Chapter 2
Thermodynamics of Combustion

2.1 Properties of Mixtures

The thermal properties of a pure substance are described by quantities including internal energy, u, enthalpy, h, specific heat, c_p, etc. Combustion systems consist of many different gases, so the thermodynamic properties of a mixture result from a combination of the properties of all of the individual gas species. The ideal gas law is assumed for gaseous mixtures, allowing the ideal gas relations to be applied to each gas component. Starting with a mixture of K different gases, the total mass, m, of the system is

$$m = \sum_{i=1}^{K} m_i, \tag{2.1}$$

where m_i is the mass of species i. The total number of moles in the system, N, is

$$N = \sum_{i=1}^{K} N_i, \tag{2.2}$$

where N_i is the number of moles of species i in the system. Mass fraction, y_i, and mole fraction, x_i, describe the relative amount of a given species. Their definitions are given by

$$y_i \equiv \frac{m_i}{m} \quad \text{and} \quad x_i \equiv \frac{N_i}{N}, \tag{2.3}$$

where $i = 1, 2, \ldots, K$. By definition,

$$\sum_{i=1}^{K} y_i = 1 \quad \text{and} \quad \sum_{i=1}^{K} x_i = 1.$$

With M_i denoting the molecular mass of species i, the average molecular mass, M, of the mixture is determined by

$$M = \frac{m}{N} = \frac{\sum\limits_i N_i M_i}{N} = \sum\limits_i x_i M_i. \tag{2.4}$$

From Dalton's law of additive pressures and Amagat's law of additive volumes along with the ideal gas law, the mole fraction of a species in a mixture can be found from the partial pressure of that species as

$$\frac{P_i}{P} = \frac{N_i}{N} = \frac{V_i}{V} = x_i, \tag{2.5}$$

where P_i is the partial pressure of species i, P is the total pressure of the gaseous mixture, V_i the partial volume of species i, and V is the total volume of the mixture. The average intrinsic properties of a mixture can be classified using either a molar base or a mass base. For instance, the internal energy per unit mass of a mixture, u, is determined by summing the internal energy per unit mass for each species weighted by the mass fraction of the species.

$$u = \frac{U}{m} = \frac{\sum\limits_i m_i u_i}{m} = \sum\limits_i y_i u_i, \tag{2.6}$$

where U is the total internal energy of the mixture and u_i is the internal energy per mass of species i. Similarly, enthalpy per unit mass of mixture is

$$h = \sum\limits_i y_i h_i$$

and specific heat at constant pressure per unit mass of mixture is

$$c_p = \sum\limits_i y_i c_{p,i}.$$

A molar base property, often denoted with a $^\wedge$ over bar, is determined by the sum of the species property per mole for each species weighted by the species mole fraction, such as internal energy per mole of mixture

$$\hat{u} = \sum\limits_i x_i \hat{u}_i,$$

enthalpy per mole of mixture

$$\hat{h} = \sum\limits_i x_i \hat{h}_i,$$

and entropy per mole of mixture

$$\hat{s} = \sum_i x_i \hat{s}_i.$$

Assuming constant specific heats during a thermodynamic process, changes of energy, enthalpy, and entropy of an individual species per unit mass are described as follows:

$$\Delta u_i = c_{v,i}(T_2 - T_1) \tag{2.7}$$

$$\Delta h_i = c_{p,i}(T_2 - T_1) \tag{2.8}$$

$$\Delta s_i = c_{p,i} \ln\frac{T_2}{T_1} - R_i \ln\frac{P_{i,2}}{P_{i,1}} \tag{2.9}$$

$P_{i,1}$ and $P_{i,2}$ denote the partial pressures of species i at state 1 and state 2, respectively. R_i is the gas constant for species i ($R_i = \hat{R}_u/M_i =$ universal gas constant/molecular mass of species i). The overall change of entropy for a combustion system is

$$\Delta S = \sum_i m_i \Delta s_i.$$

A summary of the thermodynamic properties of mixtures is provided at the end of the chapter.

2.2   Combustion Stoichiometry

For a given combustion device, say a piston engine, how much fuel and air should be injected in order to completely burn both? This question can be answered by balancing the combustion reaction equation for a particular fuel. A stoichiometric mixture contains the exact amount of fuel and oxidizer such that after combustion is completed, all the fuel and oxidizer are consumed to form products. This ideal mixture approximately yields the maximum flame temperature, as all the energy released from combustion is used to heat the products. For example, the following reaction equation can be written for balancing methane-air combustion
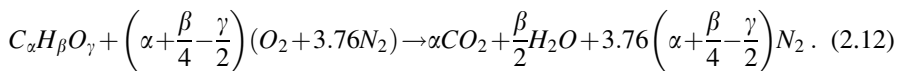
$$CH_4 + \underline{?}\left(O_2 + \frac{79}{21}N_2\right) \rightarrow \underline{?}CO_2 + \underline{?}H_2O + \underline{?}N_2, \tag{2.10}$$
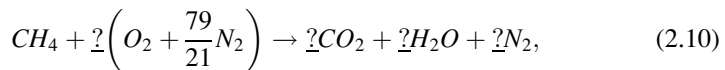
where air consisting of 21% O_2 and 79% N_2 is assumed.[1] The coefficients associated with each species in the above equation are unknown. By balancing the atomic

abundance on both the reactant and product sides, one can find the coefficient for each species. For instance, let's determine the coefficient for CO_2: on the reactant side, we have 1 mol of C atoms; hence the product side should also have 1 mol of C atoms. The coefficient of CO_2 is therefore unity. Using this procedure we can determine all the coefficients. These coefficients are called the reaction stoichiometric coefficients. For stoichiometric methane combustion with air, the balanced reaction equation reads:

$$CH_4 + \underline{2}(O_2 + 3.76N_2) \rightarrow \underline{1}CO_2 + \underline{2}H_2O + \underline{7.52}N_2. \qquad (2.11)$$
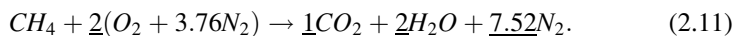
Note that on the reactant side there are $2\cdot(1+3.76)$ or 9.52 mol of air and its molecular mass is 28.96 kg/kmol. In this text, the reactions are balanced using 1 mol of fuel. This is done here to simplify the calculations of the heat of reaction and flame temperature later in the chapter. Combustion stoichiometry for a general hydrocarbon fuel, $C_\alpha H_\beta O_\gamma$, with air can be expressed as

$$C_\alpha H_\beta O_\gamma + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)(O_2 + 3.76N_2) \rightarrow \alpha CO_2 + \frac{\beta}{2}H_2O + 3.76\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)N_2. \quad (2.12)$$
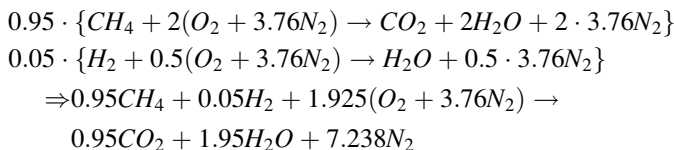
The amount of air required for combusting a stoichiometric mixture is called *stoichiometric* or *theoretical* air. The above formula is for a single-component fuel and cannot be applied to a fuel consisting of multiple components. There are two typical approaches for systems with multiple fuels. Examples are given here for a fuel mixture containing 95% methane and 5% hydrogen. The first method develops the stoichiometry of combustion using the general principle of atomic balance, making sure that the total number of each type of atom (C, H, N, O) is the same in the products and the reactants.

$$0.95CH_4 + 0.05H_2 + 1.925(O_2 + 3.76N_2) \rightarrow$$
$$0.95CO_2 + 1.95H_2O + 7.238N_2.$$
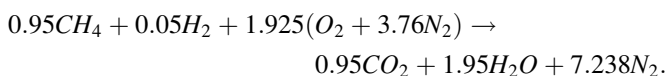
The other method of balancing a fuel mixture is to first develop stoichiometry relations for CH_4 and H_2 individually:

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 2\cdot3.76N_2$$

$$H_2 + 0.5(O_2 + 3.76N_2) \rightarrow H_2O + 0.5\cdot3.76N_2$$
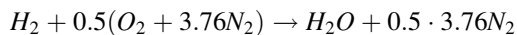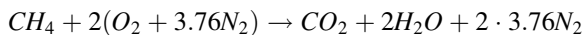
Then, multiply the individual stoichiometry equations by the mole fractions of the fuel components and add them:

$$0.95 \cdot \{CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 2 \cdot 3.76N_2\}$$
$$0.05 \cdot \{H_2 + 0.5(O_2 + 3.76N_2) \rightarrow H_2O + 0.5 \cdot 3.76N_2\}$$
$$\Rightarrow 0.95CH_4 + 0.05H_2 + 1.925(O_2 + 3.76N_2) \rightarrow$$
$$0.95CO_2 + 1.95H_2O + 7.238N_2$$

2.2.1 Methods of Quantifying Fuel and Air Content of Combustible Mixtures

In practice, fuels are often combusted with an amount of air different from the stoichiometric ratio. If less air than the stoichiometric amount is used, the mixture is described as fuel rich. If excess air is used, the mixture is described as fuel lean. For this reason, it is convenient to quantify the combustible mixture using one of the following commonly used methods:

Fuel-Air Ratio (FAR): The fuel-air ratio, f, is given by

$$f = \frac{m_f}{m_a}, \tag{2.13}$$

where m_f and m_a are the respective masses of the fuel and the air. For a stoichiometric mixture, Eq. 2.13 becomes

$$f_s = \frac{m_f}{m_a}\bigg|_{stoichiometric} = \frac{M_f}{(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}) \cdot 4.76 \cdot M_{air}}, \tag{2.14}$$

where M_f and M_{air} (~28.84 kg/kmol) are the average masses per mole of fuel and air, respectively. The range of f is bounded by zero and ∞. Most hydrocarbon fuels have a stoichiometric fuel-air ratio, f_s, in the range of 0.05–0.07. The air-fuel ratio (AFR) is also used to describe a combustible mixture and is simply the reciprocal of FAR, as AFR $= 1/f$. For instance, the stoichiometric AFR of gasoline is about 14.7. For most hydrocarbon fuels, 14–20 kg of air is needed for complete combustion of 1 kg of fuel.

Equivalence Ratio: Normalizing the actual fuel-air ratio by the stoichiometric fuel-air ratio gives the equivalence ratio, ϕ.

$$\phi = \frac{f}{f_s} = \frac{m_{as}}{m_a} = \frac{N_{as}}{N_a} = \frac{N_{O2s}}{N_{O2,a}} \tag{2.15}$$

The subscript s indicates a value at the stoichiometric condition. $\phi < 1$ is a *lean* mixture, $\phi = 1$ is a *stoichiometric* mixture, and $\phi > 1$ is a *rich* mixture. Similar to f, the range of ϕ is bounded by zero and ∞ corresponding to the limits of pure air and fuel respectively. Note that equivalence ratio is a normalized quantity that provides the information regarding the content of the combustion mixture. An alternative

variable based on AFR is frequently used by combustion engineers and is called lambda (λ). Lambda is the ratio of the actual air-fuel ratio to the stoichiometric air-fuel ratio defined as

$$\lambda = \frac{AFR}{AFR_s} = \frac{1/f}{1/f_s} = \frac{1}{f/f_s} = \frac{1}{\phi} \tag{2.16}$$

Lambda of stoichiometric mixtures is 1.0. For rich mixtures, lambda is less than 1.0; for lean mixtures, lambda is greater than 1.0.
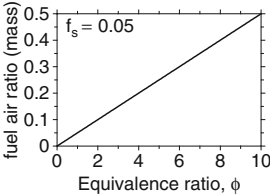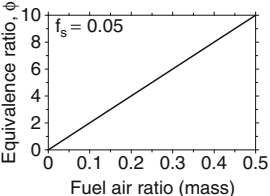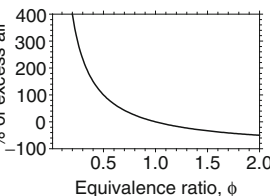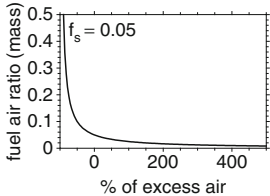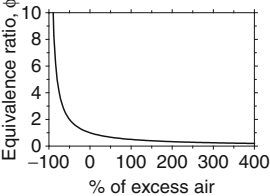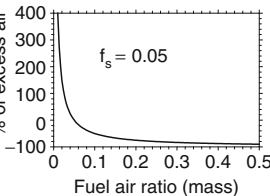
Percent Excess Air: The amount of air in excess of the stoichiometric amount is called excess air. The percent excess air, *%EA*, is defined as

$$\%EA = 100 \frac{m_a - m_{as}}{m_{as}} = 100 \left(\frac{m_a}{m_{as}} - 1 \right) \tag{2.17}$$

For example, a mixture with $\%EA = 50$ contains 150% of the theoretical (stoichiometric) amount of air.

Converting between quantification methods: Given one of the three variables (f, ϕ, and %EA), the other two can be deduced as summarized in Table 2.1 with their graphic relations. In general, the products of combustion include many different

Table 2.1 Relations among the three variables for describing reacting mixtures

f (fuel air ratio by mass)	ϕ (equivalence ratio)	%EA (% of excess air)
$f = f_s \cdot \phi$	$\phi = \dfrac{f}{f_s}$	$\%EA = 100 \dfrac{1 - \phi}{\phi}$
$f = \dfrac{100 \cdot f_s}{\%EA + 100}$	$\phi = \dfrac{100}{\%EA + 100}$	$\%EA = 100 \dfrac{1 - f/f_s}{f/f_s}$

species in addition to the major species (CO_2, H_2O, N_2, O_2), and the balance of the stoichiometric equation requires the use of thermodynamic e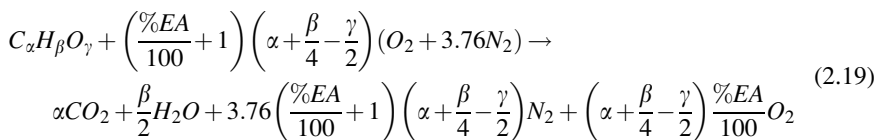quilibrium relations. However, assuming that the products contain major species only (complete combustion) and excess air, the global equation for lean combustion $\phi \leqslant 1$ is

$$
C_\alpha H_\beta O_\gamma + \frac{1}{\phi}\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)(O_2 + 3.76N_2) \rightarrow
$$
$$
\alpha CO_2 + \frac{\beta}{2}H_2O + \frac{3.76}{\phi}\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)N_2 + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)\left(\frac{1}{\phi} - 1\right)O_2
$$

$$(2.18)$$
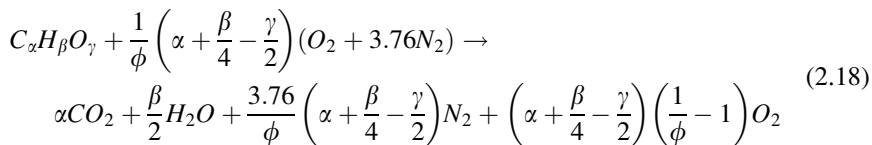
In terms of %EA, we replace ϕ by $\dfrac{100}{\%EA + 100}$ and the result is

$$
C_\alpha H_\beta O_\gamma + \left(\frac{\%EA}{100} + 1\right)\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)(O_2 + 3.76N_2) \rightarrow
$$
$$
\alpha CO_2 + \frac{\beta}{2}H_2O + 3.76\left(\frac{\%EA}{100} + 1\right)\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)N_2 + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)\frac{\%EA}{100}O_2
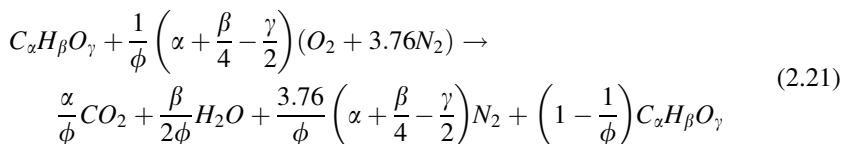$$

$$(2.19)$$

The amount of excess air can be deduced from measurements of exhaust gases. The ratio of mole fractions between CO_2 and O_2 is

$$
\frac{x_{CO2}}{x_{O2}} = \frac{\alpha}{\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)\frac{\%EA}{100}} \rightarrow \frac{\%EA}{100} = \frac{\alpha}{\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)\frac{x_{CO_2}}{x_{O_2}}}
$$

or using Table 2.1

$$
\phi = \frac{100}{100 + \%EA} \rightarrow \phi = \frac{1}{1 + \dfrac{\alpha}{\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)\frac{x_{CO_2}}{x_{O_2}}}}
$$

$$(2.20)$$

For rich combustion ($\phi > 1$), the products may contain CO, unburned fuels, and other species formed by the degradation of the fuel. Often additional information on the products is needed for complete balance of the chemical reaction. If the products are assumed to contain only unburned fuel and major combustion products, the corresponding global equation can be written as

$$
C_\alpha H_\beta O_\gamma + \frac{1}{\phi}\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)(O_2 + 3.76N_2) \rightarrow
$$
$$
\frac{\alpha}{\phi}CO_2 + \frac{\beta}{2\phi}H_2O + \frac{3.76}{\phi}\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)N_2 + \left(1 - \frac{1}{\phi}\right)C_\alpha H_\beta O_\gamma
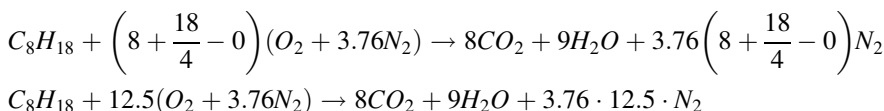$$

$$(2.21)$$

Example 2.1 Considering a stoichiometric mixture of isooctane and air, determine:

(a) the mole fraction of fuel
(b) the fuel-air ratio
(c) the mole fraction of H_2O in the products
(d) the temperature of products below which H_2O starts to condense into liquid at 101.3 kPa

Solution:

The first step is writing and balancing the stoichiometric reaction equation. Using Eq. 2.12,

$$C_8H_{18} + \left(8 + \frac{18}{4} - 0\right)(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 3.76\left(8 + \frac{18}{4} - 0\right)N_2$$

$$C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 3.76 \cdot 12.5 \cdot N_2$$

From here:

(a) $x_{C_8H_{18}} = \dfrac{N_{C_8H_{18}}}{N_{C_8H_{18}} + N_{air}} = \dfrac{1}{1 + 12.5 \cdot 4.76} = 0.0165$

(b) $f_s = \dfrac{M_f}{\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right) \cdot 4.76 \cdot M_{air}} = \dfrac{114}{12.5 \cdot 4.76 \cdot 28.96} = 0.066$

(c) $x_{H_2O} = \dfrac{N_{H_2O}}{N_{CO_2} + N_{H_2O} + N_{N_2}} = \dfrac{9}{8 + 9 + 3.76 \cdot 12.5} = 0.141$

(d) The partial pressure of water is 101 kPa $\cdot$ 0.141 $= 14.2$ kPa. A saturation table for steam gives the saturation temperature at this water pressure $\cong 53°C$.

Example 2.2 How many kg (lb) of air are used to combust 55.5 L (~14.7 US gallons) of gasoline?

Solution:

We will use isooctane C_8H_{18} to represent gasoline. The stoichiometric fuel-air ratio is

$$f_s = \frac{M_f}{\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right) \cdot 4.76 \cdot M_{air}}$$

$$= \frac{114 \text{ kg/kmol}}{(8 + 18/4 - 0) \cdot 4.76 \cdot 28.84 \text{ kg/kmol}}$$

$$= 0.066$$

One gallon of gasoline weighs about 2.7 kg (6 lb). The total fuel thus weighs about 40 kg (88 lb). The required air weighs about $40/f_s \approx 610$ kg $\approx 1,300$ lb. This is a lot of weight if it must be carried. Hence, for transportation applications, free ambient air is preferred.

Example 2.3 In a model "can-combustor" combustion chamber, n-heptane (C_7H_{16}) is burned under an overall lean condition. Measurements of dry exhaust give mole fractions of CO_2 and O_2 as $x_{CO_2} = 0.084$ and $x_{O_2} = 0.088$. Determine the %EA, equivalence ratio ϕ, and λ.

Solution:

To avoid condensation of water inside the instruments, measurements of exhaust gases are taken on a 'dry' mixture that is obtained by passing the exhaust gases through an ice bath so that most water is condensed. Further removal of water can be done with desiccants. The mole fractions measured under dry conditions will be larger than at real conditions since water is removed. However, this will not impact the relation deduced above, as both x_{CO_2} and x_{O_2} are increased by the same factor.

$$\frac{\%EA}{100} = \frac{\alpha}{\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)\frac{x_{CO_2}}{x_{O_2}}} = \frac{7}{(7 + 16/4 - 0)(0.084/0.088)} = 0.667 \rightarrow \%EA$$

$$= 66.7$$

Next we use the relations given in Table 2.1 to convert %EA to ϕ and λ

$$\phi = \frac{100}{\%EA + 100} = \frac{100}{66.7 + 100} = 0.6$$

$$\lambda = \frac{1}{\phi} = 1.67$$

2.3 Heating Values

Heating values of a fuel (units of kJ/kg or MJ/kg) are traditionally used to quantify the maximum amount of heat that can be generated by combustion with air at standard conditions (STP) (25°C and 101.3 kPa). The amount of heat release from combustion of the fuel will depend on the phase of water in the products. If water is in the gas phase in the products, the value of total heat release is denoted as the lower heating value (LHV). When the water vapor is condensed to liquid, additional energy (equal to the latent heat of vaporization) can be extracted and the total energy release is called the higher heating value (HHV). The value of the LHV can be calculated from the HHV by subtracting the amount of energy released during the phase change of water from vapor to liquid as

$$LHV = HHV - \frac{N_{H2O,P}M_{H2O}h_{fg}}{N_{fuel}M_{fuel}} \quad \text{(MJ/kg)}, \tag{2.22}$$

where $N_{H2O,P}$ is the number of moles of water in the products. Latent heat for water at STP is $h_{fg} = 2.44$ MJ/kg $= 43.92$ MJ/kmol. In combustion literature, the LHV is normally called the enthalpy or heat of combustion (Q_C) and is a positive quantity.

2.3.1 Determination of HHV for Combustion Processes at Constant Pressure

A control volume analysis at constant pressure with no work exchanged can be used to theoretically determine the heating values of a particular fuel. Suppose reactants with 1 kmol of fuel enter the inlet of a control volume at standard conditions and products leave at the exit. A maximum amount of heat is extracted when the products are cooled to the inlet temperature and the water is condensed. Conservation of energy for a constant pressure reactor, with H_P and H_R denoting the respective total enthalpies of products and reactants, gives

$$- Q_{rxn,p} = H_R - H_p. \tag{2.23}$$

The negative value of $Q_{rxn,p}$ indicates heat transfer out of the system to the surroundings. It follows from above that the heating value of the fuel is the difference in the enthalpies of the reactants and the products. However, in combustion systems, the evaluation of the enthalpies is not straightforward because the species entering the system are different than those coming out due to chemical reactions. $Q_{rxn,p}$ is often referred to as the enthalpy of reaction or heat of reaction, with the subscript p indicating that the value was calculated at constant pressure. The enthalpy of reaction is related to the enthalpy of combustion by $Q_{rxn,p} = -Q_C$.

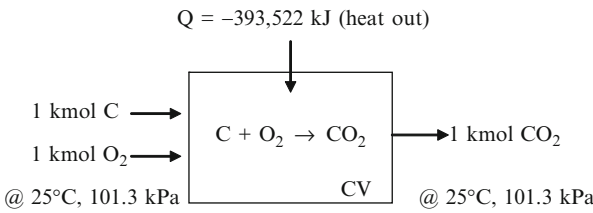#### 2.3.1.1 Enthalpy of Formation

In combustion processes, reactants are consumed to form products and energy is released. This energy comes from a rearrangement of chemical bonds in the reactants to form the products. The standard enthalpy of formation, $\Delta \hat{h}_i^o$, quantifies the chemical bond energy of a chemical species at standard conditions. The enthalpy of formation of a substance is the energy needed for the formation of that substance from its constituent elements at STP conditions (25°C and 1 atm). The molar base enthalpy of formation, $\Delta \hat{h}_i^o$, has units of *MJ/kmol*, and the mass base enthalpy of formation, $\Delta \hat{h}_i^o$, has units of MJ/kg. Elements in their most stable forms, such as $C_{(graphite)}$, H_2, O_2, and N_2, have enthalpies of formation of zero. Enthalpies of formation of commonly encountered chemical species are tabulated in Table 2.2.

A departure from standard conditions is accompanied by an enthalpy change. For thermodynamic systems without chemical reactions, the change of enthalpy of an ideal gas is described by the sensible enthalpy,

Table 2.2 Enthalpy of formation of common combustion species

Species	$\Delta\hat{h}^o$ (MJ/kmol)	Species	$\Delta\hat{h}^o$ (MJ/kmol)
H_2O (g)	−241.83	H	+217.99
CO_2	−393.52	N	+472.79
CO	−110.53	NO	+90.29
CH_4	−74.87	NO_2	+33.10
C_3H_8	−104.71	O	+249.19
C_7H_{16} (g) (n-heptane)	−224.23	OH	+39.46
C_8H_{18} (g) (isooctane)	−259.25	C (g)	+715.00
CH_3OH (g) (methanol)	−201.54	C_2H_2 (acetylene)	+226.73
CH_3OH (l) (methanol)	−238.43	C_2H_4 (ethylene)	+52.28
C_2H_6O (g) (ethanol)	−235.12	C_2H_6 (ethane)	−84.68
C_2H_6O (l) (ethanol)	−277.02	C_4H_{10} (n-butane)	−126.15

Fig. 2.1 Constant-pressure flow reactor for determining enthalpy of formation

$Q = -393,522$ kJ (heat out)

1 kmol C →

1 kmol O_2 →

$C + O_2 \rightarrow CO_2$

→ 1 kmol CO_2

CV

@ 25°C, 101.3 kPa   @ 25°C, 101.3 kPa

$$\hat{h}_{si} = \int_{T_o}^{T} \hat{c}_p(T)dT,$$

where the subscript i refers to species i, T_0 denotes the standard temperature (25°C), and $\hat{}$ indicates that a quantity is per mole. Note that the sensible enthalpy of any species is zero at standard conditions. The 'absolute' or 'total' enthalpy, $\hat{h}_i$, is thus the sum of the sensible enthalpy and the enthalpy of formation:[2]

$$\hat{h}_i = \Delta\hat{h}_i^o + \hat{h}_{si} \qquad (2.24)$$

One way to determine the enthalpy of formation of a species is to use a constant-pressure flow reactor. For instance, the enthalpy of formation of CO_2 is determined by reacting 1 kmol of $C_{(graphite)}$ with 1 kmol of O_2 at 25°C at a constant pressure of 101.3 kPa. The product, 1 kmol of CO_2, flows out of this reactor at 25°C as sketched in Fig. 2.1. An amount of heat produced in the reaction is transferred

---

[2] When phase change is encountered, the total enthalpy needs to include the latent heat, $\hat{h}_i = \Delta\hat{h}_i^o + \hat{h}_{si} + \hat{h}_{latent}$.

out of this system, therefore the enthalpy formation of CO_2 is negative $\Delta\hat{h}^o_{CO2} = -393.52$ MJ/kmol. This means that CO_2 at 25°C contains less energy than its constituent elements $C_{(graphite)}$ and O_2, which have zero enthalpy of formation. The enthalpy of formation is not negative for all chemical species. For instance, the enthalpy formation of NO is $\Delta\hat{h}^o_{NO} = +90.29$ MJ/kmol, meaning that energy is needed to form NO from its elements, O_2 and N_2. For most unstable or "radical" species, such as O, H, N, and CH_3, the enthalpy of formation is positive.

2.3.1.2 Evaluation of the Heat of Combustion from a Constant-Pressure Reactor

Using the conservation of energy equation (2.23), we can now evaluate the enthalpies of the reactants and products. Inserting the expression for the total enthalpy,

$$-Q_{rxn.p} = H_R - H_p = \sum_i N_{i,R}\left(\Delta\hat{h}^o_{i,R} + \hat{h}_{si,R}\right) - \sum_i N_{i,P}\left(\Delta\hat{h}^o_{i,P} + \hat{h}_{si,P}\right)$$
$$= \left[\sum_i N_{i,R}\Delta\hat{h}^o_{i,R} - \sum_i N_{i,P}\Delta\hat{h}^o_{i,P}\right] + \sum_i N_{i,R}\hat{h}_{si,R} - \sum_i N_{i,P}\hat{h}_{si,P}, \tag{2.25}$$

where N_i is the number of moles of species i. The sensible enthalpies of common reactants and products can be found in Appendix 1. When the products are cooled to the same conditions as the reactants, the amount of heat transfer from the constant-pressure reactor to the surroundings is defined as the heating value. At STP the sensible enthalpy terms drop out for both reactants and products and the heat release is

$$-Q^0_{rxn,p} = \sum_i N_{i,R}\Delta\hat{h}^o_{i,R} - \sum_i N_{i,P}\Delta\hat{h}^o_{i,P} \tag{2.26}$$

Usually excess air is used in such a test to ensure complete combustion. The amount of excess air used will not affect $-Q^0_{rxn,p}$ at STP. Unless the reactant mixtures are heavily diluted, the water in the products at STP normally will be liquid.[3] Assuming that water in the products is liquid, HHV is determined:

$$HHV = \frac{-Q^0_{rxn,p}}{N_{fuel}M_{fuel}}. \tag{2.27}$$

The negative sign in front of $Q^0_{rxn,p}$ ensures that HHV is positive.

_____

2.3.2   Determination of HHV for Combustion Processes from a Constant-Volume Reactor

A constant-volume reactor is more convenient than the constant-pressure reactor to experimentally determine the HHV of a particular fuel. For a closed system, conservation of energy yields

$$- Q_{rxn,v} = U_R - U_p \tag{2.28}$$

Because of the combustion process, the same type of accounting must be used to include the change in chemical bond energies. The internal energy will be evaluated by using its relation to enthalpy. Note that relation $h = u + pv$ is mass based and the corresponding molar base relation is $\hat{h} = \hat{u} + \hat{R}_u T$. At STP (T $= T_0 = 25°$C), the total internal energy of the reactants, U_R, inside the closed system is

$$\begin{aligned}
U_R &= H_R - PV \\
&= H_R - \sum_i N_{i,R}\hat{R}_u T_0 \\
&= \sum_i N_{i,R}\Delta\hat{h}^o_{i,R} - \sum_i N_{i,R}\hat{R}_u T_0
\end{aligned} \tag{2.29}$$

The total internal energy of products is evaluated in a similar manner:

$$U_P = \sum_i N_{i,P}\Delta\hat{h}^o_{i,P} - \sum_i N_{i,P}\hat{R}_u T_0 \tag{2.30}$$

Using the internal energy relations, we can re-express the heat release at constant volume in terms of enthalpies as

$$\begin{aligned}
-Q^0_{rxn,v} &= U_R - U_P \\
&= \sum_i N_{i,R}\Delta\hat{h}^o_{i,R} - \sum_i N_{i,R}\hat{R}_u T_0 - \left[\sum_i N_{i,P}\Delta\hat{h}^o_{i,P} - \sum_i N_{i,P}\hat{R}_u T_0\right] \\
&= \sum_i N_{i,R}\Delta\hat{h}^o_{i,R} - \sum_i N_{i,P}\Delta\hat{h}^o_{i,P} + \left(\sum_i N_{i,P} - \sum_i N_{i,R}\right)\hat{R}_u T_0
\end{aligned} \tag{2.31}$$

Therefore, HHV for combustion processes is calculated as

$$HHV = \frac{-Q^0_{rxn,v} - \left(\sum_i N_{i,P} - \sum_i N_{i,R}\right)\hat{R}_u T_0}{N_{fuel}M_{fuel}}, \tag{2.32}$$

where N_{fuel} is the number of moles of fuel burned and M_{fuel} is the molecular mass of the fuel. The negative sign in front of $Q_{rxn,v}^0$ is to make sure that HHV is positive. For a general fuel, $C_\alpha H_\beta O_\gamma$, the difference between $-Q_{rxn,v}$ and $-Q_{rxn,p}$ is

$$\left(\sum_i N_{i,P} - \sum_i N_{i,R}\right)\hat{R}_u T_0 = \Delta N \hat{R}_u T_0 = \left(\frac{\beta}{4} + \frac{\gamma}{2} - 1\right)\hat{R}_u T_0 \qquad (2.33)$$

and is usually small in comparison to HHV; therefore normally no distinction is made between the heat of reaction at constant pressure or constant volume.

2.3.2.1 Experimental Determination of HHV: The Bomb Calorimeter

To experimentally measure the heating value of a fuel, the fuel and air are often enclosed in an explosive-proof steel container (see Fig. 2.2), whose volume does not change during a reaction. The vessel is then submerged in water or another liquid that absorbs the heat of combustion. The heat capacitance of the vessel plus the liquid is then measured using the same technique as other calorimeters. Such an instrument is called a bomb calorimeter.

A constant-volume analysis of the bomb calorimeter data is used to determine the heating value of a particular fuel. The fuel is burned with sufficient oxidizer in a closed system. The closed system is cooled by heat transfer to the surroundings such that the final temperature is the same as the initial temperature. The standard conditions are set for evaluation of heating values. Conservation of energy gives
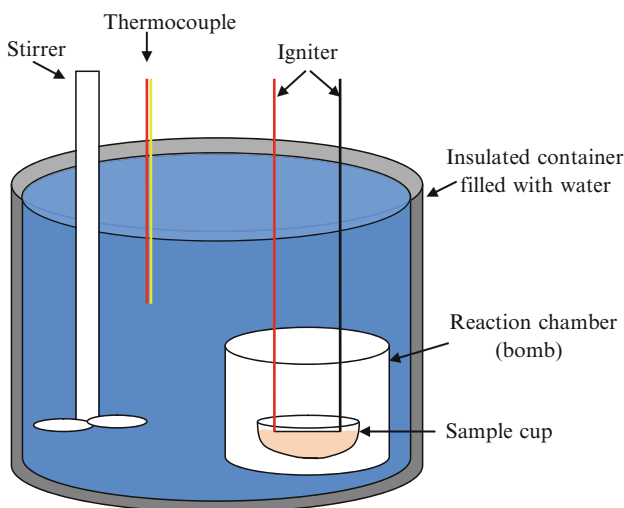
$$U_P - U_R = Q_{rxn,v}^0 \qquad (2.34)$$

Fig. 2.2 Bomb calorimeter

Because the final water temperature is close to room temperature, the water in the combustion products is usually in liquid phase. Therefore the measurement leads to the HHV from a constant-volume combustion process as described by Eq. 2.32:

$$HHV = \left\{ -Q_{rxn,v}^0 - \left(\sum_i N_{i,P} - \sum_i N_{i,R} \right) \hat{R}_u T_0 \right\} / \left[N_{fuel} M_{fuel} \right],$$

where N_{fuel} is the number of moles of fuel burned and M_{fuel} is the molecular weight of the fuel. The negative sign in front of $Q_{rxn,v}^0$ ensures that HHV is positive. In a bomb calorimeter, if the final temperature of the combustion products is higher than the reactants by only a few degrees ($<10°C$), the error is negligible. The amount of heat transfer is estimated by

$$- Q_{rxn,v}^0 = (m_{steel} \cdot c_{p,steel} + m_{water} \cdot c_{p,water}) \Delta T, \tag{2.35}$$

where ΔT is the temperature change of the water and the steel container.

The bomb calorimeter can also measure the enthalpy of formation of a chemical species. For instance, to determine enthalpy of formation of H_2O, we start out with 1 mol of H_2 and 0.5 mol of O_2. These element species have zero enthalpy of formation; therefore

$$\sum_i N_{i,R} \Delta \hat{h}_{i,R}^0 = 0.$$

The only product is the species of interest, namely H_2O. We therefore can write the enthalpy of formation of H_2O, $\Delta \hat{h}_{i,P}^0$, as

$$\Delta \hat{h}_{i,P}^0 = \frac{Q_{rxn,v}^0 + \left(\sum_i N_{i,P} - \sum_i N_{i,R} \right) \hat{R}_u T_0}{N_{i,P}} = \frac{Q_{rxn,v}^0 + \Delta N \hat{R}_u T_0}{N_{i,P}} \tag{2.36}$$

where

$$\Delta N = \sum_i N_{i,P} - \sum_i N_{i,R}.$$

2.3.3 Representative HHV Values

Listed in Table 2.3 are higher heating values of some common and less common fuels.

Example 2.4 A table of thermodynamic data gives the enthalpy of formation for liquid water as $\Delta \hat{h}_{H_2O(l)}^0 = -285.8$ kJ/mol. A bomb calorimeter burning 1 mol of H_2 with O_2 measures 282.0 kJ of heat transfer out of the reacted mixture. Estimate the error of the enthalpy measurement.

Solution:

We start out with the combustion stoichiometry

$$H_2(g) + 0.5O_2(g) = H_2O(liq),$$
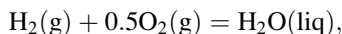
$$\Delta N = -1.5 \quad \text{(Change in moles of } gas \text{ in the mixture)}$$

Applying the ideal gas approximation to the energy balance with $Q^0_{rxn,v} = -282.0$ kJ,

$$\Delta \hat{h}^0_{H_2O(l)} = Q^0_{rxn,v} + \Delta N \hat{R}_u T_0,$$
$$= -282.0 \text{ kJ/mol} \cdot 1 \text{ mol} + (-1.5 \text{ mol} \cdot 8.314 \text{ J/mol} - \text{K} \cdot 298 \text{K} \cdot 0.001 \text{ kJ/J})$$
$$= (-282.0 - 3.72) \text{kJ} = -285.7 \text{ kJ}$$

The error is $(285.8 - 285.7)/285.8 = 0.03\%$. In this case, more heat is given off if the reaction is carried out at constant pressure, since the *P-V* work ($1.5\hat{R}_u T_0$) due to the compression of 1.5 mol of gases in the reactants would contribute to $\Delta \hat{h}^0_{H_2O(l)}$. However, this difference is only about 1–2% of the enthalpy of formation. The enthalpy of formation for gaseous H_2O is obtained by adding the latent heat to $\Delta \hat{h}^0_{H_2O(l)}$:

$$\Delta \hat{h}^0_{H_2O(g)} = \Delta \hat{h}^0_{H_2O(l)} + \hat{h}_{fg} = -241.88 \text{ kJ/mol},$$

Table 2.3 Heat values of various fuels

| Fuel	Heating value		
	MJ/kg	BTU/lb	kJ/mol
Hydrogen	141.8	61,100	286
Methane	55.5	23,900	890
Ethane	51.9	22,400	1,560
Propane	50.35	21,700	2,220
Butane	49.5	20,900	2,877
Gasoline	47.3	20,400	~5,400
Paraffin	46	19,900	16,300
Diesel	44.8	19,300	~4,480
Coal	15–27	8,000–14,000	200–350
Wood	15	6,500	300
Peat	6–15	2,500–6,500	
Methanol	22.7	9,800	726
Ethanol	29.7	12,800	1,368
Propanol	33.6	14,500	2,020
Acetylene	49.9	21,500	1,300
Benzene	41.8	18,000	3,270
Ammonia	22.5	9,690	382
Hydrazine	19.4	8,370	622
Hexamine	30.0	12,900	4,200
Carbon	32.8	14,100	393.5

where

$$\hat{h}_{fg} = 43.92\,\text{kJ/mol}.$$

Example 2.5 The heat released by 1 mol of sugar in a bomb calorimeter experiment is 5,648 kJ/mol. Calculate the enthalpy of combustion per mole of sugar.

Solution:
The balanced chemical reaction equation is

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) = 12CO_2(g) + 11H_2O(liq)$$
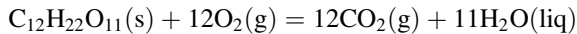
Since the total number of moles of gas is constant (12) in the products and reactants, $\Delta N = 0$. Therefore, work is zero and the enthalpy of combustion equals the heat transfer: $-5{,}648$ kJ/mol.

2.4   Adiabatic Flame Temperature

One of the most important features of a combustion process is the highest temperature of the combustion products that can be achieved. The temperature of the products will be greatest when there are no heat losses to the surrounding environment and all of the energy released from combustion is used to heat the products. In the next two sections, the methodology used to calculate the maximum temperature, or *adiabatic flame temperature*, will be presented.

2.4.1   Constant-Pressure Combustion Processes

An adiabatic constant-pressure analysis is used here to calculate the adiabatic flame temperature. Under this idealized condition, conservation of energy is:

$$H_P(T_P) = H_R(T_R), \tag{2.37}$$

where

$$H_P(T_P) = \sum_i N_{i,P}\hat{h}_{i,P} = \sum_i N_{i,P}[\Delta\hat{h}^o_{i,P} + \hat{h}_{si,P}(T_P)]$$

and

$$H_R(T_R) = \sum_i N_{i,R}\hat{h}_{i,R} = \sum_i N_{i,R}[\Delta\hat{h}^o_{i,R} + \hat{h}_{si,R}(T_R)].$$

Figure 2.3 is a graphic explanation of how the adiabatic flame temperature is determined. At the initial reactant temperature, the enthalpy of the product mixture
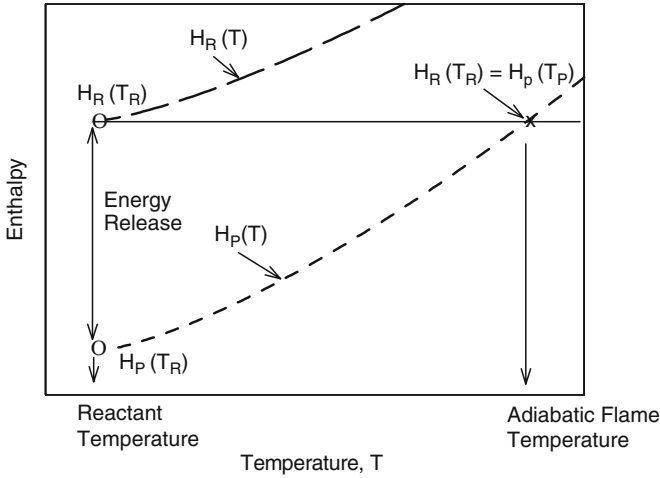
Fig. 2.3 Graphical interpretation of adiabatic flame temperature

is lower than that of the reactant mixture. The energy released from combustion is used to heat up the products such that the condition $H_P(T_P) = H_R(T_R)$ is met.

The task is finding the product temperature given the enthalpy of reactants. Three different methods can be used to obtain T_P:

1. Using an average c_p value,
2. An iterative enthalpy balance,
3. Finding the equilibrium state using computer software (such as Cantera).

The first two methods can be performed manually if complete combustion is considered and provide only quick estimates. An equilibrium state solver takes into account dissociation of products at high temperature, making it more accurate than the first two methods.

Method 1: Constant, average c_p
From conservation of energy, $H_p(T_p) = H_R(T_R)$, which can be expressed as

$$\sum_i N_{i,P}[\Delta\hat{h}_{i,P}^o + \hat{h}_{si,P}(T_P)] = \sum_i N_{i,R}[\Delta\hat{h}_{i,R}^o + \hat{h}_{si,R}(T_R)]$$

Rearranging yields

$$\sum_i N_{i,P}\hat{h}_{si,P}(T_P) = -\left\{\sum_i N_{i,P}\Delta\hat{h}_{i,P}^o - \sum_i N_{i,R}\Delta\hat{h}_{i,R}^o\right\} + \sum_i N_{i,R}\hat{h}_{si,R}(T_R)$$

$$= -Q_{rxn,p}^0 + \sum_i N_{i,R}\hat{h}_{si,R}(T_R) \tag{2.38}$$

with

$$-Q^0_{rxn,p} = \sum_i N_{i,R}\Delta\hat{h}^o_{i,R} - \sum_i N_{i,P}\Delta\hat{h}^o_{i,P}. \tag{2.39}$$

Note that water in the products is likely in gas phase due to the high combustion temperature; therefore $-Q^0_{rxn,p} = \text{LHV}\cdot N_{fuel}\cdot M_{fuel} = \text{LHV}\cdot m_f$ when the fuel is completely consumed. The second term, $\sum_i N_{i,R}\hat{h}_{si,R}(T_R)$, in Eq. 2.38 represents the difference of sensible enthalpy between T_R and T_0 (25°C) for the reactant mixture. With the assumption that the sensible enthalpy can be approximated by $\hat{h}_{si,P}(T_P) \approx \hat{c}_{pi}(T_P - T_0)$ with $\hat{c}_{pi} \approx$ constant, we have

$$(T_P - T_0)\sum_i N_{i,P}\hat{c}_{pi} \equiv \hat{c}_p(T_P - T_0)\sum_i N_{i,P} = -Q^0_{rxn,p} + \sum_i N_{i,R}\hat{h}_{si,R}(T_R) \tag{2.40}$$

Rearranging the equation one finds T_P as

$$\begin{aligned}
T_P &= T_0 + \frac{-Q^0_{rxn,p} + \sum_i N_{i,R}\hat{h}_{si,R}(T_R)}{\sum_i N_{i,P}\hat{c}_{pi}} \\
&\approx T_R + \frac{-Q^0_{rxn,p}}{\sum_i N_{i,P}\hat{c}_{pi}} \\
&= T_R + \frac{\text{LHV}\cdot N_{fuel}\cdot M_{fuel}}{\sum_i N_{i,P}\hat{c}_{pi}},
\end{aligned} \tag{2.41}$$

where the following approximation has been applied[4]

$$\frac{\sum_i N_{i,R}\hat{h}_{si,R}(T_R)}{\sum_i N_{i,P}\hat{c}_{pi}} = \frac{\sum_i N_{i,R}\hat{c}_{pi,R}(T_R - T_0)}{\sum_i N_{i,P}\hat{c}_{pi}} \approx T_R - T_0$$

When reactants enter the combustor at the standard conditions, the above equation reduces to (as sensible enthalpies of reactants are zero at T_0)

$$T_P = T_0 + \frac{\text{LHV}\cdot N_{fuel}\cdot M_{fuel}}{\sum_i N_{i,P}\hat{c}_{pi}}. \tag{2.42}$$

---

[4] $\sum_i N_{i,R}\hat{c}_{pi,R}$ and $\sum_i N_{i,p}\hat{c}_{pi}$ are assumed to be approximately equal.

The above procedure is general and can be applied to any mixture. Note that the specific heat is a function of temperature, so the accuracy of this approach depends on the value selected for the specific heat $\hat{c}_p$.

If the heating value of a fuel is given, a mass-based analysis for the same control volume can be conducted. The initial mixture consists of fuel and air with m_f and m_a, respectively. By mass conservation, the products have a total mass of $m_f + m_a$. The sensible enthalpy of the products is approximated by $H_{s,P} = (m_a + m_f) \cdot \bar{c}_{p,P} \cdot (T_P - T_0)$, where $\bar{c}_{p,P}$ is an average value of specific heat evaluated at the average temperature of the reactants and products, i.e., $\bar{c}_{p,P} = c_p(\bar{T})$, where $\bar{T} = (T_p + T_R)/2$. Similarly, the sensible enthalpy of the reactants is estimated by $H_{s,R} = (m_a + m_f) \cdot \bar{c}_{p,R} \cdot (T_R - T_0)$, where $\bar{c}_{p,R}$ is an average value of specific heat evaluated at the average temperature of reactants and the standard temperature, i.e., $\bar{c}_{p,R} = c_p(\bar{T})$, where $\bar{T} = (T_R + T_0)/2$. From conservation of energy, $H_{s,P}$ equals the amount of heat released from combustion plus the sensible enthalpy of the reactants, $H_{s,P} = -Q^0_{rxn,p} + H_{s,R} = m_{fb}$ $\cdot LHV + H_{s,R}$, where m_{fb} is the amount of fuel burned. For $\phi \leqslant 1$, $m_{fb} = m_f$ since there is enough air to consume all the fuel in a lean mixture. For rich combustion ($\phi > 1$), the limiting factor is the amount of air available, m_a. Therefore, for $\phi > 1$, the amount of fuel burned (with air, m_a) is $m_{fb} = m_a f_s$, where f_s is the stoichiometric fuel/air ratio by mass. Then the adiabatic flame temperature is calculated for a lean mixture as $\phi \leqslant 1$

$$
\begin{aligned}
T_P &\cong T_0 + \frac{m_f \cdot LHV + (m_a + m_f)\bar{c}_{p,R}(T_R - T_0)}{(m_a + m_f)\bar{c}_{p,P}} \\
&\approx T_R + \frac{m_f \cdot LHV}{(m_a + m_f)\bar{c}_{p,P}} = T_R + \frac{m_f/m_a \cdot LHV}{(1 + m_f/m_a)\bar{c}_{p,P}} \\
&= T_R + \frac{f \cdot LHV}{(1+f)\bar{c}_{p,P}} = T_R + \frac{\phi \cdot f_s \cdot LHV}{(1 + \phi \cdot f_s)\bar{c}_{p,P}}
\end{aligned}
\tag{2.43}
$$

where $\bar{c}_{p,R} \approx \bar{c}_{p,P}$ is used in deriving the second line. Similarly, for the rich mixtures one gets

$$
\phi \geqslant 1 \quad T_p = T_R + \frac{f_s \cdot LHV}{(1+f)\bar{c}_{p,P}} = T_R + \frac{f_s \cdot LHV}{(1 + \phi \cdot f_s)\bar{c}_{p,P}}
\tag{2.44}
$$

Note that f_s is very small for hydrocarbon fuels (e.g., $f_s = 0.058$ for methane). As such, the product (flame) temperature increases almost linearly with equivalence ratio, ϕ, for lean combustion as shown in Fig. 2.4. As expected, the flame temperature peaks at the stoichiometric ratio. In rich combustion, the flame temperature decreases with ϕ.

Method 2: Iterative enthalpy balance
A more accurate approach is to find the flame temperature by iteratively assigning the flame temperature T_p until $H_p(T_p) \approx H_R(T_R)$. The enthalpy of reactants is assumed given. The enthalpy of products can be expressed in the following form
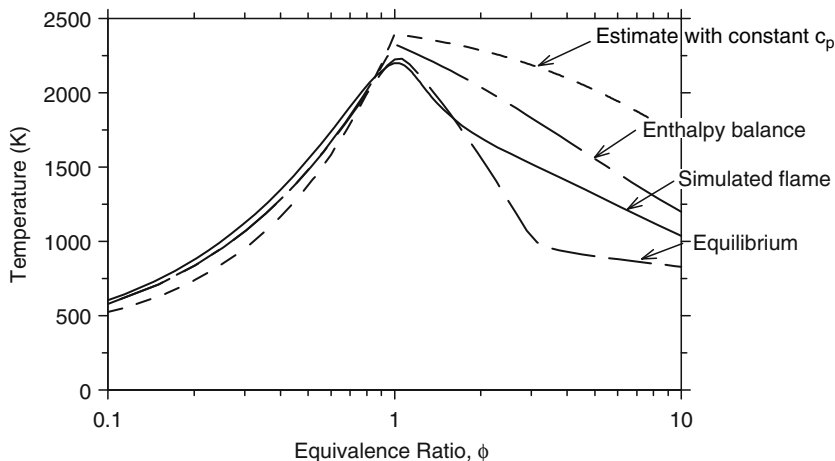
Fig. 2.4 Comparison of flame temperatures with different approaches

$$H_P(T_P) = \sum_i N_{i,P}\hat{h}_{i,P} = \sum_i N_{i,P}[\Delta\hat{h}^o_{i,P} + \hat{h}_{si,P}(T_P)] = H_R(T_R) = \sum_i N_{i,R}\hat{h}_{i,R}$$

Next, we rearrange the above equation to find an expression for the sensible enthalpy of the products as

$$\sum_i N_{i,P}\Delta\hat{h}^o_{i,P} + \sum_i N_{i,P}\hat{h}_{si,P}(T_P) = \sum_i N_{i,R}\Delta\hat{h}^o_{i,R} + \sum_i N_{i,R}\hat{h}_{si,R}(T_R)$$

$$\sum_i N_{i,P}\hat{h}_{si,P}(T_P) = \sum_i N_{i,R}\Delta\hat{h}^o_{i,R} - \sum_i N_{i,P}\Delta\hat{h}^o_{i,P} + \sum_i N_{i,R}\hat{h}_{si,R}(T_R) \quad (2.45)$$

$$\sum_i N_{i,P}\hat{h}_{si,P}(T_P) = -Q^0_{rxn,p} + \sum_i N_{i,P}\hat{h}_{si,R}(T_R).$$

With an initial guess of flame temperature, T_{p1}, one evaluates $H_p(T_{p1})$ from tables such as those in Appendix 3. If $H_p(T_{p1}) < H_R(T_R)$, we guess a higher flame temperature, T_{p2}. One repeats this process until the two closest temperatures are found such that $H_p(T_{f1}) < H_R(T_R) < H_p(T_{f2})$. The product temperature can be estimated by linear interpolation. This method, although more accurate, still assumes complete combustion to the major products.

Method 3: Equilibrium State (Free software: Cantera; Commercial software: Chemkin)
Dissociation[5] of products at high temperature ($T > 1,500$ K at ambient pressure) can take a significant portion of energy from combustion and hence the product

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[5] Dissociation is the separation of larger molecules into smaller molecules. For example, $2H_2O \leftrightarrow 2H_2 + O_2$.

temperature is lower than that calculated with only major components as products. The equilibrium state determines the species concentrations and temperature under certain constraints such as constant enthalpy, pressure, or temperature. The equilibrium flame temperature is expected to be lower than the temperatures estimated with Method 1 or Method 2. In addition, the chemical equilibrium state is often used in combustion engineering as a reference point for chemical kinetics (the subject of Chap. 3) if infinite time is available for chemical reactions. At this ideal state, forward and backward reaction rates of any chemical reaction steps are balanced. By constraining certain variables such as constant pressure and enthalpy, the chemical equilibrium state can be determined by minimizing the Gibbs free energy, even without knowledge of the chemical kinetics. Computer programs (such as STANJAN, Chemkin, Cantera) are preferred for this task, as hand calculations are time consuming.

2.4.2 Comparison of Adiabatic Flame Temperature Calculation Methods

The presented methods of estimating adiabatic flame temperature will produce different values from each other. Predicted adiabatic flame temperatures of a methane/air mixture at ambient pressure using these methods are compared in Fig. 2.4 for a range of equivalence ratios. Also included are the results from a flame calculation using a detailed, non-equilibrium flame model. On the lean side, the results agree reasonably well among all methods, as the major products are CO_2, H_2O, unburned O_2, and N_2. Visible deviations arise near stoichiometric conditions and become larger in richer mixtures. One reason for the deviation is the assumptions made about product species in the rich mixtures. For rich mixtures at the equilibrium state, CO is preferred over CO_2 due to the deficiency in O_2. Because the conversion of CO into CO_2 releases a large amount of energy, the rich mixture equilibrium temperatures are lower than those from the flame calculation, which has a residence time of less than 1 s. Among the methods, the results from the detailed flame model calculations are closest to reality, as real flames have finite residence times and generally do not reach equilibrium.

Example 2.6. Estimate the adiabatic flame temperature of a constant-pressure reactor burning a stoichiometric mixture of H_2 and air at 101.3 kPa and 25°C at the inlet.

Solution:
The combustion stoichiometry is $H_{2(g)} + 0.5 \ (O_{2(g)} + 3.76 \ N_{2(g)}) \rightarrow H_2O_{(g)} + 1.88 \ N_{2(g)}$

$$-Q^0_{rxn,p} = \sum_i N_{i,R}\Delta\hat{h}^o_{i,R} - \sum_i N_{i,P}\Delta\hat{h}^o_{i,P}$$
$$= \Delta\hat{h}^o_{H2} + 0.5\Delta\hat{h}^o_{O2} + 1.88\Delta\hat{h}^o_{N2} - 1\cdot\Delta\hat{h}^o_{H2O}$$
$$= 0 + 0 + 0 - 1\,\text{mol}\cdot(-241.88\,\text{kJ/mol}) = 241.88\,\text{kJ}$$

Method 1: Assuming a constant (average) $\hat{c}_p$ at 1,500 K, $\hat{c}_{p,H_2O}(1,500\,\text{K}) = 0.0467\,\text{kJ/mol} - \text{K}$
and

$$\hat{c}_{p,N_2}(1,500\,\text{K}) = 0.0350\,\text{kJ/mol} - \text{K}:$$

$$T_p = T_0 + \frac{-Q_{rxn,p}^0 + \sum_i N_{i,R}\hat{h}_{si,R}(T_R)}{\sum_i N_{i,p}\hat{c}_{p,i}}$$

$$= 300 + \frac{(241.88 + 0)\text{kJ/mol}}{(0.047 + 1.88 \cdot 0.035)\ \text{kJ/mol} - \text{K}}$$

$$\sim 2{,}148\,\text{K}$$

The average temperature of the products and reactants is now (2,148 K + 298 K)/ 2 ~ 1,223 K, indicating that the initial assumption of $T_{ave} = 1{,}500$ K was too high. Using the new average temperature of 1,223 K to evaluate the specific heats, the calculated flame temperature becomes $T_p \sim 2{,}253$ K. The average temperature is now $T_{ave} = 1{,}275$ K. This new average temperature can be used to calculate the specific heats and the process should be continued until the change in the average temperature is on the order of 20 K. By doing this procedure, we obtain $T_P \sim 2{,}230$ K.

Method 2: Iterative enthalpy balance:

$$H_P(T_P) = H_R(T_R)$$

$$\sum_i N_{i,p}\Delta\hat{h}_{i,p}^o + \sum_i N_{i,p}\hat{h}_{si,p}(T_p) = \sum_i N_{i,R}\Delta\hat{h}_{i,R}^o + \sum_i N_{i,R}\hat{h}_{si,R}(T_R)$$

$$N_{H_2O}\Delta\hat{h}_{H_2O}^o + N_{H_2O}\hat{h}_{s,H_2O}(T_P) + N_{N_2}\Delta\hat{h}_{N_2}^o + N_{N_2}\hat{h}_{s,N_2}(T_P)$$
$$= N_{H_2}\Delta\hat{h}_{H_2}^o + N_{H_2}\hat{h}_{s,H_2}(T_R) + N_{O_2}\Delta\hat{h}_{O_2}^o + N_{O_2}\hat{h}_{s,O_2}(T_R)$$
$$+ N_{N_2}\Delta\hat{h}_{N_2}^o + N_{N_2}\hat{h}_{s,N_2}(T_R)$$

$$1 \cdot \Delta\hat{h}_{H_2O}^0 + \hat{h}_{s,H_2O}(T_P) + 0 + 1.88 \cdot \hat{h}_{s,N_2}(T_P) = 0 + 0 + 0 + 0 + 0 + 0$$

$$\Delta\hat{h}_{H_2O}^0 + \hat{h}_{s,H_2O}(T_P) + 1.88 \cdot \hat{h}_{s,N_2}(T_P) = 0.$$

The first step is to guess the product temperature. For this case, let's pick $T_P = 2{,}000$ K. We now plug in the value for the heat of formation of water and use thermodynamic property tables to evaluate the sensible enthalpy terms.

T_P (K)	$H_P(T_P)$ (MJ)
2,000 K	$-241.83 + 72.69 + 1.88 \cdot 56.14 = -63.6$ MJ
2,500 K	$-241.83 + 98.96 + 1.88 \cdot 74.31 = -3.1$ MJ

Our initial guess of $T_P = 2,000$ K was too low. The process was repeated with a higher guess of $T_P = 2,500$ K which resulted in a much smaller remainder, implying that $T_P \sim 2,500$ K. For more accuracy, we can use linear extrapolation (or interpolation if we bracketed the real value):

$$\frac{T_P - 2,500}{2,500 - 2,000} = \frac{0 + 3.1}{-3.1 + 63.6}$$

$$T_P = 2,526K$$

Method 3: Cantera. Assume H_2, O_2, and H_2O are the only species in the system; equilibrium temperature is 2,425.1 K. The equilibrium mole fractions are listed below
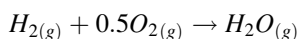
Mole fractions		
Species	$x_{reactant}$	$x_{product}$
H_2	0.2958	0.0153
O_2	0.1479	0.0079
N_2	0.5563	0.6478
H_2O	0	0.3286

Note that there is a small amount (~1.5%) of H_2 existing in the products due to the dissociation of H_2O at high temperature. Results of the above three methods agree with each other within 100–200 K which is less than 12% of the flame temperature. If radicals, such as H, OH, and O, are also included in the products, the equilibrium temperature drops to 2,384 K because additional dissociation occurs. This 41 K difference is about 1.7% of the flame temperature.

Example 2.7 The space shuttle burns liquid hydrogen and oxygen in the main engine. To estimate the maximum flame temperature, consider combustion of 1 mol of gaseous hydrogen with 0.5 mol of gaseous O_2 at 101.3 kPa. Determine the adiabatic flame temperatures using the average c_p method.

Solution:
The combustion stoichiometry is

$$H_{2(g)} + 0.5O_{2(g)} \rightarrow H_2O_{(g)}$$

$$- Q^0_{rxn,p} = \text{ LHV of } H_2 \text{ at constant pressure}$$

$$-Q^0_{rxn,p} = \sum_i N_{i,R}\Delta\hat{h}^o_{i,R} - \sum_i N_{i,P}\Delta\hat{h}^o_{i,P} = \Delta\hat{h}^o_{H2} + 0.5\Delta\hat{h}^o_{O2} - 1\Delta\hat{h}^o_{H2O}$$

$$= 0 + 0 - 1 \text{ mol}(-241.88 \text{ kJ/mol}) = 241.88 \text{ kJ}$$

Guessing a final temperature of about 3,000 K, we use average specific heats evaluated at 1,500 K

$$T_P = T_0 + \frac{-Q^0_{rxn,p} + \sum_i N_{i,R}\hat{h}_{si,R}(T_R)}{\sum_i N_{i,P}\hat{c}_{pi}}$$

$$= 300\,\text{K} + \frac{241.88\,\text{kJ/mol}}{0.047\,\text{kJ/mol} - \text{K}}$$

$$\sim 5,822\,\text{K}$$

Discussion:

This temperature is evidently much higher than the NASA reported value of ~3,600 K. What is the main reason for such a **BIG** discrepancy? The estimated temperature is well above 2,000 K and one expects a substantial dissociation of H_2O back to H_2 and O_2. That is, $H_2(g) + 0.5\,O_2\,(g) \leftrightarrow H_2O\,(g)$. Now we use Cantera or a commercial software program, such as Chemkin, to compute the equilibrium temperature with only three species H_2, O_2, and H_2O. The predicted adiabatic flame temperature drops to 3508.7 K. The mole fractions of these three before reaction and after combustion are listed below.

Species	Reactant	Product
H_2	0.6667	0.2915
O_2	0.3333	0.1457
H_2O	0	0.5628

As seen in the table, the dissociation is *very significant*; about 30% of the products is H_2. Let's find out how much fuel is not burned by considering the following stoichiometric reaction:

$$H_2(g) + 0.5O_2(g) \rightarrow X \cdot H_2 + 0.5X \cdot O_2 + (1 - X) \cdot H_2O(g)$$
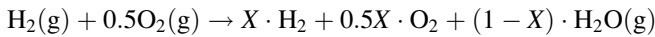
The mole fraction of H_2 in the products is

$$x_{H_2} = \frac{X}{X + 0.5X + 1 - X} = \frac{X}{0.5X + 1}.$$

With $x_{H_2} = 0.2915$, we get $X = 0.3412$. If we assume 66% of fuel is burned, a new estimate based on $\hat{c}_p$ at 1,500 K leads to

$$T_p = 300\,\text{K} + \frac{0.66 \cdot 241.88\,\text{kJ/mol}}{0.047\,\text{kJ/mol} - \text{K}} \sim 3,700\,\text{K}$$

that is in much better agreement with the equilibrium result. If we estimate $\hat{c}_p$ at 1,800 K we get

$$T_p = 300\,\text{K} + \frac{0.66 \cdot 241.88\,\text{kJ/mole}}{0.04966\,\text{kJ/mole} - \text{K}} \sim 3,514.7\,\text{K}.$$

If we include additional species, H, OH, and O in the products, the predicted equilibrium temperature drops to 3,076 K. The table below shows the mole fractions of each species in this case.

Species	Reactant	Product
H_2	0.6667	0.1503
O_2	0.3333	0.0510
H_2O	0	0.5809
OH	0	0.1077
O	0	0.0330
H	0	0.0771

Evidently, the radicals OH, H, and O take some energy to form; note that their values for enthalpy of formation are positive. Because the space shuttle engine operates at 18.94 MPa (2,747 psi, ~186 atm) at 100% power, the pressure needs to be taken into consideration as the combination of radicals occurs faster at higher pressures. The predicted equilibrium temperature at 18.94 MPa is 3,832.4 K and the mole fractions are listed below.

Species	Reactant	Product
H_2	0.6667	0.1169
O_2	0.3333	0.0336
H_2O	0	0.7051
OH	0	0.1005
O	0	0.0143
H	0	0.0296

The energy needed to vaporize liquid H_2 and O_2 and heat them from their boiling temperatures to 25°C are estimated to be 8.84 kJ/mol and 12.92 kJ/mol (energy = latent heat + sensible energy from boiling point to STP). With $H_2 + 0.5O_2$, the total energy required is then $8.84 + 0.5 \cdot 12.92$ or about 15.3 kJ/mol. The temperature drop due to this process is about ~15.3 kJ/(0.049 kJ/mol-K) = 148 K. With this, we estimate the space shuttle main engine temperature is $3,832 - 148$ K or ~3,675 K. The following information is used for estimating energy to vaporize H_2 and O_2: (1) for H_2, latent heat of vaporization 445.7 kJ/kg, boiling temperature = −252.8°C, $c_p \sim 4.12$ kJ/kg-K; (2) for O_2, latent heat of vaporization 212.7 kJ/kg, boiling temperature = −183°C, $c_p \sim 0.26$ kJ/kg-K.

2.5   Chapter Summary

The following shows the relations among different thermodynamics properties expressed in terms of mass fractions and mole fractions.

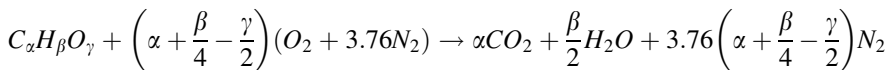| Property	Mass fraction, y_i	Mole fraction x_i
Species density ρ_i (kg/m^3)	ρy_i	$\rho \dfrac{x_i M_i}{\sum_{j=1}^{K} x_j M_j}$
Mole fraction, x_i [$-$]	$\dfrac{y_i/M_i}{\sum_{j=1}^{K} y_j/M_j}$	$-$
Mass fraction, y_i,	$-$	$\dfrac{x_i M_i}{\sum_{j=1}^{K} x_j M_j}$
Mixture molecular mass, M (kg/kmol)	$\dfrac{1}{\sum_{j=1}^{K} y_j/M_j}$	$\sum_{j=1}^{K} x_j M_j$
Internal energy of mixture, u (kJ/kg)	$\sum_{j=1}^{K} y_j \cdot u_j$	$\dfrac{1}{M} \sum_{j=1}^{K} x_j \cdot \hat{u}_j$
Enthalpy of mixture, h (kJ/kg)	$\sum_{j=1}^{K} y_j \cdot h_j$	$\dfrac{1}{M} \sum_{j=1}^{K} x_j \cdot \hat{h}_j$
Entropy of mixture, s (kJ/kg-K)	$\sum_{j=1}^{K} s_j \cdot h_j$	$\dfrac{1}{M} \sum_{j=1}^{K} x_j \cdot \hat{s}_j$
Specific heat at constant pressure c_p (kJ/kg-K)	$\sum_{j=1}^{K} y_j \cdot c_{pj}$	$\dfrac{1}{M} \sum_{j=1}^{K} x_j \cdot \hat{c}_{pj}$
Specific heat at constant volume c_v (kJ/kg-K)	$\sum_{j=1}^{K} y_j \cdot c_{vj}$	$\dfrac{1}{M} \sum_{j=1}^{K} x_j \cdot \hat{c}_{vj}$
Internal energy of mixture, $\hat{u}$ (kJ/kmol)	$M \sum_{j=1}^{K} y_j \cdot u_j$	$\sum_{j=1}^{K} x_j \cdot \hat{u}_j$
Enthalpy of mixture, $\hat{h}$ (kJ/kmol)	$M \sum_{j=1}^{K} y_j \cdot h_j$	$\sum_{j=1}^{K} x_j \cdot \hat{h}_j$
Entropy of mixture, $\hat{s}$ (kJ/kmol-K)	$M \sum_{j=1}^{K} y_j \cdot s_j$	$\sum_{j=1}^{K} x_j \cdot \hat{s}_j$
Specific heat at constant pressure $\hat{c}_p$ (kJ/kmol-K)	$M \sum_{j=1}^{K} y_j \cdot c_{pj}$	$\sum_{j=1}^{K} x_j \cdot \hat{c}_{pj}$
Specific heat at constant volume $\hat{c}_v$ (kJ/kmol-K)	$M \sum_{j=1}^{K} y_j \cdot c_{vj}$	$\sum_{j=1}^{K} x_j \cdot \hat{c}_{vj}$

Definitions

Enthalpy of combustion or heat of combustion: Ideal amount of energy that can be released by burning a unit amount of fuel.

Enthalpy of reaction or heat of reaction: Energy that must be supplied in the form of heat to keep a system at constant temperature and pressure during a reaction.

Enthalpy of formation or heat of formation: Heat of reaction per unit of product needed to form a species by reaction from the elements at the most stable conditions.

Combustion stoichiometry for a general hydrocarbon fuel, $C_\alpha H_\beta O_\gamma$

$$C_\alpha H_\beta O_\gamma + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)(O_2 + 3.76N_2) \rightarrow \alpha CO_2 + \frac{\beta}{2}H_2O + 3.76\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)N_2$$

Variables to quantify combustible mixtures
Fuel/air ratio by weight: $f = \frac{m_f}{m_a}$
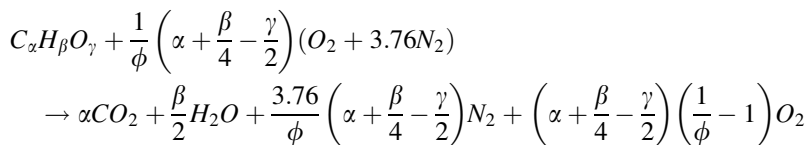For stoichiometric mixture: $f_s = \frac{m_f}{m_{as}}$
Equivalence ratio: $\phi = \frac{f}{f_s} = \frac{m_{as}}{m_a}$
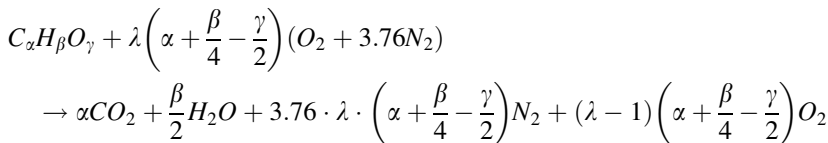Normalized air/fuel ratio $\lambda = \frac{AFR}{AFR_s} = \frac{1/f}{1/f_s} = \frac{1}{f/f_s} = \frac{1}{\phi}$
Percent of excess air

$$\%EA = 100\frac{(m_a - m_{as})}{m_{as}} = 100\left(\frac{m_a}{m_{as}} - 1\right) = 100\left(\frac{1}{\phi} - 1\right)$$

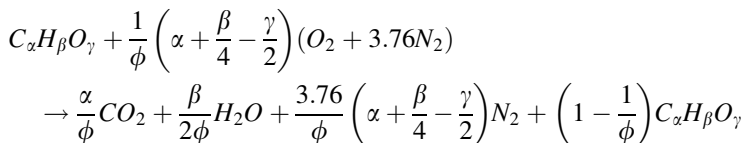Global equation for lean combustion $\phi \leqslant 1$

$$C_\alpha H_\beta O_\gamma + \frac{1}{\phi}\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)(O_2 + 3.76N_2)$$

$$\rightarrow \alpha CO_2 + \frac{\beta}{2}H_2O + \frac{3.76}{\phi}\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)N_2 + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)\left(\frac{1}{\phi} - 1\right)O_2$$

in terms of λ

$$C_\alpha H_\beta O_\gamma + \lambda\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)(O_2 + 3.76N_2)$$

$$\rightarrow \alpha CO_2 + \frac{\beta}{2}H_2O + 3.76 \cdot \lambda \cdot \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)N_2 + (\lambda - 1)\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)O_2$$

Global equation for rich combustion $\phi > 1$ with the assumption that products contain unburned fuel

$$C_\alpha H_\beta O_\gamma + \frac{1}{\phi}\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)(O_2 + 3.76N_2)$$

$$\rightarrow \frac{\alpha}{\phi}CO_2 + \frac{\beta}{2\phi}H_2O + \frac{3.76}{\phi}\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)N_2 + \left(1 - \frac{1}{\phi}\right)C_\alpha H_\beta O_\gamma$$

Enthalpy of formation (heat of formation) determined by bomb calorimeter

$$\Delta\hat{h}_i^o = \frac{Q_{rxn,v}^0 + \Delta N \cdot \hat{R}_u T_0}{N_{i,P}}$$

$$\Delta N = \sum_i N_{i,P} - \sum_i N_{i,R} = \frac{\beta}{4} + \frac{\gamma}{2} - 1$$

where $Q^0_{rxn,v}$ is the heat released from a constant-volume reactor where the products and reactants are at STP.

Heating values at STP (T_0) from a constant-volume reactor

$$HHV = \frac{\sum_i N_{i,R}\Delta\hat{h}^o_{i,R} - \sum_i N_{i,P}\Delta\hat{h}^o_{i,P} + \left(\sum_i N_{i,p} - \sum_i N_{i,R}\right)\hat{R}_u T_0}{N_{fuel}M_{fuel}}\ \text{(MJ/kg)}$$

$$LHV = HHV - \frac{N_{H2O,P}M_{H2O}h_{fg}}{N_{fuel}M_{fuel}},\ h_{fg} = 2{,}440 kJ/kg$$

Heating values at STP (T_0) determined from a constant-pressure reactor

$$HHV = \frac{\sum_i N_{i,R}\Delta\hat{h}^o_{i,R} - \sum_i N_{i,P}\Delta\hat{h}^o_{i,P}}{N_{fuel}M_{fuel}}$$

Adiabatic flame temperature for reactants at standard conditions
Method 1: Estimate based on average $\hat{c}_p$ values

$$T_P = T_0 + \frac{N_{fuel}M_{fuel}LHV + \sum_i N_{i,R}\hat{h}_{si,R}(T_R)}{\sum_i N_{i,P}\hat{c}_{pi}}$$

$$T_P \approx T_R + \frac{N_{fuel}M_{fuel}LHV}{\sum_i N_{i,P}\hat{c}_{pi}}$$

or if mixture is not stoichiometric: mass-base analysis using LHV and ϕ

$$\phi \leqslant 1\ T_P = T_R + \frac{f \cdot LHV}{(1+f)\bar{c}_p} = T_R + \frac{\phi \cdot f_s \cdot LHV}{(1 + \phi \cdot f_s)\bar{c}_p}$$

$$\phi > 1\ T_P = T_R + \frac{f_s \cdot LHV}{(1+f)\bar{c}_p} = T_R + \frac{f_s \cdot LHV}{(1 + \phi \cdot f_s)\bar{c}_p}$$

Method 2: Enthalpy Balance

$$H_P(T_P) = H_R(T_R)$$
$$H_P(T_P) = \sum_i N_{i,P}\hat{h}_{i,P} = \sum_i N_{i,P}[\Delta\hat{h}^o_{i,P} + \hat{h}_{si,P}(T_P)]$$

Trial and error of T_P such that $H_P(T_P)$ matches $H_R(T_R)$

Exercises

2.1 Consider an isentropic combustion system with a total of K species. Assuming constant specific heats, show that the mixture temperature and pressure at two different states are related to the respective pressures as

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}$$

where

$$\gamma = \frac{\sum_{i=1}^{K} m_i c_{p,i}}{\sum_{i=1}^{K} m_i c_{v,i}}.$$

2.2 Measurements of exhaust gases from a methane-air combustion system show 3% of oxygen by volume (dry base) in the exhaust. Assuming complete combustion, determine the excess percentage of air, equivalence ratio, and fuel/air ratio.

2.3 There has been a lot of interest about replacing gasoline with ethanol, but is this really a good idea? We're going to compare a blend of ethanol (70% ethanol and 30% gasoline by volume) to gasoline. Calculate the lower heating value (LHV) of a 70% ethanol/30% isooctane mixture in terms of kJ/mol of fuel. Assume complete combustion. How does this compare to the tabulated value for gasoline (isooctane)? Assuming a 20% thermal efficiency, if you need to get 100 kW of power from an engine, how much of each fuel (in mol/s) do you need? If you have a stoichiometric mixture of the ethanol/gasoline blend and air in your 100 kW engine, how much CO_2 are you emitting in g/s? How does this compare to the same engine running a stoichiometric mixture of 100% gasoline and air?

2.4 Gasoline is assumed to have a chemical composition of $C_{8.26} H_{15.5}$.

   (a) Determine the mole fractions of CO_2 and O_2 in the exhaust for an engine with normalized air/fuel ratio $\lambda = 1.2$ with the assumption of complete combustion.

   (b) The enthalpy of formation of $C_{8.26} H_{15.5}$ is -250 MJ/kmol. Determine the LHV of gasoline in terms of MJ/kg. The molecular mass of $C_{8.26} H_{15.5}$ is 114.62 kg/kmol.

   (c) Using an average c_p for the products at 1,200 K, estimate the adiabatic flame temperature at constant pressure of 1 atm for the lean ($\lambda = 1.2$) mixture.

2.5 A mixture of methane gas and air at 25°C and 1 atm is burned in a water heater at 150% theoretical air. The mass flow rate of methane is 1.15 kg/h. The exhaust gas temperature was measured to be 500°C and approximately
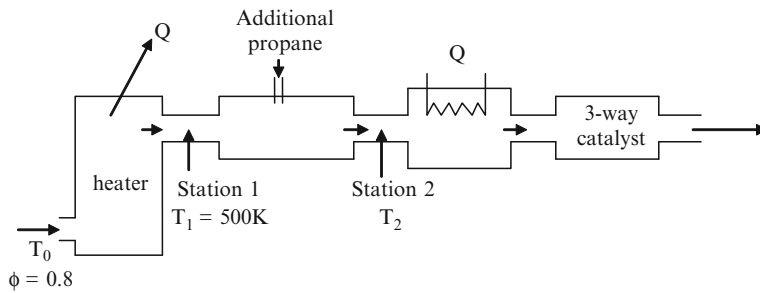
Fig. 2.5 Exercise 2.7

1 atm. The volumetric flow rate of cold water (at 22°C) to the heater is 4 L/min.

(a) Draw a schematic of the water heater and name its most important elements.
(b) Using Cantera, determine the amount of heat generated from burning of 1 kg of methane.
(c) Calculate the temperature of the hot water if the heat exchanger were to have an efficiency of 1.0, i.e., perfect heat transfer.

2.6 An acetylene-oxygen torch is used in industry for cutting metals.

(a) Estimate the maximum flame temperature using average specific heat c_p.
(b) Measurements indicate a maximum flame temperature of about 3,300 K. Compare with the result from (a) and discuss the main reasons for the discrepancy.

2.7 A space heater burns propane and air with intake temperature at $T_0 = 25°C$ and pressure at 1 atm (see Fig. 2.5). The combustible mixture enters the heater at an equivalence ratio $\phi = 0.8$. The exhaust gases exit at temperature $T_1 = 500$ K and contain CO_2, H_2O, O_2, and N_2 only at station 1. In order to use a 3-way catalyst for exhaust treatment, additional propane is injected into the exhaust to consume all the remaining oxygen in the exhaust such that the gases entering the catalyst contain only CO_2, H_2O, and N_2 at station 2. Assume that the entire system is at $P = 1$ atm and complete combustion occurs in both the heater and in the exhaust section.

(a) The volumetric flow rate of propane entering the heater is 1 L/min. Determine the injection rate of propane into the exhaust between station 1 and station 2 (see Fig. 2.5). Note that the propane at the injection station is at the same conditions as heater inlet, i.e., $T = 25°C$ and $P = 1$ atm.
(b) With the assumption of constant specific heats for the gases, estimate the temperature at station 2, T_2. The specific heat can be approximated by that of N_2 at 700 K as $\hat{c}_p = 30.68 \, kJ/kmol - K$,

Fuel:
$T_{fuel} = 25°C$
$P_{fuel} = 1\ atm$

Air:
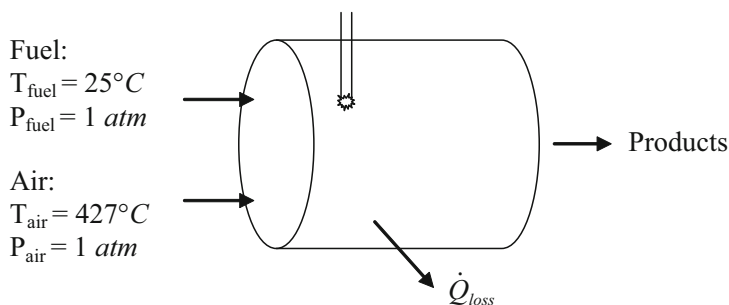$T_{air} = 427°C$
$P_{air} = 1\ atm$

Products

$\dot{Q}_{loss}$

Fig. 2.6 Exercise 2.9

2.8 Two grams of solid carbon, C(s), are combusted with pure oxygen in a 500 cm³ bomb calorimeter initially at 300 K. After the carbon is placed inside the bomb, the chamber is evacuated and then filled with gaseous oxygen from a pressurized tank.

   (a) Determine the minimum O_2 pressure inside the bomb necessary to allow complete combustion of the solid carbon.
   (b) When the bomb is cooled back to its initial temperature of 300 K, determine the pressure inside the bomb.

2.9 Consider the combustion chamber in a jet engine at cruising altitude. For simplicity, the combustor is operated at 1 atm of pressure and burns a stoichiometric ($\phi = 1$) mixture of n-heptane (C_7H_{16}) and air. The intake conditions are as indicated in Fig. 2.6.

   (a) Write the stoichiometric chemical reaction for the fuel with air.
   (b) If the mass flow rate of fuel is 1 kg/s, what is the mass flow rate of air?
   (c) What is the rate of heat loss from the combustion chamber if 10% of the LHV (heat of combustion) of the fuel is lost to surroundings?
   (d) What is the temperature of the products?
   (e) How does the temperature change if we burn fuel rich ($\phi > 1$)? How about fuel lean ($\phi < 1$)? (Hint: Easiest to show with a plot)

2.10 An afterburner is a device used by jet planes to increase thrust by injecting fuel after the main combustor. A schematic of this system is shown in Fig. 2.7. In the main combustor, hexane is burned with air at an equivalence ratio of $\phi = 0.75$. The products of the main combustor are CO_2, H_2O, O_2 and N_2, all of which enter the afterburner. In the afterburner, additional hexane is injected such that the equivalence ratio is $\phi = 1.25$. In the afterburner the hexane reacts with the excess O_2 from the main combustor to form CO, H_2O, and CO_2 only. Combined with the products of the main combustor, the gases exiting the afterburner are CO, CO_2, H_2O, O_2 and N_2. The entire system is
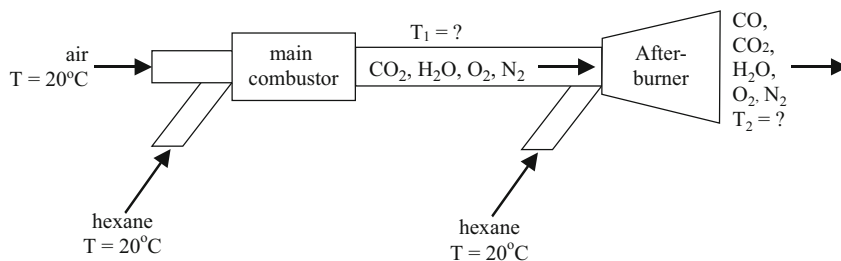
Fig. 2.7 Exercise 2.10

insulated, and the pressure everywhere is atmospheric. The inlet temperature of the hexane and air is $20°C$. Determine the temperature of the exhaust gases at each stage (Fig. 2.7). **Note:** An approximate answer is sufficient and it can be assumed that the specific heats for the gases are constant and approximately equal to that of N_2 at 1,000 K.