

Thermodynamics: An Engineering Approach

8th Edition

Yunus A. Çengel, Michael A. Boles
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CHAPTER 15

CHEMICAL REACTIONS

Vaibhav Arghode, Department of Aerospace Engineering
Indian Institute of Technology Kanpur

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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
- Apply energy balances to reacting systems for both steady-flow control volumes and fixed mass systems
- Calculate the 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 C_nH_m

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

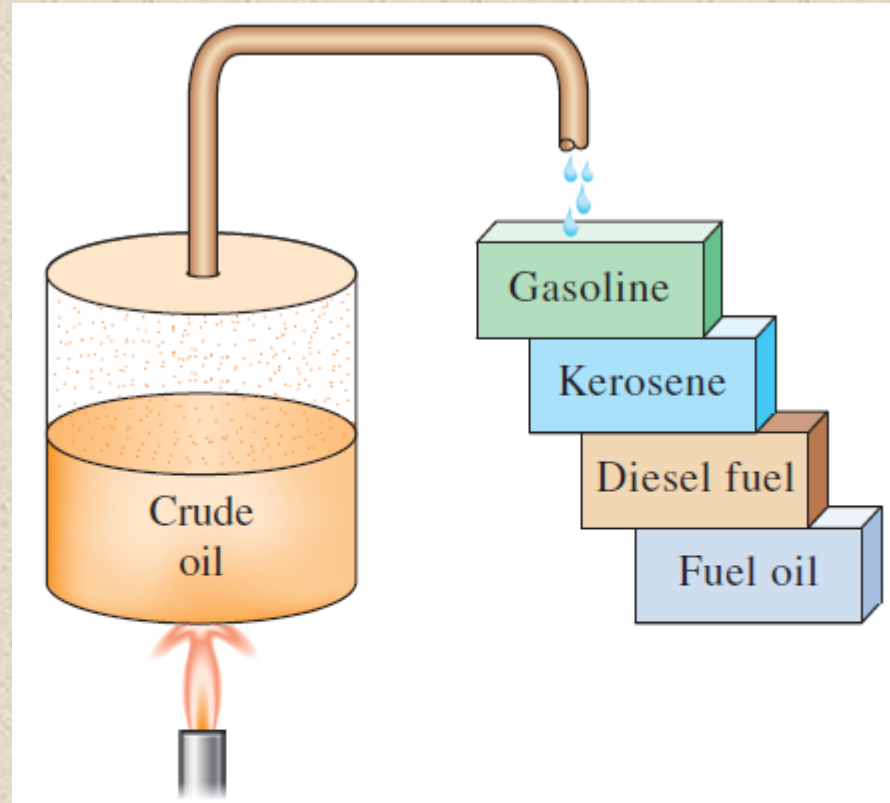


FIGURE 15-1

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

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.

AIR AS AN OXIDIZER

The oxidizer most often used in combustion processes is air. 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. Here nitrogen is assumed to remain perfectly inert (i.e. it does not react with other elements)

$$79 / 21 = 3.76$$

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

$$\begin{aligned} M_{\text{air}} & \text{ (Molecular weight of air)} \\ &= (N_{\text{O}_2} M_{\text{O}_2} + N_{\text{N}_2} M_{\text{N}_2}) / (N_{\text{O}_2} + N_{\text{N}_2}) \\ &= (1 \times 32 + 3.76 \times 28) / (1 + 3.76) \\ &= 28.84 \cong 29 \text{ kg/kmol} \end{aligned}$$

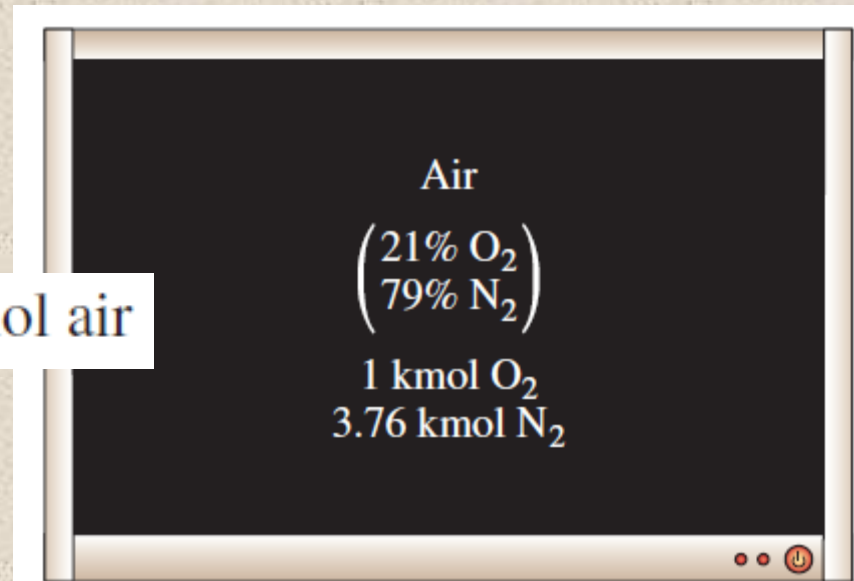


FIGURE 15–2

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

REACTANTS AND PRODUCTS

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

During a combustion process, the components that exist before the reaction are called **reactants** and the components that exist after the reaction are called **products**

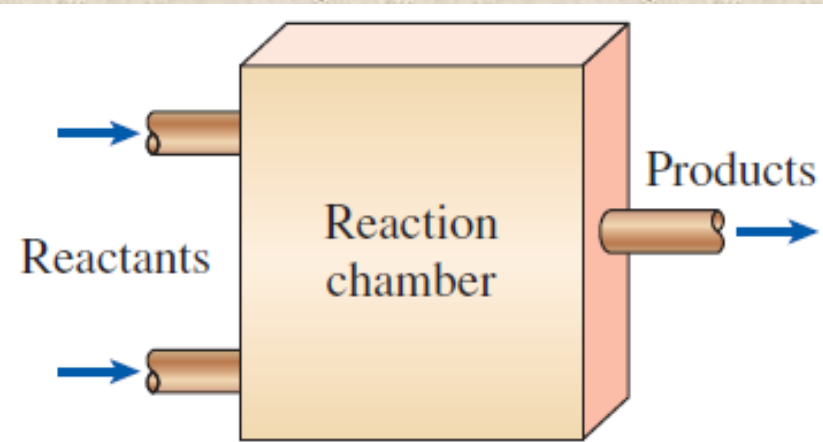


FIGURE 15–3

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

IGNITION

Bringing a fuel into intimate contact with oxygen is not sufficient to start combustion process

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%.

MASS BALANCE IN A CHEMICAL REACTION

The total mass of each element is conserved during a chemical reaction

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

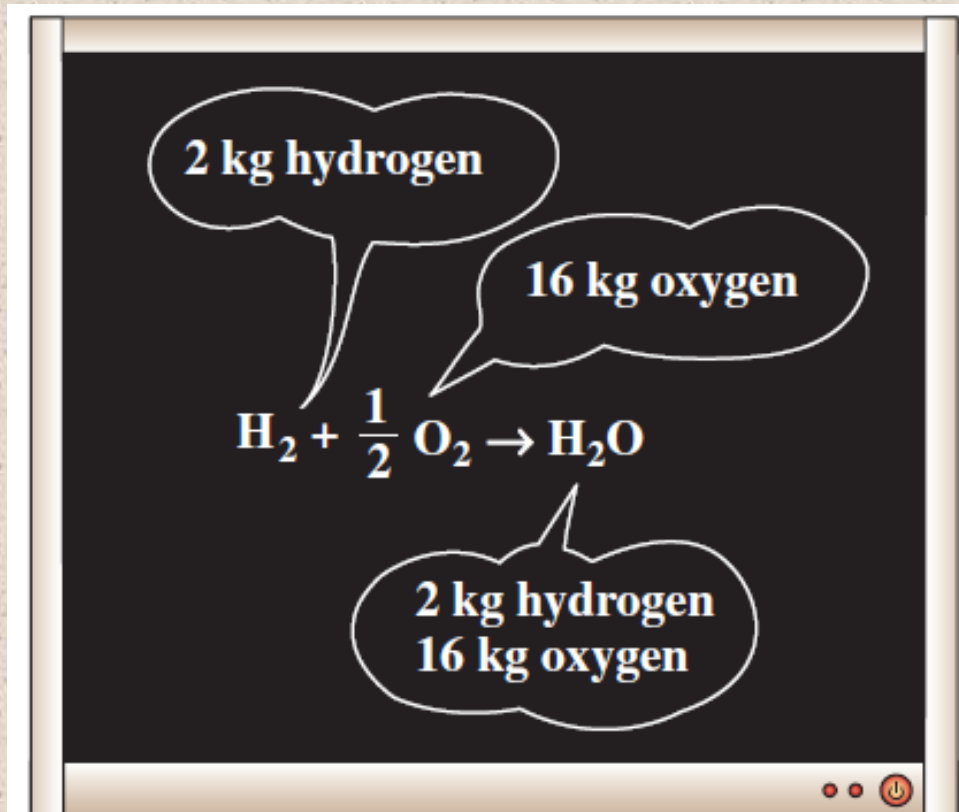
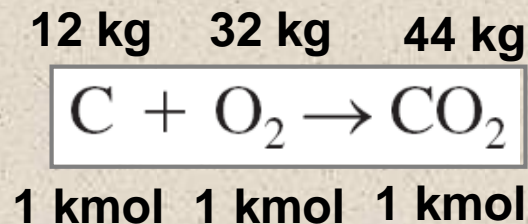


FIGURE 15–4

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

AIR-FUEL RATIO

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

$$m = NM$$

m mass

N number of moles

M molar mass

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

Fuel–air ratio (FA): The reciprocal of air–fuel ratio ($FA = 1 / AF$)

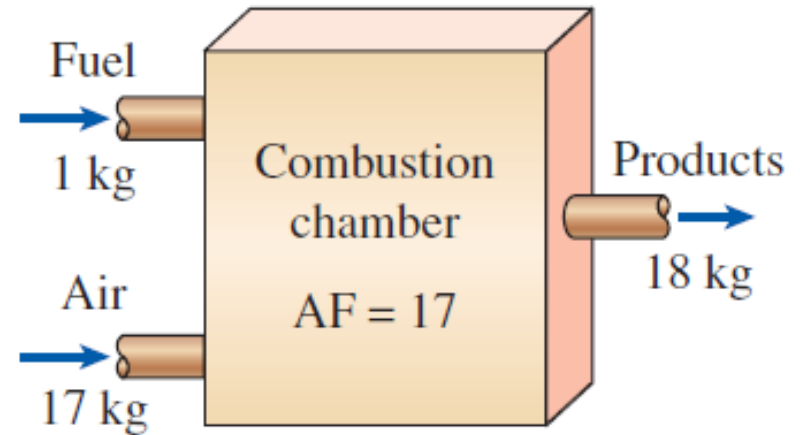


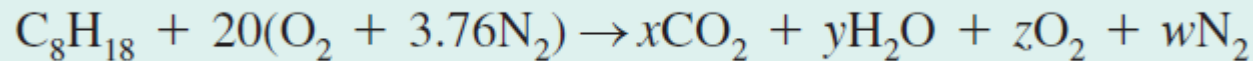
FIGURE 15–5

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

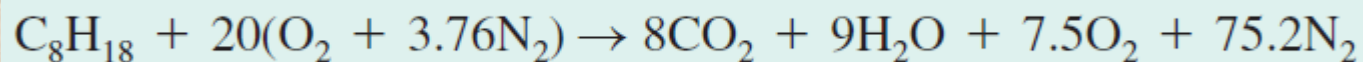
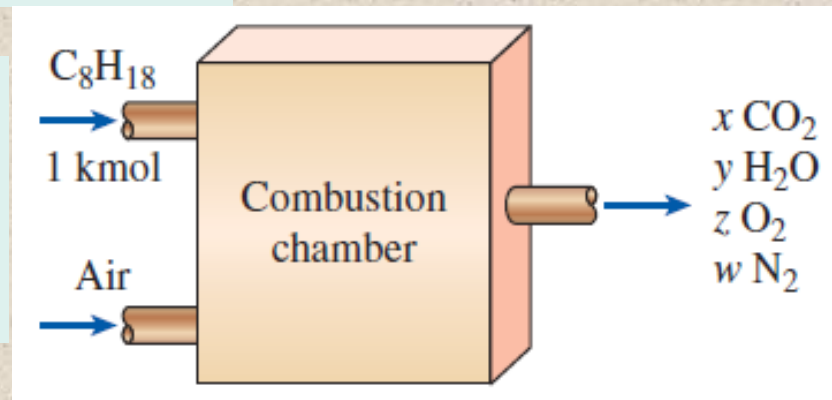
EXAMPLE

Balancing the Combustion Equation

One kmol of octane (C_8H_{18}) is burned with air that contains 20 kmol of O_2 , as shown. 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.



$$\begin{array}{ll} \text{C:} & 8 = x \rightarrow x = \mathbf{8} \\ \text{H:} & 18 = 2y \rightarrow y = \mathbf{9} \\ \text{O:} & 20 \times 2 = 2x + y + 2z \rightarrow z = \mathbf{7.5} \\ \text{N}_2: & (20)(3.76) = w \rightarrow w = \mathbf{75.2} \end{array}$$



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

COMPLETE COMBUSTION

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)

COMPLETE COMBUSTION

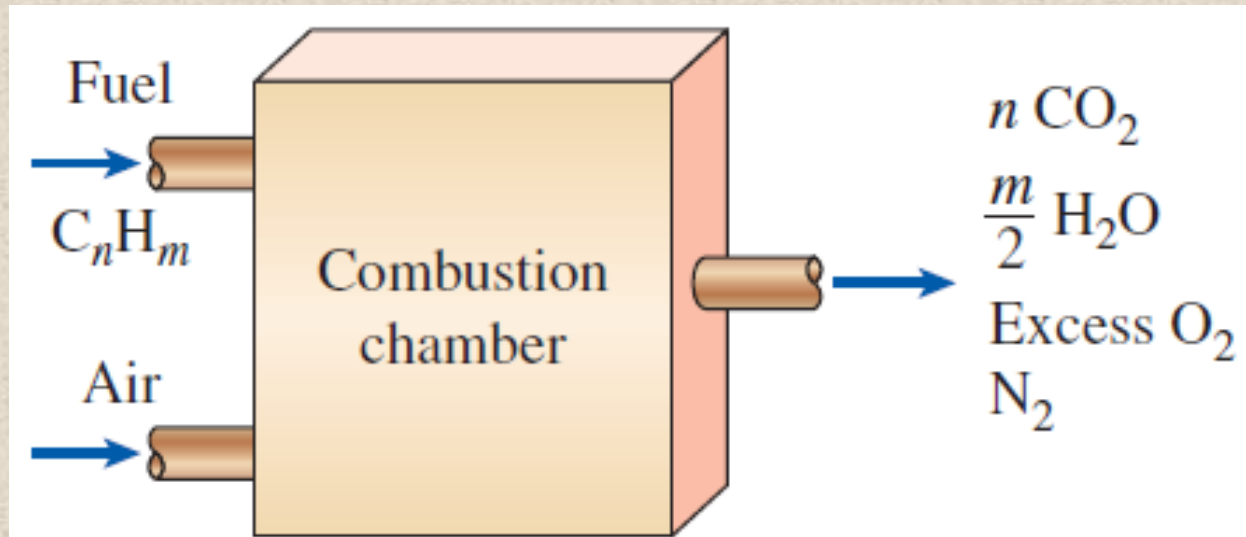


FIGURE 15-7

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

STOICHIOMETRIC COMBUSTION

Stoichiometric or theoretical air: The minimum amount of air needed for the **complete combustion** of a fuel

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**

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

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

$$\text{Equivalence ratio} = \frac{(AF)_{\text{stoichiometric}}}{(AF)_{\text{actual}}}$$

Stoichiometric or theoretical combustion of methane



- no unburned fuel
- no free oxygen in products

$$(AF)_{stoichiometric} = \frac{2 \times 32 + 2 \times 3.76 \times 28}{1 \times 12 + 4 \times 1} = 17.16$$

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

ACTUAL COMBUSTION

Predicting the composition of the products is relatively easy when the combustion process is assumed to be complete and the exact amounts of the fuel and air used are known (by simply applying mass balance to each element)

Actual combustion process are hardly ever complete, even in the presence of excess air. Therefore, it is impossible to predict the composition of the products on the basis of the mass balance alone.

Then the only alternative we have is to measure the amount of each component in the products directly

A commonly used device to analyze the composition of combustion gases is the **Orsat gas analyzer**

INTERNAL ENERGY

The molecules of a system possess energy in various forms such as *sensible* and *latent energy* (associated with a change of state), *chemical energy* (associated with molecular structure), and *nuclear energy* (associated with the atomic structure)

Here we do not intend to deal with *nuclear energy*

Until now we also ignored *chemical energy* since the systems considered previously involved no changes in their chemical structure

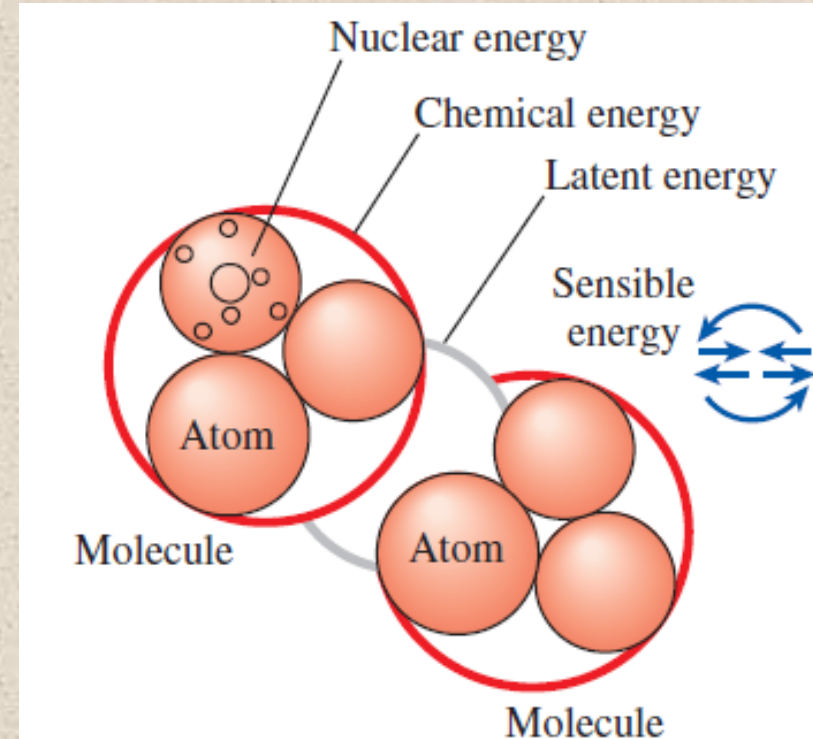


FIGURE 15-13

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

CHEMICAL ENERGY

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

A process that involves chemical reactions involves changes in chemical energies, which must be accounted for in an energy balance

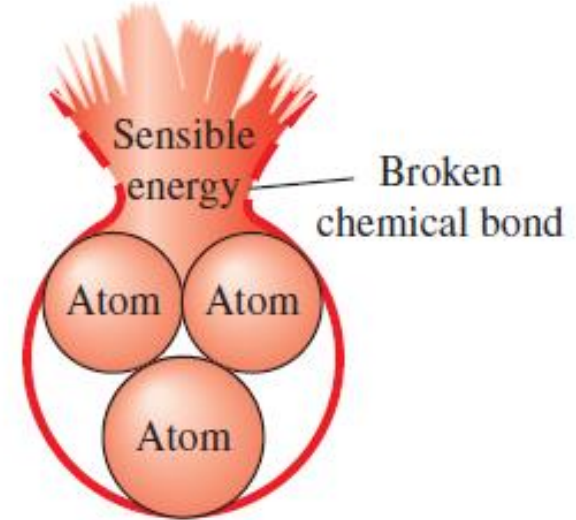


FIGURE 15–14

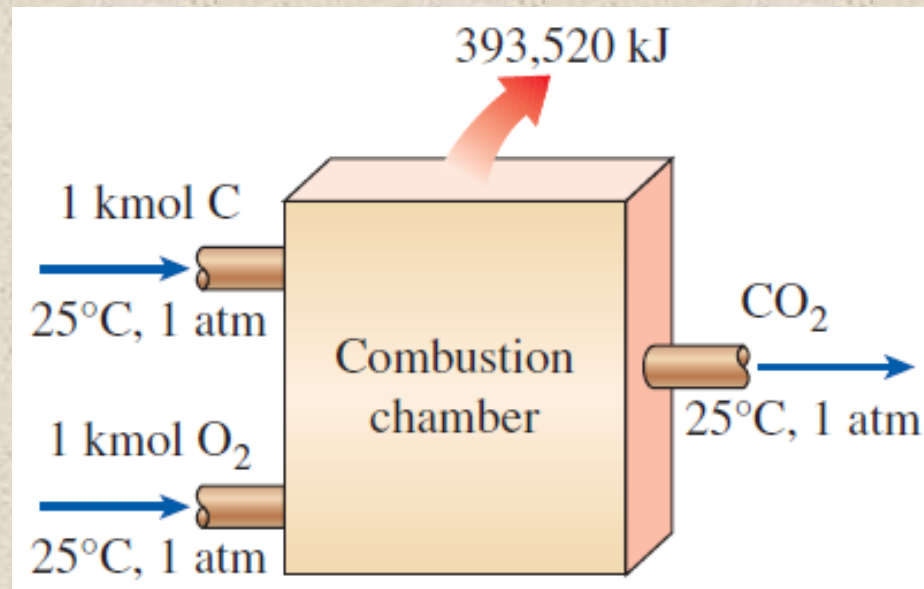
When the existing chemical bonds are destroyed and new ones are formed during a combustion process, usually a large amount of sensible energy is absorbed or released.

CHEMICAL ENERGY

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:

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

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



ENTHALPY OF FORMATION

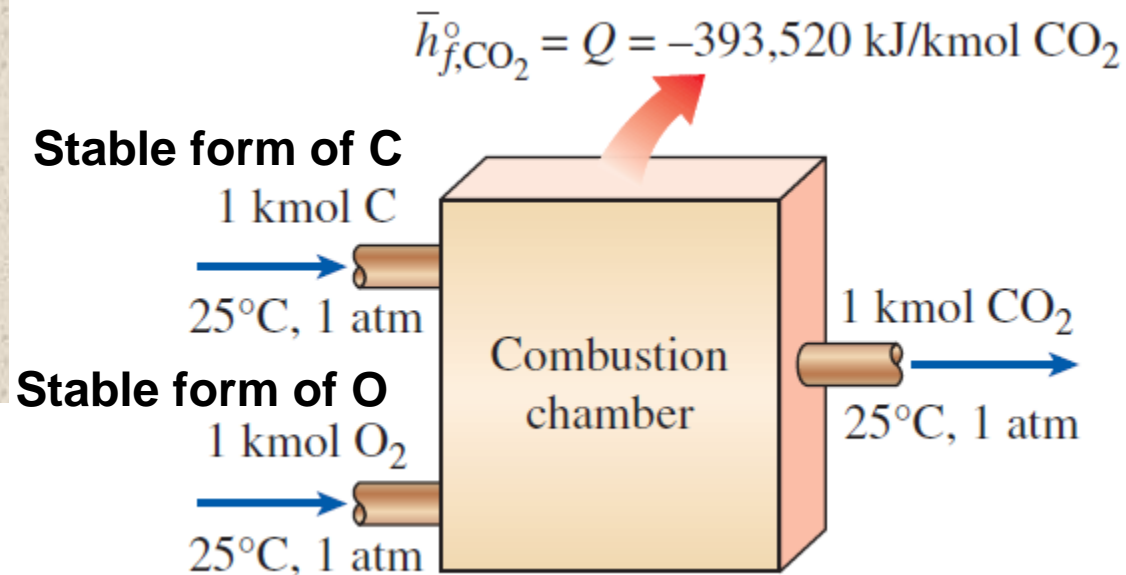
Enthalpy of formation at standard reference state h_f° : The amount of energy absorbed as the component is formed at the standard reference state from its **stable elemental forms** during a steady-flow process

Standard reference state $\rightarrow 25^\circ\text{C}$ and 1 atm

$$\bar{h}_{f,CO_2}^\circ = Q = -393,520 \text{ kJ/kmol CO}_2$$

Negative enthalpy of formation for a compound indicates that heat is released during formation of that compound from its stable form of elements

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



STABLE FORMS OF ELEMENTS

Stable form of an element: The chemically stable form of that element at 25°C and 1 atm (standard reference state)

e.g. nitrogen, exists in diatomic form (N_2) at 25°C and 1 atm. Therefore, the stable form of nitrogen at the standard reference state is diatomic nitrogen N_2 , and not monoatomic nitrogen N

To establish a starting point, we assign the enthalpy of formation of all stable forms of 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

<u>Element</u>		<u>Stable form</u>	<u>Enthalpy of formation at standard reference state (\bar{h}_f°)</u>
C	→	C (solid, graphite) (not diamond)	0
H	→	H_2 (gas)	0
N	→	N_2 (gas)	0
O	→	O_2 (gas)	0

ENTHALPY OF FORMATION: Table

TABLE A-26

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

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)	0	0	130.68
Nitrogen	N ₂ (g)	0	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

Difference is h_{fg} of water at 25°C (2441.7 kJ/kg, 44,000 kJ/kmol)

Positive sign suggests heat is absorbed while forming C₂H₂ from C and H₂

ENTHALPY OF COMBUSTION

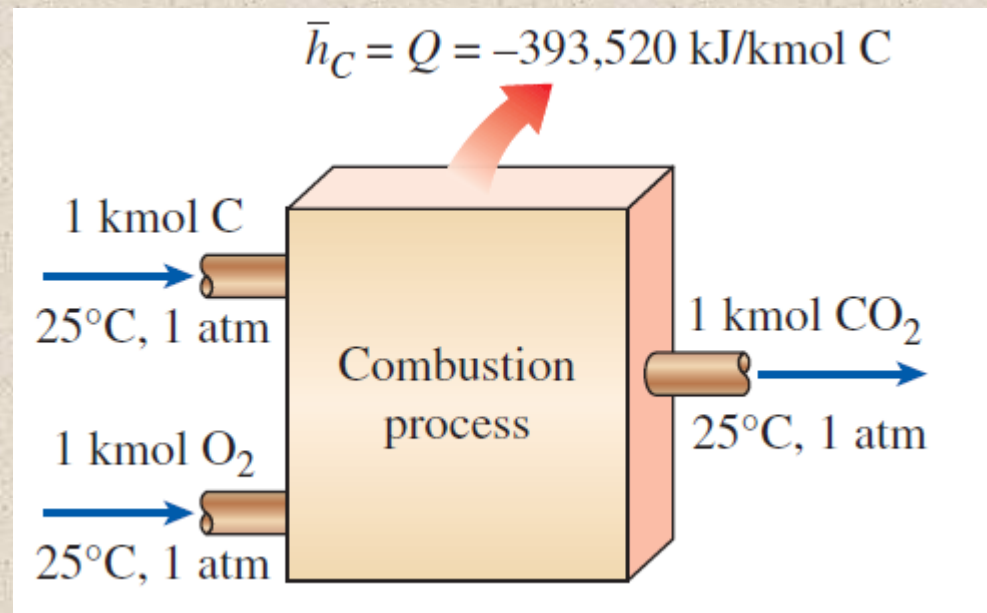
Enthalpy of combustion h_C : It represents the amount of heat absorbed during a steady-flow combustion process when 1 kmol (or 1 kg) of fuel is burned completely at a specified temperature and pressure and the products are returned to the state of reactants

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

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

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

at the standard reference state of 25°C and 1 atm



HEATING VALUE

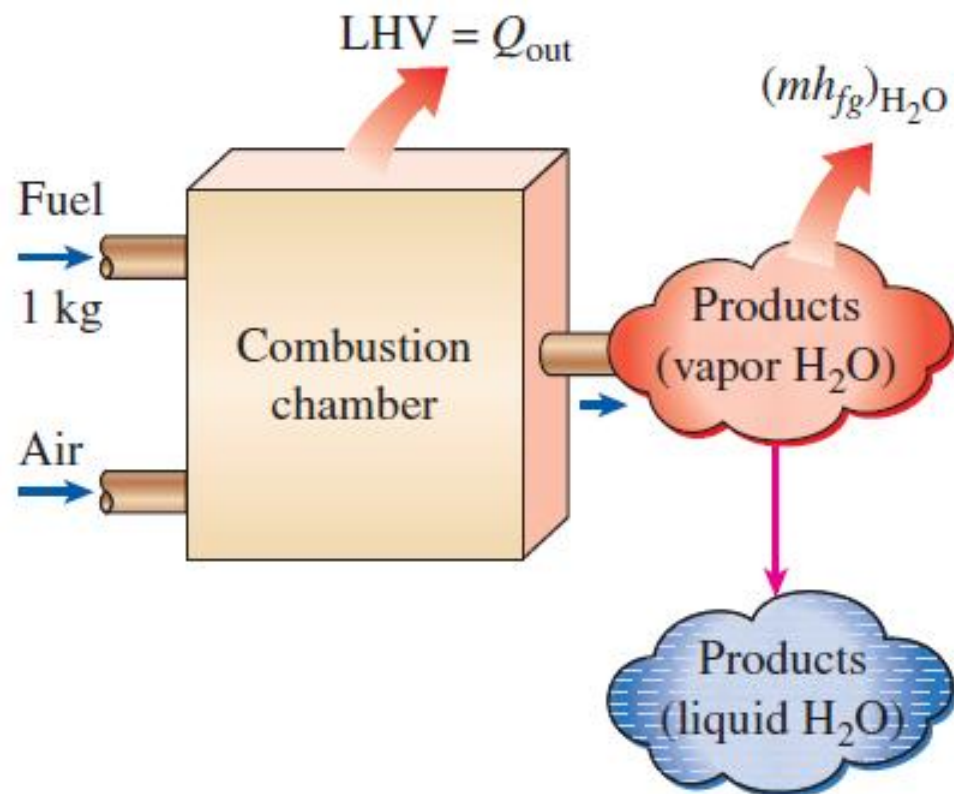
Heating value: The amount of heat released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants. The heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel.

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

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

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



$$\text{HHV} = \text{LHV} + (mh_{fg})_{\text{H}_2\text{O}}$$

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.

HEATING VALUE OF FUELS: Table

TABLE A-27

Properties of some common fuels and hydrocarbons

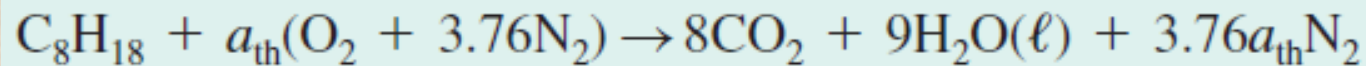
Fuel (phase)	Formula	Molar mass, kg/kmol	Density, ¹ kg/L	Enthalpy of vaporization, ² kJ/kg	Specific heat, ¹ c_p kJ/kg·K	Higher heating value, ³ kJ/kg	Lower heating value, ³ kJ/kg
Carbon (s)	C	12.011	2	—	0.708	32,800	32,800
Hydrogen (g)	H ₂	2.016	—	—	14.4	141,800	120,000
Carbon monoxide (g)	CO	28.013	—	—	1.05	10,100	10,100
Methane (g)	CH ₄	16.043	—	509	2.20	55,530	50,050
Methanol (ℓ)	CH ₄ 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 ₆ 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

~45 MJ/kg

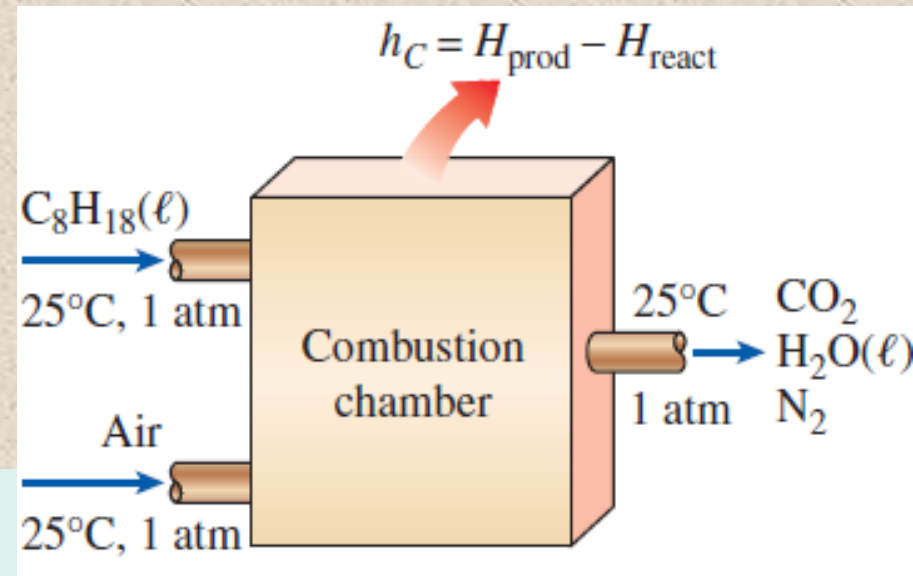
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EXAMPLE 15–5**Evaluation of the Enthalpy of Combustion**

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



Note: Calculation of a_{th} is not required as the enthalpy of formation of O_2 and N_2 is zero ($\bar{h}_{f,\text{O}_2}^\circ = 0$, $\bar{h}_{f,\text{N}_2}^\circ = 0$), and not required in estimation of enthalpy of combustion for this case



$$\bar{h}_C = H_{\text{prod}} - H_{\text{react}}$$

$$= \sum N_p \bar{h}_{f,p}^\circ - \sum N_r \bar{h}_{f,r}^\circ = (N \bar{h}_f^\circ)_{\text{CO}_2} + (N \bar{h}_f^\circ)_{\text{H}_2\text{O}} - (N \bar{h}_f^\circ)_{\text{C}_8\text{H}_{18}}$$

$$\begin{aligned} \bar{h}_C &= (8 \text{ kmol})(-393,520 \text{ kJ/kmol}) + (9 \text{ kmol})(-285,830 \text{ kJ/kmol}) \\ &\quad - (1 \text{ kmol})(-249,950 \text{ kJ/kmol}) \\ &= -5,471,000 \text{ kJ/kmol C}_8\text{H}_{18} = -47,891 \text{ kJ/kg C}_8\text{H}_{18} \end{aligned}$$

TABLE A-26

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

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)	0	0	130.68
Nitrogen	N ₂ (g)	0	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
<i>n</i> -Butane	C ₄ H ₁₀ (g)	-126,150	-15,710	310.12
<i>n</i> -Octane	C ₈ H ₁₈ (g)	-208,450	+16,530	466.73
<i>n</i> -Octane	C ₈ H ₁₈ (l)	-249,950	+6,610	360.79

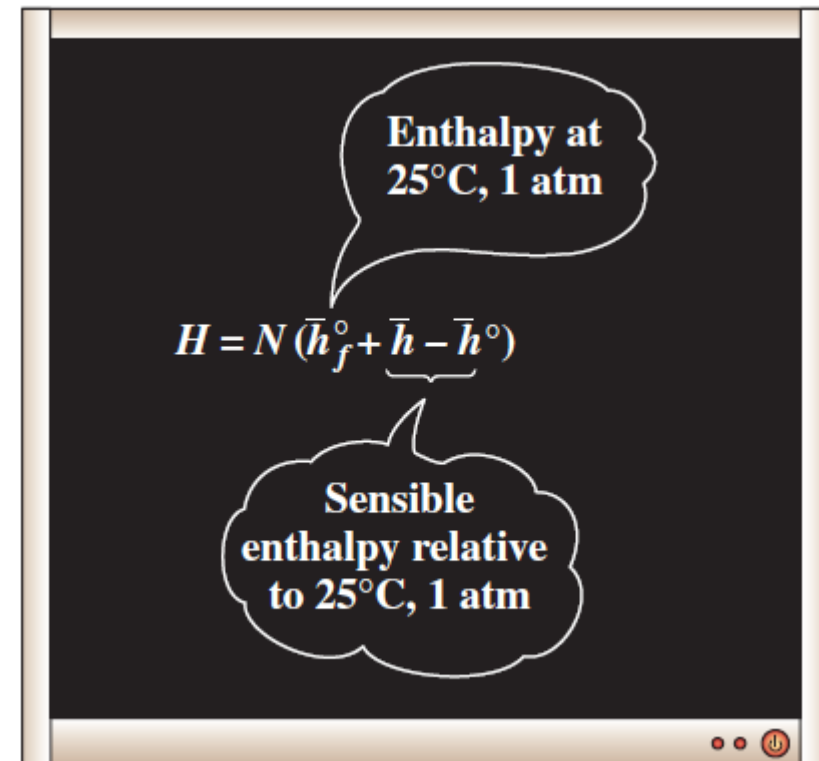
ENTHALPY

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

\bar{h}_f° - *Enthalpy of formation: Table A26*

$(\bar{h} - \bar{h}^\circ)$ *Sensible enthalpy: Table A17-A25*

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



Nitrogen: Table

(@ 25°C and 1 atm)

Formula	\bar{h}_f° kJ/kmol
C(s)	0
H ₂ (g)	0
N ₂ (g)	0
O ₂ (g)	0
CO(g)	-110,530
CO ₂ (g)	-393,520

TABLE A-18

Ideal-gas properties of nitrogen, N₂

T K	Sensible enthalpy \bar{h} kJ/kmol	\bar{u} kJ/kmol	\bar{s}° kJ/kmol·K
0	0	0	0
220	6,391	4,562	182.639
230	6,683	4,770	183.938
240	6,975	4,979	185.180
250	7,266	5,188	186.370
260	7,558	5,396	187.514
270	7,849	5,604	188.614
280	8,141	5,813	189.673
290	8,432	6,021	190.695
298	8,669	6,190	191.502
300	8,723	6,229	191.682
310	9,014	6,437	192.638
320	9,306	6,645	193.562
330	9,597	6,853	194.459
340	9,888	7,061	195.328
350	10,180	7,270	196.173
360	10,471	7,478	196.995
370	10,763	7,687	197.794
380	11,055	7,895	198.572
390	11,347	8,104	199.331

Enthalpy(350 K)

= $\bar{h}_f^\circ(298 K)$

+ [$\bar{h}(350 K) - \bar{h}^\circ$]

$\bar{h}(298 K)$

Enthalpy(350 K) =

0 + [10,180 - 8,669] =

1511 $\frac{kJ}{kmol}$

Carbon Dioxide: Table

(@ 25°C and 1 atm)

Formula	\bar{h}_f° kJ/kmol
C(s)	0
H ₂ (g)	0
N ₂ (g)	0
O ₂ (g)	0
CO(g)	-110,530
CO ₂ (g)	-393,520

$$\begin{aligned} \text{Enthalpy}(350 \text{ K}) \\ = \bar{h}_f^\circ(298 \text{ K}) + \bar{h}(298 \text{ K}) \\ + [\bar{h}(350 \text{ K}) - \bar{h}^\circ] \end{aligned}$$

$$\begin{aligned} \text{Enthalpy}(350 \text{ K}) &= \\ &- 393,520 + \\ &[11,351 - 9,364] = \\ &- 391,533 \frac{\text{kJ}}{\text{kmol}} \end{aligned}$$

TABLE A-20

Ideal-gas properties of carbon dioxide, CO₂

T K	Sensible enthalpy \bar{h} kJ/kmol	\bar{u} kJ/kmol	\bar{s}° kJ/kmol·K
0	0	0	0
220	6,601	4,772	202.966
230	6,938	5,026	204.464
240	7,280	5,285	205.920
250	7,627	5,548	207.337
260	7,979	5,817	208.717
270	8,335	6,091	210.062
280	8,697	6,369	211.376
290	9,063	6,651	212.660
298	9,364	6,885	213.685
300	9,431	6,939	213.915
310	9,807	7,230	215.146
320	10,186	7,526	216.351
330	10,570	7,826	217.534
340	10,959	8,131	218.694
350	11,351	8,439	219.831
360	11,748	8,752	220.948
370	12,148	9,068	222.044
380	12,552	9,392	223.122
390	12,960	9,718	224.182

FIRST-LAW ANALYSIS OF REACTING SYSTEMS

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

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

Steady-Flow Systems

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

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

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

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

Steady-Flow 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

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

where

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

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

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:

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

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

Utilizing the definition of enthalpy:

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

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

The $P\bar{v}$ terms are negligible for solids and liquids

The $P\bar{v}$ terms can be replaced by $R_u T$ for gases that behave as an ideal gas

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

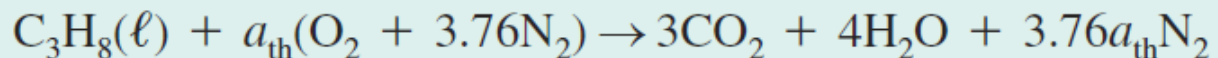
FIGURE 15–21

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

EXAMPLE

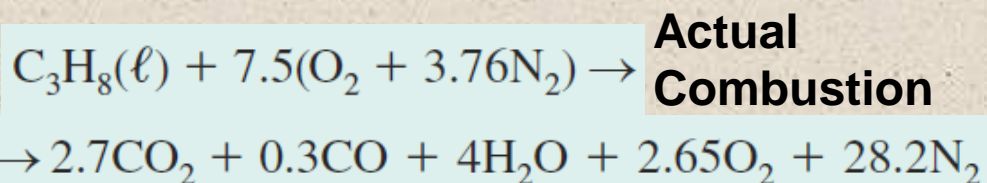
First-Law Analysis of Steady-Flow Combustion

Liquid propane (C_3H_8) enters a combustion chamber at 25°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°C , as shown. 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.



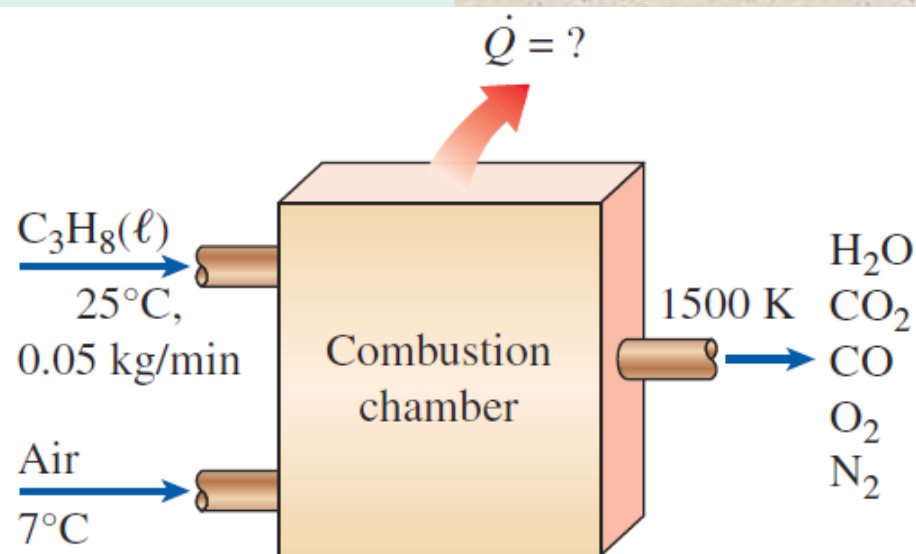
O_2 balance: $a_{\text{th}} = 3 + 2 = 5$

Stoichiometric Combustion



Actual Combustion

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



steady-flow energy balance $E_{\text{out}} = E_{\text{in}}$

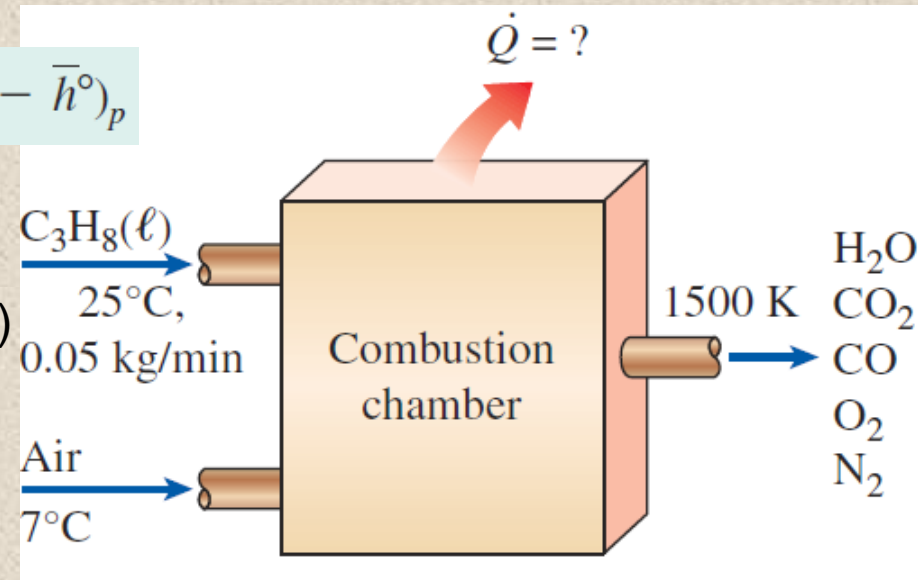
$$Q_{\text{out}} = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r - \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p$$

$$= 363,880 \text{ kJ/kmol of C}_3\text{H}_8$$

Thus 363,880 kJ of heat is transferred from the combustion chamber for each kmol (44 kg) of propane. This corresponds to $363,880/44 = 8270$ kJ of heat loss per kilogram of propane.

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

$$= 413.5 \text{ kJ/min} = \mathbf{6.89 \text{ kW}}$$



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° kJ/kmol	$\bar{h}_{280 \text{ K}}$ kJ/kmol	$\bar{h}_{298 \text{ K}}$ kJ/kmol	$\bar{h}_{1500 \text{ K}}$ kJ/kmol
$\text{C}_3\text{H}_8(\ell)$	-118,590	—	—	—
O_2	0	8150	8682	49,292
N_2	0	8141	8669	47,073
$\text{H}_2\text{O}(g)$	-241,820	—	9904	57,999
CO_2	-393,520	—	9364	71,078
CO	-110,530	—	8669	47,517

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

$$\begin{aligned} Q_{\text{out}} &= (1 \text{ kmol } C_3H_8)[(-118,590 + \bar{h}_{298} - \bar{h}_{298}) \text{ kJ/kmol } C_3H_8] \\ &\quad + (7.5 \text{ kmol } O_2)[(0 + 8150 - 8682) \text{ kJ/kmol } O_2] \\ &\quad + (28.2 \text{ kmol } N_2)[(0 + 8141 - 8669) \text{ kJ/kmol } N_2] \\ &\quad - (2.7 \text{ kmol } CO_2)[(-393,520 + 71,078 - 9364) \text{ kJ/kmol } CO_2] \\ &\quad - (0.3 \text{ kmol } CO)[(-110,530 + 47,517 - 8669) \text{ kJ/kmol } CO] \\ &\quad - (4 \text{ kmol } H_2O)[(-241,820 + 57,999 - 9904) \text{ kJ/kmol } H_2O] \\ &\quad - (2.65 \text{ kmol } O_2)[(0 + 49,292 - 8682) \text{ kJ/kmol } O_2] \\ &\quad - (28.2 \text{ kmol } N_2)[(0 + 47,073 - 8669) \text{ kJ/kmol } N_2] \\ &= 363,880 \text{ kJ/kmol of } C_3H_8 \end{aligned}$$

(Table A-27) Enthalpy of vaporization (kJ/kg) for Propane, $C_3H_8 = 335$ kJ/kg (@25°C) = 335×44 (molar mass of C_3H_8) = 14,740 kJ/kmol

Enthalpy of formation for liquid propane, $C_3H_8(l) = -103,850 - 14,740 = -118,590$ kJ/kmol

TABLE A-26

Enthalpy of formation,
25°C, 1 atm

Substance	Formula	\bar{h}_f° kJ/kmol
Carbon	C(s)	0
Hydrogen	H ₂ (g)	0
Nitrogen	N ₂ (g)	0
Oxygen	O ₂ (g)	0
Carbon monoxide	CO(g)	-110,530
Carbon dioxide	CO ₂ (g)	-393,520
Water vapor	H ₂ O(g)	-241,820
Water	H ₂ O(l)	-285,830
Hydrogen peroxide	H ₂ O ₂ (g)	-136,310
Ammonia	NH ₃ (g)	-46,190
Methane	CH ₄ (g)	-74,850
Acetylene	C ₂ H ₂ (g)	+226,730
Ethylene	C ₂ H ₄ (g)	+52,280
Ethane	C ₂ H ₆ (g)	-84,680
Propylene	C ₃ H ₆ (g)	+20,410
Propane	C ₃ H ₈ (g)	-103,850
<i>n</i> -Butane	C ₄ H ₁₀ (g)	-126,150
<i>n</i> -Octane	C ₈ H ₁₈ (g)	-208,450
<i>n</i> -Octane	C ₈ H ₁₈ (l)	-249,950
<i>n</i> -Dodecane	C ₁₂ H ₂₆ (g)	-291,010
Benzene	C ₆ H ₆ (g)	+82,930

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 temperature** or **adiabatic combustion temperature**

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

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

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

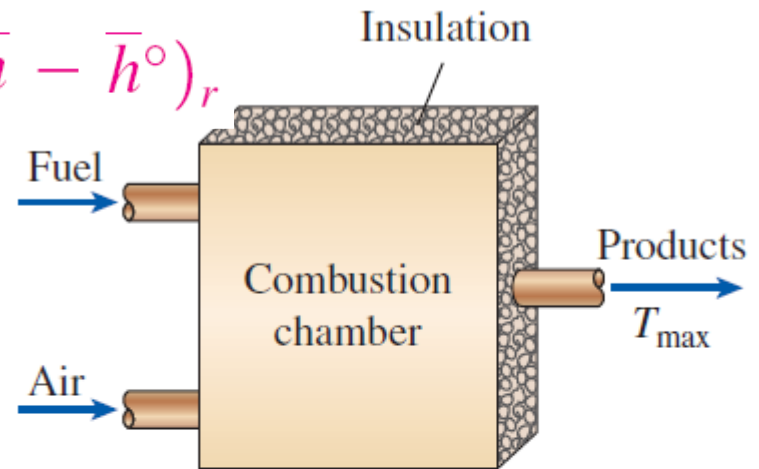


FIGURE 15–24

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

ADIABATIC FLAME TEMPERATURE

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*

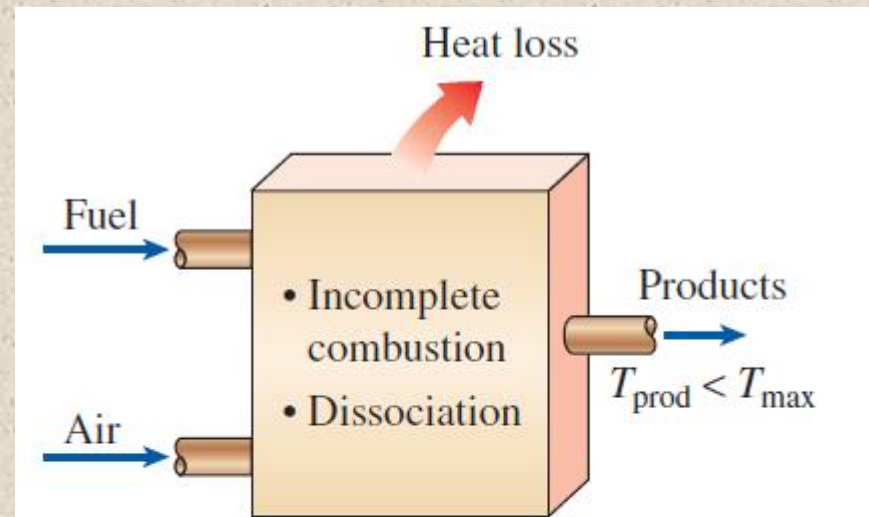


FIGURE 15–25

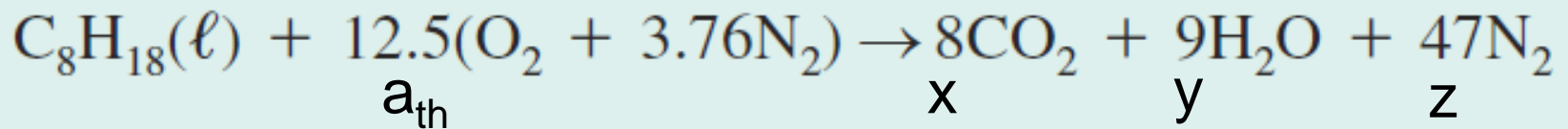
The maximum temperature encountered in a combustion chamber is lower than the theoretical adiabatic flame temperature.

EXAMPLE

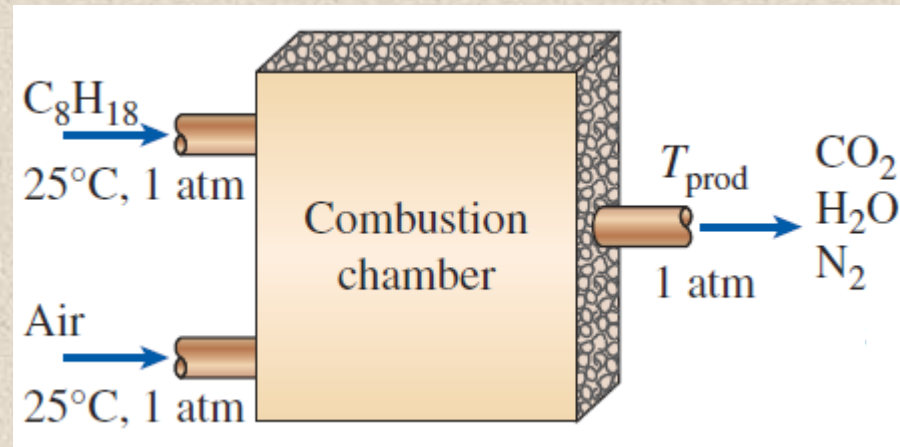
Adiabatic Flame Temperature in Steady Combustion

Liquid octane (C_8H_{18}) enters the combustion chamber of a gas turbine steadily at 1 atm and 25°C , and it is burned with air that enters the combustion chamber at the same state, as shown. Determine the adiabatic flame temperature for complete combustion with 100 percent theoretical air,

Stoichiometric Combustion (no oxygen in the products, balance C, H, O, N atoms)



$$\begin{aligned} \text{C: } 8 &= x && \rightarrow x = 8 \\ \text{H: } 18 &= 2y && \rightarrow y = 9 \\ \text{O: } 2 \times a_{th} &= 2x + y && \rightarrow a_{th} = 12.5 \\ \text{N: } 3.76 \times 2 \times a_{th} &= 2z && \rightarrow z = 47 \end{aligned}$$



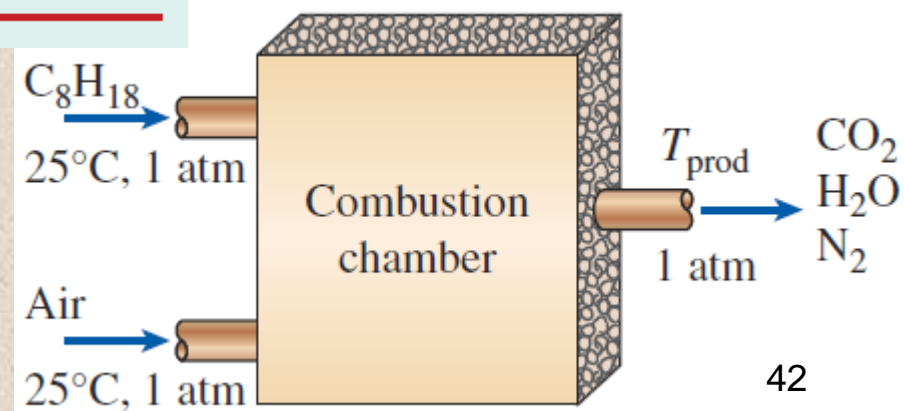
adiabatic flame temperature relation $H_{\text{prod}} = H_{\text{react}}$

$$\begin{aligned} \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p &= \sum N_r \bar{h}_{f,r}^\circ = (N\bar{h}_f^\circ)_{\text{C}_8\text{H}_{18}} \\ (8 \text{ kmol CO}_2)[(-393,520 + \bar{h}_{\text{CO}_2} - 9364) \text{ kJ/kmol CO}_2] \\ + (9 \text{ kmol H}_2\text{O})[(-241,820 + \bar{h}_{\text{H}_2\text{O}} - 9904) \text{ kJ/kmol H}_2\text{O}] \\ + (47 \text{ kmol N}_2)[(0 + \bar{h}_{\text{N}_2} - 8669) \text{ kJ/kmol N}_2] \\ &= (1 \text{ kmol C}_8\text{H}_{18})(-249,950 \text{ kJ/kmol C}_8\text{H}_{18}) \end{aligned}$$

Substance	\bar{h}_f° KJ/kmol	$\bar{h}_{298\text{K}}$ KJ/kmol
C ₈ H ₁₈ (ℓ)	-249,950	—
O ₂	0	8682
N ₂	0	8669
H ₂ O(g)	-241,820	9904
CO ₂	-393,520	9364

$$8\bar{h}_{\text{CO}_2} + 9\bar{h}_{\text{H}_2\text{O}} + 47\bar{h}_{\text{N}_2} = 5,646,081 \text{ kJ}$$

It appears that we have one equation with three unknowns. **Actually we have only one unknown—the temperature of the products T_{prod} , since $h = h(T)$**



trial-and-error approach

A first guess is obtained by dividing the right-hand side of the equation by the total number of moles, which yields $5,646,081/(8 + 9 + 47) = 88,220$ 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,

$$\begin{aligned} 8\bar{h}_{CO_2} + 9\bar{h}_{H_2O} + 47\bar{h}_{N_2} &= 8 \times 125,152 + 9 \times 103,508 + 47 \times 79,320 \\ &= 5,660,828 \text{ kJ} \quad (\text{at } T = 2400 \text{ K}) \end{aligned}$$

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

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

(at $T = 2350$ K)

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

$$T_{\text{prod}} = \mathbf{2395 \text{ K.}}$$

ENTROPY CHANGE OF REACTING SYSTEMS

entropy balance for *any* system (including reacting systems) undergoing *any* process

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

Net entropy transfer by heat and mass

Entropy generation

Change in entropy

for a *closed* or *steady-flow* reacting system

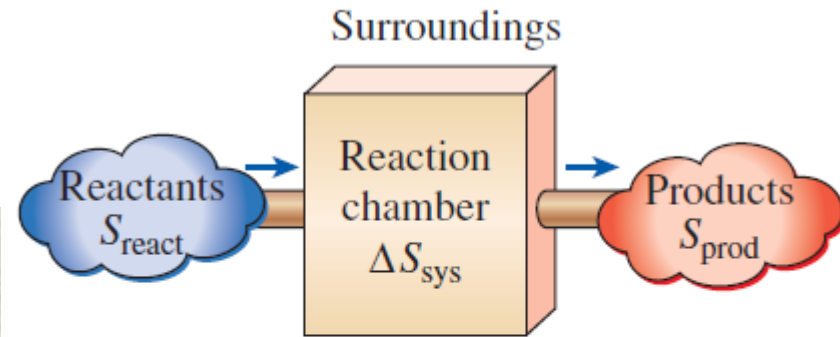


FIGURE 15–27

(kJ/K) entropy change associated with a chemical relation.

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

for an *adiabatic* process ($Q = 0$)

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

$$S_{\text{prod}} = \sum_{i=1}^k (N_i \bar{s}_i)_p$$

$$S_{\text{reac}} = \sum_{i=1}^k (N_i \bar{s}_i)_r$$

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

Exergy destruction

ENTROPY OF A COMPONENT

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

$P_0 = 1 \text{ atm}$

P_i partial pressure

y_i mole fraction

P_m total pressure of mixture

Entropy of a component

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

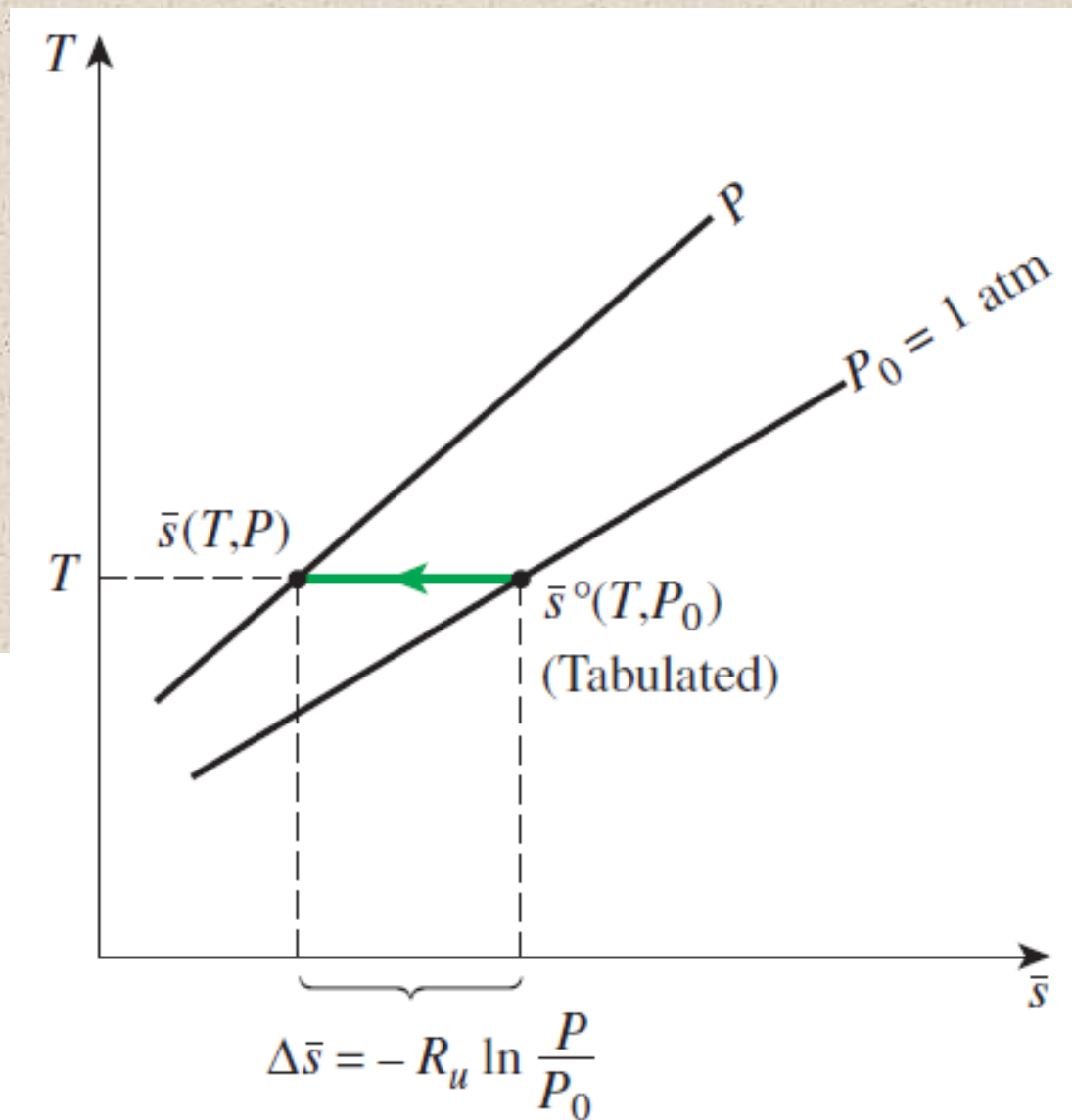
When evaluating the entropy of a component of an ideal-gas mixture, we should use the temperature and the **partial pressure** of the component ($P_i = y_i P_m$)

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 atm₄₅

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.



Nitrogen: Table

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

Find entropy of nitrogen
at 350 K and 3 atm

$$\begin{aligned} \bar{s}(350 \text{ K}, 3 \text{ atm}) &= \\ \bar{s}^{\circ}(350 \text{ K}, 1 \text{ atm}) &- \\ 8.314 \ln \frac{3 \text{ atm}}{1 \text{ atm}} \end{aligned}$$

$$\begin{aligned} \bar{s}(350 \text{ K}, 3 \text{ atm}) &= \\ 196.173 - 9.134 &= \\ 187.039 \frac{\text{kJ}}{\text{kmol-K}} \end{aligned}$$

TABLE A-18

Ideal-gas properties of nitrogen, N_2

T K	\bar{h} kJ/kmol	\bar{u} kJ/kmol	entropy @1 atm \bar{s}° kJ/kmol·K
0	0	0	0
220	6,391	4,562	182.639
230	6,683	4,770	183.938
240	6,975	4,979	185.180
250	7,266	5,188	186.370
260	7,558	5,396	187.514
270	7,849	5,604	188.614
280	8,141	5,813	189.673
290	8,432	6,021	190.695
298	8,669	6,190	191.502
300	8,723	6,229	191.682
310	9,014	6,437	192.638
320	9,306	6,645	193.562
330	9,597	6,853	194.459
340	9,888	7,061	195.328
350	10,180	7,270	196.173
360	10,471	7,478	196.995
370	10,763	7,687	197.794
380	11,055	7,895	198.572
390	11,347	8,104	199.331

TABLE A-26

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

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)	0	0	130.68
Nitrogen	N ₂ (g)	0	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

Find: Entropy of 4.76 kmol of air (1 kmol of O₂ and 3.76 kmol of N₂) at 298 K and 1 atm

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

$$\begin{aligned} \text{Mole fraction of O}_2 \text{ in air } (y_{\text{O}_2}) &= 1 / (1 + 3.76) = 0.21 \\ \text{Mole fraction of N}_2 \text{ in air } (y_{\text{N}_2}) &= 3.76 / (1 + 3.76) = 0.79 \end{aligned}$$

$$\text{Air (or the mixture) pressure } (P_m) = 1 \text{ atm}$$

$$\begin{aligned} \text{Partial pressure of O}_2 \text{ in air } (P_{\text{O}_2}) &= y_{\text{O}_2} P_m = 0.21 \text{ atm} \\ \text{Partial pressure of N}_2 \text{ in air } (P_{\text{N}_2}) &= y_{\text{N}_2} P_m = 0.79 \text{ atm} \end{aligned}$$

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

$$\begin{aligned} \text{For O}_2: \quad \bar{s}(298 \text{ K}, 0.21 \text{ atm}) &= \bar{s}^\circ(298 \text{ K}, 1 \text{ atm}) - R_u \ln \frac{0.21 \text{ atm}}{1 \text{ atm}} = \\ &= 205.033 - 8.314 \ln \frac{0.21}{1} = 218.008 \frac{\text{kJ}}{\text{kmol-K}} \end{aligned}$$

$$\begin{aligned} \text{For N}_2: \quad \bar{s}(298 \text{ K}, 0.79 \text{ atm}) &= \bar{s}^\circ(298 \text{ K}, 1 \text{ atm}) - R_u \ln \frac{0.79 \text{ atm}}{1 \text{ atm}} = \\ &= 191.502 - 8.314 \ln \frac{0.79}{1} = 193.462 \frac{\text{kJ}}{\text{kmol-K}} \end{aligned}$$

$$S_m = \sum_{i=1}^k S_i = \sum_{i=1}^k m_i s_i = \sum_{i=1}^k N_i \bar{s}_i$$

$$S_{\text{air}} = 1 \times 218.008 + 3.76 \times 193.462 = 945.425 \text{ kJ/K}$$

SECOND-LAW ANALYSIS OF REACTING SYSTEMS

The **reversible work** W_{rev} represents the maximum work that can be done during a process

In the absence of any changes in kinetic and potential energies, the reversible work relation for a steady-flow process that involves heat transfer with only environment at T_0 :

$$\dot{W}_{rev} = \dot{m}(\psi_1 - \psi_2)$$

reactants

products

(difference between the exergy of reactants and the products, no additional heat addition or rejection)

neglect

$$\psi_1 - \psi_2 = (h_1 - h_2) - T_0(s_1 - s_2) + \frac{V_1^2 - V_2^2}{2} + g(z_1 - z_2)$$

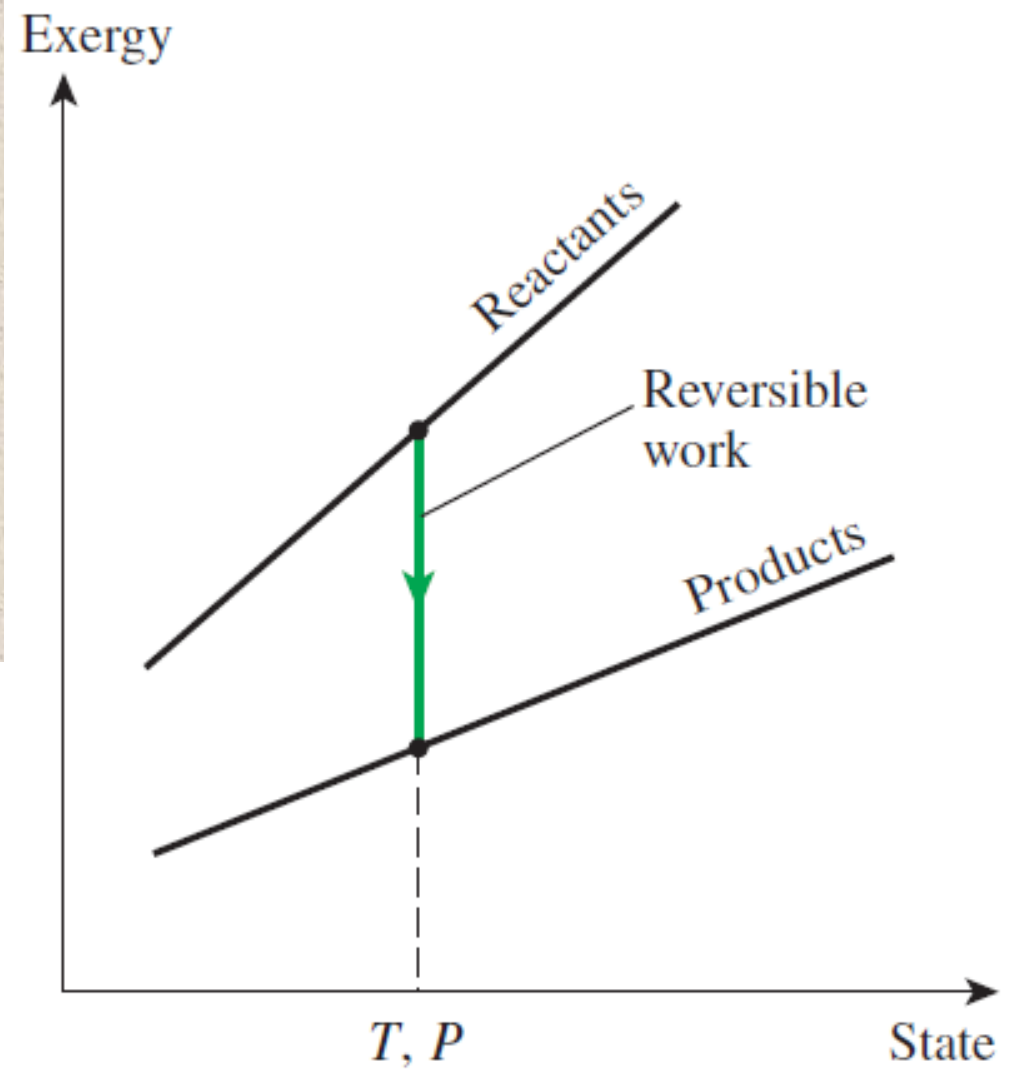
enthalpy

enthalpy

$$W_{rev} = \underbrace{\sum N_r (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0 \bar{s})}_\text{reactants} - \underbrace{\sum N_p (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0 \bar{s})}_\text{products}$$

FIGURE 15–29

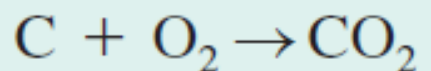
The difference between the exergy of the reactants and of the products during a chemical reaction is the reversible work associated with that reaction.



EXAMPLE

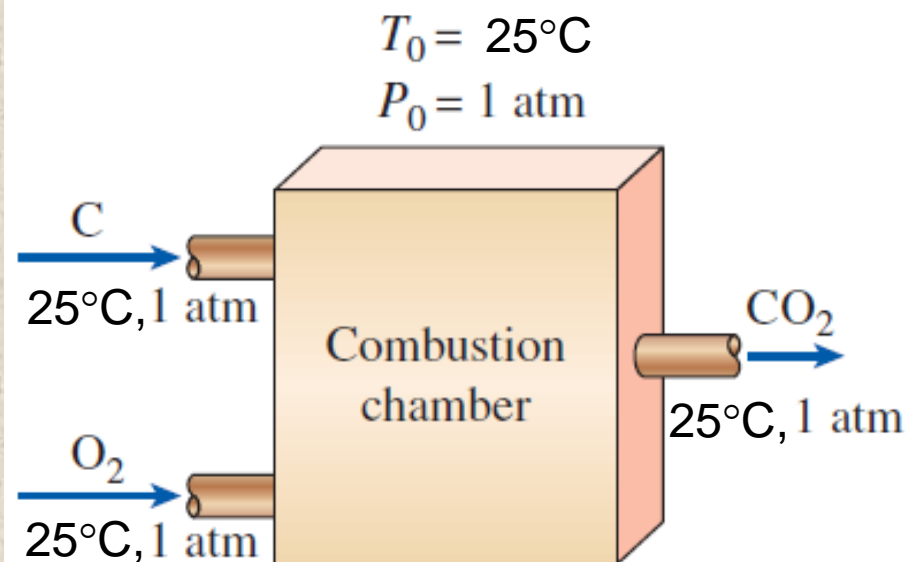
Reversible Work Associated with a Combustion Process

One kmol of carbon at 25°C and 1 atm is burned steadily with 1 kmol of oxygen at the same state as shown. The CO₂ 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.

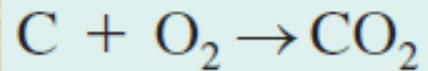


1 kmol 1 kmol 1 kmol

The C, O₂, and CO₂ are at 25°C and 1 atm, which is the standard reference state and also the state of the environment ($T_0 = 25^\circ\text{C}$)



$$\begin{aligned} W_{\text{rev}} &= \sum N_r (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0 \bar{s})_r - \sum N_p (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0 \bar{s})_p \\ &= \sum N_r (\bar{h}_f^\circ - T_0 \bar{s})_r - \sum N_p (\bar{h}_f^\circ - T_0 \bar{s})_p \\ &= N_C (\bar{h}_f^\circ - T_0 \bar{s}^\circ)_C + N_{\text{O}_2} (\bar{h}_f^\circ - T_0 \bar{s}^\circ)_{\text{O}_2} - N_{\text{CO}_2} (\bar{h}_f^\circ - T_0 \bar{s}^\circ)_{\text{CO}_2} \end{aligned}$$



1 kmol 1 kmol 1 kmol

$$\begin{aligned} W_{\text{rev}} &= \sum N_r (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0 \bar{s})_r - \sum N_p (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0 \bar{s})_p \\ &= \sum N_r (\bar{h}_f^\circ - T_0 \bar{s})_r - \sum N_p (\bar{h}_f^\circ - T_0 \bar{s})_p \\ &= N_C (\bar{h}_f^\circ - T_0 \bar{s}^\circ)_C + N_{\text{O}_2} (\bar{h}_f^\circ - T_0 \bar{s}^\circ)_{\text{O}_2} - N_{\text{CO}_2} (\bar{h}_f^\circ - T_0 \bar{s}^\circ)_{\text{CO}_2} \end{aligned}$$

$$\begin{aligned} W_{\text{rev}} &= (1 \text{ kmol C}) [0 - (298 \text{ K}) (5.74 \text{ kJ/kmol-K})] \\ &\quad + (1 \text{ kmol O}_2) [0 - (298 \text{ K}) (205.04 \text{ kJ/kmol-K})] \\ &\quad - (1 \text{ kmol CO}_2) [-393,520 \text{ kJ/kmol} - (298 \text{ K}) (213.80 \text{ kJ/kmol-K})] \\ &= \mathbf{394,420 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} H_{\text{react}} - H_{\text{prod}} &= (1 \text{ kmol of C}) (0) + (1 \text{ kmol of O}_2) (0) - (1 \text{ kmol of CO}_2) (-393,520 \text{ kJ/kmol}) \\ &= \mathbf{393,520 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} S_{\text{react}} - S_{\text{prod}} &= (1 \text{ kmol of C}) (5.74 \text{ kJ/kmol-K}) + (1 \text{ kmol of O}_2) (205.04 \text{ kJ/kmol-K}) - \\ &\quad (1 \text{ kmol of CO}_2) (213.80 \text{ kJ/kmol-K}) = \mathbf{-3.02 \text{ kJ-K (entropy would increase)}} \end{aligned}$$

$$W_{\text{rev}} = \underbrace{(H_{\text{react}} - H_{\text{prod}})}_{\mathbf{393,520 \text{ kJ}}} - \underbrace{T_0(S_{\text{react}} - S_{\text{prod}})}_{\mathbf{(-900 \text{ kJ})}} = \mathbf{394,420 \text{ kJ}}$$

TABLE A-26

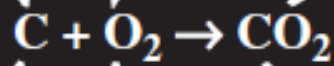
Enthalpy of formation, Gibbs function of formation, and absolute entropy at 25°C, 1 atm

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)	0	0	130.68
Nitrogen	N ₂ (g)	0	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
<i>n</i> -Butane	C ₄ H ₁₀ (g)	-126,150	-15,710	310.12
<i>n</i> -Octane	C ₈ H ₁₈ (g)	-208,450	+16,530	466.73
<i>n</i> -Octane	C ₈ H ₁₈ (l)	-249,950	+6,610	360.79

$$T_0 = 25^\circ\text{C}$$

Stable
elements

Compound



25°C,
1 atm

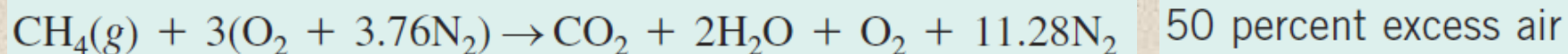
25°C,
1 atm

25°C,
1 atm

$$W_{\text{rev}} = 394,420 \text{ kJ/kmol C}$$

EXAMPLE 15–10**Second-Law Analysis of Adiabatic Combustion**

Methane (CH_4) gas enters a steady-flow adiabatic combustion chamber at 25°C and 1 atm. It is burned with 50 percent excess air that also enters at 25°C and 1 atm, as shown. Assuming complete combustion, determine (a) the temperature of the products, (b) the entropy generation, and (c) the exergy destruction. Assume that $T_0 = 298\text{ K}$ and the products leave the combustion chamber at 1 atm pressure.



adiabatic flame temperature $H_{\text{prod}} = H_{\text{react}} \quad \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p = \sum N_r \bar{h}_{f,r}^\circ = (N\bar{h}_f^\circ)_{\text{CH}_4}$

$$(1 \text{ kmol CO}_2)[(-393,520 + \bar{h}_{\text{CO}_2} - 9364) \text{ kJ/kmol CO}_2]$$

$$+ (2 \text{ kmol H}_2\text{O})[(-241,820 + \bar{h}_{\text{H}_2\text{O}} - 9904) \text{ kJ/kmol H}_2\text{O}]$$

$$+ (11.28 \text{ kmol N}_2)[(0 + \bar{h}_{\text{N}_2} - 8669) \text{ kJ/kmol N}_2]$$

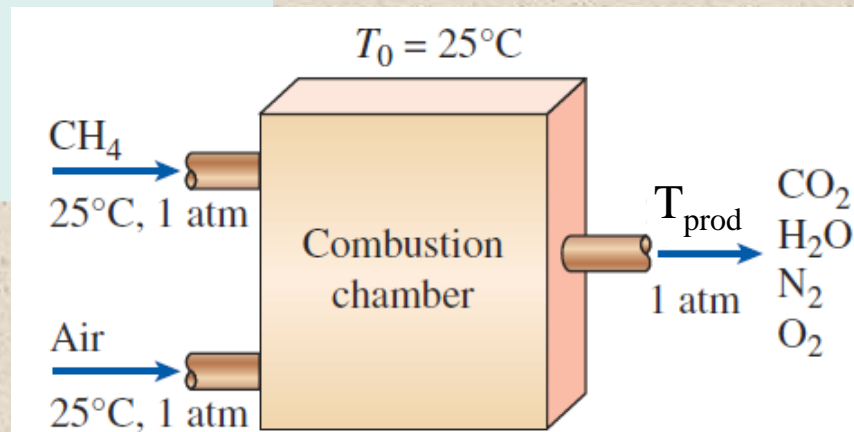
$$+ (1 \text{ kmol O}_2)[(0 + \bar{h}_{\text{O}_2} - 8682) \text{ kJ/kmol O}_2]$$

$$= (1 \text{ kmol CH}_4)(-74,850 \text{ kJ/kmol CH}_4)$$

$$\bar{h}_{\text{CO}_2} + 2\bar{h}_{\text{H}_2\text{O}} + \bar{h}_{\text{O}_2} + 11.28\bar{h}_{\text{N}_2} = 937,950 \text{ kJ}$$

trial and error,

$$T_{\text{prod}} = \mathbf{1789 \text{ K}}$$



combustion is adiabatic,

$$S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}} = \sum N_p \bar{s}_p - \sum N_r \bar{s}_r$$

$$S_i = N_i \bar{s}_i(T, P_i) = N_i [\bar{s}_i^\circ(T, P_0) - R_u \ln y_i P_m]$$

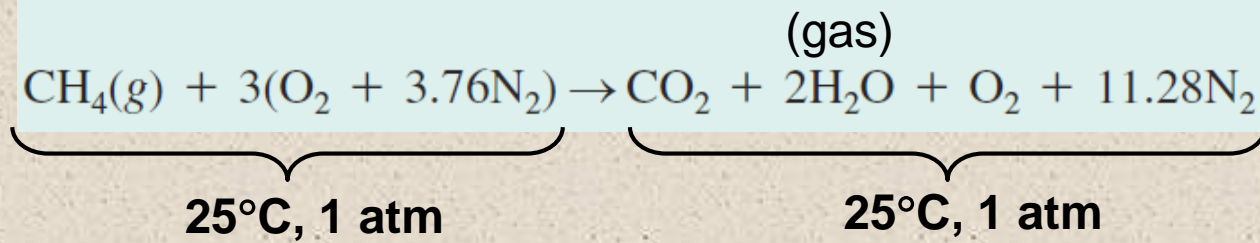
$$\begin{aligned} S_{\text{gen}} &= S_{\text{prod}} - S_{\text{react}} = (3989.71 - 3023.69) \text{ kJ/kmol} \cdot \text{K CH}_4 \\ &= \mathbf{966.0 \text{ kJ/kmol} \cdot \text{K}} \end{aligned}$$

$$\begin{aligned} X_{\text{destroyed}} &= T_0 S_{\text{gen}} = (298 \text{ K})(966.0 \text{ kJ/kmol} \cdot \text{K}) \\ &= \mathbf{288 \text{ MJ/kmol CH}_4 = 18 \text{ MJ/kg CH}_4} \end{aligned}$$

That is, 288 MJ of work potential is wasted during this combustion process for each kmol of methane burned. This example shows that even complete combustion processes are highly irreversible.

Substance	\bar{h}_f° kJ/kmol	$\bar{h}_{298\text{ K}}$ kJ/kmol
CH ₄ (g)	-74,850	—
O ₂	0	8682
N ₂	0	8669
H ₂ O(g)	-241,820	9904
CO ₂	-393,520	9364

	N_i	y_i	$\bar{s}_i^\circ(T, 1 \text{ atm})$	$-R_u \ln y_i P_m$	$N_i \bar{s}_i^\circ$
CH ₄	1	1.00	186.16	—	186.16
O ₂	3	0.21	205.04	12.98	654.06
N ₂	11.28	0.79	191.61	1.96	2183.47
$S_{\text{react}} = 3023.69$					
CO ₂	1	0.0654	302.517	22.674	325.19
H ₂ O	2	0.1309	258.957	16.905	551.72
O ₂	1	0.0654	264.471	22.674	287.15
N ₂	11.28	0.7382	247.977	2.524	2825.65
$S_{\text{prod}} = 3989.71$					



$$S_{\text{react}} = 3023.69 \text{ kJ/kmol-K CH}_4$$

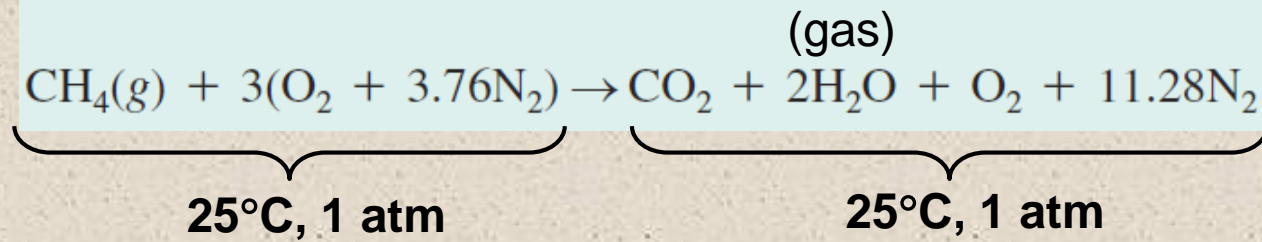
$$S_{\text{prod}} = 3065.45 \text{ kJ/kmol-K CH}_4$$

$$S_{\text{react}} - S_{\text{prod}} = -41.76 \text{ kJ/kmol-K CH}_4 \quad (\text{entropy would increase})$$

	N_i	y_i	$\bar{s}_i^\circ(T, 1 \text{ atm})$	$-R_u \ln y_i P_m$	$N_i \bar{s}_i$
H ₂ O	2	0.1309	188.83	16.91	411.48
CO ₂	1	0.0654	213.80	22.67	236.47
O ₂	1	0.0654	205.04	22.67	227.71
N ₂	11.28	0.7382	191.61	2.52	2189.79
$S_{\text{prod}} =$					3065.45

$$H_{\text{react}} - H_{\text{prod}} = 802,310 \text{ kJ/kmol CH}_4 \text{ (try this!!!)}$$

$$W_{\text{rev}} = \underbrace{(H_{\text{react}} - H_{\text{prod}})}_{802,310 \text{ kJ/kmol CH}_4} - \underbrace{T_0(S_{\text{react}} - S_{\text{prod}})}_{(-12,444 \text{ kJ/kmol CH}_4)} = 814,754 \text{ kJ/kmol CH}_4$$



$$\begin{aligned}
 H_{\text{react}} - H_{\text{prod}} &= (1 \text{ kmol CH}_4)(-74,850 \text{ kJ/kmol CH}_4) \\
 &\quad - (1 \text{ kmol CO}_2)(-393,520 \text{ kJ/kmol CO}_2) \\
 &\quad - [2 \text{ kmol H}_2\text{O}(\text{g})](-241,820 \text{ kJ/kmol H}_2\text{O}(\text{g})) \\
 &= 802,310 \text{ kJ/kmol CH}_4
 \end{aligned}$$

Fuels like methane are commonly burned to provide thermal energy at high temperatures for use in heat engines.

However, a comparison of the reversible works obtained in the last two examples reveals that the exergy of the reactants (815 MJ/kmol CH_4 , 51 MJ/kg CH_4) decreases by 288 MJ/kmol, 18 MJ/kg as a result of the irreversible adiabatic combustion process alone.

That is, the exergy of the hot combustion gases at the end of the adiabatic combustion process is $815 - 288 = 527$ MJ/kmol CH_4 , 33 MJ/kg CH_4 .

In other words, the work potential of the hot combustion gases is about 65 percent of the work potential of the reactants. It seems that when methane is burned, 35 percent of the work potential is lost before we even start using the thermal energy.

fuel cells.

FIGURE 15–34

The availability of methane decreases by 35 percent as a result of irreversible combustion process.

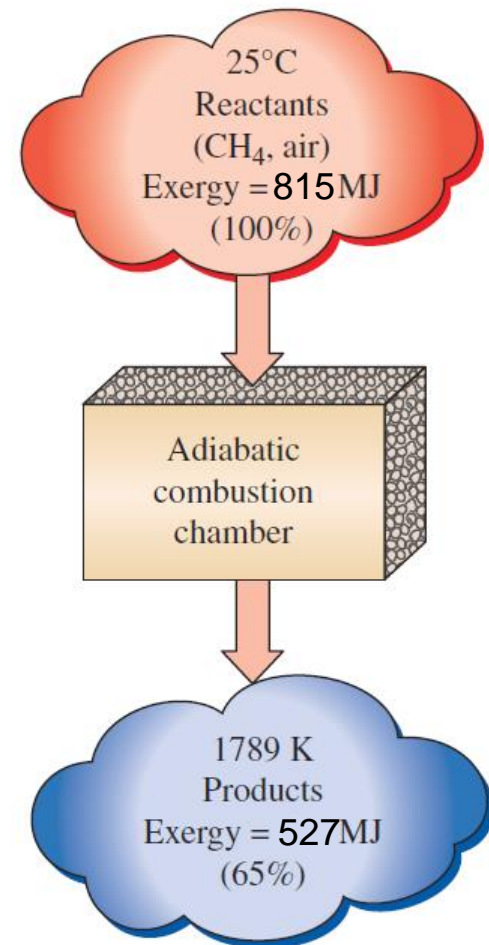


FIGURE 15–34

The availability of methane decreases by 35 percent as a result of irreversible combustion process.

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

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

$$m_{\text{air}} = (NM)_{\text{air}} \text{ and } m_{\text{fuel}} = \sum (N_i M_i)_{\text{fuel}}$$

standard reference state of 25°C and 1 atm

steady-flow systems

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

closed system

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

adiabatic flame temperature of a steady-flow combustion process is determined from $H_{\text{prod}} = H_{\text{react}}$

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

closed system or steady-flow combustion chamber

$$\sum \frac{Q_k}{T_k} + S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}}$$

adiabatic process

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

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

$$\bar{s}_i(T, P_i) = \bar{s}_i^\circ(T, P_0) - R_u \ln \frac{y_i P_m}{P_0}$$

P_i is the partial pressure, y_i is the mole fraction

P_m is the total pressure of the mixture

$$X_{\text{destroyed}} = W_{\text{rev}} - W_{\text{act}} = T_0 S_{\text{gen}}$$

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

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