

Chapter 3: Fuels and combustion

3.1. Introduction

- ▶ In the preceding chapters we limited our consideration to **non-reacting systems**—systems whose **chemical composition remains unchanged during a process**.
- ▶ This was the case even with mixing processes during which a homogeneous mixture is formed from two or more fluids without the occurrence of any chemical reactions.
- ▶ In this chapter, we specifically deal with systems whose **chemical composition changes during a process**, i.e., systems that involve *chemical reactions*.
- ▶ When dealing with **non-reacting systems**, we need to consider only the *sensible internal energy* (associated with temperature and pressure changes) and the *latent internal energy* (associated with **phase changes**).
- ▶ When dealing with **reacting systems**, however, we also need to consider the *chemical internal energy*, which is the energy associated with the **destruction** and **formation** of **chemical bonds** between the atoms. The energy balance relations developed for non-reacting systems are equally applicable to reacting systems, but the energy terms in the latter case should include the **chemical energy of the system**.

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

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3.2. Fuels and combustion

- ▶ Any material that can be burned to release **thermal energy** is called a **fuel**.
- ▶ Most familiar fuels consist primarily of **hydrogen** and **carbon**.
 - They are called **hydrocarbon fuels** and are denoted by the general formula C_nH_m .
- ▶ **Hydrocarbon fuels** exist in **all phases**, some examples being
 - coal,
 - gasoline, and
 - natural gas.
- ▶ The main constituent of coal is **carbon**.
- ▶ Coal also contains varying amounts of oxygen, hydrogen, nitrogen, sulfur, moisture, and ash.
- ▶ It is difficult to give an exact mass analysis for coal since its composition varies considerably from one geographical area to the next and even within the same geographical location.

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- ▶ **Most liquid hydrocarbon fuels** are a mixture of numerous hydrocarbons and are obtained from crude oil by distillation (Fig. 3–1).

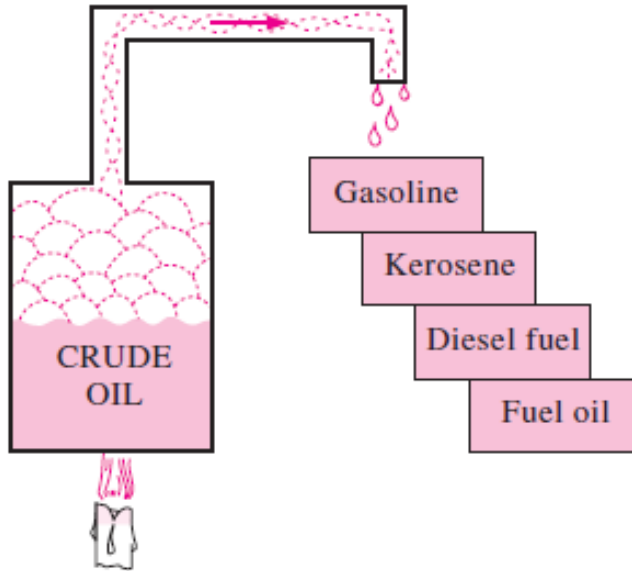


FIGURE 3–1: Most liquid hydrocarbon fuels are obtained from crude oil by distillation.

- ▶ The most volatile hydrocarbons vaporize first, forming what we know as **gasoline**. The less volatile fuels obtained during distillation are kerosene, diesel fuel, and fuel oil. The composition of a particular fuel depends on the source of the crude oil as well as on the refinery.
- ▶ Although liquid hydrocarbon fuels are mixtures of many different hydrocarbons, they are usually considered to be a **single hydrocarbon** for convenience.

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- For example, gasoline is treated as **octane**, C_8H_{18} , and the diesel fuel as **dodecane**, $C_{12}H_{26}$.
- ▶ Another common liquid hydrocarbon fuel is **methyl alcohol**, CH_3OH , which is also called ***methanol*** and is used in some gasoline blends.
- ▶ The gaseous hydrocarbon fuel **natural gas**, which is a mixture of methane and smaller amounts of other gases, is often treated as **methane**, CH_4
- ▶ **Natural gas** is produced from **gas wells** or **oil wells** rich in natural gas.
 - It is composed mainly of **methane**, but it also contains small amounts of ethane, propane, hydrogen, helium, carbon dioxide, nitrogen, hydrogen sulfate, and water vapor.
 - On vehicles, it is stored either in the
 - **gas phase** at pressures of 150 to 250 atm as **CNG** (compressed natural gas), or
 - **Liquid phase** at $-162^\circ C$ as **LNG** (liquefied natural gas).

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- ▶ Over a million vehicles in the world, mostly buses, run on natural gas. Liquefied petroleum gas (LPG) is a byproduct of natural gas processing or the crude oil refining. It consists mainly of propane and thus LPG is usually referred to as propane. However, it also contains varying amounts of butane, propylene, and butylenes. Propane is commonly used in fleet vehicles, taxis, school buses, and private cars. Ethanol is obtained from corn, grains, and organic waste. Methanol is produced mostly from natural gas, but it can also be obtained from coal and biomass. Both alcohols are commonly used as additives in oxygenated gasoline and reformulated fuels to reduce air pollution.
- ▶ Vehicles are a major source of **air pollutants** such as nitric oxides, carbon monoxide, and hydrocarbons, as well as the greenhouse gas carbon dioxide, and thus there is a growing shift in the transportation industry from the traditional petroleum-based fuels such as gasoline and diesel fuel to the cleaner burning *alternative fuels* friendlier to the environment such as natural gas, alcohols (ethanol and methanol), liquefied petroleum gas (LPG), and hydrogen.

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The use of electric and hybrid cars is also on the rise. A comparison of some alternative fuels for transportation to gasoline is given in Table below.

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

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

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

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

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- ▶ A chemical reaction during which **a fuel is oxidized** and a large quantity of energy is released is called **combustion**
- ▶ **The oxidizer** most often used in combustion processes is **air**, b/c
 - it is free and
 - readily available.
- ▶ Pure oxygen O_2 is used as an oxidizer only in some **specialized applications**, such as
 - cutting and
 - welding, where air cannot be used.
- ▶ **On a mole or a volume basis, dry air** is composed of
 - 20.9 percent oxygen,
 - 78.1 percent nitrogen,
 - 0.9 percent argon, and
 - small amounts of carbon dioxide, helium, neon, and hydrogen.
- ▶ **In the analysis of combustion processes**, the argon in the air is treated as nitrogen, and the gases that exist in trace amounts are disregarded. **Then dry air** can be approximated as:
 - **21 percent oxygen** and
 - **79 percent nitrogen** by mole numbers.

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- ▶ Therefore, each mole of oxygen entering a combustion chamber is accompanied by $0.79/0.21 = 3.76$ mol of nitrogen (Fig. 3–2). That is,

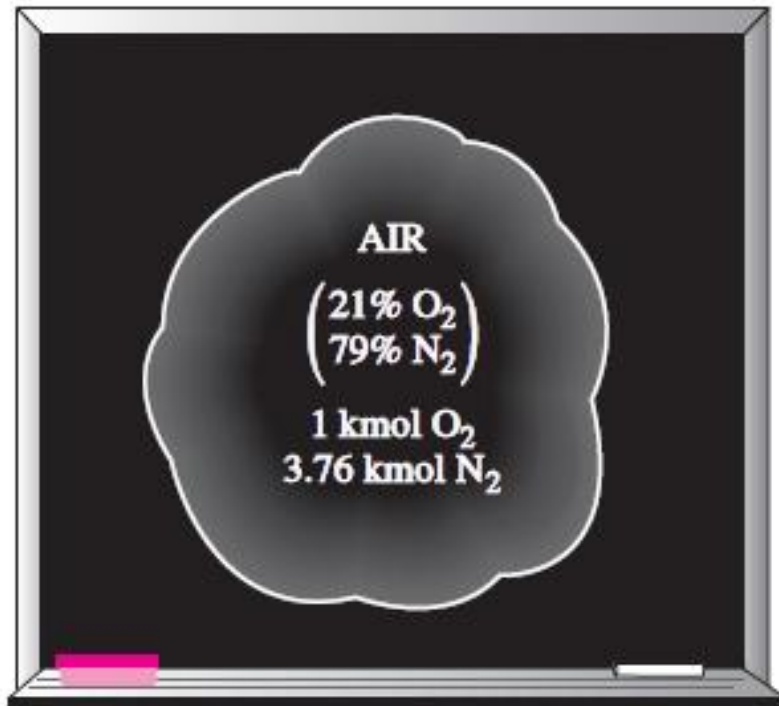


Figure 3–2: Each kmol of O₂ in air is accompanied by 3.76 kmol of N₂.

- During combustion, nitrogen behaves as an **inert gas** and does not react with other elements, other than forming a very small amount of nitric oxides.

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- ▶ However, even then the presence of nitrogen greatly affects the outcome of a combustion process since **nitrogen usually enters a combustion chamber in large quantities at low temperatures and exits at considerably higher temperatures**, absorbing a large proportion of the chemical energy released during combustion. Throughout this chapter, nitrogen is assumed to remain **perfectly inert**. Keep in mind, however, that at **very high temperatures**, such as those encountered in **internal combustion engines**, a small fraction of nitrogen reacts with oxygen, forming hazardous gases such as **nitric oxide**.
- ▶ Air that enters a combustion chamber normally contains some water vapor (or moisture), which also deserves consideration.
- ▶ For most combustion processes, the moisture in the air and the H_2O that forms during combustion can also be treated as an **inert gas**, like nitrogen.
- ▶ At very high temperatures, however, some water vapor dissociates into H_2 and O_2 as well as into H , O , and OH .
- ▶ When the combustion gases are cooled **below the dew-point temperature** of the **water vapor**, some **moisture condenses**. It is important to be able to predict the **dew-point temperature** since the water droplets often combine with the **sulfur dioxide** that may be present in the combustion gases, forming **sulfuric acid**, which is highly corrosive.

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- ▶ During a combustion process,
 - the components that exist before the reaction are called **reactants** and
 - the components that exist after the reaction are called **products as shown below**

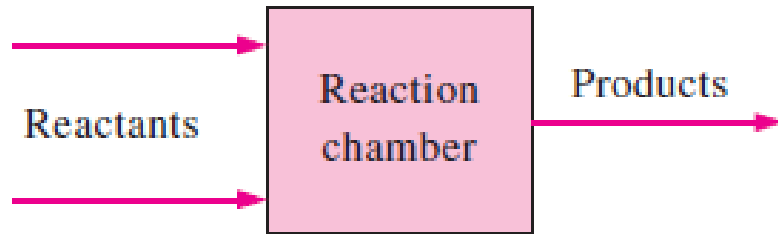


Figure : In a steady-flow combustion process, the components that enter the reaction chamber are called reactants and the components that exit are called products.

Consider, for example, the combustion of 1 kmol of carbon with 1 kmol of pure oxygen, forming carbon dioxide



Here C and O₂ are the reactants since they exist before combustion, and CO₂ is the product since it exists after combustion. **Note that** a reactant does not have to react chemically in the combustion chamber. For example, if carbon is burned with air instead of pure oxygen, both sides of the combustion equation will include N₂. That is, the N₂ will appear both as a reactant and as a product.

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- ▶ We should also mention that **bringing a fuel into intimate contact with oxygen** is **not sufficient to start a combustion process**. (Thank goodness it is not. Otherwise, the whole world would be on fire now.)
 - The fuel must be brought above its **ignition temperature** to start the combustion.
 - The minimum ignition temperatures of various substances in atmospheric air are approximately 260°C for gasoline, 400°C for carbon, 580°C for hydrogen, 610°C for carbon monoxide, and 630°C for methane.
 - Moreover, the proportions of the fuel and air must be in the proper range for combustion to begin. For example, natural gas does not burn in air in concentrations less than 5 percent or greater than about 15 percent.
- ▶ As you may recall from your chemistry courses, chemical equations are balanced on the basis of the **conservation of mass principle** (or the **mass balance**), which can be stated as follows:
 - *The total mass of each element is conserved during a chemical reaction* (Fig. 3–3). That is, the total mass of each element on the right-hand side of the reaction equation (the products) must be equal to the total mass of that element on the left-hand side (the reactants) even though the elements exist in different chemical compounds in the reactants and products.
 - Also, the total number of atoms of each element is conserved during a chemical reaction since the total number of atoms is equal to the total mass of the element divided by its atomic mass.

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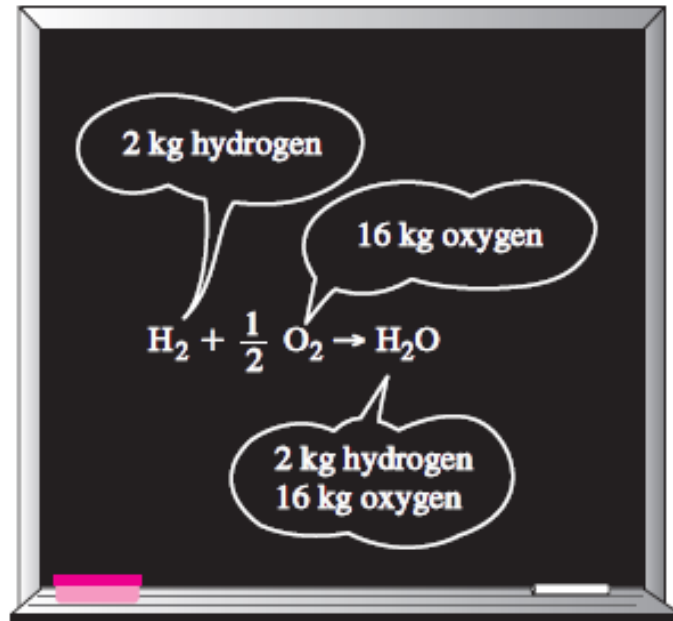


FIGURE 3.3: The mass (and number of atoms) of each element is conserved during a chemical reaction.

For example, $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ 3.1

- both sides of Eq. 3.1 contain 12 kg of carbon and 32 kg of oxygen, even though the carbon and the oxygen exist as elements in the reactants and as a compound in the product. Also, the total mass of reactants is equal to the total mass of products, each being 44 kg.
- However, notice that the **total mole number** of the reactants (2 kmol) is not equal to the total mole number of the products (1 kmol). That is, *the total number of moles is not conserved during a chemical reaction.*

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- ▶ In the analysis of combustion processes to quantify the amounts of fuel and air, frequently used quantity is the **air–fuel ratio** denoted by AF.
 - AF It is usually expressed on a mass basis and is defined as *the ratio of the mass of air to the mass of fuel* for a combustion process (Fig. 3.4). That is,

$$AF = \frac{m_{\text{air}}}{m_{\text{fuel}}} \dots\dots\dots 3.2$$

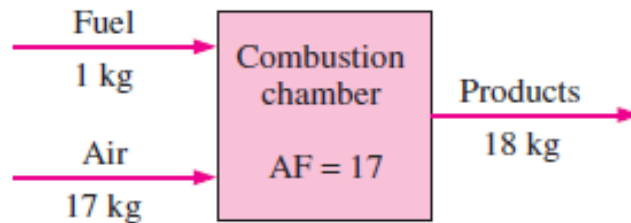


FIGURE 3.4: The air–fuel ratio (AF) represents the amount of air used per unit mass of fuel during a combustion process.

Recalling that, $m = NM$, where M is the molar mass and N is the number of moles.

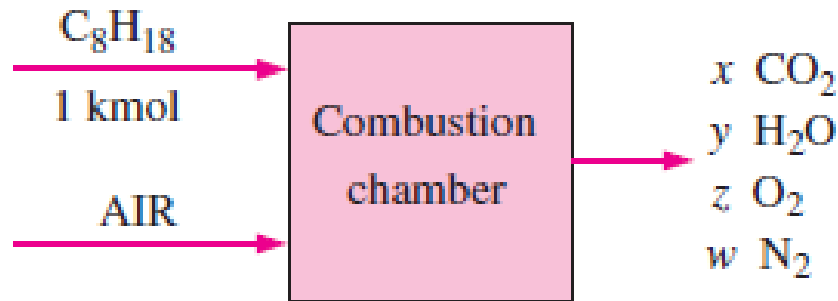
- ▶ The air–fuel ratio can also be expressed on a mole basis as the ratio of the mole numbers of air to the mole numbers of fuel, But this is not common definition.
- ▶ The reciprocal of air–fuel ratio is called the **fuel–air ratio**.

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Example

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

Solution



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

Analysis The chemical equation for this combustion process can be



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

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$$\text{C:} \quad 8 = x \quad \rightarrow \quad x = 8$$

$$\text{H:} \quad 18 = 2y \quad \rightarrow \quad y = 9$$

$$\text{O:} \quad 20 \times 2 = 2x + y + 2z \quad \rightarrow \quad z = 7.5$$

$$\text{N}_2: \quad (20)(3.76) = w \quad \rightarrow \quad w = 75.2$$

Substituting yields



Note that the coefficient 20 in the balanced equation above represents the number of moles of *oxygen*, not the number of moles of air. The latter is obtained by adding $20 \times 3.76 = 75.2$ moles of nitrogen to the 20 moles of oxygen, giving a total of 95.2 moles of air. The air–fuel ratio (AF) is determined by taking the ratio of the mass of the air and the mass of the fuel,

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

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

3.2: Theoretical and actual combustion processes

- A combustion process is **complete** if all the carbon in the fuel burns to CO_2 , all the hydrogen burns to H_2O , and all the sulfur (if any) burns to SO_2 .
That is, all the combustible components of a fuel are burned to completion during a complete combustion process (Fig. 3–5).

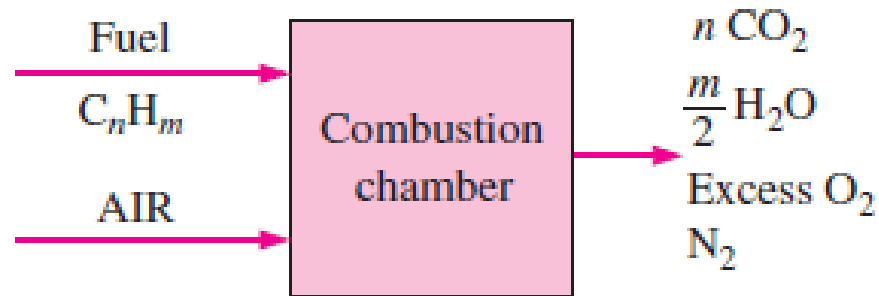


FIGURE 3–5: A combustion process is complete if all the combustible components of the fuel are burned to completion.

- Conversely, the combustion process is **incomplete** if the combustion products contain any unburned fuel or components such as C , H_2 , CO , or OH .
- Incomplete combustion occurs when there is
 - Insufficient oxygen:** is an obvious reason for incomplete combustion, but it is not the only one.
 - Occurs even when more oxygen is present in the combustion chamber than is needed for complete combustion. This may be attributed to **insufficient mixing in the combustion chamber** during the limited time that the fuel and the oxygen are in contact.
 - Another cause of incomplete combustion is **dissociation**, which becomes important at high temperatures.

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- Oxygen has a much greater tendency to combine with hydrogen than it does with carbon. Therefore, the hydrogen in the fuel normally burns to completion, forming H_2O , even when there is less oxygen than needed for complete combustion. Some of the carbon, however, ends up as CO or just as plain C particles (soot) in the products.
- The **minimum amount of air** needed for the complete combustion of a fuel is called the **stoichiometric** or **theoretical air**. Thus, when a fuel is completely burned with theoretical air, no uncombined oxygen is present in the product gases. The theoretical air is also referred to as the *chemically correct amount of air*, or **100 percent theoretical air**. A combustion process with less than the theoretical air is bound to be **incomplete**. The ideal combustion process during which a fuel is burned completely with theoretical air is called the **stoichiometric** or **theoretical combustion** of that fuel (Fig. 3–6). For example, the theoretical combustion of methane is



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



- no unburned fuel
- no free oxygen in products

FIGURE 3–6: The complete combustion process with no free oxygen in the products is called theoretical combustion.

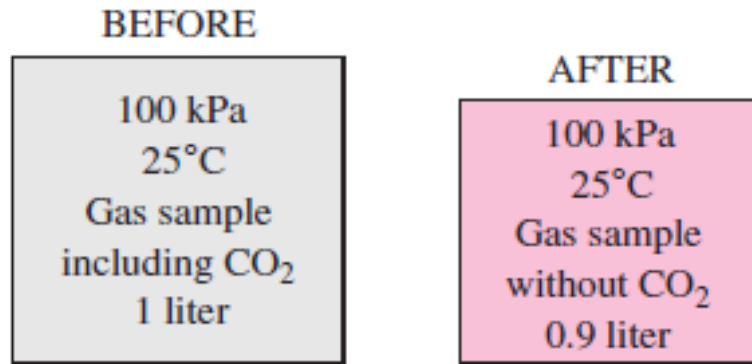
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- ▶ In actual combustion processes, it is common practice to use **more air than the stoichiometric amount** to increase the chances of complete combustion or to control the temperature of the combustion chamber.
- ▶ The amount of air in excess of the stoichiometric amount is called **excess air**.
- ▶ The amount of excess air is usually expressed in terms of the stoichiometric air as **percent excess air** or **percent theoretical air**.
 - For example, 50 percent excess air is equivalent to 150 percent theoretical air, and 200 percent excess air is equivalent to 300 percent theoretical air. Of course, the stoichiometric air can be expressed as 0 percent excess air or 100 percent theoretical air.
- ▶ Amounts of air less than the stoichiometric amount are called **deficiency of air** and are often expressed as **percent deficiency of air**.
 - For example, 90 percent theoretical air is equivalent to 10 percent deficiency of air.
- ▶ The amount of air used in combustion processes is also expressed in terms of the **equivalence ratio**, which is the ratio of the actual fuel–air ratio to the stoichiometric fuel–air ratio.

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- ▶ Predicting the composition of the products is relatively easy when the combustion process is assumed to be complete and the exact amounts of the fuel and air used are known. All one needs to do in this case is simply apply the mass balance to each element that appears in the combustion equation, without needing to take any measurements. Things are not so simple, however, when one is dealing with actual combustion processes. For one thing, actual combustion processes are hardly ever complete, even in the presence of excess air. Therefore, it is impossible to predict the composition of the products on the basis of the mass balance alone. Then the only alternative we have is to measure the amount of each component in the products directly.
- ▶ A commonly used device to analyze the composition of combustion gases is the **Orsat gas analyzer**. In this device, a sample of the combustion gases is collected and cooled to room temperature and pressure, at which point its volume is measured. The sample is then brought into contact with a chemical that absorbs the CO_2 . The remaining gases are returned to the room temperature and pressure, and the new volume they occupy is measured. The ratio of the reduction in volume to the original volume is the volume fraction of the CO_2 , which is equivalent to the mole fraction if ideal-gas behavior is assumed (Fig. 3–7). The volume fractions of the other gases are determined by repeating this procedure. In **Orsat analysis** the gas sample is collected over water and is maintained saturated at all times. Therefore, the vapor pressure of water remains constant during the entire test. For this reason the presence of water vapor in the test chamber is ignored and data are reported on a dry basis. However, the amount of H_2O formed during combustion is easily determined by balancing the combustion equation.

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$$y_{\text{CO}_2} = \frac{V_{\text{CO}_2}}{V} = \frac{0.1}{1} = 0.1$$

FIGURE 3–7: Determining the mole fraction of the CO₂ in combustion gases by using the Orsat gas analyzer.

Example: See boles starting from page 757 – to – 761

3.3: Enthalpy of formation and enthalpy of combustion

- ▶ Recalling that, (in Chap. 2), the molecules of a system possess energy in various forms such as
 - **sensible and latent energy** (associated with a change of state),
 - **chemical energy** (associated with the molecular structure), and
 - **nuclear energy** (associated with the atomic structure), as illustrated in Fig. 3.8.

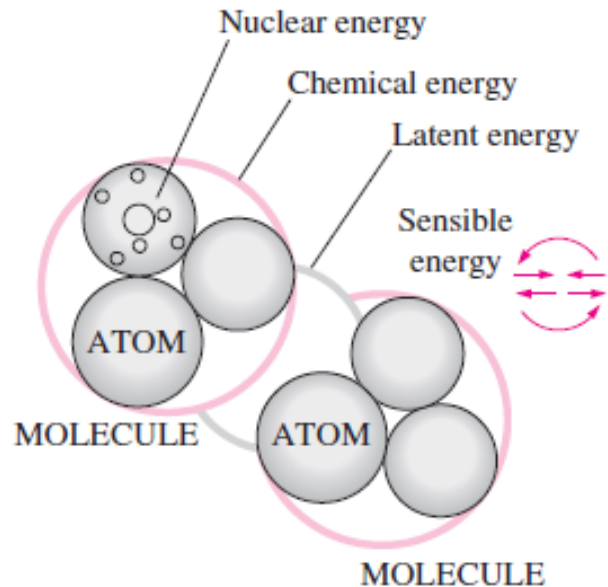


FIGURE 3.8: The microscopic form of energy of a substance consists of sensible, latent, chemical, and nuclear energies.

- ▶ In this text we do not intend to deal with nuclear energy. We also ignored chemical energy until now since the systems considered in previous chapters involved no changes in their chemical structure, and thus no changes in chemical energy. Consequently, all we

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

$$\Delta E_{\text{sys}} = \Delta E_{\text{state}} + \Delta E_{\text{chem}} \dots\dots\dots 3.3$$

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

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- ▶ In thermodynamics we are concerned with the changes in the **energy of a system** during a process, and **not the energy values at the particular states**.
- ▶ Therefore, we can choose any state as the **reference state** and **assign a value of zero** to the **internal energy** or **enthalpy** of a substance at that state.
- ▶ When a process involves no changes in chemical composition, the reference state chosen has no effect on the results.
- ▶ When the process involves chemical reactions, however, the composition of the system at the end of a process is no longer the same as that at the beginning of the process. In this case it becomes necessary to have a common reference state for all substances. The chosen reference state is **25°C (77°F)** and **1 atm**, which is known as the **standard reference state**. Property values at the **standard reference state** are indicated by a superscript (°) (such as h° and u°).
- ▶ When analyzing reacting systems, we must use property values relative to the **standard reference state**. However, it is not necessary to prepare a new set of property tables for this purpose. We can use the existing tables by subtracting the property values at the standard reference state. For example, the enthalpy of H_2O at 500 K is $h_{500\text{ K}} - h^\circ = 14,581 - 8669 = 5912 \text{ kJ/kmol}$.

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- Consider the formation of CO_2 from its elements, carbon and oxygen, during a steady-flow combustion process (Fig. 3.9). Both the carbon and the oxygen enter the combustion chamber at 25°C and 1 atm. The CO_2 formed during this process also leaves the combustion chamber at 25°C and 1 atm. The combustion of carbon is an **exothermic reaction** (a reaction during which chemical energy is released in the form of heat). Therefore, some heat is transferred from the combustion chamber to the surroundings during this process,

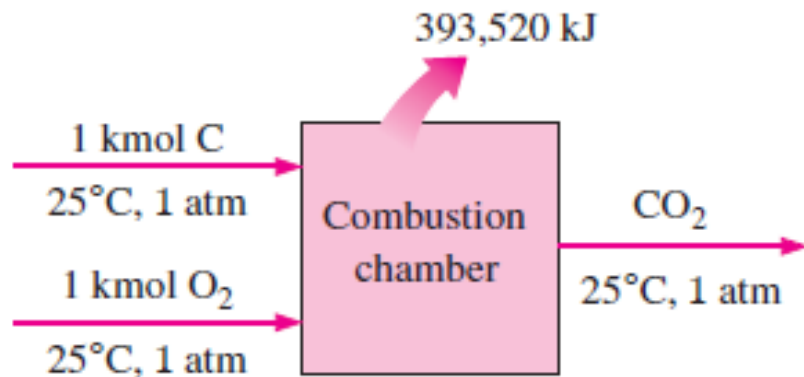


FIGURE 3.9: The formation of CO_2 during a steady flow combustion process at 25°C and 1 atm.

- The process described above involves **no work interactions**. Therefore, from the steady-flow energy balance relation, the heat transfer during this process must be equal to the **difference between the enthalpy of the products and the enthalpy of the reactants**. That is, $Q = H_{\text{prod}} - H_{\text{react}} = -393,520 \text{ kJ/kmol}$ 3.4

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- ▶ Since both the **reactants** and the **products** are at the same state, the enthalpy change during this process is solely due to the **changes in the chemical composition** of the system. This enthalpy change is different for different reactions, and it is very desirable to have a property to represent the changes in chemical energy during a reaction.
- ▶ This property is the **enthalpy of reaction** h_R , which is defined as *the difference between the enthalpy of the products at a specified state and the enthalpy of the reactants at the same state for a complete reaction*.
- ▶ For combustion processes, the **enthalpy of reaction** is usually referred to as the **enthalpy of combustion** h_C , which represents the amount of heat released during a steady-flow combustion process

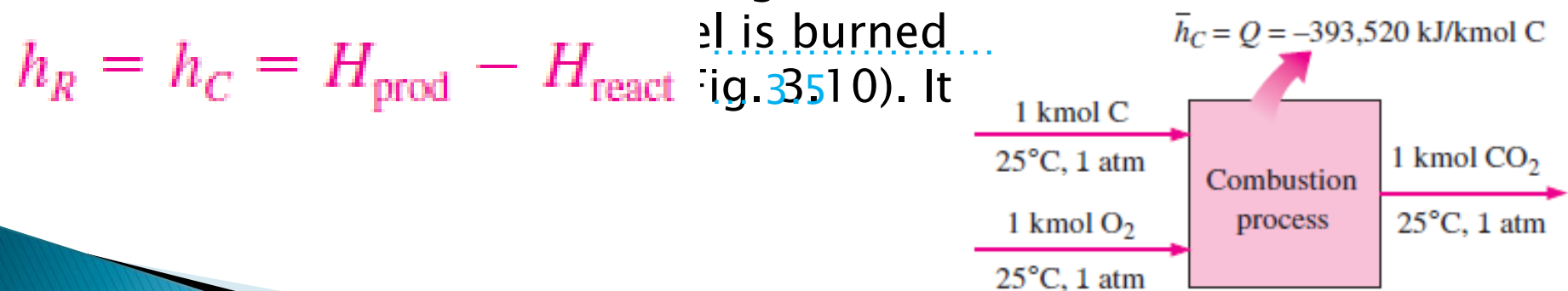


FIGURE 3.10: The enthalpy of combustion represents the amount of energy released as a fuel is burned during a steady-flow combustion process.

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which is $-393,520 \text{ kJ/kmol}$ for carbon at the standard reference state.

Note that: The enthalpy of combustion of a particular fuel is different at different **temperatures** and **pressures**.

- ▶ The enthalpy of combustion is not of much use when the combustion is incomplete. Therefore a more practical approach would be to have a more fundamental property to represent the chemical energy of an element or a compound at some reference state. This property is the **enthalpy of formation** denoted by:

$$\bar{h}_f$$

- ▶ The **enthalpy of formation**, can be viewed as *the enthalpy of a substance at a specified state due to its chemical composition*.
- ▶ To establish a starting point, we assign the enthalpy of formation of all stable elements (such as O_2 , N_2 , H_2 , and C) a **value of zero** at the standard reference state of 25°C and 1 atm. That is

$$\bar{h}_f = 0 \text{ for all stable elements.}$$

(This is no different from assigning the internal energy of saturated liquid water a value of zero at 0.01°C .) see table A-4 for saturated water at 0.01°C

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- ▶ Perhaps we should clarify what we mean by *stable*.
- ▶ **The stable form of an element** is simply the **chemically stable form** of that element at 25°C and 1 atm.
 - Nitrogen, for example, exists in diatomic form (N_2) at 25°C and 1 atm. Therefore, the stable form of nitrogen at the standard reference state is diatomic nitrogen N_2 , not monatomic nitrogen N.
- ▶ If an element exists in **more than one stable form** at 25°C and 1 atm, one of the forms should be specified as the stable form.
 - Carbon, for example, the stable form is assumed to be **graphite**, not diamond.

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- Now reconsider the formation of CO_2 (a compound) from its elements C and O_2 at 25°C and 1 atm during a steady-flow process. The enthalpy change during this process was determined to be $-393,520 \text{ kJ/kmol}$. However, $H_{\text{react}} = 0$ since both reactants are elements at the standard reference state, and the products consist of 1 kmol of CO_2 at the same state.
- Therefore, the enthalpy of formation of CO_2 at the standard reference state is -393.520 kJ/kmol (Fig. 3.11). The

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

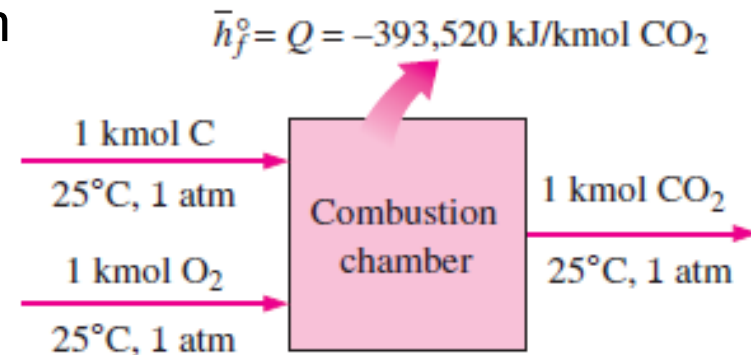


FIGURE 3.11: The enthalpy of formation of a compound represents the amount of energy absorbed or released as the component is formed from its stable elements during a steady-flow process at a specified state.

- The negative sign shows that 393,520 kJ of chemical energy is released (leaving the system as heat) when C and O_2 combine to form

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- ▶ Therefore, a negative enthalpy of formation for a compound indicates that heat is released during the formation of that compound from its stable elements. A positive value indicates heat is absorbed.
- ▶ Another term commonly used in conjunction with the combustion of fuels is the **heating value** of the fuel, which is defined as:
 - The amount of heat released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants.
- ▶ In other words, the heating value of a fuel is equal to **the absolute value of the enthalpy of combustion of the fuel**. That is,
$$\text{Heating value} = |h_c| \quad (\text{kJ/kg fuel})$$
- ▶ The heating value depends on the *phase* of the H₂O in the products.
- ▶ The heating value is called
 - the **higher heating value** (HHV) when the H₂O in the products is in the liquid form, and
 - it is called the **lower heating value** (LHV) when the H₂O in the products is in the vapor form (Fig. 3.12).

Cont...

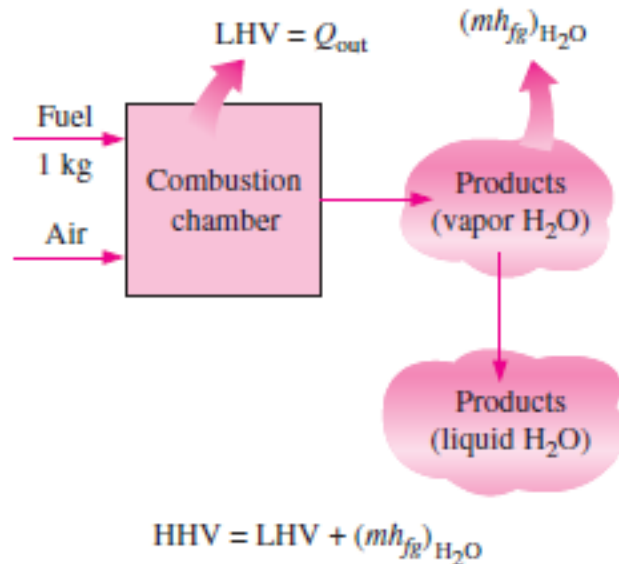


FIGURE 3.12: The higher heating value of a fuel is equal to the sum of the lower heating value of the fuel and the latent heat of vaporization of the H₂O in the products.

- The two heating values are related by

$$\text{HHV} = \text{LHV} + (mh_{fg})_{\text{H}_2\text{O}} \quad (\text{kJ/kg fuel}) \quad \dots 3.6$$

where m is the mass of H₂O in the products per unit mass of fuel and h_{fg} is the enthalpy of vaporization of water at the specified temperature.

- Higher and lower heating values of common fuels are given in **Table A-27**.

Cont...

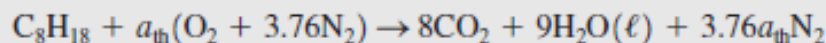
EXAMPLE: Evaluation of the Enthalpy of Combustion

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

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

Properties The enthalpy of formation at 25°C and 1 atm is $-393,520$ kJ/kmol for CO_2 , $-285,830$ kJ/kmol for $H_2O(\ell)$, and $-249,950$ kJ/kmol for $C_8H_{18}(\ell)$ (Table A-26).

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



Both the reactants and the products are at the standard reference state of 25°C and 1 atm. Also, N_2 and O_2 are stable elements, and thus their enthalpy of formation is zero. Then the enthalpy of combustion of C_8H_{18} becomes (Eq. 15-6)

$$\begin{aligned}\bar{h}_C &= H_{\text{prod}} - H_{\text{react}} \\ &= \sum N_p \bar{h}_{f,p}^\circ - \sum N_r \bar{h}_{f,r}^\circ = (N\bar{h}_f^\circ)_{CO_2} + (N\bar{h}_f^\circ)_{H_2O} - (N\bar{h}_f^\circ)_{C_8H_{18}}\end{aligned}$$

Substituting,

$$\begin{aligned}\bar{h}_C &= (8 \text{ kmol})(-393,520 \text{ kJ/kmol}) + (9 \text{ kmol})(-285,830 \text{ kJ/kmol}) \\ &\quad - (1 \text{ kmol})(-249,950 \text{ kJ/kmol}) \\ &= -5,471,000 \text{ kJ/kmol } C_8H_{18} = -47,891 \text{ kJ/kg } C_8H_{18}\end{aligned}$$

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

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

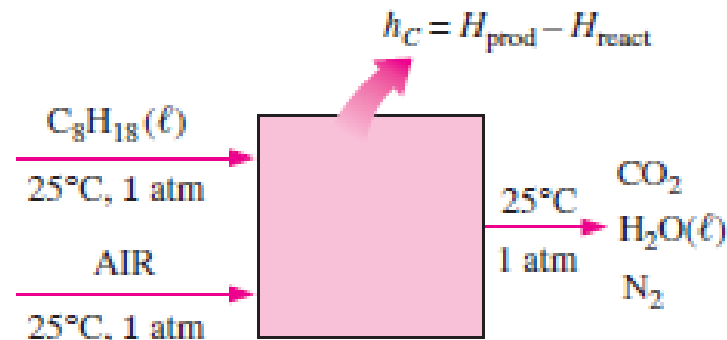


FIGURE 15-20

Schematic for Example 15-5.

Cont...

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

Adiabatic flame temperature

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

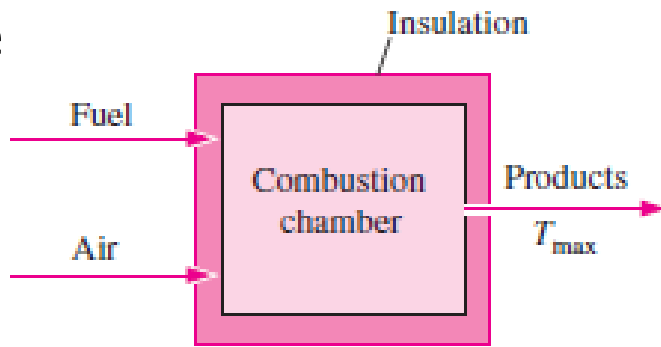


FIGURE 3.13: The temperature of a combustion chamber becomes maximum when combustion is complete and no heat is lost to the surroundings ($Q = 0$).

- The adiabatic flame temperature of a steady-flow combustion process is determined from the knowledge of the conservation of energy $Q - W = H_{prod} - H_{react}$ (kJ/kmol fuel) c & potential energy terms are disre

$$H_{prod} = H_{react}$$