{\text{fuel}} \tag{2.37}$$

or

$$\Delta h_R\left(\frac{\text{kJ}}{\text{kg}_{\text{fuel}}}\right) = (-802{,}405/16.043) = -50{,}016.$$

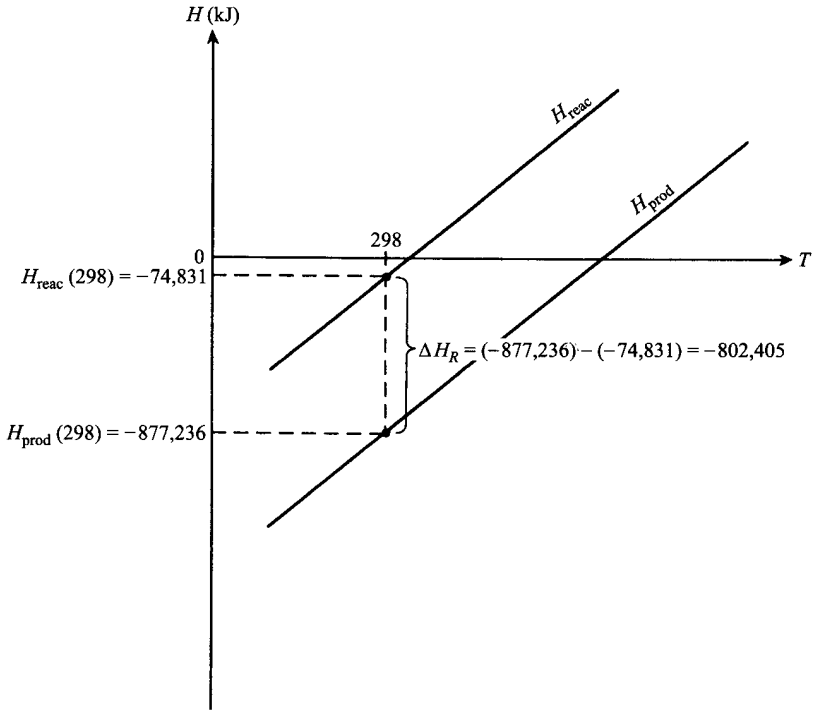

Figure 2.8 Enthalpy of reaction using representative values for a stoichiometric methane–air mixture. The water in the products is assumed to be in the vapor state.

This value can, in turn, be converted to a per-unit-mass-of-mixture basis:

$$\Delta h_R\left(\frac{\text{kJ}}{\text{kg}_{\text{mix}}}\right) = \Delta h_R\left(\frac{\text{kJ}}{\text{kg}_{\text{fuel}}}\right)\frac{m_{\text{fuel}}}{m_{\text{mix}}}, \tag{2.38}$$

where

$$\frac{m_{\text{fuel}}}{m_{\text{mix}}} = \frac{m_{\text{fuel}}}{m_{\text{air}} + m_{\text{fuel}}} = \frac{1}{(A/F) + 1}. \tag{2.39}$$

From Table 2.1, we see that the stoichiometric air–fuel ratio for CH_4 is 17.11; thus,

$$\Delta h_R\left(\frac{\text{kJ}}{\text{kg}_{\text{mix}}}\right) = \frac{-50{,}016}{17.11 + 1} = -2761.8.$$

Note that the value of the enthalpy of combustion depends on the temperature chosen for its evaluation since the enthalpies of both the reactants and products vary with temperature; i.e., the distance between the H_{prod} and H_{reac} lines in Fig. 2.8 is not constant.

The **heat of combustion**, Δh_c (known also as the **heating value**), is numerically equal to the enthalpy of reaction, but with opposite sign. The **upper** or **higher heating value, HHV**, is the heat of combustion calculated assuming that all of the water in the products has condensed to liquid. This scenario liberates the most amount of energy, hence the designation "upper." The **lower heating value, LHV**, corresponds to the case where none of the water is assumed to condense. For CH_4, the upper heating value is approximately 11 percent larger than the lower. Standard-state heating values for a variety of hydrocarbon fuels are given in Appendix B.

Example 2.4

A. Determine the upper and lower heating values at 298 K of gaseous *n*-decane, $C_{10}H_{22}$, per kilomole of fuel and per kilogram of fuel. The molecular weight of *n*-decane is 142.284.

B. If the enthalpy of vaporization of *n*-decane is 359 $\text{kJ/kg}_{\text{fuel}}$ at 298 K, what are the upper and lower heating values of liquid *n*-decane?

Solution

A. For 1 mole of $C_{10}H_{22}$, the combustion equation can be written as

$$C_{10}H_{22}(\text{g}) + 15.5(O_2 + 3.76N_2) \rightarrow 10CO_2 + 11H_2O(\text{l or g}) + 15.5(3.76)N_2.$$

For either the upper or lower heating value,

$$\Delta H_c = -\Delta H_R = H_{\text{reac}} - H_{\text{prod}},$$

where the numerical value of H_{prod} depends on whether the H_2O in the products is liquid (determining higher heating value) or gaseous (determining lower heating value). The sensible enthalpies for all species involved are zero since we desire ΔH_c at the reference state (298 K). Furthermore, the enthalpies of formation of the O_2 and N_2 are also zero at 298 K. Recognizing that

$$H_{\text{reac}} = \sum_{\text{reac}} N_i \bar{h}_i \qquad \text{and} \qquad H_{\text{prod}} = \sum_{\text{prod}} N_i \bar{h}_i,$$

we obtain

$$\Delta H_{c,H_2O(l)} = \text{HHV} = (1)\bar{h}^o_{f,C_{10}H_{22}} - \left[10\bar{h}^o_{f,CO_2} + 11\bar{h}^o_{f,H_2O(l)}\right].$$

Table A.6 (Appendix A) gives the enthalpy of formation for gaseous water and the enthalpy of vaporization. With these values, we can calculate the enthalpy of formation for the liquid water (Eqn. 2.18):

$$\bar{h}^o_{f,H_2O(l)} = \bar{h}^o_{f,H_2O(g)} - \bar{h}_{fg} = -241{,}847 - 44{,}010 = -285{,}857\,\text{kJ/kmol}.$$

Using this value, together with enthalpies of formation given in Appendices A and B, we obtain the higher heating value:

$$\begin{aligned}\Delta H_{c,H_2O,(l)} &= (1)\left(-249{,}659\,\frac{\text{kJ}}{\text{kmol}}\right) \\ &\quad - \left[10\left(-393{,}546\,\frac{\text{kJ}}{\text{kmol}}\right) + 11\left(-285{,}857\,\frac{\text{kJ}}{\text{kmol}}\right)\right] \\ &= 6{,}830{,}096\,\text{kJ}\end{aligned}$$

and

$$\boxed{\Delta\bar{h}_c = \frac{\Delta H_c}{N_{C_{10}H_{22}}} = \frac{6{,}830{,}096\ \text{kJ}}{1\,\text{kmol}} = 6{,}830{,}096\,\text{kJ/kmol}_{C_{10}H_{22}}}$$

or

$$\boxed{\Delta h_c = \frac{\Delta\bar{h}_c}{MW_{C_{10}H_{22}}} = \frac{6{,}830{,}096\ \frac{\text{kJ}}{\text{kmol}}}{142.284\ \frac{\text{kg}}{\text{kmol}}} = 48{,}003\,\text{kJ/kg}_{C_{10}H_{22}}}$$

For the lower heating value, we use $\bar{h}^o_{f,H_2O(g)} = -241{,}847\,\text{kJ/kmol}$ in place of $\bar{h}^o_{f,H_2O(l)} = -285{,}857\,\text{kJ/kmol}$. Thus,

$$\boxed{\Delta\bar{h}_c = 6{,}345{,}986\,\text{kJ/kmol}_{C_{10}H_{22}}}$$

or

$$\boxed{\Delta h_c = 44{,}601\,\text{kJ/kg}_{C_{10}H_{22}}}$$

B. For $C_{10}H_{22}$, in the liquid state,

$$H_{\text{reac}} = (1)\left(\bar{h}^o_{f,C_{10}H_{22}(g)} - \bar{h}_{fg}\right),$$

or

$$\Delta h_c\left(\begin{matrix}\text{liquid}\\ \text{fuel}\end{matrix}\right) = \Delta h_c\left(\begin{matrix}\text{gaseous}\\ \text{fuel}\end{matrix}\right) - h_{fg}.$$

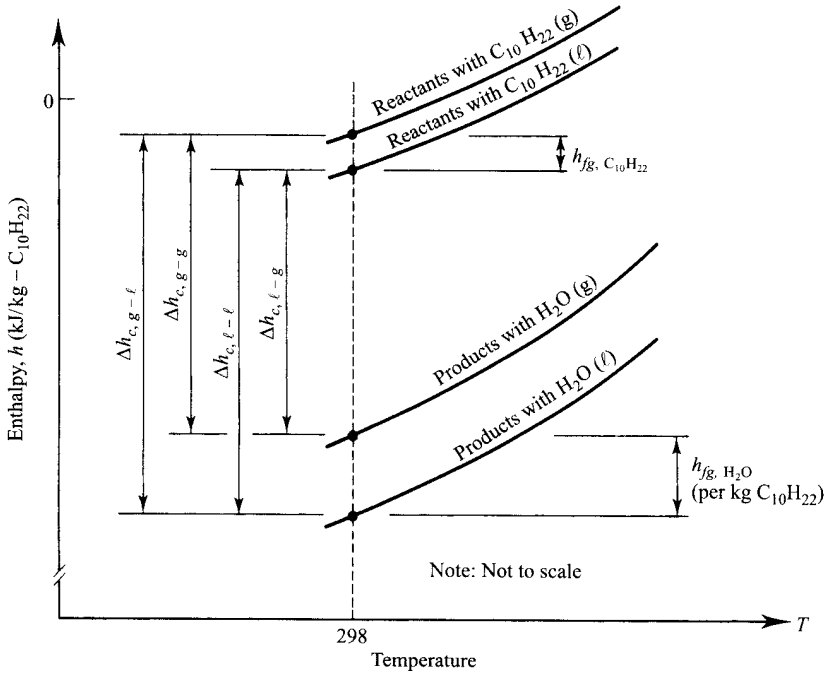

Figure 2.9 Enthalpy–temperature plot illustrating calculation of heating values in Example 2.4.

Thus,

$$\Delta h_c \text{ (higher)} = 48{,}003 - 359 = 47{,}644\ \text{kJ/kg}_{C_{10}H_{22}}$$

$$\Delta h_c \text{ (lower)} = 44{,}601 - 359 = 44{,}242\ \text{kJ/kg}_{C_{10}H_{22}}$$

Comment

Graphical representations of the various definitions and/or thermodynamic processes are valuable aids in setting up problems or in checking their solutions. Figure 2.9 illustrates, on h–T coordinates, the important quantities used in this example. Note that the enthalpy of vaporization given for n-decane is for the standard-state temperature (298.15 K), while the value given in Appendix B is at the boiling point (447.4 K).

ADIABATIC FLAME TEMPERATURES

We define two adiabatic flame temperatures: one for constant-pressure combustion and one for constant-volume. If a fuel–air mixture burns adiabatically at constant pressure, the absolute enthalpy of the reactants at the initial state (say, $T = 298\,\text{K}$, $P = 1\,\text{atm}$) equals the absolute enthalpy of the products at the final state ($T = T_{ad}$, $P = 1\,\text{atm}$), i.e., application of Eqn. 2.28 results in

$$H_{\text{reac}}(T_i, P) = H_{\text{prod}}(T_{ad}, P), \tag{2.40a}$$

or, equivalently, on a per-mass-of-mixture basis,

$$h_{\text{reac}}(T_i, P) = h_{\text{prod}}(T_{ad}, P). \tag{2.40b}$$

This first-law statement, Eqn. 2.40, defines what is called the **constant-pressure adiabatic flame temperature**. This definition is illustrated graphically in Fig. 2.10. Conceptually, the adiabatic flame temperature is simple; however, evaluating this quantity requires knowledge of the composition of the combustion products. At typical flame temperatures, the products dissociate and the

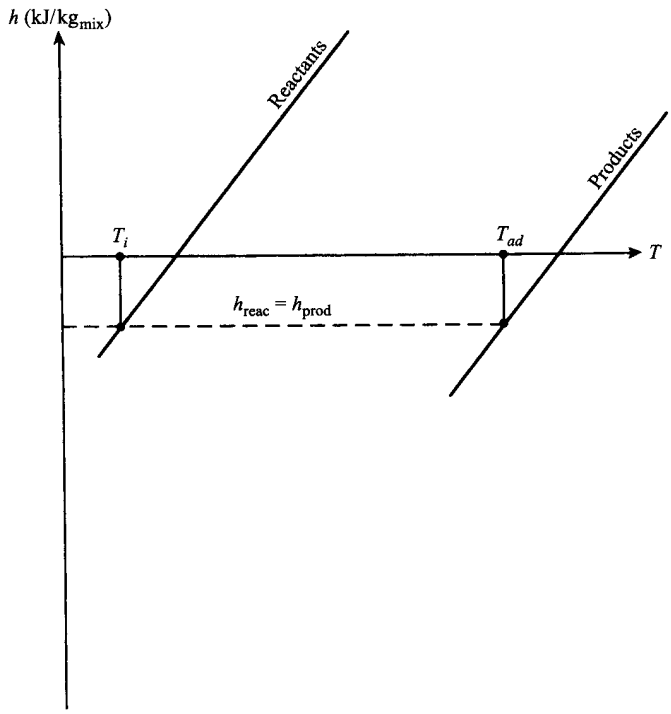

Figure 2.10 Illustration of constant-pressure adiabatic flame temperature on h–T coordinates.

mixture comprises many species. As shown in Table 2.1 and Table B.1 in Appendix B, flame temperatures are typically several thousand kelvins. Calculating the complex composition by invoking chemical equilibrium is the subject of the next section. The following example illustrates the fundamental concept of constant-pressure adiabatic flame temperatures, while making crude assumptions regarding the product mixture composition and evaluation of the product mixture enthalpy.

Example 2.5

Estimate the constant-pressure adiabatic flame temperature for the combustion of a stoichiometric CH_4–air mixture. The pressure is 1 atm and the initial reactant temperature is 298 K.

Use the following assumptions:

1. "Complete combustion" (no dissociation), i.e., the product mixture consists of only CO_2, H_2O, and N_2.
2. The product mixture enthalpy is estimated using constant specific heats evaluated at 1200 K ($\approx 0.5(T_i + T_{ad})$, where T_{ad} is guessed to be about 2100 K).

Solution

Mixture composition:

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow 1\,CO_2 + 2H_2O + 7.52N_2$$

$$N_{CO_2} = 1,\ N_{H_2O} = 2,\ N_{N_2} = 7.52.$$

Properties (Appendices A and B):

Species	Enthalpy of Formation @ 298 K $\bar{h}^o_{f,i}$ (kJ/kmol)	Specific Heat @ 1200 K $\bar{c}_{p,i}$ (kJ/kmol-K)
CH_4	−74,831	—
CO_2	−393,546	56.21
H_2O	−241,845	43.87
N_2	0	33.71
O_2	0	—

First law (Eqn. 2.40):

$$H_{\text{react}} = \sum_{\text{react}} N_i \bar{h}_i = H_{\text{prod}} = \sum_{\text{prod}} N_i \bar{h}_i$$

$$H_{\text{react}} = (1)(-74{,}831) + 2(0) + 7.52(0)$$
$$= -74{,}831\ \text{kJ}$$

$$H_{\text{prod}} = \sum N_i[\bar{h}^o_{f,i} + \bar{c}_{p,i}(T_{ad} - 298)]$$
$$= (1)[-393{,}546 + 56.21(T_{ad} - 298)]$$
$$+ (2)[-241{,}845 + 43.87(T_{ad} - 298)]$$
$$+ (7.52)[0 + 33.71(T_{ad} - 298)].$$

Equating H_{react} to H_{prod} and solving for T_{ad} yields

$$\boxed{T_{ad} = 2318\ \text{K}}$$

Comments

Comparing the above result with the equilibrium-composition based computation shown in Table 2.1 ($T_{ad,eq} = 2226\,\text{K}$) shows that the simplified approach overestimates T_{ad} by slightly less than 100 K. Considering the crudeness of the assumptions, this appears to be rather surprisingly good agreement. Removing assumption 2 and re-calculating T_{ad} using variable specific heats, i.e.,

$$\bar{h}_i = \bar{h}^o_{f,i} + \int_{298}^{T} \bar{c}_{p,i}\, \mathrm{d}T,$$

yields $T_{ad} = 2328\,\text{K}$. (Note that Appendix A provides tabulations of these integrated quantities. Similar tabulations are found in the JANAF tables [6].) Since this result is quite close to our constant-c_p solution, we conclude that the $\sim 100\,\text{K}$ difference is the result of neglecting dissociation. Note that dissociation causes a lowering of T_{ad} since more energy is tied up in chemical bonds (enthalpies of formation) at the expense of the sensible enthalpy.

In the above, we dealt with a constant-pressure system, which would be appropriate in dealing with a gas-turbine combustor, or a furnace. Let us look now at **constant-volume adiabatic flame temperatures**, which we might require in an ideal Otto-cycle analysis, for example. The first law of thermodynamics (Eqn. 2.20) requires

$$U_{\text{reac}}(T_{\text{init}}, P_{\text{init}}) = U_{\text{prod}}(T_{ad}, P_f), \tag{2.41}$$

where U is the absolute (or standardized) internal energy of the mixture. Graphically, Eqn. 2.41 resembles the sketch (Fig. 2.10) used to illustrate the constant-pressure adiabatic flame temperature, except the internal energy replaces the enthalpy. Since most compilations or calculations of thermodynamic properties provide values for H (or h) rather than U (or u) [1, 6], we can rearrange Eqn. 2.41 to the following form:

$$H_{\text{reac}} - H_{\text{prod}} - V(P_{\text{init}} - P_f) = 0. \tag{2.42}$$

We can apply the ideal-gas law to eliminate the PV terms:

$$P_{\text{init}} V = \sum_{\text{reac}} N_i R_u T_{\text{init}} = N_{\text{reac}} R_u T_{\text{init}}$$

$$P_f V = \sum_{\text{prod}} N_i R_u T_{ad} = N_{\text{prod}} R_u T_{ad}.$$

Thus,

$$H_{\text{reac}} - H_{\text{prod}} - R_u(N_{\text{reac}} T_{\text{init}} - N_{\text{prod}} T_{ad}) = 0. \tag{2.43}$$

An alternative form of Eqn. 2.43, on a per-mass-of-mixture basis, can be obtained by dividing Eqn. 2.43 by the mass of mixture, m_{mix}, and recognizing that

$$m_{\text{mix}}/N_{\text{reac}} \equiv MW_{\text{reac}}$$

or

$$m_{\text{mix}}/N_{\text{prod}} \equiv MW_{\text{prod}}.$$

We thus obtain

$$h_{\text{reac}} - h_{\text{prod}} - R_u\left(\frac{T_{\text{init}}}{MW_{\text{reac}}} - \frac{T_{ad}}{MW_{\text{prod}}}\right) = 0. \tag{2.44}$$

Since the equilibrium composition of the product mixture depends upon both temperature and pressure, as we will see in the next section, utilizing Eqn. 2.43 or 2.44 with the ideal-gas law and appropriate calorific equations of state, e.g., $h = h(T, P) = h$ (T only, ideal gas), to find T_{ad} is straightforward, but non-trivial.

Example 2.6

Estimate the constant-volume adiabatic flame temperature for a stoichiometric CH_4–air mixture using the same assumtions as in Example 2.5. Initial conditions are $T_i = 298\,\text{K}$, $P = 1\,\text{atm}$ (= 101,325 Pa).

Solution

The same composition and properties used in Example 2.5 apply here. We note, however, that the $c_{p,i}$ values should be evaluated at a temperature somewhat greater than 1200 K, since the constant-volume T_{ad} will be higher than the constant-pressure T_{ad}. Nonetheless, we will use the same values as before.

First law (Eqn. 2.43):

$$H_{\text{reac}} - H_{\text{prod}} - R_u(N_{\text{reac}}T_{\text{init}} - N_{\text{prod}}T_{ad}) = 0$$

or

$$\sum_{\text{reac}} N_i\bar{h}_i - \sum_{\text{prod}} N_i\bar{h}_i - R_u(N_{\text{reac}}T_{\text{init}} - N_{\text{prod}}T_{ad}) = 0.$$

Substituting numerical values, we have

$$\begin{aligned} H_{\text{react}} &= (1)(-74{,}831) + 2(0) + 7.52(0) \\ &= -74{,}831\,\text{kJ} \\ H_{\text{prod}} &= (1)[-393{,}546 + 56.21(T_{ad} - 298)] \\ &\quad + (2)[-241{,}845 + 43.87(T_{ad} - 298)] \\ &\quad + (7.52)[0 + 33.71(T_{ad} - 298)] \\ &= -877{,}236 + 397.5(T_{ad} - 298)\,\text{kJ} \end{aligned}$$

and

$$R_u(N_{\text{reac}}T_{\text{init}} - N_{\text{prod}}T_{ad}) = 8.315(10.52)(298 - T_{ad}),$$

where $N_{\text{reac}} = N_{\text{prod}} = 10.52\,\text{kmol}$.

Reassembling Eqn. 2.43 and solving for T_{ad} yields

$$\boxed{T_{ad} = 2889\,\text{K}}$$