

Fall_12

Thermodynamics II

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Objectives

- Give an overview of fuels and combustion.
- Apply the conservation of mass to reacting systems to determine balanced reaction equations.
- Define the parameters used in combustion analysis, such as air–fuel ratio, percent theoretical air, and dew-point temperature.
- Apply energy balances to reacting systems for both steady-flow control volumes and fixed mass systems.
- Calculate the enthalpy of reaction, enthalpy of combustion, and the heating values of fuels.
- Determine the adiabatic flame temperature for reacting mixtures.
- Evaluate the entropy change of reacting systems.
- Analyze reacting systems from the second-law perspective.

FUELS AND COMBUSTION

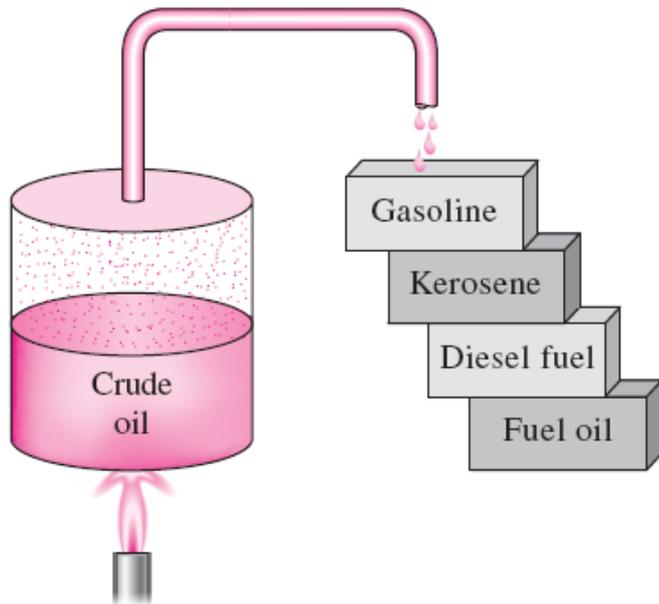
Fuel: Any material that can be burned to release thermal energy.

Most familiar fuels consist primarily of hydrogen and carbon.

They are called **hydrocarbon fuels** and are denoted by the general formula



Hydrocarbon fuels exist in all phases, some examples being coal, gasoline (usually treated as octane C_8H_{18}), and natural gas.



Most liquid hydrocarbon fuels are obtained from crude oil

 distillation.

TABLE 15-1

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

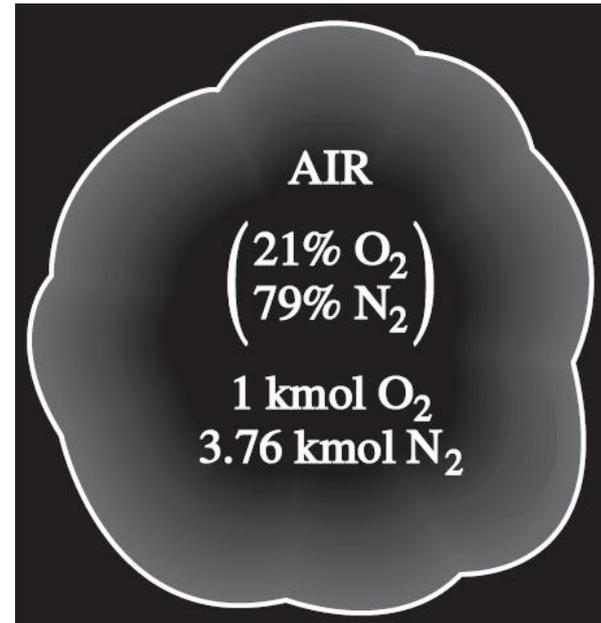
| Fuel | Energy content kJ/L | Gasoline equivalence,* L/L-gasoline |
|--|------------------------|--|
| Gasoline | 31,850 | 1 |
| Light diesel | 33,170 | 0.96 |
| Heavy diesel | 35,800 | 0.89 |
| LPG (Liquefied petroleum gas, primarily propane) | 23,410 | 1.36 |
| Ethanol (or ethyl alcohol) | 29,420 | 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.

The oxidizer most often used in combustion processes is air. Why?

On a mole or a volume basis, dry air is composed of 20.9% O₂, 78.1% N₂, 0.9% Ar, and small amounts of CO₂, He, Ne, H₂.

In the analysis of combustion processes, dry air is approximated as 21% O₂ and 79% N₂ by mole numbers.

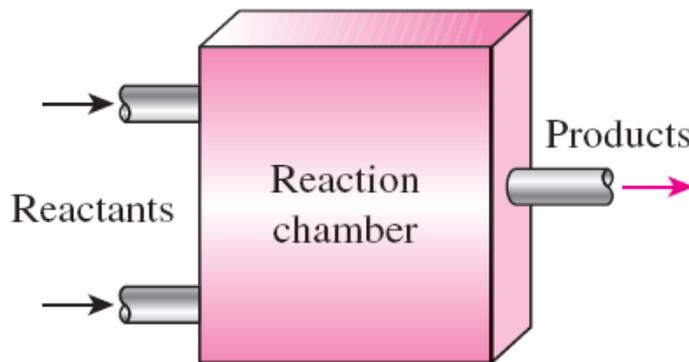
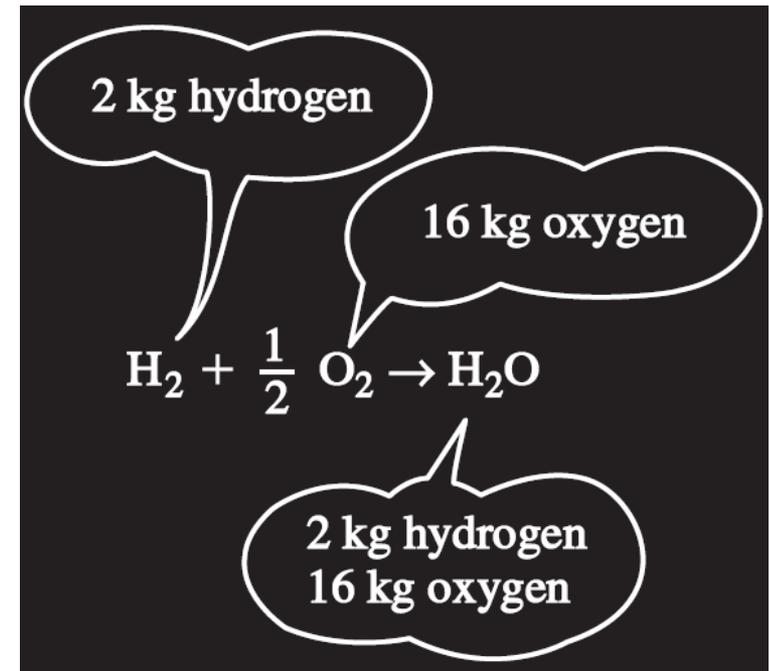


Combustion is a chemical reaction during which a fuel is oxidized and a large quantity of energy is released.

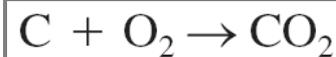
Each kmol of O₂ in air is accompanied by 3.76 kmol of N₂.

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

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% or greater than about 15%.



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



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

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

Air-fuel ratio (AF) 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

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

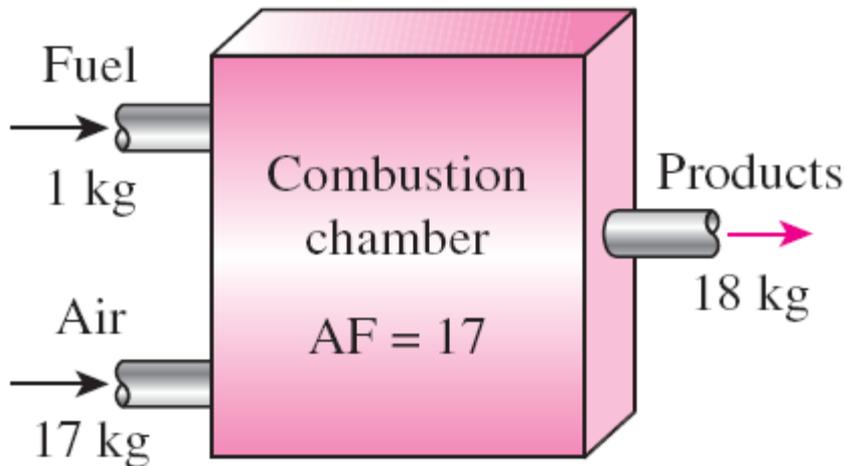
$$m = NM$$

m mass

N number of moles

M molar mass

Fuel–air ratio (FA): The reciprocal of air–fuel ratio.



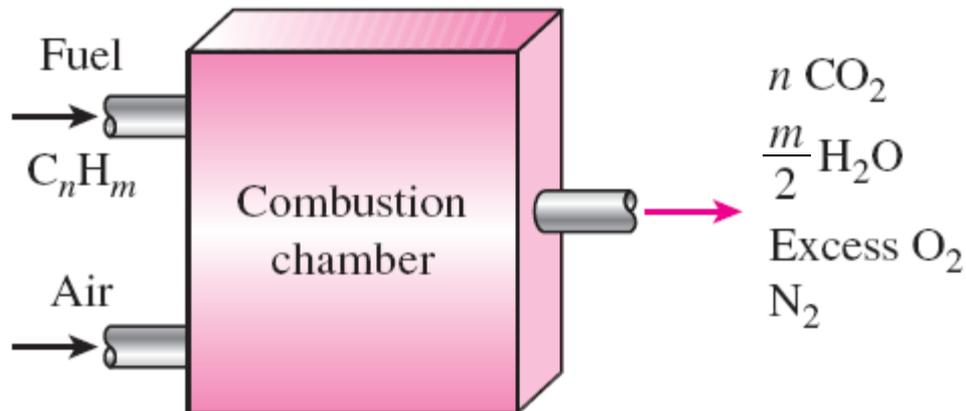
The air–fuel ratio (AF) represents the amount of air used per unit mass of fuel during a combustion process.

THEORETICAL AND ACTUAL COMBUSTION PROCESSES

Complete combustion: 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 .

Incomplete combustion: If the combustion products contain any unburned fuel or components such as C, H_2 , CO, or OH.

Reasons for incomplete combustion: 1 **Insufficient oxygen**, 2 **insufficient mixing** in the combustion chamber during the limited time that the fuel and the oxygen are in contact, and 3 **dissociation** (at high temperatures).



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 .

A combustion process is complete if all the combustible components of the fuel are burned to completion.

Stoichiometric or theoretical air: The minimum amount of air needed for the complete combustion of a fuel. Also referred to as the *chemically correct amount of air*, or *100% theoretical air*.

Stoichiometric or theoretical combustion: The ideal combustion process during which a fuel is burned completely with theoretical air.

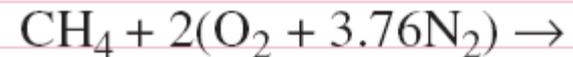
Excess air: The amount of air in excess of the stoichiometric amount. Usually expressed in terms of the stoichiometric air as *percent excess air* or *percent theoretical air*.

Deficiency of air: Amounts of air less than the stoichiometric amount. Often expressed as *percent deficiency of air*.

Equivalence ratio: The ratio of the actual fuel–air ratio to the stoichiometric fuel–air ratio.

50% excess air = 150% theoretical air
200% excess air = 300% theoretical air.

90% theoretical air = 10% deficiency of air



- no unburned fuel
- no free oxygen in products

The complete combustion process with no free oxygen in the products is called theoretical combustion.

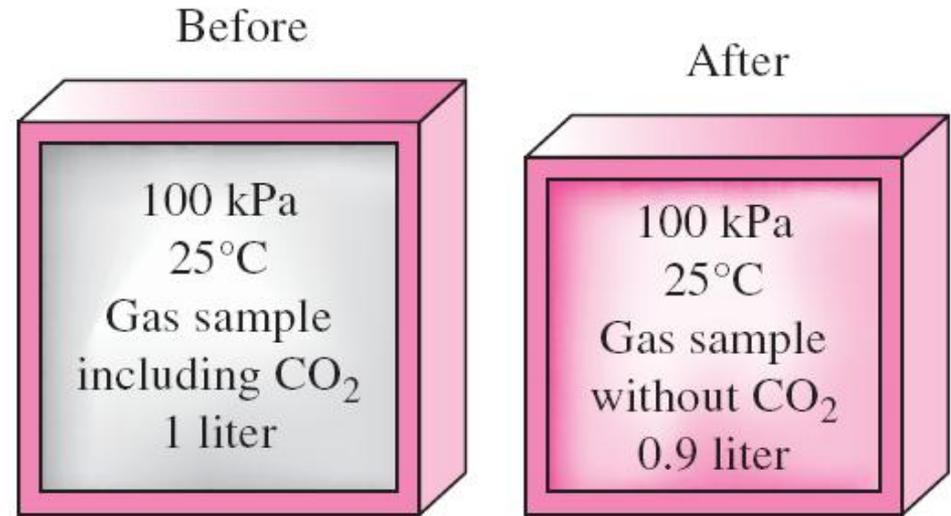
Predicting the composition of the products is relatively easy when the combustion process is assumed to be complete.

With actual combustion processes, 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**.

The results are reported on a dry basis.



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

Determining the mole fraction of the CO₂ in combustion gases by using the Orsat gas analyzer.

EXAMPLE 15–1 Balancing the Combustion Equation

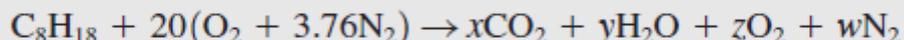
One kmol of octane (C_8H_{18}) is burned with air that contains 20 kmol of O_2 , as shown in Fig. 15–7. Assuming the products contain only CO_2 , H_2O , O_2 , and N_2 , determine the mole number of each gas in the products and the air–fuel ratio for this combustion process.

Solution The amount of fuel and the amount of oxygen in the air are given. The amount of the products and the AF are to be determined.

Assumptions The combustion products contain CO_2 , H_2O , O_2 , and N_2 only.

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

Analysis The chemical equation for this combustion process can be written as



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 the reactants be equal to that in the products:

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

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

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

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

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 from Eq. 15–3 by taking the ratio of the mass of the air and the mass of the fuel,

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

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

EXAMPLE 15-4 Reverse Combustion Analysis

Octane (C_8H_{18}) is burned with dry air. The volumetric analysis of the products on a dry basis is (Fig. 15-13)

CO_2 : 10.02 percent

O_2 : 5.62 percent

CO : 0.88 percent

N_2 : 83.48 percent

Determine (a) the air–fuel ratio, (b) the percentage of theoretical air used, and (c) the amount of H_2O that condenses as the products are cooled to $25^\circ C$ at 100 kPa.

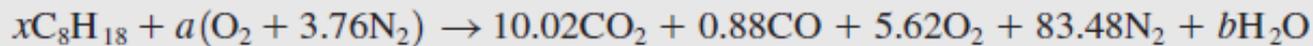
Solution Combustion products whose composition is given are cooled to $25^\circ C$. The AF, the percent theoretical air used, and the fraction of water vapor that condenses are to be determined.

Assumptions Combustion gases are ideal gases.

Properties The saturation pressure of water at $25^\circ C$ is 3.1698 kPa (Table A-4).

Analysis Note that we know the relative composition of the products, but we do not know how much fuel or air is used during the combustion process. However, they can be determined from mass balances. The H_2O in the combustion gases will start condensing when the temperature drops to the dew-point temperature.

For ideal gases, the volume fractions are equivalent to the mole fractions. Considering 100 kmol of dry products for convenience, the combustion equation can be written as



The unknown coefficients x , a , and b are determined from mass balances,

$$N_2: \quad 3.76a = 83.48 \quad \rightarrow \quad a = 22.20$$

$$C: \quad 8x = 10.02 + 0.88 \quad \rightarrow \quad x = 1.36$$

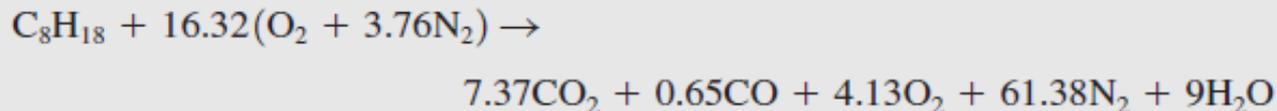
$$H: \quad 18x = 2b \quad \rightarrow \quad b = 12.24$$

$$O_2: \quad a = 10.02 + 0.44 + 5.62 + \frac{b}{2} \quad \rightarrow \quad 22.20 = 22.20$$

The O_2 balance is not necessary, but it can be used to check the values obtained from the other mass balances, as we did previously. Substituting, we get



The combustion equation for 1 kmol of fuel is obtained by dividing the above equation by 1.36,



(a) The air–fuel ratio is determined by taking the ratio of the mass of the air to the mass of the fuel (Eq. 15–3),

$$\begin{aligned} AF &= \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{(16.32 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(8 \text{ kmol})(12 \text{ kg/kmol}) + (9 \text{ kmol})(2 \text{ kg/kmol})} \\ &= \mathbf{19.76 \text{ kg air/kg fuel}} \end{aligned}$$

(b) To find the percentage of theoretical air used, we need to know the theoretical amount of air, which is determined from the theoretical combustion equation of the fuel,



$$\text{O}_2: \quad a_{\text{th}} = 8 + 4.5 \rightarrow a_{\text{th}} = 12.5$$

Then,

$$\begin{aligned} \text{Percentage of theoretical air} &= \frac{m_{\text{air,act}}}{m_{\text{air,th}}} = \frac{N_{\text{air,act}}}{N_{\text{air,th}}} \\ &= \frac{(16.32)(4.76) \text{ kmol}}{(12.50)(4.76) \text{ kmol}} \\ &= \mathbf{131\%} \end{aligned}$$

That is, 31 percent excess air was used during this combustion process. Notice that some carbon formed carbon monoxide even though there was considerably more oxygen than needed for complete combustion.

(c) For each kmol of fuel burned, $7.37 + 0.65 + 4.13 + 61.38 + 9 = 82.53$ kmol of products are formed, including 9 kmol of H_2O . Assuming that the dew-point temperature of the products is above $25^\circ C$, some of the water vapor will condense as the products are cooled to $25^\circ C$. If N_w kmol of H_2O condenses, there will be $(9 - N_w)$ kmol of water vapor left in the products. The mole number of the products in the gas phase will also decrease to $82.53 - N_w$ as a result. By treating the product gases (including the remaining water vapor) as ideal gases, N_w is determined by equating the mole fraction of the water vapor to its pressure fraction,

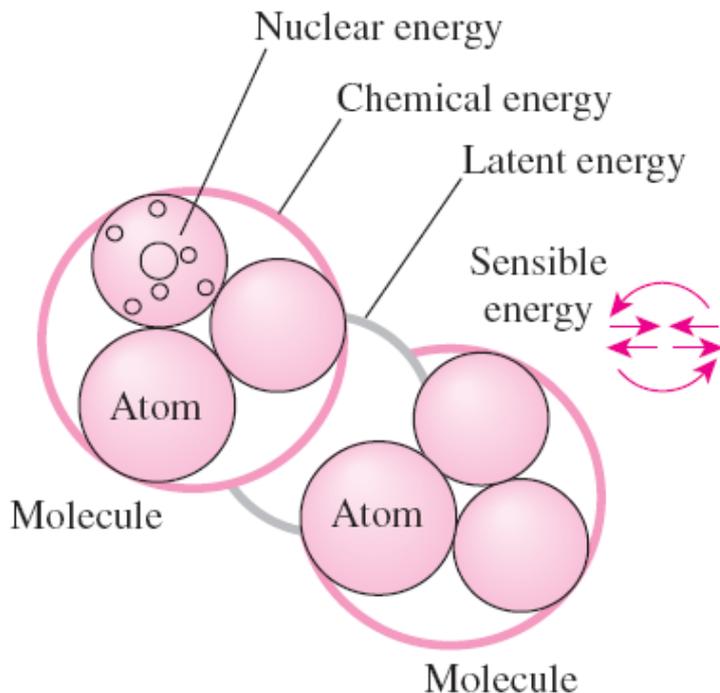
$$\frac{N_v}{N_{\text{prod, gas}}} = \frac{P_v}{P_{\text{prod}}}$$
$$\frac{9 - N_w}{82.53 - N_w} = \frac{3.1698 \text{ kPa}}{100 \text{ kPa}}$$
$$N_w = \mathbf{6.59 \text{ kmol}}$$

Therefore, the majority of the water vapor in the products (73 percent of it) condenses as the product gases are cooled to $25^\circ C$.

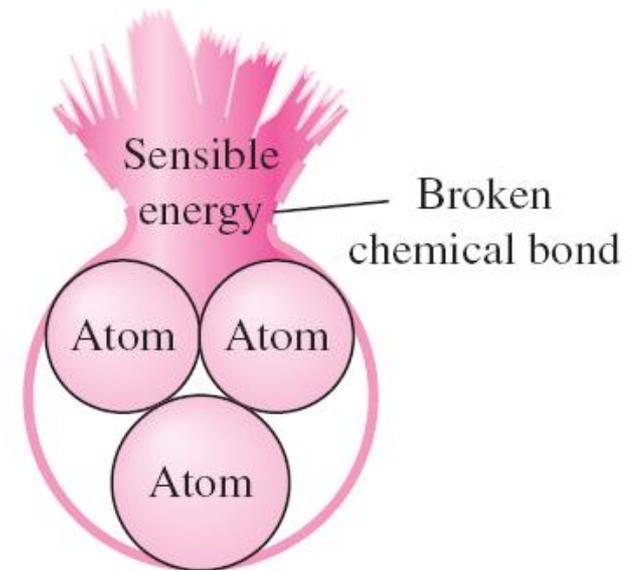
ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

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:

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



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



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.

Enthalpy of reaction h_R : 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.

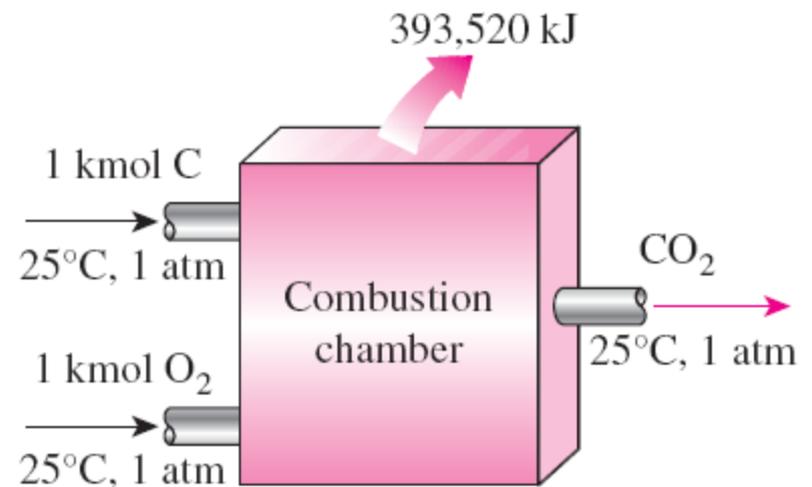
Enthalpy of combustion h_C : It is the enthalpy of reaction for combustion processes. It represents the amount of heat released during a steady-flow combustion process when 1 kmol (or 1 kg) of fuel is burned completely at a specified temperature and pressure.

The enthalpy of formation h_f : 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.

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.

$$Q = H_{\text{prod}} - H_{\text{react}} = -393,520 \text{ kJ/kmol}$$
$$\bar{h}_C = Q = -393,520 \text{ kJ/kmol C}$$

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



$$h_R = h_C = H_{\text{prod}} - H_{\text{react}}$$

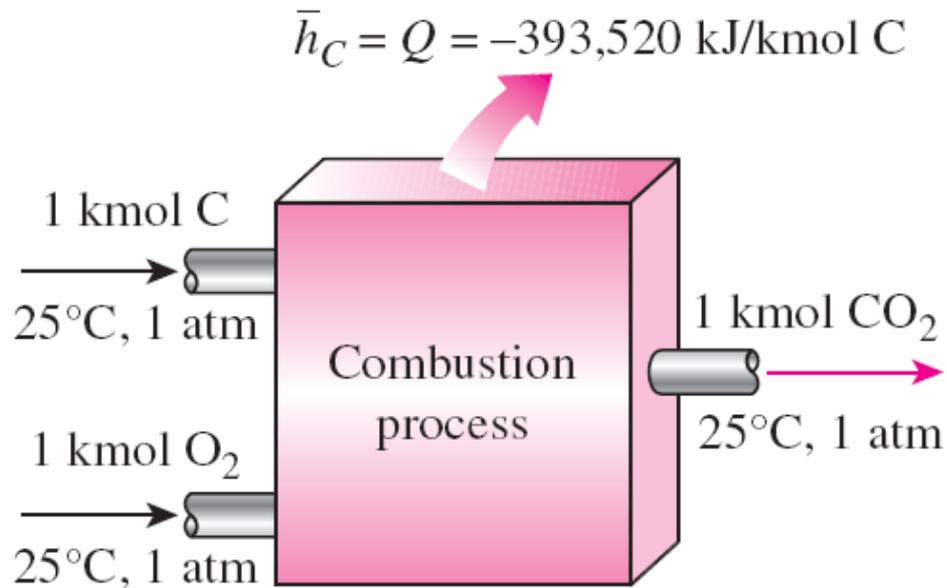
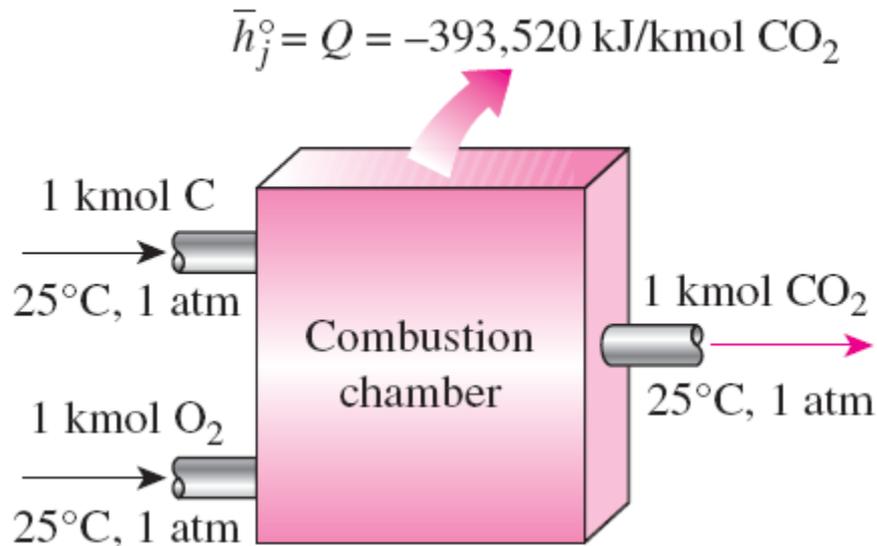


FIGURE 15–17

The enthalpy of combustion represents the amount of energy released as a fuel is burned during a steady-flow process at a specified state.



Enthalpy of formation:
The enthalpy of a substance at a specified state due to its chemical composition.

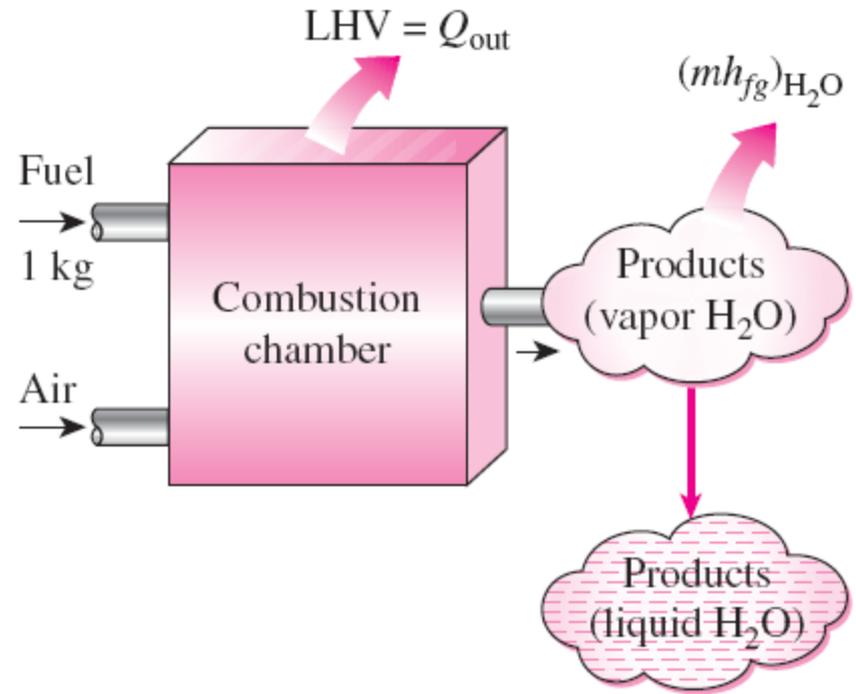
FIGURE 15–18

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.

Heating value: 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. The heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel.

Higher heating value (HHV): When the H_2O in the products is in the liquid form.

Lower heating value (LHV): When the H_2O in the products is in the vapor form.



$$HHV = LHV + (mh_{fg})_{H_2O}$$

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 H_2O in the products.

$$\text{Heating value} = |h_c| \quad (\text{kJ/kg fuel})$$

$$HHV = LHV + (mh_{fg})_{H_2O} \quad (\text{kJ/kg fuel})$$

For the fuels with variable composition (i.e., coal, natural gas, fuel oil), the heating value may be determined by burning them directly in a **bomb calorimeter**.

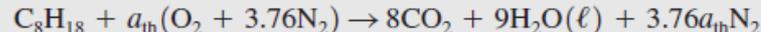
EXAMPLE 15–5 Evaluation of the Enthalpy of Combustion

Determine the enthalpy of combustion of liquid octane (C_8H_{18}) at $25^\circ C$ 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 $25^\circ C$ 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 $25^\circ C$ 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,

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

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.

FIRST-LAW ANALYSIS OF REACTING SYSTEMS

The energy balance (the first-law) relations developed in Chaps. 4 and 5 are applicable to both reacting and nonreacting systems. We rewrite the energy balance relations including the changes in chemical energies.

Steady-Flow Systems

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

When the changes in kinetic and potential energies are negligible, the steady-flow energy balance for a *chemically reacting steady-flow system*:

$$\dot{E}_{\text{in}} = \dot{E}_{\text{out}}$$

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

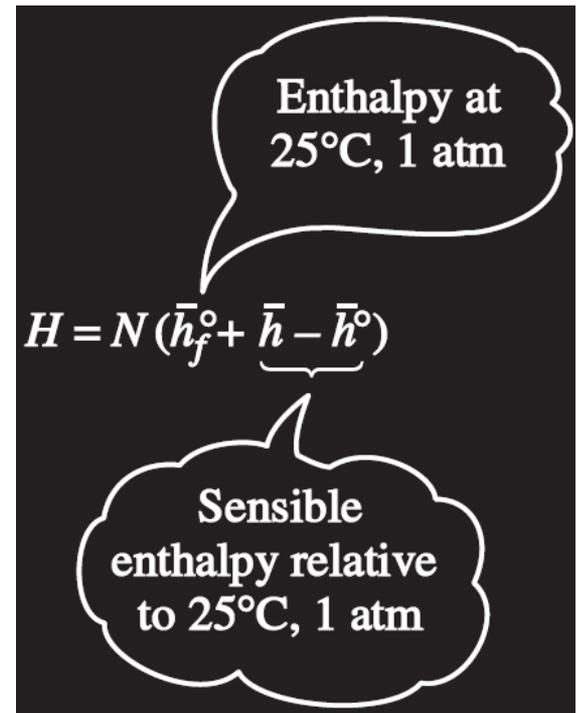
Rate of net energy transfer in by heat, work, and mass

Rate of net energy transfer out by heat, work, and mass

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

Energy transfer in per mole of fuel by heat, work, and mass

Energy transfer out per mole of fuel by heat, work, and mass



The enthalpy of a chemical component at a specified state

Taking **heat transfer to the system** and **work done by the system** to be *positive* quantities, the energy balance relation is

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

or as

$$Q - W = H_{\text{prod}} - H_{\text{react}} \quad (\text{kJ/kmol fuel})$$

where

$$H_{\text{prod}} = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p \quad (\text{kJ/kmol fuel})$$

$$H_{\text{react}} = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r \quad (\text{kJ/kmol fuel})$$

If the enthalpy of combustion for a particular reaction is available:

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

Most steady-flow combustion processes do not involve any work interactions. Also, combustion chamber normally involves heat output but no heat input:

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

Closed Systems

Taking **heat transfer to the system** and **work done by the system** to be *positive* quantities, the general closed-system energy balance relation can be expressed for a stationary *chemically reacting closed system* as

$$E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$$

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

$$\begin{aligned} U &= H - PV \\ &= N(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ) - PV \\ &= N(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v}) \end{aligned}$$

An expression for the internal energy of a chemical component in terms of the enthalpy.

Utilizing the definition of enthalpy:

$$\bar{u} = \bar{h} - P\bar{v} \quad \bar{u}_f^\circ + \bar{u} - \bar{u}^\circ = \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v}$$

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

The Pv terms are negligible for solids and liquids, and can be replaced by $R_u T$ for gases that behave as an ideal gas.

EXAMPLE 15–6**First-Law Analysis of Steady-Flow Combustion**

Liquid propane (C_3H_8) enters a combustion chamber at $25^\circ C$ at a rate of 0.05 kg/min where it is mixed and burned with 50 percent excess air that enters the combustion chamber at $7^\circ C$, as shown in Fig. 15–23. An analysis of the combustion gases reveals that all the hydrogen in the fuel burns to H_2O but only 90 percent of the carbon burns to CO_2 , with the remaining 10 percent forming CO . If the exit temperature of the combustion gases is 1500 K , determine (a) the mass flow rate of air and (b) the rate of heat transfer from the combustion chamber.

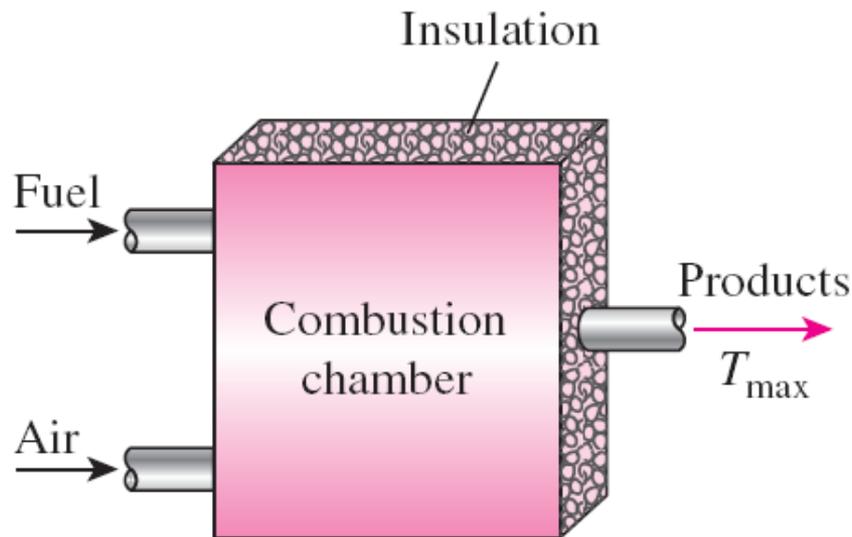
ADIABATIC FLAME TEMPERATURE

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**.

$$H_{\text{prod}} = H_{\text{react}} \quad \text{since } Q = 0 \text{ and } W = 0$$

$$\sum N_p (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p = \sum N_r (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r$$

The determination of the adiabatic flame temperature by hand requires the use of an iterative technique.

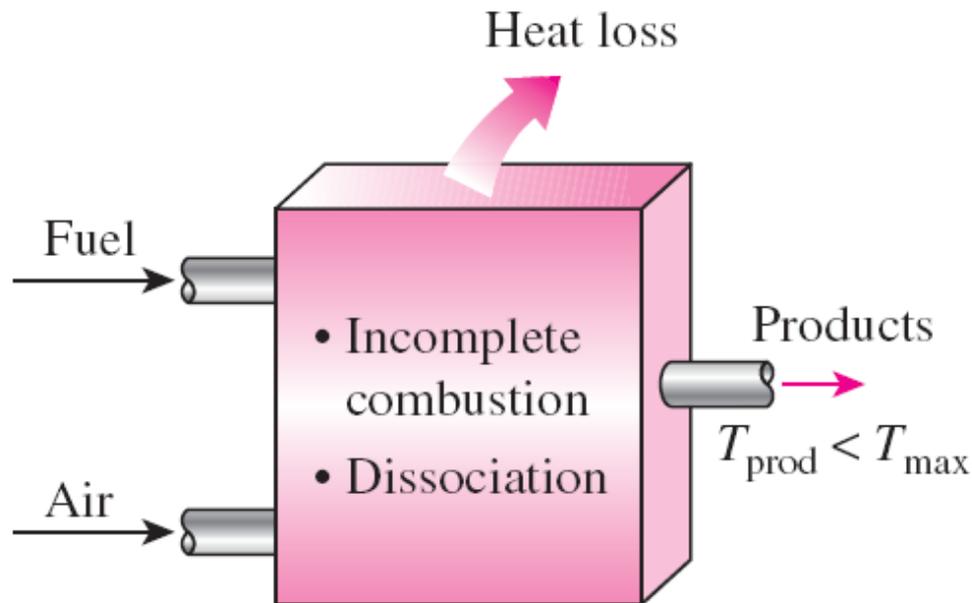


The temperature of a combustion chamber becomes maximum when combustion is complete and no heat is lost to the surroundings ($Q = 0$).

The adiabatic flame temperature of a fuel depends on

- (1) the state of the reactants
- (2) the degree of completion of the reaction
- (3) the amount of air used

For a specified fuel at a specified state burned with air at a specified state, *the adiabatic flame temperature attains its maximum value when complete combustion occurs with the theoretical amount of air.*



The maximum temperature encountered in a combustion chamber is lower than the theoretical adiabatic flame temperature.

EXAMPLE 15-8 **Adiabatic Flame Temperature in Steady Combustion**

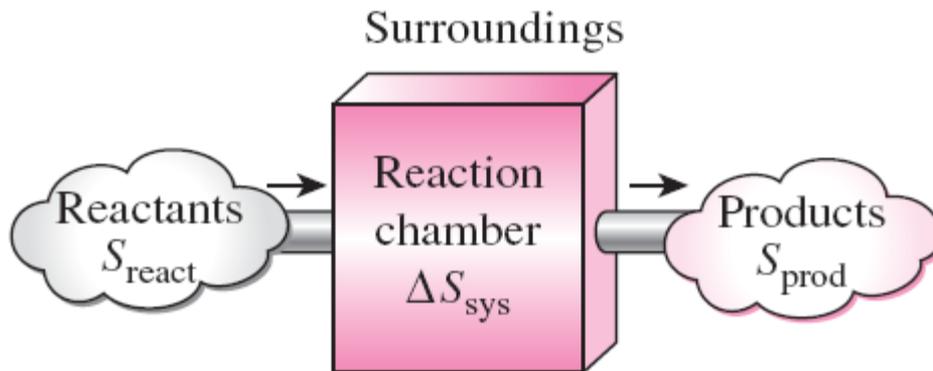
Liquid octane (C_8H_{18}) enters the combustion chamber of a gas turbine steadily at 1 atm and $25^\circ C$, and it is burned with air that enters the combustion chamber at the same state, as shown in Fig. 15-27. Determine the adiabatic flame temperature for (a) complete combustion with 100 percent theoretical air, (b) complete combustion with 400 percent theoretical air, and (c) incomplete combustion (some CO in the products) with 90 percent theoretical air.

ENTROPY CHANGE OF REACTING SYSTEMS

$$\underbrace{S_{\text{in}} - S_{\text{out}}}_{\text{Net entropy transfer by heat and mass}} + \underbrace{S_{\text{gen}}}_{\text{Entropy generation}} = \underbrace{\Delta S_{\text{system}}}_{\text{Change in entropy}} \quad (\text{kJ/K}) \text{ entropy balance for any system (including reacting systems) undergoing any process}$$

$$\sum \frac{Q_k}{T_k} + S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}} \quad (\text{kJ/K}) \text{ for a closed or steady-flow reacting system}$$

$$S_{\text{gen,adiabatic}} = S_{\text{prod}} - S_{\text{react}} \geq 0 \quad \text{for an adiabatic process (} Q = 0 \text{)}$$



The entropy change associated with a chemical relation.

$$\bar{s}(T,P) = \bar{s}^\circ(T,P_0) - R_u \ln \frac{P}{P_0}$$

Entropy of a component

$P_0 = 1 \text{ atm}$

P_i partial pressure

y_i mole fraction

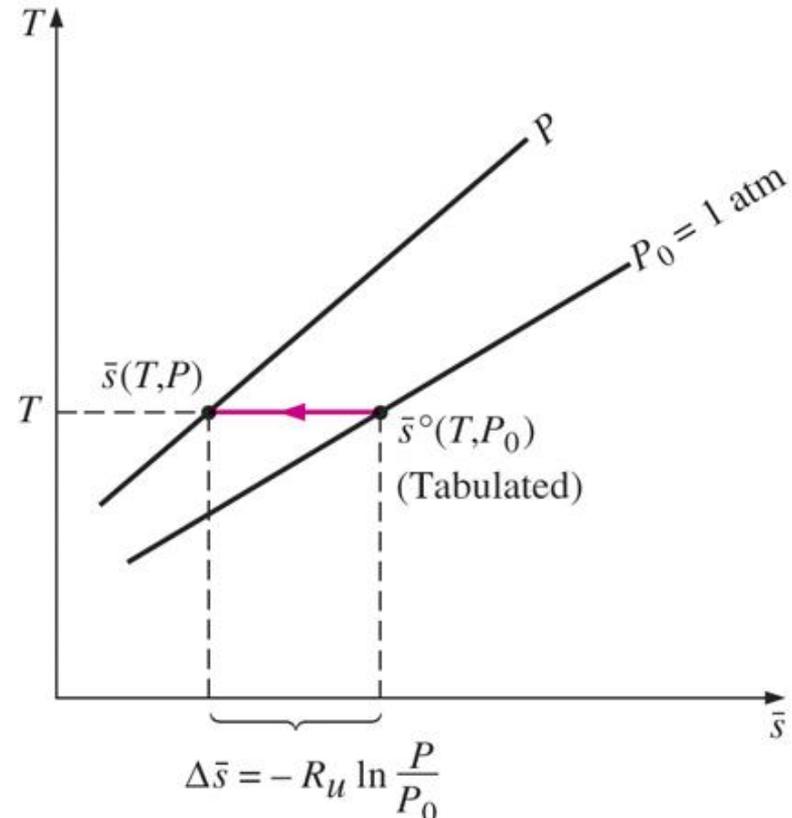
P_m total pressure of mixture.

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

When evaluating the entropy of a component of an ideal-gas mixture, we should use the temperature and the partial pressure of the component.

The absolute entropy values are listed in Tables A-18 through A-25 for various ideal gases at the specified temperature and *at a pressure of 1 atm*. The absolute entropy values for various fuels are listed in Table A-26 at the standard reference state of 25°C and 1 atm.

At a specified temperature, the absolute entropy of an ideal gas at pressures other than $P_0 = 1 \text{ atm}$ can be determined by subtracting $R_u \ln (P/P_0)$ from the tabulated value at 1 atm.



SECOND-LAW ANALYSIS OF REACTING SYSTEMS

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} \quad (\text{kJ}) \quad \text{Exergy destruction}$$

The reversible work for a steady-flow combustion process that involves heat transfer with only the surroundings at T_0

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

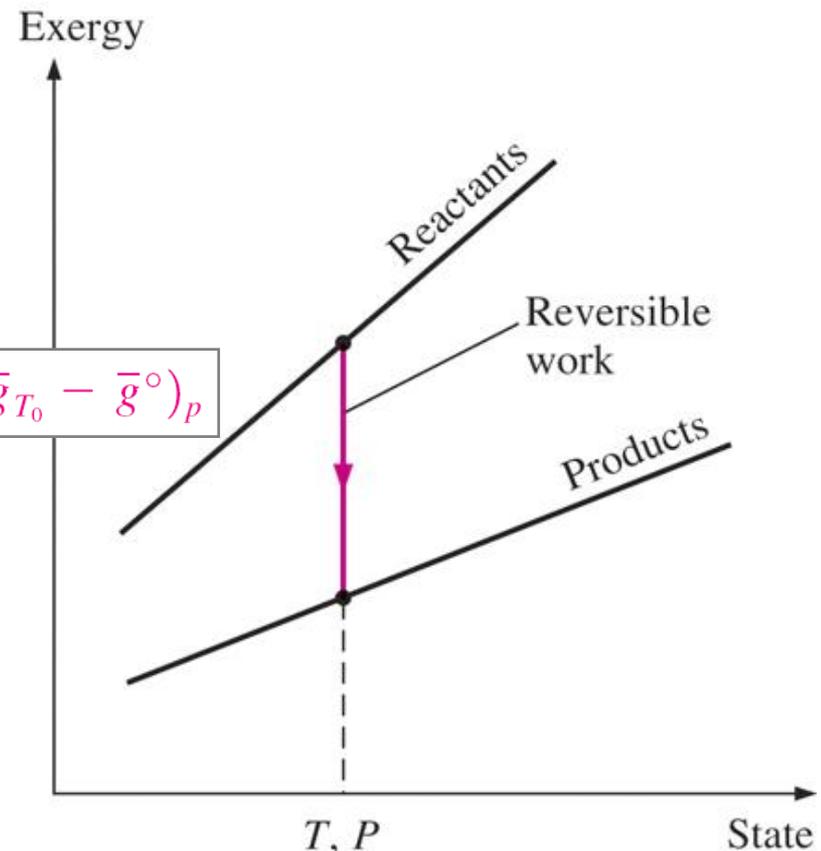
When both the reactants and the products are at T_0

$$\bar{h} - T_0 \bar{s} = (\bar{h} - T_0 \bar{s})_{T_0} = \bar{g}_0 \quad \text{Gibbs function}$$

$$W_{\text{rev}} = \sum N_r \bar{g}_{0,r} - \sum N_p \bar{g}_{0,p}$$

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

The difference between the exergy of the reactants and of the products during a chemical reaction is the reversible work associated with that reaction.



For the very special case of

$$T_{\text{react}} = T_{\text{prod}} = T_0 = 25^\circ\text{C}$$

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

We can conclude from the above equation that the $-\bar{g}_f^\circ$ value (the negative of the Gibbs function of formation at 25°C and 1 atm) of a compound represents the *reversible work* associated with the formation of that compound from its stable elements at 25°C and 1 atm in an environment at 25°C and 1 atm.

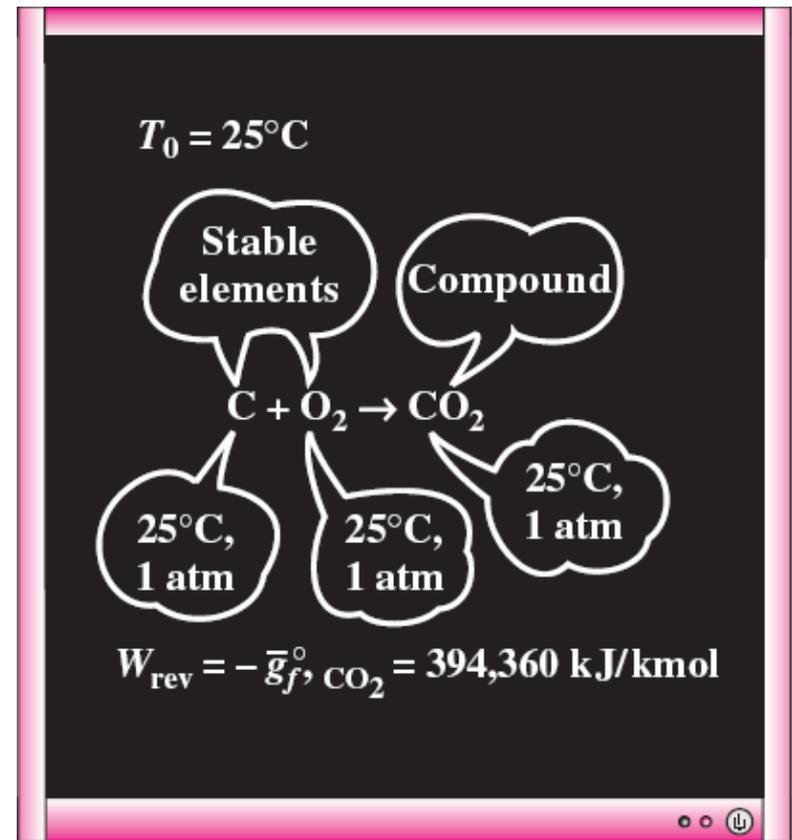


FIGURE 15–31

The negative of the Gibbs function of formation of a compound at 25°C , 1 atm represents the reversible work associated with the formation of that compound from its stable elements at 25°C , 1 atm in an environment that is at 25°C , 1 atm.

EXAMPLE 15–9**Reversible Work Associated
with a Combustion Process**

One kmol of carbon at 25°C and 1 atm is burned steadily with 1 kmol of oxygen at the same state as shown in Fig. 15–32. The CO_2 formed during the process is then brought to 25°C and 1 atm, the conditions of the surroundings. Assuming the combustion is complete, determine the reversible work for this process.

EXAMPLE 15–11**Second-Law Analysis
of Isothermal Combustion**

Methane (CH_4) gas enters a steady-flow combustion chamber at 25°C and 1 atm and is burned with 50 percent excess air, which also enters at 25°C and 1 atm, as shown in Fig. 15–34. After combustion, the products are allowed to cool to 25°C . Assuming complete combustion, determine (a) the heat transfer per kmol of CH_4 , (b) the entropy generation, and (c) the reversible work and exergy destruction. Assume that $T_0 = 298\text{ K}$ and the products leave the combustion chamber at 1 atm pressure.

Summary

- Fuels and combustion
- Theoretical and actual combustion processes
- Enthalpy of formation and enthalpy of combustion
- First-law analysis of reacting systems
 - Steady-flow systems
 - Closed systems
- Adiabatic flame temperature
- Entropy change of reacting systems
- Second-law analysis of reacting systems