Chapter 15 **CHEMICAL REACTIONS**

15–1 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.

Liquefied petroleum gas (LPG)

CNG (compressed natural gas) gas phase at pressures of 150 to 250 atm

LNG (liquefied natural gas) liquid phase at -162°C

TABLE 15–1

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.*

A chemical reaction during which a fuel is oxidized and a large quantity of energy is released is called **combustion.**

Pure oxygen O_2 is used as an oxidizer only in some specialized applications, such as cutting and welding, where air cannot be used.

$$0.79/0.21 = 3.76$$

$$1 \text{ kmol } O_2 + 3.76 \text{ kmol } N_2 = 4.76 \text{ kmol air} \quad \textbf{(15–1)}$$

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. 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.

Air that enters a combustion chamber normally contains some water vapor (or moisture), which also deserves consideration. When the combustion gases are cooled below the dew-point temperature of the water vapor, some moisture condenses.

The fuel must be brought above its **ignition temperature** to start the combustion.

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.

Conservation of mass principle (or the **mass balance**): *The total mass of each element is conserved during a chemical reaction.*

The total number of moles is not conserved during a chemical reaction.

Air–fuel ratio

$$\text{AF} = \frac{m_{\text{air}}}{m_{\text{fuel}}} \quad \textbf{(15–3)}$$

15–2 THEORETICAL AND ACTUAL COMBUSTION PROCESSES

It is often instructive to study the combustion of a fuel by assuming that the combustion is complete. 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.

Reasons for incomplete combustion:

- *Insufficient oxygen.*
- *Excess oxygen (insufficient mixing in the combustion chamber during the limited time that the fuel and the oxygen are in contact).*
- *Dissociation, which becomes important at high temperatures.*

The minimum amount of air needed for the complete combustion of a fuel is called the **stoichiometric** or **theoretical air**.

The theoretical air is also referred to as the *chemically correct amount of air,* or *100 percent theoretical air.*

The ideal combustion process during which a fuel is burned completely with theoretical air is called the **stoichiometric** or **theoretical combustion** of that fuel

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.**

Amounts of air less than the stoichiometric amount are called **deficiency of air** and are often expressed as **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.

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. 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.

15–3 ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

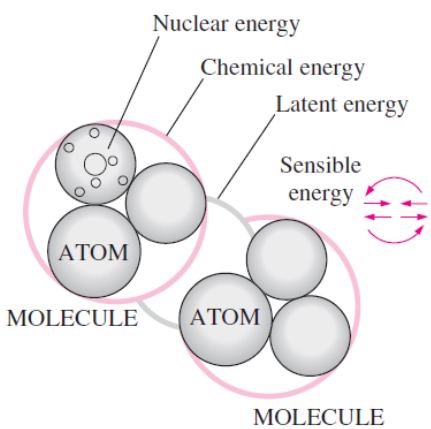

FIGURE 15–14

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

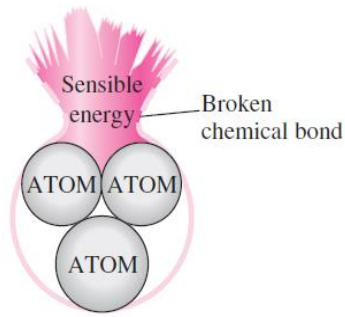

FIGURE 15–15

When the existing chemical bonds are destroyed and new ones are formed during a combustion process, usually a large amount of sensible energy is absorbed or released.

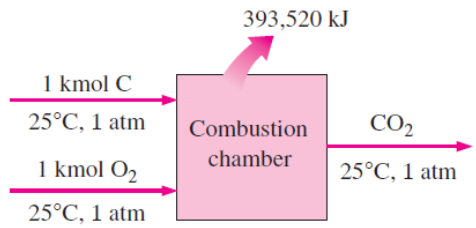

FIGURE 15–16

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

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 $u°$).

Exothermic reaction: a reaction during which chemical energy is released in the form of heat.

The heat transfer during a process that don't involve work must be equal to the difference between the enthalpy of the products and the enthalpy of the reactants.

Enthalpy of reaction h_R: it 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 when 1 kmol (or 1 kg) of fuel is burned completely at a specified temperature and pressure. It is expressed as

$$h_R = h_C = H_{\text{prod}} - H_{\text{react}} \qquad \textbf{(15–6)}$$

Enthalpy of formation ($\bar{h}_f$): *the enthalpy of a substance at a specified state due to its chemical composition*.

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

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.

Heating value of the fuel: it 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,

$$\text{Heating value} = |h_C| \qquad (\text{kJ/kg fuel})$$

The heating value depends on the *phase* of the H_2O in the products. The heating value is called the **higher heating value** (HHV) when the H_2O in the products is in the liquid form, and it is called the **lower heating value** (LHV) when the H_2O in the products is in the vapor form. The two heating values are related by

$$\text{HHV} = \text{LHV} + (mh_{fg})_{H_2O} \qquad (\text{kJ/kg fuel}) \qquad \textbf{(15–7)}$$

where m is the mass of H_2O in the products per unit mass of fuel and h_{fg} is the enthalpy of vaporization of water at the specified temperature.

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.

15–4 FIRST-LAW ANALYSIS OF REACTING SYSTEMS

Steady-Flow Systems

We express the enthalpy of a component on a unit mole basis as

$$\text{Enthalpy} = \bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ) \qquad (\text{kJ/kmol})$$

where the term in the parentheses represents the sensible enthalpy relative to the standard reference state, which is the difference between $\bar{h}$ the sensible enthalpy at the specified state) and $\bar{h}^\circ$ (the sensible enthalpy at the standard reference state of 25°C and 1 atm).

For a chemically reacting steady-flow system:

$$\underbrace{\dot{Q}_{in} + \dot{W}_{in} + \sum \dot{n}_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r}_{\text{Rate of net energy transfer in by heat, work, and mass}} = \underbrace{\dot{Q}_{out} + \dot{W}_{out} + \sum \dot{n}_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p}_{\text{Rate of net energy transfer out by heat, work, and mass}} \quad \textbf{(15–8)}$$

In combustion analysis, it is more convenient to work with quantities expressed *per mole of fuel*. Such a relation is obtained by dividing each term of the equation above by the molar flow rate of the fuel, yielding

$$\underbrace{Q_{in} + W_{in} + \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r}_{\text{Energy transfer in per mole of fuel by heat, work, and mass}} = \underbrace{Q_{out} + W_{out} + \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p}_{\text{Energy transfer out per mole of fuel by heat, work, and mass}} \quad \textbf{(15–9)}$$

Taking heat transfer *to* the system and work done *by* the system to be *positive* quantities, the energy balance relation just discussed can be expressed more compactly as

$$Q - W = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p - \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r \quad \textbf{(15–10)}$$

$$Q - W = H_{prod} - H_{react} \qquad \text{(kJ/kmol fuel)} \quad \textbf{(15–11)}$$

If the enthalpy of combustion $\bar{h}_c^\circ$ *for* a particular reaction is available, the steady-flow energy equation per mole of fuel can be expressed as

$$Q - W = \bar{h}_C^\circ + \sum N_p(\bar{h} - \bar{h}^\circ)_p - \sum N_r(\bar{h} - \bar{h}^\circ)_r \qquad \text{(kJ/kmol)} \quad \textbf{(15–12)}$$

A combustion chamber normally involves heat output but no heat input. Then the energy balance for a *typical steady-flow combustion process* becomes

$$Q_{\text{out}} = \underbrace{\sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r}_{\substack{\text{Energy in by mass}\\ \text{per mole of fuel}}} - \underbrace{\sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p}_{\substack{\text{Energy out by mass}\\ \text{per mole of fuel}}} \qquad \textbf{(15–13)}$$

Closed Systems

$$(Q_{\text{in}} - Q_{\text{out}}) + (W_{\text{in}} - W_{\text{out}}) = U_{\text{prod}} - U_{\text{react}} \qquad (\text{kJ/kmol fuel}) \quad \textbf{(15–14)}$$

To avoid using another property— *the internal energy of formation* $\bar{u}_f{}^\circ$—we utilize the definition of enthalpy

$$(\bar{u} = \bar{h} - P\bar{v} \text{ or } \bar{u}_f^\circ + \bar{u} - \bar{u}^\circ = \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - Pv)$$

and express the above equation as

$$Q - W = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_p - \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_r \qquad \textbf{(15–15)}$$

where we have taken heat transfer *to* the system and work done *by* the system to be *positive* quantities. The $P\bar{v}$ terms are negligible for solids and liquids, and can be replaced by R_uT for gases that behave as an ideal gas. Also, if desired, the $\bar{h} - P\bar{v}$ terms in Eq. 15–15 can be replaced by $\bar{u}$.

There are several important considerations in the analysis of reacting systems.

For example, we need to know whether the fuel is a solid, a liquid, or a gas since the enthalpy of formation $h_f{}^\circ$ of a fuel depends on the phase of the fuel. We also need to know the state of the fuel when it enters the combustion chamber in order to determine its enthalpy. For entropy calculations it is especially important to know if the fuel and air enter the combustion chamber premixed or separately. When the combustion products are cooled to low temperatures, we need to consider the possibility of condensation of some of the water vapor in the product gases.

15–5 ADIABATIC FLAME TEMPERATURE

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** or **adiabatic combustion temperature** of the reaction (Fig. 15–25).

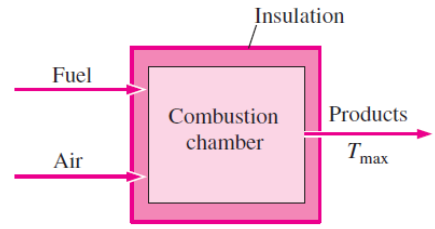

FIGURE 15–25
The temperature of a combustion chamber becomes maximum when combustion is complete and no heat is lost to the surroundings ($Q = 0$).

The adiabatic flame temperature of a steady-flow combustion process is determined from Eq. 15–11 by setting Q = 0 and W = 0. It yields

$$H_{prod} = H_{react} \qquad \textbf{(15–16)}$$

or

$$\sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r \qquad \textbf{(15–17)}$$

The determination of the adiabatic flame temperature requires the use of an iterative technique unless equations for the sensible enthalpy changes of the combustion products are available. A temperature is assumed for the product gases, and the H_{prod} is determined for this temperature. If it is not equal to H_{react}, calculations are repeated with another temperature. The adiabatic flame temperature is then determined from these two results by interpolation. When the oxidant is air, the product gases mostly consist of N_2, and a good first guess for the adiabatic flame temperature is obtained by treating the entire product gases as N_2.

Note that the adiabatic flame temperature of a fuel is not unique. Its value depends on (1) the state of the reactants, (2) the degree of completion of the reaction, and (3) the amount of air used.

15–6 ENTROPY CHANGE OF REACTING SYSTEMS

$$\underbrace{S_{in} - S_{out}}_{\text{Net entropy transfer by heat and mass}} + \underbrace{S_{gen}}_{\text{Entropy generation}} = \underbrace{\Delta S_{system}}_{\text{Change in entropy}} \qquad (\text{kJ/K}) \qquad \textbf{(15–18)}$$

The entropy balance relation can be expressed more explicitly for a *closed* or *steady-flow* reacting system as

$$\sum \frac{Q_k}{T_k} + S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}} \qquad (\text{kJ/K}) \qquad \textbf{(15–19)}$$

For an *adiabatic process* (Q = 0), the entropy transfer term drops out and Eq. 15–19 reduces to

$$S_{\text{gen,adiabatic}} = S_{\text{prod}} - S_{\text{react}} \geq 0 \qquad \textbf{(15–20)}$$

The **third law of thermodynamics** was expressed in Chap. 7 as follows: *The entropy of a pure crystalline substance at absolute zero temperature is zero*.

Therefore, the third law of thermodynamics provides an absolute base for the entropy values for all substances. Entropy values relative to this base are called the **absolute entropy ($\bar{s}$°)**.

The entropy calculations can be simplified somewhat if the gaseous components of the reactants and the products are approximated as ideal gases. However, entropy calculations are never as easy as enthalpy or internal energy calculations, since entropy is a function of both temperature and pressure even for ideal gases.

Note that the temperature of a component is the same as the temperature of the mixture, and the partial pressure of a component is equal to the mixture pressure multiplied by the mole fraction of the component.

For an ideal-gas:

$$\bar{s}(T,P) = \bar{s}^{\circ}(T,P_0) - R_u \ln \frac{P}{P_0} \qquad \textbf{(15–21)}$$

For the component i of an ideal-gas mixture, this relation can be written as

$$\bar{s}_i(T,P_i) = \bar{s}_i^{\circ}(T,P_0) - R_u \ln \frac{y_i P_m}{P_0} \qquad (\text{kJ/kmol} \cdot \text{K}) \qquad \textbf{(15–22)}$$

where P_0 = 1 atm, P_i is the partial pressure, y_i is the mole fraction of the component, and P_m is the total pressure of the mixture.

If a gas mixture is at a relatively high pressure or low temperature, the deviation from the ideal-gas behavior should be accounted for by incorporating more accurate equations of state or the generalized entropy charts.

15–7 SECOND-LAW ANALYSIS OF REACTING SYSTEMS

Exergy destroyed:

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} \qquad (\text{kJ}) \qquad \textbf{(15–23)}$$

The **reversible work:** $\boldsymbol{W_{rev}}$ represents the maximum work that can be done during a process.

$$W_{\text{rev}} = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0\bar{s})_r - \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0\bar{s})_p \qquad \textbf{(15–24)}$$

An interesting situation arises when both the reactants and the products are at the temperature of the surroundings T_0. In that case $\bar{h} - T_0\bar{s} = (\bar{h} - T_0\bar{s})_{T_0} = \bar{g}_0$ which is, by definition, the **Gibbs function** of a unit mole of a substance at temperature T_0.

$$W_{\text{rev}} = \sum N_r\bar{g}_{0,r} - \sum N_p\bar{g}_{0,p} \qquad \textbf{(15–25)}$$

$$W_{\text{rev}} = \sum N_r(\bar{g}_f^\circ + \bar{g}_{T_0} - \bar{g}^\circ)_r - \sum N_p(\bar{g}_f^\circ + \bar{g}_{T_0} - \bar{g}^\circ)_p \qquad \textbf{(15–26)}$$

where $\bar{g}_f^\circ$ is the Gibbs function of formation ($\bar{g}_f^\circ = 0$ for stable elements like N_2 and O_2 at the standard reference state of 25°C and 1 atm, just like the enthalpy of formation) and $\bar{g}_{T_0} - \bar{g}^\circ$ represents the value of the sensible Gibbs function of a substance at temperature T_0 relative to the standard reference state.

For the very special case of $T_{react} = T_{prod} = T_0$ = 25°C and the partial pressure

P_i = 1 atm for each component of the reactants and the products, Eq. 15–26 reduces to

$$W_{\text{rev}} = \sum N_r \bar{g}^{\circ}_{f,r} - \sum n_p \bar{g}^{\circ}_{f,p} \qquad (\text{kJ}) \qquad \textbf{(15–27)}$$