

Topic3: Chemical Reactions

Further Reading

Chapter 15

Chemical Reactions



Content

- Fuels and combustion
- Theoretical and actual combustion processes
- Enthalpy of formation and enthalpy of combustion
- First-law analysis of reacting systems
- Adiabatic flame temperature

Optional Reading

- Entropy change of reacting systems
- Second-law analysis of reacting systems

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.
- Calculate the enthalpy of reaction, enthalpy of combustion, and the heating values of fuels.
- Apply energy balances to reacting systems for both steady-flow control volumes and fixed mass systems.
- Determine the adiabatic flame temperature for reacting mixtures.
- Evaluate the entropy change of reacting systems.
- Analyze reacting systems from the second-law perspective

15–1 Fuels and Combustion

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

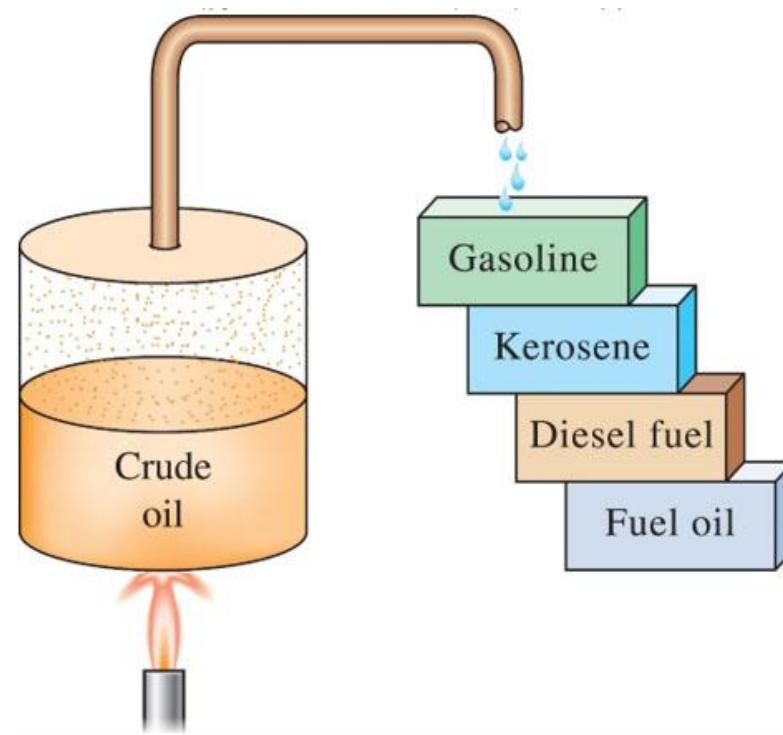
Most familiar fuels consist primarily of hydrogen and carbon.

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

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

Figure 15–1

Most liquid hydrocarbon fuels are obtained from crude oil by distillation.



15–1 Fuels and Combustion

Although liquid hydrocarbon fuels are mixtures of many different hydrocarbons, they are usually considered to be a single hydrocarbon for convenience. For example, gasoline is treated as **octane**, C₈H₁₈, and diesel fuel as **dodecane**, C₁₂H₂₆. Another common liquid hydrocarbon fuel is **methyl alcohol**, CH₃OH, 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**, CH₄, for simplicity.

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 in the liquid phase at -162°C as LNG (liquefied natural gas). Over a million vehicles in the world, mostly buses, run on natural gas. Liquefied petroleum gas (LPG) is a by-product of natural gas processing or 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.

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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.

Vehicles are a major source of air pollutants. So 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 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% Argon, and small amounts of CO₂, Helium, Neon, Hydrogen.

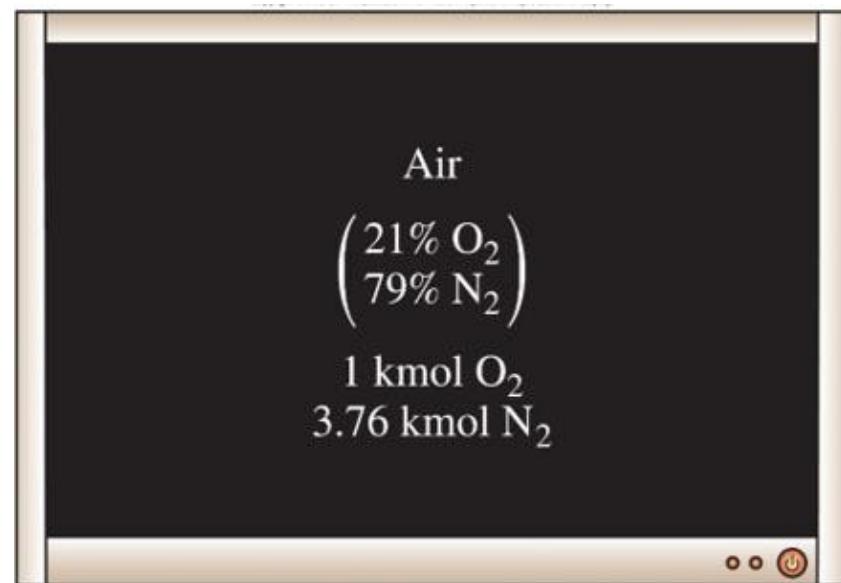
In the analysis of combustion processes, dry air is approximated as 21% O₂ and 79% N₂ by mole numbers (with 0.79/0.21=3.76). Thus,

$$1 \text{ kmol O}_2 + 3.76 \text{ kmol N}_2 = 4.76 \text{ kmol air}$$

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.

Figure 15–2

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



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

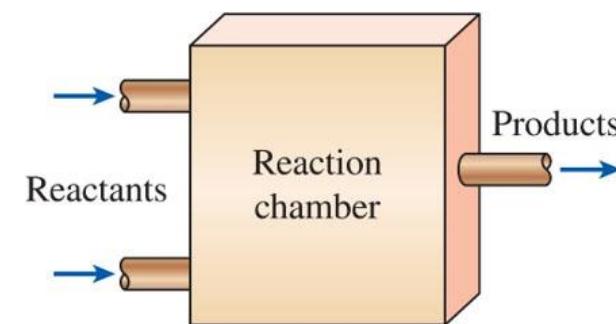
15–1 Fuels and Combustion ⁴

For most combustion processes, the moisture in the air and the H₂O that forms during combustion can also be treated as an inert gas, like nitrogen. At very high temperatures, however, some water vapor dissociates into H₂ and O₂ 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 ('sulphur' in British English) dioxide (SO₂) that may be present in the combustion gases, forming sulfuric acid, which is highly corrosive.

- 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%.

Figure 15–3

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



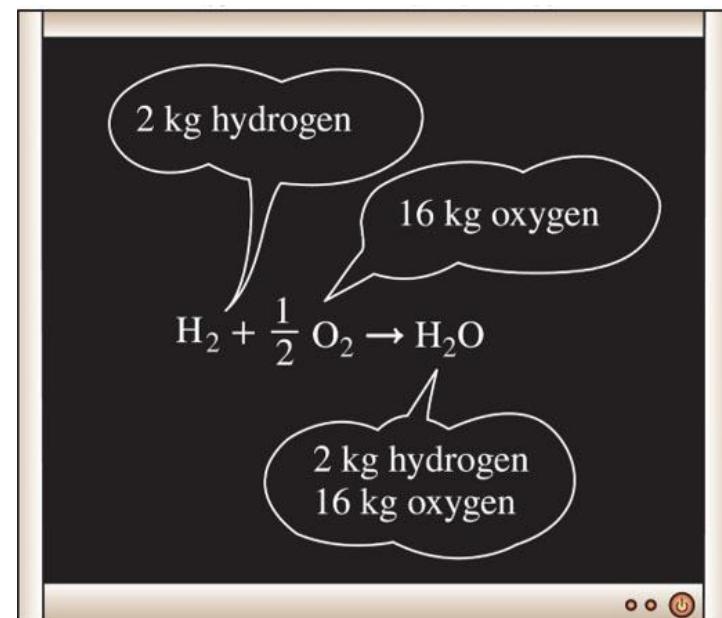
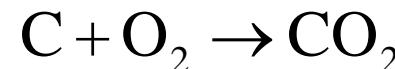
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Figure 15–4

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

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.

But the total number of moles is *not* conserved during a chemical reaction.



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Air-fuel ratio (AF): The ratio of the mass of air to the mass of fuel for a combustion process.

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

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

$$m = NM$$

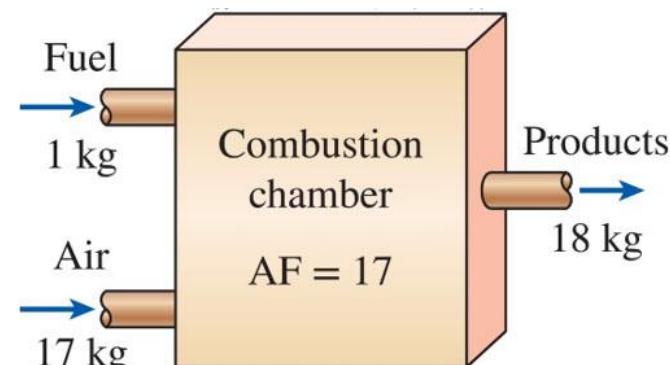
m mass

N number of moles

M molar mass

Figure 15–5

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



15–1 Fuels and Combustion

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EXAMPLE 15–1 Balancing the Combustion Equation

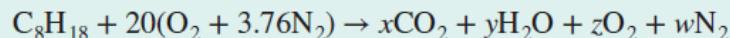
One kmol of octane (C_8H_{18}) is burned with air that contains 20 kmol of O_2 , as shown in Fig. 15–6. Assuming the products contain only CO_2 , H_2O , O_2 , and N_2 , determine the mole number of each gas in the products and the air–fuel ratio for this combustion process.

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:

$$\begin{aligned} C: \quad & 8 = x \rightarrow x = 8 \\ H: \quad & 18 = 2y \rightarrow y = 9 \\ O: \quad & 20 \times 2 = 2x + y + 2z \rightarrow z = 7.5 \\ N_2: \quad & (20)(3.76) = w \rightarrow w = 75.2 \end{aligned}$$

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,

$$\begin{aligned} AF &= \frac{m_{air}}{m_{fuel}} = \frac{(NM)_{air}}{(NM)_C + (NM)_{H_2}} \\ &= \frac{(20 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(8 \text{ kmol})(12 \text{ kg/kmol}) + (9 \text{ kmol})(2 \text{ kg/kmol})} \\ &= 24.2 \text{ kg air/kg fuel} \end{aligned}$$

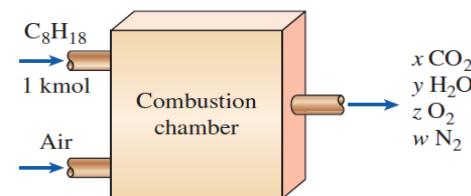
9 kmol of H_2 or 18 kmol of H

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

TABLE A–1

Molar mass, gas constant, and critical-point properties

Substance	Formula	Molar mass, $M \text{ kg/kmol}$	Gas constant, $R \text{ kJ/kg-K}^*$	Critical-point properties		
				Temperature, K	Pressure, MPa	Volume, m^3/kmol
Air	—	28.97	0.2870	132.5	3.77	0.0883
Ammonia	NH_3	17.03	0.4882	405.5	11.28	0.0724
Argon	Ar	39.948	0.2081	151	4.86	0.0749
Benzene	C_6H_6	78.115	0.1064	562	4.92	0.2603
Bromine	Br_2	159.808	0.0520	584	10.34	0.1355
<i>n</i> -Butane	C_4H_{10}	58.124	0.1430	425.2	3.80	0.2547
Carbon dioxide	CO_2	44.01	0.1889	304.2	7.39	0.0943
Carbon monoxide	CO	28.011	0.2968	133	3.50	0.0930
Carbon tetrachloride	CCl_4	153.82	0.05405	556.4	4.56	0.2759
Chlorine	Cl_2	70.906	0.1173	417	7.71	0.1242
Chlorofor	$CHCl_3$	119.38	0.06964	536.6	5.47	0.2403
Dichlorodifluoromethane (R–12)	CCl_2F_2	120.91	0.06876	384.7	4.01	0.2179
Dichlorofluoromethane (R–21)	$CHCl_2F$	102.92	0.08078	451.7	5.17	0.1973
Ethane	C_2H_6	30.070	0.2765	305.5	4.48	0.1480
Ethyl alcohol	C_2H_5OH	46.07	0.1805	516	6.38	0.1673
Ethylene	C_2H_4	28.054	0.2964	282.4	5.12	0.1242
Helium	He	4.003	2.0769	5.3	0.23	0.0578
<i>n</i> -Hexane	C_6H_{14}	86.179	0.09647	507.9	3.03	0.3677
Hydrogen (normal)	H_2	2.016	4.1240	33.3	1.30	0.0649
Krypton	Kr	83.80	0.09921	209.4	5.50	0.0924
Methane	CH_4	16.043	0.5182	191.1	4.64	0.0993
Methyl alcohol	CH_3OH	32.042	0.2595	513.2	7.95	0.1180
Methyl chloride	CH_3Cl	50.488	0.1647	416.3	6.68	0.1430
Neon	Ne	20.183	0.4119	44.5	2.73	0.0417
Nitrogen	N_2	28.013	0.2968	126.2	3.39	0.0899
Nitrous oxide	N_2O	44.013	0.1889	309.7	7.27	0.0961
Oxygen	O_2	31.999	0.2598	154.8	5.08	0.0780
Propane	C_3H_8	44.097	0.1885	370	4.26	0.1998
Propylene	C_3H_6	42.081	0.1976	365	4.62	0.1810
Sulfur dioxide	SO_2	64.063	0.1298	430.7	7.88	0.1217
Tetrafluoroethane (R–134a)	CF_3CH_2F	102.03	0.08149	374.2	4.059	0.1993
Trichlorofluoromethane (R–11)	CCl_3F	137.37	0.06052	471.2	4.38	0.2478
Water	H_2O	18.015	0.4615	647.1	22.06	0.0560
Xenon	Xe	131.30	0.06332	289.8	5.88	0.1186



15–2 Theoretical and Actual Combustion Processes

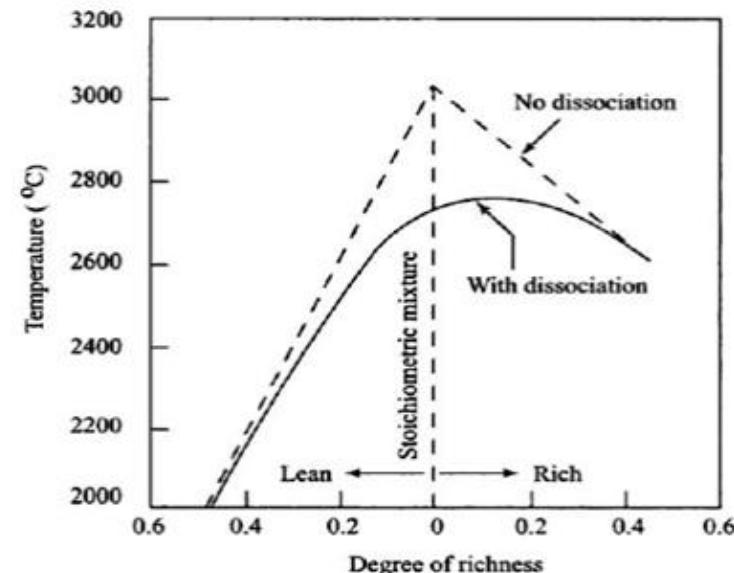
Complete combustion: If all the carbon in the fuel burns to CO_2 , all the hydrogen burns to H_2O , and all the sulfur (if any) burns to SO_2 .

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.
3. ***Dissociation*** (at high temperatures) i.e. Dissociation process can be considered as the disintegration of combustion produce at high temperature and can be viewed as the reverse process to combustion.

A typical curve that indicates the reduction in the temperature of the exhaust gas mixtures due to dissociation with respect to A/F ratio. With no dissociation maximum temperature is attained at chemically correct air-fuel ratio.



15–2 Theoretical and Actual Combustion Processes

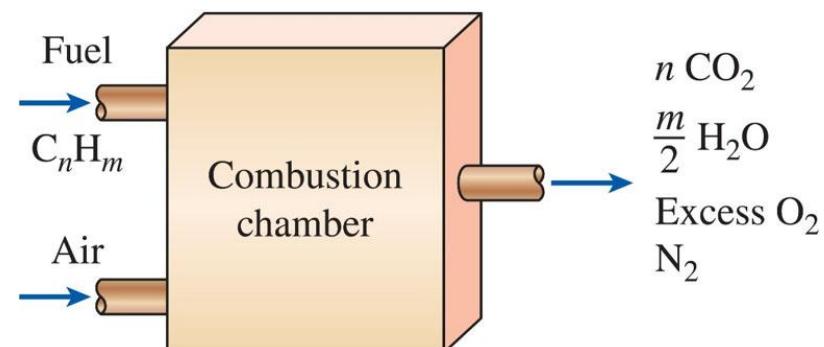
Oxygen has a much greater tendency to combine with hydrogen than it does with carbon. Therefore, the hydrogen in the fuel normally burns to completion, forming H_2O , even when there is less oxygen than needed for complete combustion. Some of the carbon, however, ends up as CO or just as plain C particles (soot) in the products.



Formation of soot

Figure 15–7

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



15–2 Theoretical and Actual Combustion Processes

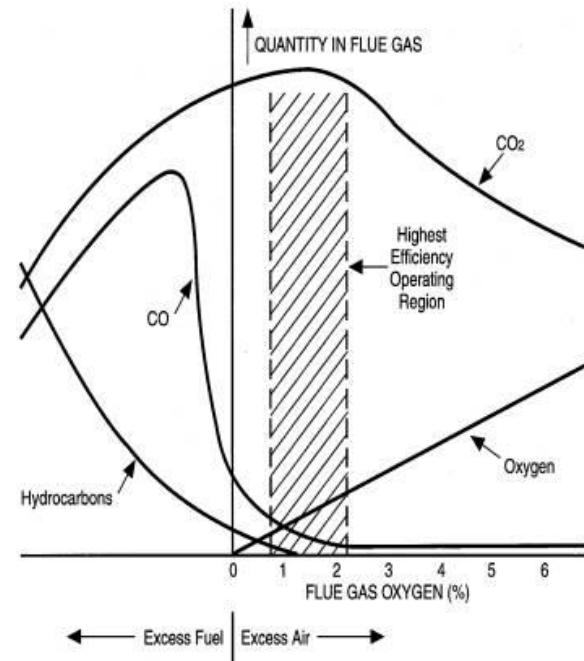
Stoichiometric or theoretical air: The minimum amount of air needed for the complete combustion of a fuel. Also referred to as the chemically correct amount of air, or 100% theoretical air.

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

Excess air: 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** and it is usually expressed in terms of the stoichiometric air as **percent excess air** or **percent theoretical air**. Too much excess air leads to lower flame temperature. That means less heat gets into the system. Also, excess air must heat up to flue gas temperature, which consumes extra energy.

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.

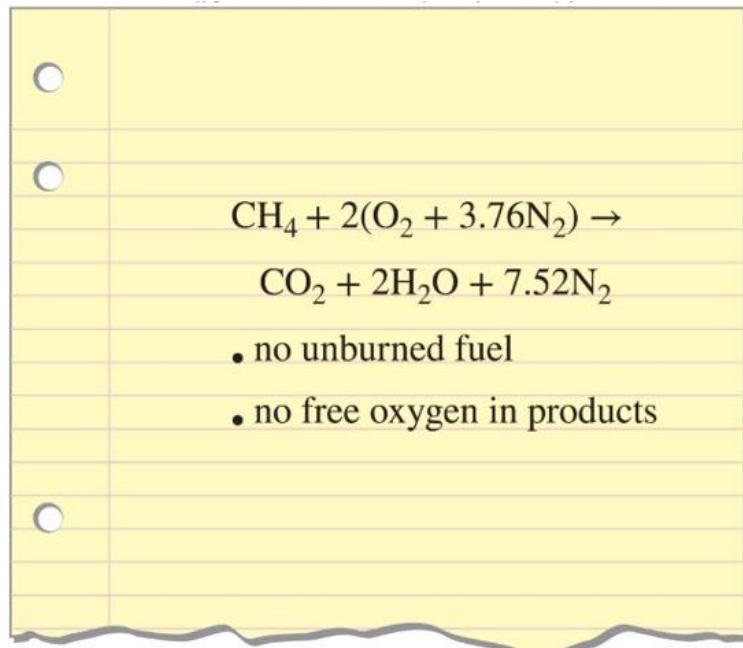


15–2 Theoretical and Actual Combustion Processes ⁴

Theoretical combustion of methane

Figure 15–8

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



50% excess air = 150% theoretical air

200% excess air = 300% theoretical air.

90% theoretical air = 10% deficiency of air

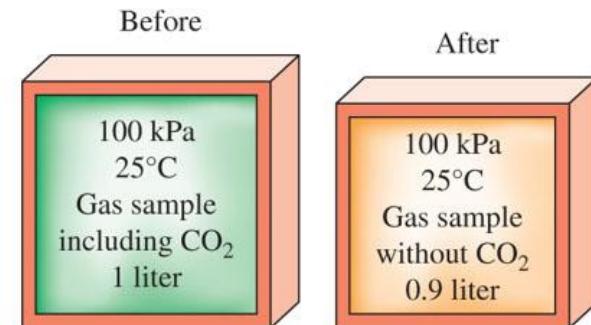
15–2 Theoretical and Actual Combustion Processes

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 device used to analyze the composition of combustion gases is the **Orsat gas analyzer**. The results are reported on a dry basis. The modern gas analyzers use nondispersive infrared technology to detect a certain gas by detecting the absorption of infrared wavelengths that is characteristic of that gas.

5 **Figure 15–9**

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



$$y_{CO_2} = \frac{V_{CO_2}}{V} = \frac{0.1}{1} = 0.1$$



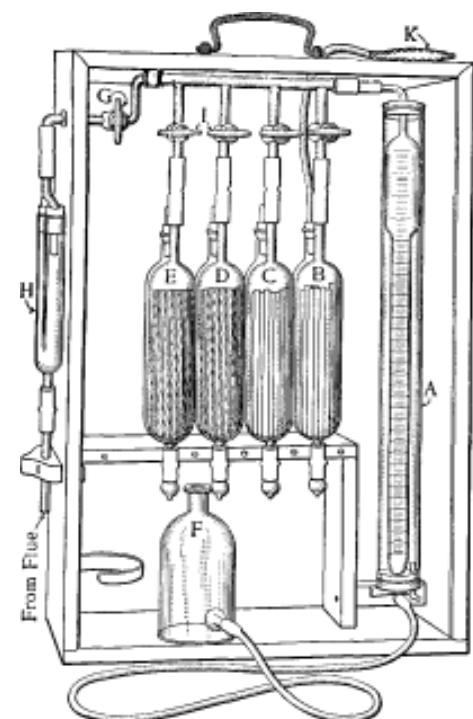
Concentration range:

- O₂: 0 to 25 vol.%
- CO (H₂ compensated): 0 to 10,000 ppm
- NO: 0 to 4,000 ppm
- NO₂: 0 to 5,000 ppm

15–2 Theoretical and Actual Combustion Processes 5

In the Orsat gas analyzer, 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 (reagent) that absorbs the CO₂. 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 CO₂, which is equivalent to the mole fraction if ideal-gas behavior is assumed (Fig. 15–9). The volume fractions of the other gases are determined by repeating this procedure.

Orsat Analyzer which analyses a gas sample for its oxygen, carbon monoxide and carbon dioxide content



EXAMPLE 15-2 Combustion of Coal with Theoretical Air

Coal from Pennsylvania which has an ultimate analysis (by mass) of 84.36 percent C, 1.89 percent H₂, 4.40 percent O₂, 0.63 percent N₂, 0.89 percent S, and 7.83 percent ash (noncombustibles) is burned with a theoretical amount of air (Fig. 15–10). Disregarding the ash content, determine the mole fractions of the products and the apparent molar mass of the product gases. Also determine the air-fuel ratio required for this combustion process.

SOLUTION Coal with known mass analysis is burned with theoretical amount of air. The mole fractions of the product gases, their apparent molar mass, and the air-fuel ratio are to be determined.

Assumptions 1 Combustion is stoichiometric and thus complete. 2 Combustion products contain CO₂, H₂O, SO₂, and N₂ only (ash disregarded). 3 Combustion gases are ideal gases.

Analysis The molar masses of C, H₂, O₂, S, and air are 12, 2, 32, 32, and 29 kg/kmol, respectively (Table A–1). We now consider 100 kg of coal for simplicity. Noting that the mass percentages in this case correspond to the masses of the constituents, the mole numbers of the constituent of the coal are determined to be

$$N_C = \frac{m_C}{M_C} = \frac{84.36 \text{ kg}}{12 \text{ kg/kmol}} = 7.030 \text{ kmol}$$

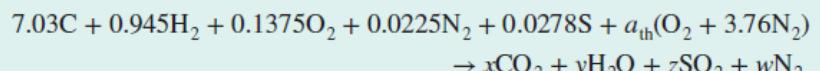
$$N_{H_2} = \frac{m_{H_2}}{M_{H_2}} = \frac{1.89 \text{ kg}}{2 \text{ kg/kmol}} = 0.9450 \text{ kmol}$$

$$N_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{4.40 \text{ kg}}{32 \text{ kg/kmol}} = 0.1375 \text{ kmol}$$

$$N_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{0.63 \text{ kg}}{28 \text{ kg/kmol}} = 0.0225 \text{ kmol}$$

$$N_S = \frac{m_S}{M_S} = \frac{0.89 \text{ kg}}{32 \text{ kg/kmol}} = 0.0278 \text{ kmol}$$

Ash consists of the noncombustible matter in coal. Therefore, the mass of ash content that enters the combustion chamber is equal to the mass content that leaves. Disregarding this nonreacting component for simplicity, the combustion equation may be written as



Performing mass balances for the constituents gives

$$\text{C balance: } x = 7.03$$

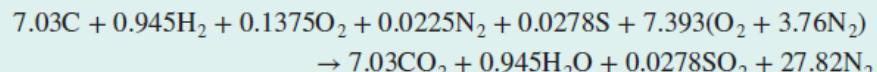
$$\text{H}_2 \text{ balance: } y = 0.945$$

$$\text{S balance: } z = 0.0278$$

$$O_2 \text{ balance: } 0.1375 + a_{th} = x + 0.5y + z \rightarrow a_{th} = 7.393$$

$$N_2 \text{ balance: } w = 0.0225 + 3.76a_{th} = 0.0225 + 3.76 \times 7.393 = 27.82$$

Substituting, the balanced combustion equation without the ash becomes



The mole fractions of the product gases are determined as follows:

$$N_{\text{prod}} = 7.03 + 0.945 + 0.0278 + 27.82 = 35.82 \text{ kmol}$$

$$y_{CO_2} = \frac{N_{CO_2}}{N_{\text{prod}}} = \frac{7.03 \text{ kmol}}{35.82 \text{ kmol}} = \mathbf{0.1963}$$

$$y_{H_2O} = \frac{N_{H_2O}}{N_{\text{prod}}} = \frac{0.945 \text{ kmol}}{35.82 \text{ kmol}} = \mathbf{0.02638}$$

$$y_{SO_2} = \frac{N_{SO_2}}{N_{\text{prod}}} = \frac{0.0278 \text{ kmol}}{35.82 \text{ kmol}} = \mathbf{0.000776}$$

$$y_{N_2} = \frac{N_{N_2}}{N_{\text{prod}}} = \frac{27.82 \text{ kmol}}{35.82 \text{ kmol}} = \mathbf{0.7767}$$

Then, the apparent molar mass of product gases becomes

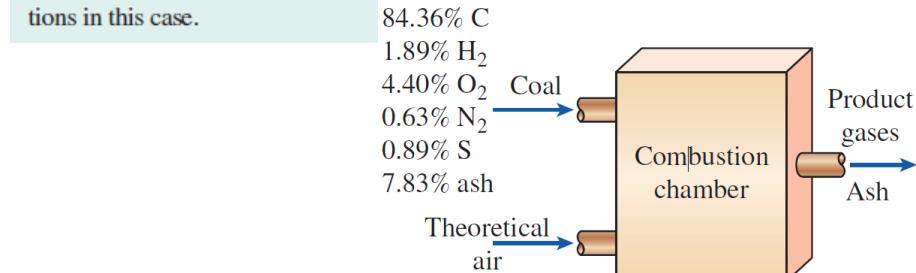
$$M_{\text{prod}} = \frac{m_{\text{prod}}}{N_{\text{prod}}} = \frac{(7.03 \times 44 + 0.945 \times 18 + 0.0278 \times 64 + 27.82 \times 28) \text{ kg}}{35.82 \text{ kmol}} = \mathbf{30.9 \text{ kg/kmol}}$$

Finally, the air-fuel mass ratio is determined from its definition to be

$$AF = \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{(7.393 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{100 \text{ kg}} = \mathbf{10.2 \text{ kg air/kg fuel}}$$

That is, 10.2 kg of air is supplied for each kg of coal in the furnace.

Discussion We could also solve this problem by considering just 1 kg of coal, and still obtain the same results. But we would have to deal with very small fractions in calculations in this case.



EXAMPLE 15–3 Combustion of a Gaseous Fuel with Moist Air

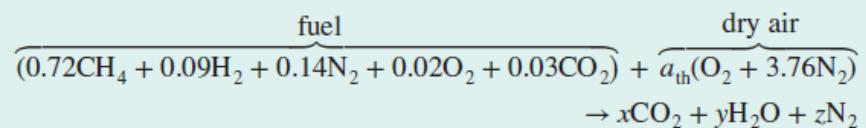
A certain natural gas has the following volumetric analysis: 72 percent CH₄, 9 percent H₂, 14 percent N₂, 2 percent O₂, and 3 percent CO₂. This gas is now burned with the stoichiometric amount of air that enters the combustion chamber at 20°C, 1 atm, and 80 percent relative humidity, as shown in Fig. 15–11. Assuming complete combustion and a total pressure of 1 atm, determine the dew-point temperature of the products.

SOLUTION A gaseous fuel is burned with the stoichiometric amount of moist air. The dew point temperature of the products is to be determined.

Assumptions 1, The fuel is burned completely and thus all the carbon in the fuel burns to CO₂ and all the hydrogen to H₂O. 2 The fuel is burned with the stoichiometric amount of air and thus there is no free O₂ in the product gases. 3 Combustion gases are ideal gases.

Properties The saturation pressure of water at 20°C is 2.3392 kPa (Table A–4).

Analysis We note that the moisture in the air does not react with anything; it simply shows up as additional H₂O in the products. Therefore, for simplicity, we balance the combustion equation by using dry air and then add the moisture later to both sides of the equation. Considering 1 kmol of fuel,



The unknown coefficients in the preceding equation are determined from mass balances on various elements,

$$\text{C: } 0.72 + 0.03 = x \rightarrow x = 0.75$$

$$\text{H: } 0.72 \times 4 + 0.09 \times 2 = 2y \rightarrow y = 1.53$$

$$\text{O}_2: \quad 0.02 + 0.03 + a_{\text{th}} = x + \frac{y}{2} \rightarrow a_{\text{th}} = 1.465$$

$$\text{N}_2: \quad 0.14 + 3.76a_{\text{th}} = z \rightarrow z = 5.648$$

Next we determine the amount of moisture that accompanies $4.76a_{\text{th}} = (4.76)(1.465) = 6.97$ kmol of dry air. The partial pressure of the moisture in the air is

$$P_{v,\text{air}} = \phi_{\text{air}} P_{\text{sat} @ 20^\circ\text{C}} = (0.80)(2.3392 \text{ kPa}) = 1.871 \text{ kPa}$$

N_{dry air}

Table A-4

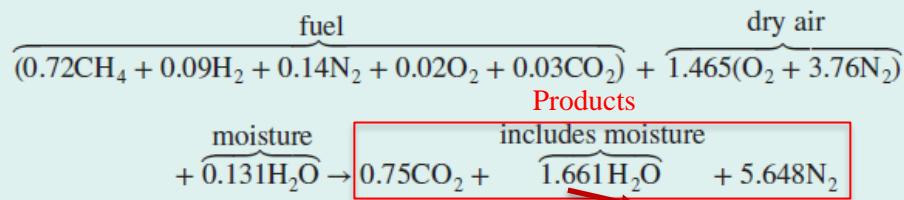
Assuming ideal-gas behavior, the number of moles of the moisture in the air is

$$\begin{aligned} (\text{pV=NRT}) \quad N_{v,\text{air}} &= \left(\frac{P_{v,\text{air}}}{P_{\text{total}}} \right) N_{\text{total}} = \left(\frac{1.871 \text{ kPa}}{101.325 \text{ kPa}} \right) (6.97 + N_{v,\text{air}}) \\ [\text{V, R, T cancel}] \quad &= N_{\text{dry air}} + N_{\text{vapour}} \end{aligned}$$

which yields

$$N_{v,\text{air}} = 0.131 \text{ kmol}$$

The balanced combustion equation is obtained by substituting the coefficients determined earlier and adding 0.131 kmol of H₂O to both sides of the equation:



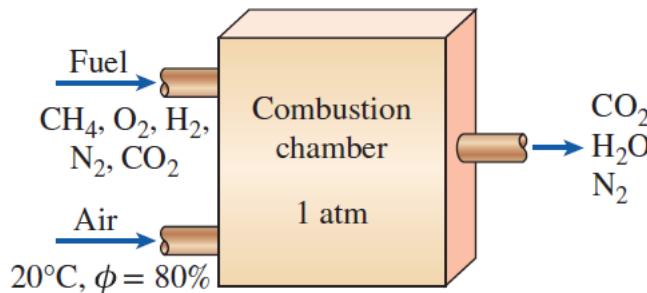
The dew-point temperature of the products is the temperature at which the water vapor in the products starts to condense as the products are cooled. Again, assuming ideal-gas behavior, the partial pressure of the water vapor in the combustion gases is

$$P_{v,\text{prod}} = \left(\frac{N_{v,\text{prod}}}{N_{\text{prod}}} \right) P_{\text{prod}} = \left(\frac{1.661 \text{ kmol}}{8.059 \text{ kmol}} \right) (101.325 \text{ kPa}) = 20.88 \text{ kPa}$$

Thus,

$$T_{dp} = T_{\text{sat} @ 20.88 \text{ kPa}} = 60.9^\circ\text{C} \quad \text{Table A-5}$$

Discussion If the combustion process were achieved with dry air instead of moist air, the products would contain less moisture, and the dew-point temperature in this case would be 59.5°C.



15–3 Enthalpy of Formation and Enthalpy of Combustion 1

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, also involves changes in chemical energies, which must be accounted for in an energy balance.

Assuming 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.

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

Therefore, when the products formed during a chemical reaction exit the reaction chamber at the inlet state of the reactants, we have $\Delta E_{state} = 0$, and the energy change of the system in this case is due to the changes in its chemical composition only. In other words, atoms bonded together represent a lower state of total energy than those same atoms existing separately, assuming all other factors being equal.

Figure 15–13

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

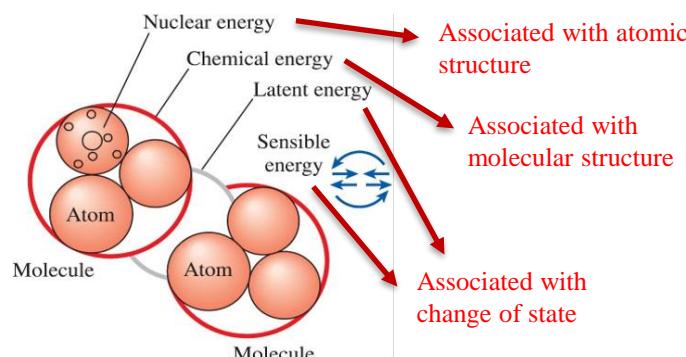
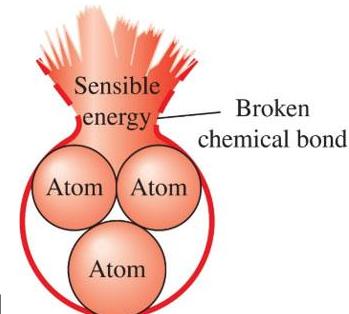


Figure 15–14

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.



15–3 Enthalpy of Formation and Enthalpy of Combustion 2

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°). (° is referred to as ‘Circ’)

The ideal-gas enthalpy of N₂ at 500 K relative to the standard reference state, for example, is

$$\bar{h}_{500\text{ K}} - \bar{h}^\circ = 14,581 - 8669 = 5912 \text{ kJ/kmol}$$

(from Table A-18 – see h at $T=500k$ and $298K$)

15–3 Enthalpy of Formation and Enthalpy of Combustion ³

Consider the formation of CO₂ from its elements, carbon and oxygen, during a steady-flow combustion process (Fig. 15–15). Both the carbon and the oxygen enter the combustion chamber at 25°C and 1 atm. The CO₂ formed during this process also leaves the combustion chamber at 25°C and 1 atm.

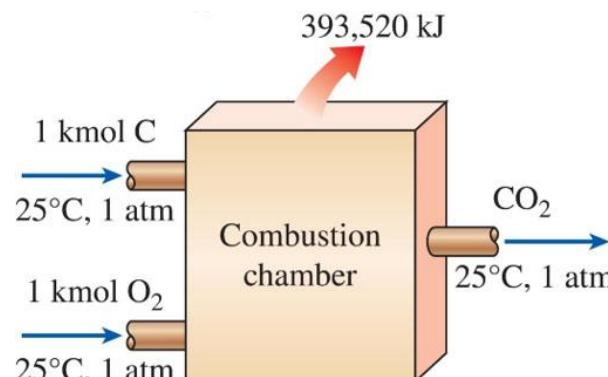
The combustion of carbon is an **exothermic reaction** (a reaction during which chemical energy is released in the form of heat – The opposite would be ‘**endothermic reaction**’). Therefore, some heat is transferred from the combustion chamber to the surroundings during this process, which is 393,520 kJ/kmol CO₂ formed.

$$Q = H_{prod} - H_{react} = -393,520 \text{ KJ/mol}$$

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.

Figure 15–15

The formation of CO₂ during a steady-flow combustion process at 25°C and 1 atm.



15–3 Enthalpy of Formation and Enthalpy of Combustion ⁴

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.

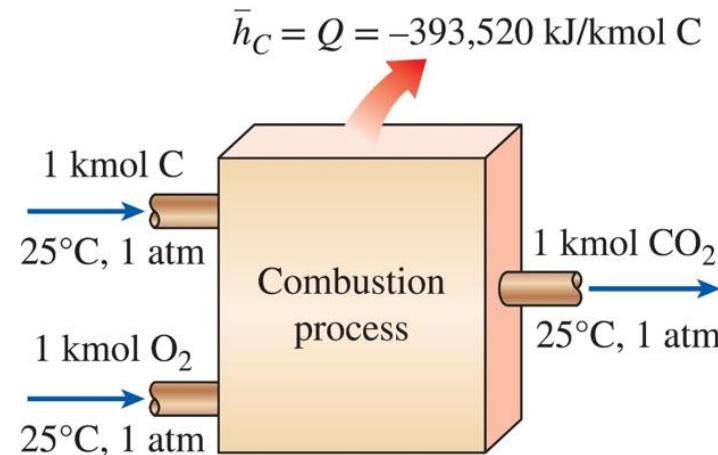
Enthalpy of combustion h_C : It is the enthalpy of reaction for combustion processes. It represents the amount of heat released during a steady-flow combustion process when 1 kmol (or 1 kg) of fuel is burned completely at a specified temperature and pressure.

$$h_R = h_c = H_{prod} - H_{react}$$

15–3 Enthalpy of Formation and Enthalpy of Combustion ⁴

Figure 15–16

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



Limitation of h_C : The enthalpy of combustion is obviously a very useful property for analysing the combustion processes of fuels. However, it has the following 2 main limitations:

- 1) there are so many different fuels and fuel mixtures that it is not practical to list h_C values for all possible cases.
- 2) 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.

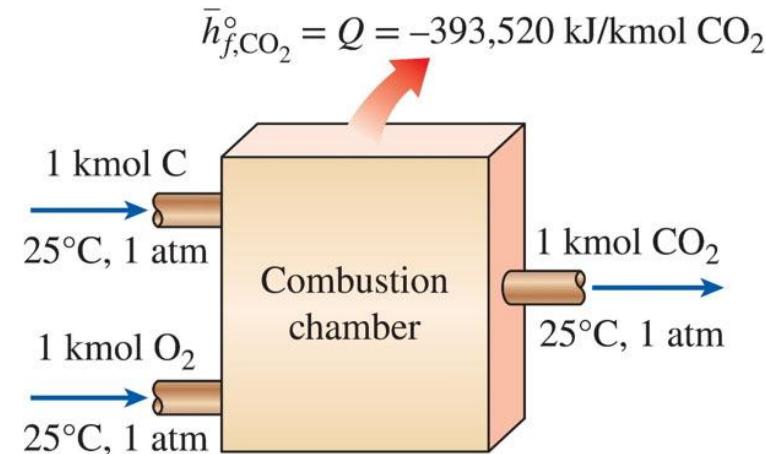
15–3 Enthalpy of Formation and Enthalpy of Combustion 5

Enthalpy of formation h_f : The amount of energy absorbed or released (depending on whether it is *endothermic* or *exothermic*) as the component is formed from its stable elements during a steady-flow process at a specified state. In other words, it is 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 O₂, N₂, H₂, and C) a value of zero at the standard reference state of 25°C and 1 atm. That is, $h_f^\circ = 0$ 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.)

Figure 15–17

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.



15–3 Enthalpy of Formation and Enthalpy of Combustion ⁶

Now reconsider the formation of CO₂ (a compound) from its elements C and O₂ at 25°C and 1 atm during a steady-flow process. The enthalpy change during this process was determined to be –393,520 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 CO₂ at the same state. Therefore, the enthalpy of formation of CO₂ at the standard reference state is –393,520 kJ/kmol (Fig. 15-17). That is,

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

The negative sign is due to the fact that the enthalpy of 1 kmol of CO₂ at 25 degree celsius and 1 atm is 393,520 kJ less than the enthalpy of 1 kmol of C and 1 kmol of O₂ at the same state.

In other words, 393,520 kJ of chemical energy is released (leaving the system as heat) when C and O₂ combine to form 1 kmol of CO₂.

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.

TABLE A-26

Enthalpy of formation, Gibbs function of formation, and absolute entropy at 25°C, 1 atm

In 'Optional Reading' section

Substance	Formula	\bar{h}_f° kJ/kmol	\bar{g}_f° kJ/kmol	\bar{s}° kJ/kmol·K
Carbon	C(s)	0	0	5.74
Hydrogen	H ₂ (g)	Stable	0	130.68
Nitrogen	N ₂ (g)	elements	0	191.61
Oxygen	O ₂ (g)	0	0	205.04
Carbon monoxide	CO(g)	-110,530	-137,150	197.65
Carbon dioxide	CO ₂ (g)	-393,520	-394,360	213.80
Water vapor	H ₂ O(g)	-241,820	-228,590	188.83
Water	H ₂ O(l)	-285,830	-237,180	69.92
Hydrogen peroxide	H ₂ O ₂ (g)	-136,310	-105,600	232.63
Ammonia	NH ₃ (g)	-46,190	-16,590	192.33
Methane	CH ₄ (g)	-74,850	-50,790	186.16
Acetylene	C ₂ H ₂ (g)	+226,730	+209,170	200.85
Ethylene	C ₂ H ₄ (g)	+52,280	+68,120	219.83
Ethane	C ₂ H ₆ (g)	-84,680	-32,890	229.49
Propylene	C ₃ H ₆ (g)	+20,410	+62,720	266.94
Propane	C ₃ H ₈ (g)	-103,850	-23,490	269.91
n-Butane	C ₄ H ₁₀ (g)	-126,150	-15,710	310.12
n-Octane	C ₈ H ₁₈ (g)	-208,450	+16,530	466.73
n-Octane	C ₈ H ₁₈ (l)	-249,950	+6,610	360.79
n-Dodecane	C ₁₂ H ₂₆ (g)	-291,010	+50,150	622.83
Benzene	C ₆ H ₆ (g)	+82,930	+129,660	269.20
Methyl alcohol	CH ₃ OH(g)	-200,670	-162,000	239.70
Methyl alcohol	CH ₃ OH(l)	-238,660	-166,360	126.80
Ethyl alcohol	C ₂ H ₅ OH(g)	-235,310	-168,570	282.59
Ethyl alcohol	C ₂ H ₅ OH(l)	-277,690	-174,890	160.70
Oxygen	O(g)	+249,190	+231,770	161.06
Hydrogen	H(g)	+218,000	+203,290	114.72
Nitrogen	N(g)	+472,650	+455,510	153.30
Hydroxyl	OH(g)	+39,460	+34,280	183.70

Source of Data: From JANAF, *Thermochemical Tables* (Midland, MI: Dow Chemical Co., 1971); Selected Values of Chemical Thermodynamic Properties, NBS Technical Note 270-3, 1968; and API Research Project 44 (Carnegie Press, 1953).

You will notice that two h_f° values are given for H₂O in Table A-26, one for liquid water and the other for water vapor. This is because both phases of H₂O are encountered at 25°C, and the effect of pressure on the enthalpy of formation is small. (Note that under equilibrium conditions, water exists only as a liquid at 25°C and 1 atm.) The difference between the two enthalpies of formation is equal to the h_{fg} of water at 25°C, which is 2441.7 kJ/kg or 44,000 kJ/kmol.

The negative and positive signs for h_f° correspond to exothermic and endothermic nature of substances, respectively.

15–3 Enthalpy of Formation and Enthalpy of Combustion 7

Other commonly used terms:

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. In other words, the heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel.

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

The heating value depends on the *phase* of the H₂O in the products.

Higher heating value (HHV): When the H₂O in the products is in the liquid form.

Lower heating value (LHV): When the H₂O in the products is in the vapor form.

$$\text{HHV} = \text{LHV} + (m h_{fg})_{\text{H}_2\text{O}} \text{ (kJ/kg fuel)}$$

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**. A bomb calorimeter by definition is a constant-volume calorimeter. These are rigid and closed, generally with a large water bath to insulate the system

15–3 Enthalpy of Formation and Enthalpy of Combustion

Figure 15–18

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.

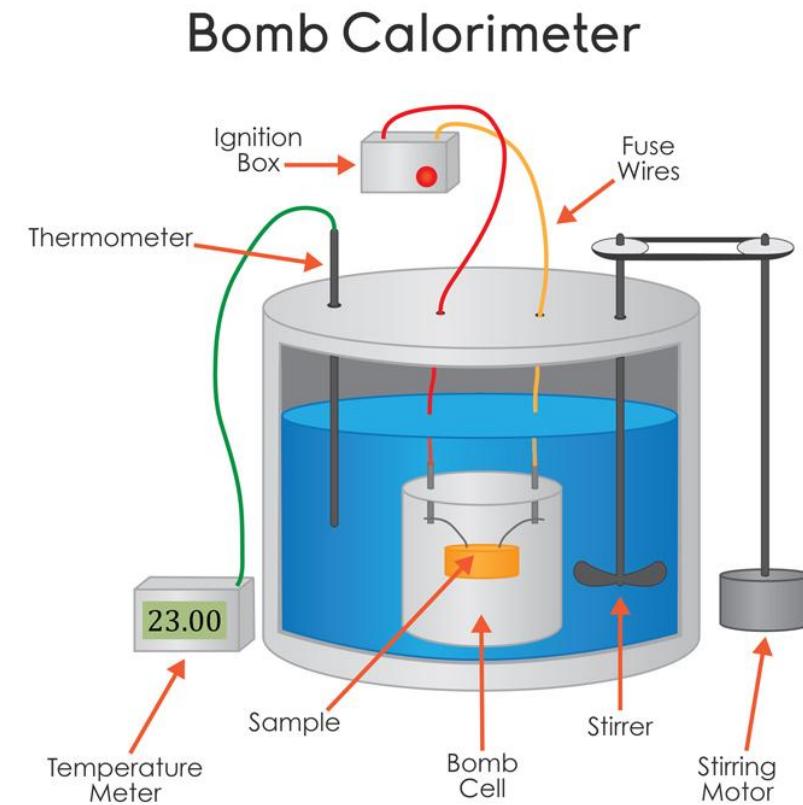
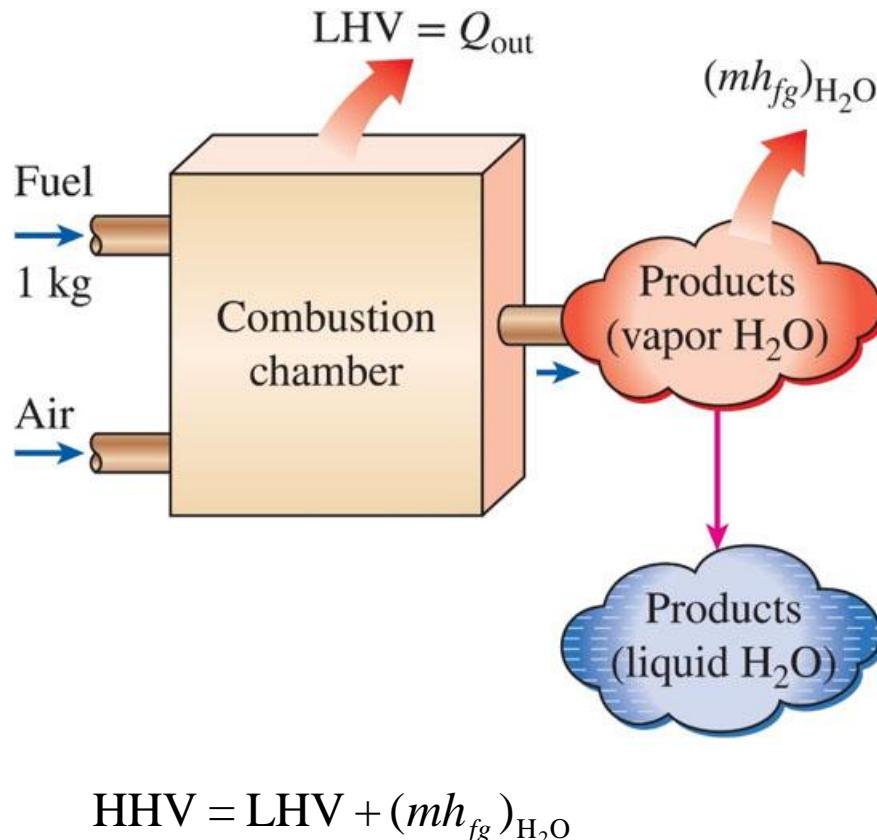


TABLE A-27

Properties of some common fuels and hydrocarbons

Fuel (phase)	Formula	Molar mass, kg/kmol	Density, ¹ kg/L	Enthalpy of vaporization, ² kJ/kg	Specific heat, ¹ c_p kJ/kg·K	Higher heating value, ³ kJ/kg	Lower heating value, ³ kJ/kg
Carbon (s)	C	12.011	2	—	0.708	32,800	32,800
Hydrogen (g)	H ₂	2.016	—	—	14.4	141,800	120,000
Carbon monoxide (g)	CO	28.013	—	—	1.05	10,100	10,100
Methane (g)	CH ₄	16.043	—	509	2.20	55,530	50,050
Methanol (l)	CH ₃ O	32.042	0.790	1168	2.53	22,660	19,920
Acetylene (g)	C ₂ H ₂	26.038	—	—	1.69	49,970	48,280
Ethane (g)	C ₂ H ₆	30.070	—	172	1.75	51,900	47,520
Ethanol (l)	C ₂ H ₅ O	46.069	0.790	919	2.44	29,670	26,810
Propane (l)	C ₃ H ₈	44.097	0.500	335	2.77	50,330	46,340
Butane (l)	C ₄ H ₁₀	58.123	0.579	362	2.42	49,150	45,370
1-Pentene (l)	C ₅ H ₁₀	70.134	0.641	363	2.20	47,760	44,630
Isopentane (l)	C ₅ H ₁₂	72.150	0.626	—	2.32	48,570	44,910
Benzene (l)	C ₆ H ₆	78.114	0.877	433	1.72	41,800	40,100
Hexene (l)	C ₆ H ₁₂	84.161	0.673	392	1.84	47,500	44,400
Hexane (l)	C ₆ H ₁₄	86.177	0.660	366	2.27	48,310	44,740
Toluene (l)	C ₇ H ₈	92.141	0.867	412	1.71	42,400	40,500
Heptane (l)	C ₇ H ₁₆	100.204	0.684	365	2.24	48,100	44,600
Octane (l)	C ₈ H ₁₈	114.231	0.703	363	2.23	47,890	44,430
Decane (l)	C ₁₀ H ₂₂	142.285	0.730	361	2.21	47,640	44,240
Gasoline (l)	C _n H _{1.87n}	100–110	0.72–0.78	350	2.4	47,300	44,000
Light diesel (l)	C _n H _{1.8n}	170	0.78–0.84	270	2.2	46,100	43,200
Heavy diesel (l)	C _n H _{1.7n}	200	0.82–0.88	230	1.9	45,500	42,800
Natural gas (g)	C _n H _{3.8n} N _{0.1n}	18	—	—	2	50,000	45,000

¹At 1 atm and 20°C.²At 25°C for liquid fuels, and 1 atm and normal boiling temperature for gaseous fuels.³At 25°C. Multiply by molar mass to obtain heating values in kJ/kmol.

15–3 Enthalpy of Formation and Enthalpy of Combustion ,

EXAMPLE 15–5 Evaluation of the HHV and LHV of Propane

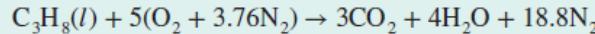
Calculate the HHV and LHV of liquid propane fuel (C_3H_8). Compare your results with the values in Table A–27.

SOLUTION The higher and lower heating values of liquid propane are to be determined and compared to the listed values.

Assumptions 1 Combustion is complete. 2 The combustion products contain CO_2 , H_2O , and N_2 . 3 Combustion gases are ideal gases.

Properties The molar masses of C, O_2 , H_2 , and air are 12, 32, 2, and 29 kg/kmol, respectively (Table A–1).

Analysis The combustion of C_3H_8 is illustrated in Fig. 15–19. The combustion reaction with stoichiometric air is



Both the reactants and the products are taken to be at the standard reference state of 25°C and 1 atm for the calculation of heating values. The heat transfer for this process is equal to enthalpy of combustion. Note that N_2 and O_2 are stable elements, and thus their enthalpy of formation is zero. Then,

$$q = \bar{h}_c = H_{\text{prod}} - H_{\text{react}} = \sum N_p \bar{h}_{f,p}^{\circ} - \sum N_r \bar{h}_{f,r}^{\circ} = (\bar{h}_f^{\circ})_{CO_2} + (\bar{h}_f^{\circ})_{H_2O} - (\bar{h}_f^{\circ})_{C_3H_8}$$

The \bar{h}_f° of liquid propane is obtained by adding \bar{h}_{fg} of propane at 25°C to \bar{h}_f° of gas propane ($103,850 + 44,097 \times 335 = 118,620$ kJ/kmol). For the HHV, the water in the products is taken to be liquid. Then,

$$\begin{aligned} \bar{h}_c &= (3 \text{ kmol})(-393,520 \text{ kJ/kmol}) + (4 \text{ kmol})(-285,830 \text{ kJ/kmol}) \\ &\quad - (1 \text{ kmol})(-118,620 \text{ kJ/kmol}) \end{aligned}$$

$$= -2,205,260 \text{ kJ/kmol propane}$$

h_f° of Liquid water in Table A-26

The HHV of the liquid propane is

$$\boxed{\text{HHV} = \frac{-\bar{h}_c}{M} = \frac{2,205,260 \text{ kJ/kmol } C_3H_8}{44,097 \text{ kg/kmol } C_3H_8} = 50,010 \text{ kJ/kg } C_3H_8}$$

M Molar mass for C_3H_8 (Table A-27)

The listed value from Table A–27 is 50,330 kJ/kg. For the LHV, the water in the products is taken to be vapor. Then,

$$\begin{aligned} \bar{h}_c &= (3 \text{ kmol})(-393,520 \text{ kJ/kmol}) + (4 \text{ kmol})(-241,820 \text{ kJ/kmol}) \\ &\quad - (1 \text{ kmol})(-118,620 \text{ kJ/kmol}) \\ &= -2,029,220 \text{ kJ/kmol propane} \end{aligned}$$

h_f° of Water Vapor (Table A-26)

The LHV of the propane is then

$$\text{LHV} = \frac{-\bar{h}_c}{M} = \frac{2,029,220 \text{ kJ/kmol } C_3H_8}{44,097 \text{ kg/kmol } C_3H_8} = 46,020 \text{ kJ/kg } C_3H_8$$

The listed value from Table A–27 is 46,340 kJ/kg. The calculated and listed values are practically identical.

Discussion The higher heating value of liquid propane is 8.7 percent higher than its lower heating value. Obtain the HHV and LHV of carbon monoxide (CO) from Table A–27. Why are the two values equal to each other?

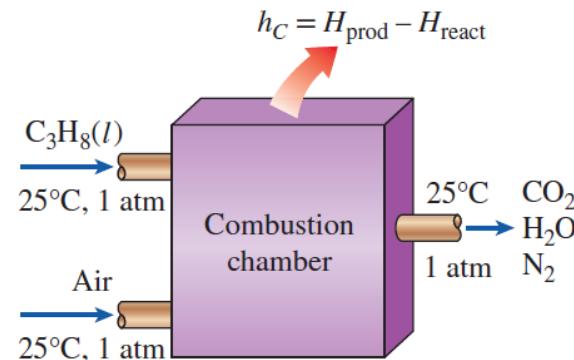


FIGURE 15–19
Schematic for Example 15–5.

Tutorial Questions

Tutorial Questions

- 1) Is the air–fuel ratio expressed on a mole basis identical to the air–fuel ratio expressed on a mass basis?
- 2) A certain natural gas has the following volumetric analysis: 65 percent CH_4 , 8 percent H_2 , 18 percent N_2 , 3 percent O_2 , and 6 percent CO_2 . This gas is now burned completely with the stoichiometric amount of moist air that enters the combustion chamber at 25°C , 1 atm, and 85 percent relative humidity. What is the air–fuel ratio for this combustion process?
- 3) Methyl alcohol (CH_3OH) is burned with 100 percent excess air. During the combustion process, 60 percent of the carbon in the fuel is converted to CO_2 and 40 percent is converted to CO . Write the balanced reaction equation and determine the air–fuel ratio.

Tutorial Questions

- 4) Determine the enthalpy of combustion of methane (CH_4) at 25°C and 1 atm, using the enthalpy of formation data from Table A–26. Assume that the water in the products is in the liquid form. Compare your result to the value listed in Table A–27.

Answer: -890,330 kJ/kmol

- 5) A constant-volume tank contains a mixture of 120 g of methane (CH_4) gas and 600 g of O_2 at 25°C and 200 kPa. The contents of the tank are now ignited, and the methane gas burns completely. If the final temperature is 1200 K, determine (a) the final pressure in the tank and (b) the heat transfer during this process.

OPTIONAL READING

15–4 First-law Analysis of Reacting Systems

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

Steady-Flow Systems

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

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}° (the sensible enthalpy at the standard reference state of 25°C and 1 atm). This definition enables us to use enthalpy values from tables regardless of the reference state used in their construction.

When the changes in kinetic and potential energies are negligible, the steady-flow energy balance relation $\dot{E}_{\text{in}} = \dot{E}_{\text{out}}$ can be expressed for a *chemically reacting steady-flow system* more explicitly as

15–4 First-law Analysis of Reacting Systems 2

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

where \dot{n}_p and \dot{n}_r represent the molar flow rates of the product p and the reactant r , respectively.

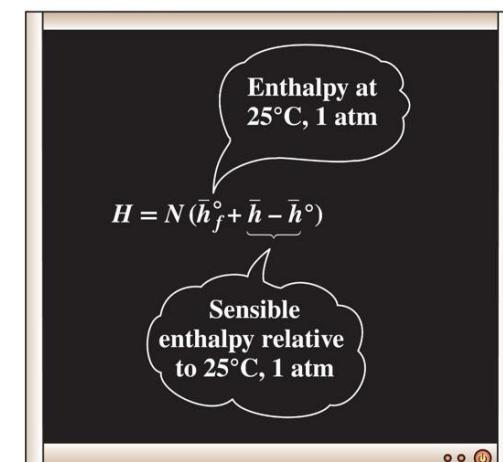
In combustion analysis, it is more convenient to work with quantities expressed *per mole of fuel*. Such a relation is obtained by dividing each term of the equation above by the molal flow rate of the fuel, yielding

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

where N_r and N_p represent the number of moles of the reactant r and the product p , respectively, per mole of fuel. Note that $N_r = 1$ for the fuel, and the other N_r and N_p values can be picked directly from the balanced combustion equation.

Figure 15–20

The enthalpy of a chemical component at a specified state is the sum of the enthalpy of the component at 25 degree celsius, 1 atm (\bar{h}_f°), and the sensible enthalpy of the component relative to 25 degree celsius, 1 atm.



15–4 First-law Analysis of Reacting Systems

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

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

The energy balance relations here are sometimes written without the work term since most steady-flow combustion processes do not involve any work interactions.

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:

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

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

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

It expresses that the heat output during a combustion process is simply the difference between the energy of the reactants entering and the energy of the products leaving the combustion chamber.

15–4 First-law Analysis of Reacting Systems⁴

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

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

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

Utilizing the definition of enthalpy:

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

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

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.

Figure 15–21

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

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

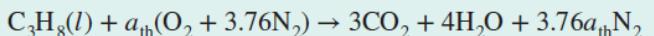
Liquid propane (C_3H_8) enters a combustion chamber at $25^\circ C$ at a rate of 0.05 kg/min where it is mixed and burned with 50 percent excess air that enters the combustion chamber at $7^\circ C$, as shown in Fig. 15–22. An analysis of the combustion gases reveals that all the hydrogen in the fuel 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.

SOLUTION Liquid propane is burned steadily with excess air. The mass flow rate of air and the rate of heat transfer are to be determined.

Assumptions 1 Steady operating conditions exist. 2 Air and the combustion gases are ideal gases. 3 Kinetic and potential energies are negligible.

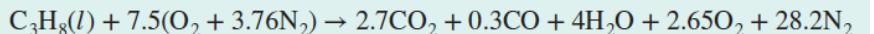
Analysis We note that all the hydrogen in the fuel burns to H_2O but 10 percent of the carbon burns incompletely and forms CO . Also, the fuel is burned with excess air, and thus there is some free O_2 in the product gases.

The theoretical amount of air is determined from the stoichiometric reaction to be



O_2 balance: $a_{th} = 3 + 2 = 5$

Then the balanced equation for the actual combustion process with 50 percent excess air and some CO in the products becomes



(a) The air-fuel ratio for this combustion process is

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{(7.5 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(3 \text{ kmol})(12 \text{ kg/kmol}) + (4 \text{ kmol})(2 \text{ kg/kmol})} = 25.53 \text{ kg air/kg fuel}$$

Thus,

$$\begin{aligned} \dot{m}_{air} &= (AF)(\dot{m}_{fuel}) \\ &= (25.53 \text{ kg air/kg fuel})(0.05 \text{ kg fuel/min}) \\ &= \mathbf{1.18 \text{ kg air/min}} \end{aligned}$$

(b) The heat transfer for this steady-flow combustion process is determined from the steady-flow energy balance $E_{out} = E_{in}$ applied on the combustion chamber per unit mole of the fuel,

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

or

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

Assuming the air and the combustion products to be ideal gases, we have $h = h(T)$, and we form the following minitable using data from the property tables:

Substance	\bar{h}_f^o kJ/kmol	$\bar{h}_{280 \text{ K}}$ kJ/kmol	$\bar{h}_{298 \text{ K}}$ kJ/kmol	$\bar{h}_{1500 \text{ K}}$ kJ/kmol
$C_3H_8(l)$	-118,910	—	—	—
O_2	0	Table A-19 8150	8682	49,292
N_2	0	Table A-18 8141	8669	47,073
$H_2O(g)$	-241,820	Table A-23 —	9904	57,999
CO_2	-393,520	Table A-20 —	9364	71,078
CO	-110,530	Table A-21 —	8669	47,517

Table A-26

The \bar{h}_f^o of liquid propane is obtained by subtracting the \bar{h}_{fg} of propane at $25^\circ C$ from the \bar{h}_f^o of gas propane. Substituting gives

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

Energy in by mass per mole of fuel Energy out by mass per mole of fuel

$$\begin{aligned} Q_{out} &= (1 \text{ kmol } C_3H_8)[(-118,910 + \bar{h}_{298} - \bar{h}_{298}) \text{ kJ/kmol } C_3H_8] \\ &\quad + (7.5 \text{ kmol } O_2)[(0 + 8150 - 8682) \text{ kJ/kmol } O_2] \\ &\quad + (28.2 \text{ kmol } N_2)[(0 + 8141 - 8669) \text{ kJ/kmol } N_2] \\ &\quad - (2.7 \text{ kmol } CO_2)[(-393,520 + 71,078 - 9364) \text{ kJ/kmol } CO_2] \\ &\quad - (0.3 \text{ kmol } CO)[(-110,530 + 47,517 - 8669) \text{ kJ/kmol } CO] \\ &\quad - (4 \text{ kmol } H_2O)[(-241,820 + 57,999 - 9904) \text{ kJ/kmol } H_2O] \\ &\quad - (2.65 \text{ kmol } O_2)[(0 + 49,292 - 8682) \text{ kJ/kmol } O_2] \\ &\quad - (28.2 \text{ kmol } N_2)[(0 + 47,073 - 8669) \text{ kJ/kmol } N_2] \\ &= 363,880 \text{ kJ/kmol of } C_3H_8 \end{aligned}$$

Thus 363,880 kJ of heat is transferred from the combustion chamber for each kmol (44 kg) of propane. This corresponds to $363,880/44 = 8270 \text{ kJ/kg}$ of heat loss per kilogram of propane. Then the rate of heat transfer for a mass flow rate of 0.05 kg/min for the propane becomes

$$\dot{Q}_{out} = \dot{m}q_{out} = (0.05 \text{ kg/min})(8270 \text{ kJ/kg}) = 413.5 \text{ kJ/min} = \mathbf{6.89 \text{ kW}}$$

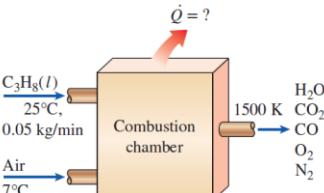


FIGURE 15–22

Schematic for Example 15–6.

15–5 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. 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** or **adiabatic combustion temperature** of the reaction (Fig. 15–24).

The adiabatic flame temperature of a steady-flow combustion process is determined from $Q - W = H_{\text{prod}} - H_{\text{react}}$ setting $Q = 0$ and $W = 0$. It yields

$$H_{\text{prod}} = H_{\text{react}} \quad (15-16)$$

or

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

15–5 Adiabatic Flame Temperature 2

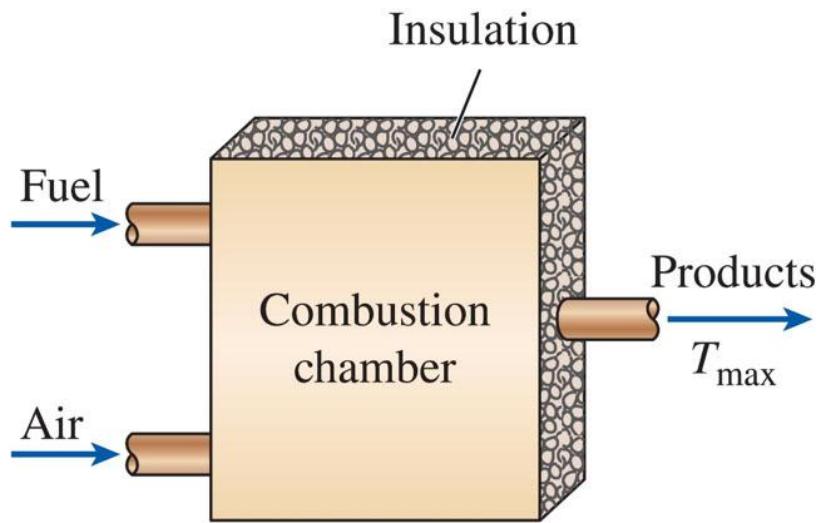


Figure 15–24

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

Once the reactants and their states are specified, the enthalpy of the reactants H_{react} can be easily determined. The calculation of the enthalpy of the products H_{prod} is not so straightforward because the temperature of the products is not known prior to the calculations. Therefore, 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.

15–5 Adiabatic Flame Temperature

In combustion chambers, the highest temperature to which a material can be exposed is limited by metallurgical considerations. Therefore, the adiabatic flame temperature is an important consideration in the design of combustion chambers, gas turbines, and nozzles.

The maximum temperature in a combustion chamber can be controlled by adjusting the amount of excess air, which serves as a coolant.

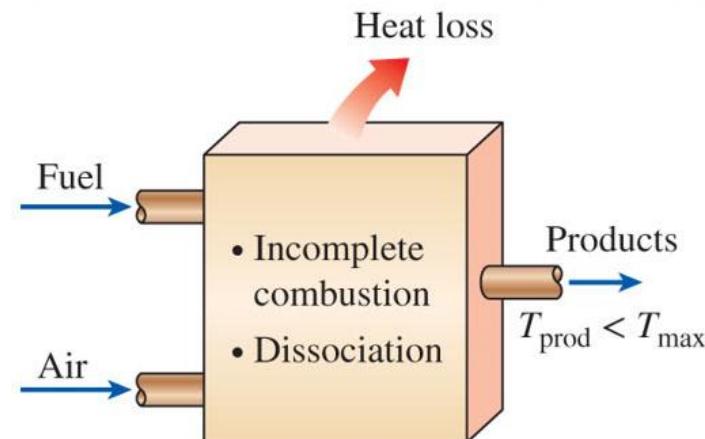
The adiabatic flame temperature of a fuel depends on

- (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.

Figure 15–25

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

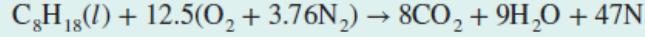


Liquid octane (C_8H_{18}) enters the combustion chamber of a gas turbine steadily at 1 atm and 25°C, and it is burned with air that enters the combustion chamber at the same state, as shown in Fig. 15–26. Determine the adiabatic flame temperature for (a) complete combustion with 100 percent theoretical air, (b) complete combustion with 400 percent theoretical air, and (c) incomplete combustion (some CO in the products) with 90 percent theoretical air.

SOLUTION Liquid octane is burned steadily. The adiabatic flame temperature is to be determined for different cases.

Assumptions 1 This is a steady-flow combustion process. 2 The combustion chamber is adiabatic. 3 There are no work interactions. 4 Air and the combustion gases are ideal gases. 5 Changes in kinetic and potential energies are negligible.

Analysis (a) The balanced equation for the combustion process with the theoretical amount of air is



The adiabatic flame temperature relation $H_{prod} = H_{react}$ in this case reduces to

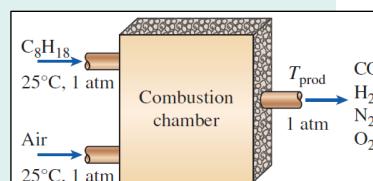
$$\sum N_p (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p = \sum N_r \bar{h}_{f,r}^\circ = (N\bar{h}_f^\circ)_{C_8H_{18}}$$

since all the reactants are at the standard reference state and $\bar{h}^\circ = 0$ for O_2 and N_2 . The \bar{h}_f° and \bar{h} values of various components at 298 K are

Substance	\bar{h}_f° kJ/kmol	$\bar{h}_{298\text{ K}}$ kJ/kmol
$C_3H_{18}(l)$	-249,950	—
O_2	0	8682
N_2	0	8669
$H_2O(g)$	-241,820	9904
CO_2	-393,520	9364

Substituting, we have

$$\begin{aligned} & (8 \text{ kmol } CO_2)[(-393,520 + \bar{h}_{CO_2} - 9364) \text{ kJ/kmol } CO_2] \\ & + (9 \text{ kmol } H_2O)[(-241,820 + \bar{h}_{H_2O} - 9904) \text{ kJ/kmol } H_2O] \\ & + (47 \text{ kmol } N_2)[(0 + \bar{h}_{N_2} - 8669) \text{ kJ/kmol } N_2] \\ & = (1 \text{ kmol } C_8H_{18})(-249,950 \text{ kJ/kmol } C_8H_{18}) \end{aligned}$$



which yields

$$8\bar{h}_{CO_2} + 9\bar{h}_{H_2O} + 47\bar{h}_{N_2} = 5,646,081 \text{ kJ}$$

It appears that we have one equation with three unknowns. Actually we have only one unknown—the temperature of the products T_{prod} —since $h = h(T)$ for ideal gases. Therefore, we have to use an equation solver or a trial-and-error approach to determine the temperature of the products.

A first guess is obtained by dividing the right-hand side of the equation by the total number of moles, which yields $5,646,081/(8 + 9 + 47) = 88,220 \text{ kJ/kmol}$. This enthalpy value corresponds to about 2650 K for N_2 , 2100 K for H_2O , and 1800 K for CO_2 . Noting that the majority of the moles are N_2 , we see that T_{prod} should be close to 2650 K, but somewhat under it. Therefore, a good first guess is 2400 K. At this temperature,

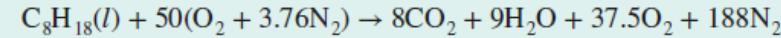
$$\begin{aligned} 8\bar{h}_{CO_2} + 9\bar{h}_{H_2O} + 47\bar{h}_{N_2} &= 8 \times 125,152 + 9 \times 103,508 + 47 \times 79,320 \\ &= 5,660,828 \text{ kJ} \end{aligned}$$

This value is higher than 5,646,081 kJ. Therefore, the actual temperature is slightly under 2400 K. Next we choose 2350 K. It yields

$$8 \times 122,091 + 9 \times 100,846 + 47 \times 77,496 = 5,526,654$$

which is lower than 5,646,081 kJ. Therefore, the actual temperature of the products is between 2350 and 2400 K. By interpolation, it is found to be $T_{prod} = 2395 \text{ K}$.

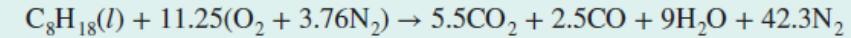
(b) The balanced equation for the complete combustion process with 400 percent theoretical air is



By following the procedure used in (a), the adiabatic flame temperature in this case is determined to be $T_{prod} = 962 \text{ K}$.

Notice that the temperature of the products decreases significantly as a result of using excess air.

(c) The balanced equation for the incomplete combustion process with 90 percent theoretical air is



Following the procedure used in (a), we find the adiabatic flame temperature in this case to be $T_{prod} = 2236 \text{ K}$.

Discussion Notice that the adiabatic flame temperature reaches its maximum value when complete combustion occurs with the theoretical amount of air (part a). It decreases as a result of incomplete combustion (part c) or using excess air (part b).

15–6 Entropy Change of Reacting Systems ¹

$$\underbrace{S_{\text{in}} - S_{\text{out}}}_{\text{Net entropy transfer by heat and mass}} + \underbrace{S_{\text{gen}}}_{\text{Entropy generation}} = \underbrace{\Delta S_{\text{system}}}_{\text{Change in entropy}}$$

(kJ/K) entropy balance for any system (including reacting systems) undergoing any process

$$\sum \frac{Q_k}{T_k} + S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}} \quad (\text{kJ/K})$$

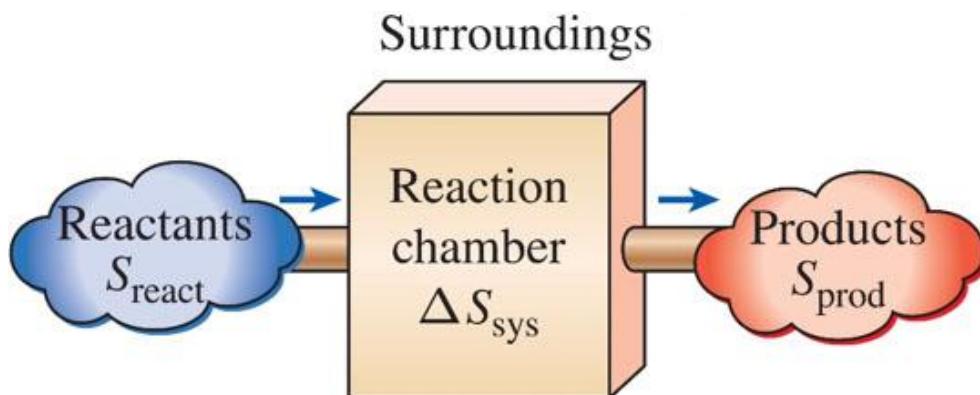
for a closed or steady-flow reacting system

$$S_{\text{gen,adiabatic}} = S_{\text{prod}} - S_{\text{react}} \geq 0$$

for an adiabatic process ($Q = 0$)

Figure 15–27

The entropy change associated with a chemical relation.



15–6 Entropy Change of Reacting Systems 2

$$\bar{s}(T, P) = \bar{s}^\circ(T, P_0) - R_u \ln \frac{P}{P_0} \quad \text{Entropy of a component}$$

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

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.

$$P_0 = 1 \text{ atm}$$

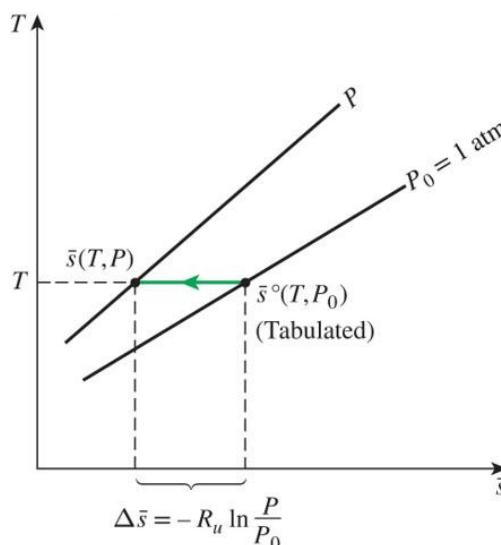
$$P_i \text{ partial pressure}$$

$$y_i \text{ mole fraction}$$

$$P_m \text{ total pressure of mixture}$$

Figure 15–28

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.



15–7 Second-law Analysis of Reacting Systems ₁

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

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

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

When both the reactants and the products are at T_0

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

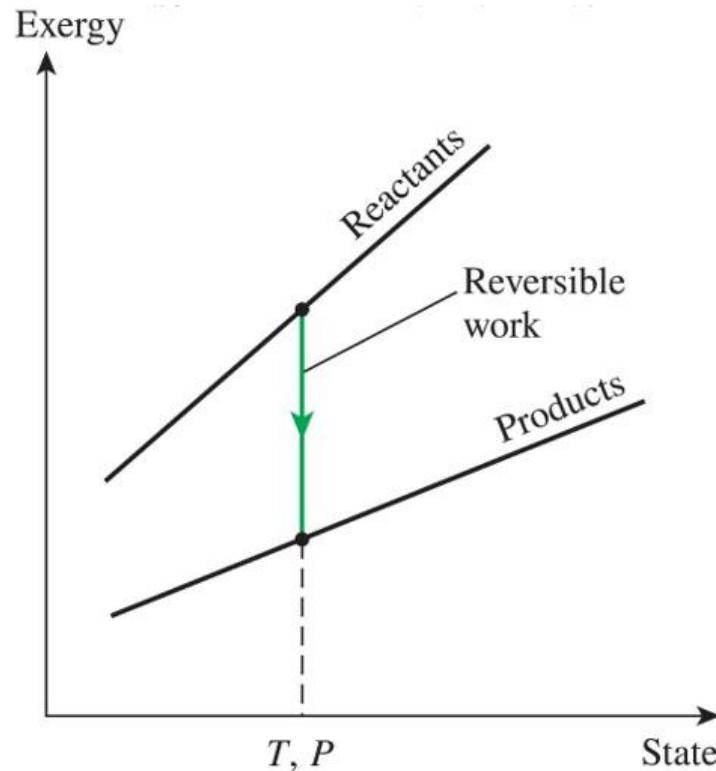
$$W_{\text{rev}} = \sum N_r \bar{g}_{0,r} - \sum N_p \bar{g}_{0,p}$$

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

15–7 Second-law Analysis of Reacting Systems 2

Figure 15–29

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



15–7 Second-law Analysis of Reacting Systems 3

For the very special case of

$$T_{\text{react}} = T_{\text{prod}} = T_0 = 25 \text{ degree celsius}$$

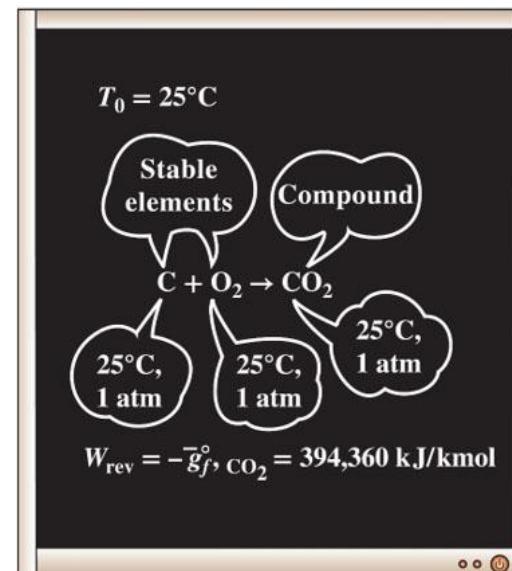
$$W_{\text{rev}} = \sum N_r \bar{g}_{f,r}^{\circ} - \sum N_p \bar{g}_{f,p}^{\circ} \quad (\text{kJ})$$

We can conclude from the above equation that the $-\bar{g}_f^{\circ}$

value (the negative of the Gibbs function of formation at 25 degree celsius and 1 atm) of a compound represents the *reversible work* associated with the formation of that compound from its stable elements at 25 degree celsius and 1 atm in an environment at 25 degree celsius and 1 atm.

Figure 15–30

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



End