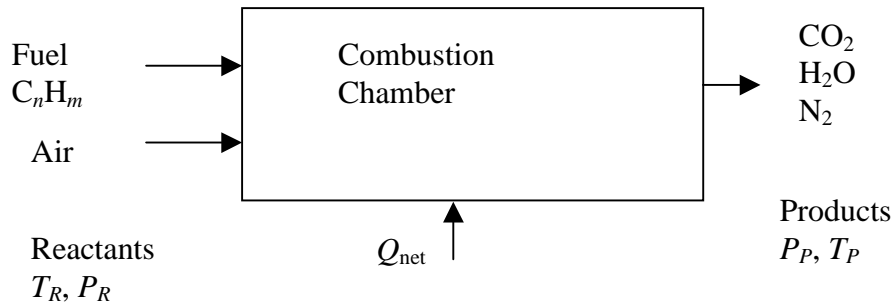


## Chapter 14: CHEMICAL REACTIONS

The combustion process is a chemical reaction whereby fuel is oxidized and energy is released.



Fuels are usually composed of some compound or mixture containing carbon, C, and hydrogen,  $H_2$ .

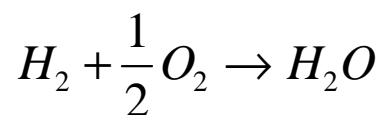
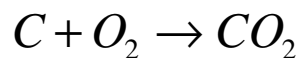
Examples of hydrocarbon fuels are

$CH_4$	Methane
$C_8H_{18}$	Octane
Coal	Mixture of C, $H_2$ , S, $O_2$ , $N_2$ and non-combustibles

Initially, we shall consider only those reactions that go to completion. The components prior to the reaction are called reactants and the components after the reaction are called products.

### Reactants $\rightarrow$ Products

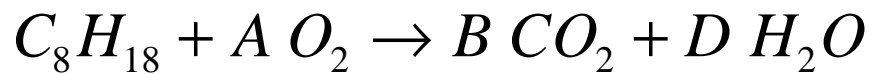
For example, all carbon is burned to carbon dioxide and all hydrogen is converted into water.



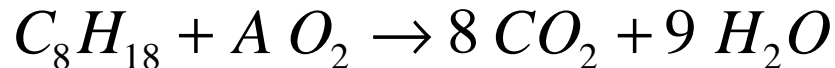
A complete combustion process is one where all carbon is burned to carbon dioxide (CO<sub>2</sub>) and all hydrogen is converted into water (H<sub>2</sub>O).

### Example 14-1

A complete combustion of octane in oxygen is represented by the balanced combustion equation. The balanced combustion equation is obtained by making sure we have the same number of atoms of each element on both sides of the equation. That is, we make sure the mass is conserved.



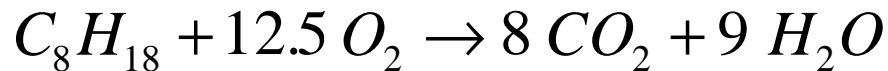
Note we often can balance the C and H for complete combustion by inspection.



The amount of oxygen is found from the oxygen balance.

$$O: A(2) = 8(2) + 9(1)$$

$$A = 12.5$$

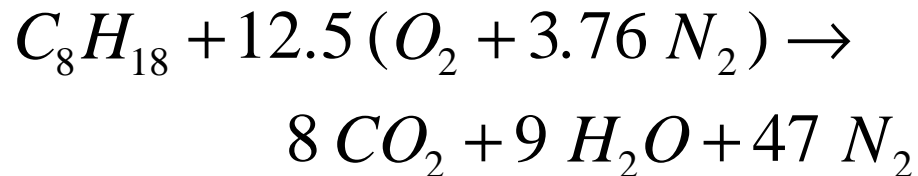


Note: Mole numbers are not conserved, but we have conserved the mass on a total basis as well as a specie basis.

The complete combustion process is also called the stoichiometric combustion, and all coefficients are called the stoichiometric coefficients.

In most combustion processes, oxygen is supplied in the form of air rather than pure oxygen.

Air is assumed to be 21 percent oxygen and 79 percent nitrogen on a volume basis. For ideal gas mixtures, percent by volume is equal to percent by moles. Thus, for each mole of oxygen in air, there exists  $79/21 = 3.76$  moles of nitrogen. Therefore, complete or theoretical combustion of octane with air can be written as



### **Air-Fuel Ratio**

Since the total moles of a mixture are equal to the sum of moles of each component, there are  $12.5(1 + 3.76) = 59.5$  moles of air required for each mole of fuel for the complete combustion process.

Often complete combustion of the fuel will not occur unless there is an excess of air present greater than just the theoretical air required for complete combustion.

To determine the amount of excess air supplied for a combustion process, let us define the air-fuel ratio  $AF$  as

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

Thus, for the above example, the theoretical air-fuel ratio is

$$AF_{th} = \frac{12.5(1 + 3.76)}{1} = 59.5 \frac{\text{kmol air}}{\text{kmol fuel}}$$

On a mass basis, the theoretical air-fuel ratio is

$$\begin{aligned} AF_{th} &= 59.5 \frac{\text{kmol air}}{\text{kmol fuel}} \frac{28.97 \frac{\text{kg air}}{\text{kmol air}}}{[8(12) + 18(1)] \frac{\text{kg fuel}}{\text{kmol fuel}}} \\ &= 15.12 \frac{\text{kg air}}{\text{kg fuel}} \end{aligned}$$

### Percent Theoretical and Percent Excess Air

In most cases, more than theoretical air is supplied to ensure complete combustion and to reduce or eliminate carbon monoxide (CO) from the products of combustion. The amount of excess air is usually expressed as percent theoretical air and percent excess air.

$$\text{Percent theoretical air} = \frac{AF_{actual}}{AF_{th}} 100\%$$

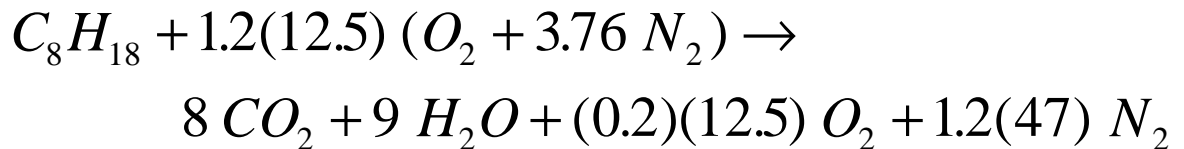
$$\text{Percent excess air} = \frac{AF_{actual} - AF_{th}}{AF_{th}} 100\%$$

Show that these results may be expressed in terms of the moles of oxygen only as

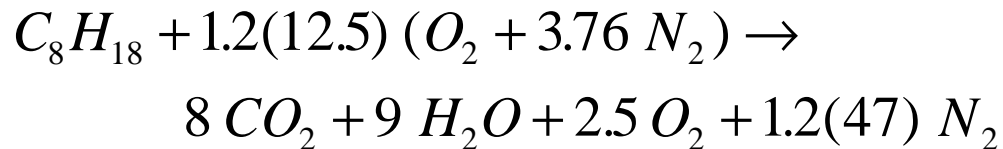
$$\text{Percent theoretical air} = \frac{N_{O_2 \text{ actual}}}{N_{O_2 \text{ th}}} 100\%$$

$$\text{Percent excess air} = \frac{N_{O_2 \text{ actual}} - N_{O_2 \text{ th}}}{N_{O_2 \text{ th}}} 100\%$$

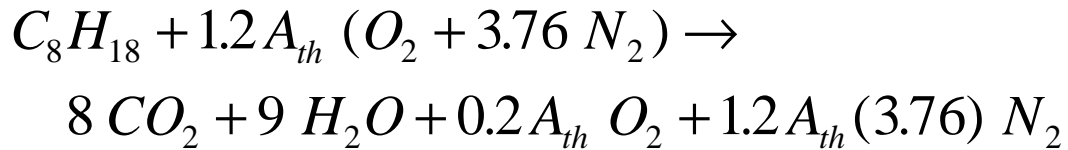
Write the combustion equation of octane with 120 percent theoretical air (20 percent excess air).



Note that (1)(12.5)O<sub>2</sub> is required for complete combustion to produce 8 kmol of carbon dioxide and 9 kmol of water; therefore, (0.2)(12.5)O<sub>2</sub> is found as excess oxygen in the products.



Second method to balance the equation for excess air (see the explanation of this technique in the solution to Example 14-2 in the text):

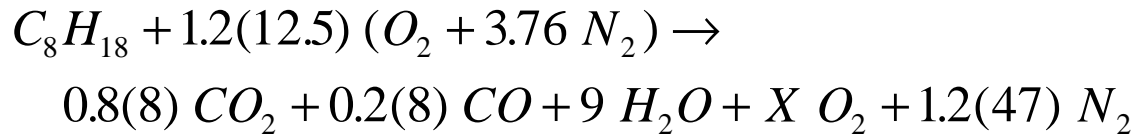


$$O: \quad 1.2 A_{th} (2) = 8(2) + 9(1) + 0.2 A_{th} (2)$$

$$A_{th} = 12.5$$

### Incomplete Combustion with Known Percent Theoretical Air

Consider combustion of  $C_8H_{18}$  with 120 % theoretical air where 80 % C in the fuel goes into  $CO_2$ .



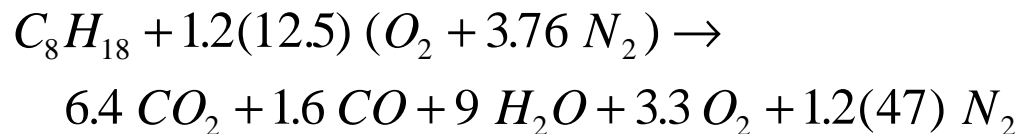
O balance gives

$$O: \quad 1.2(12.5)(2) = 0.8(8)(2) + 0.2(8)(1) + 9(1) + X(2)$$

$$X = 3.3$$

Why is  $X > 2.5$ ?

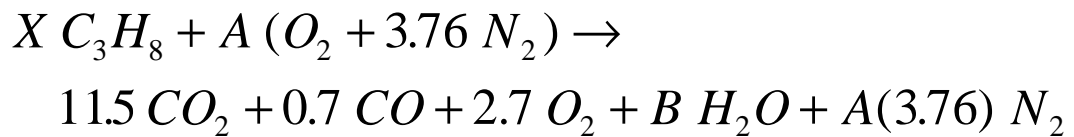
Then the balanced equation is



### Combustion Equation When Product Gas Analysis Is Known

Propane gas  $C_3H_8$  is reacted with air such that the dry product gases are 11.5 percent  $CO_2$ , 2.7 percent  $O_2$ , and 0.7 percent  $CO$  by volume. What percent theoretical air was supplied? What is the dew point temperature of the products if the product pressure is 100 kPa?

We assume 100 kmol of dry product gases; then the percent by volume can be interpreted to be mole numbers. But we do not know how much fuel and air were supplied or water formed to get the 100 kmol of dry product gases.



The unknown coefficients  $A$ ,  $B$ , and  $X$  are found by conservation of mass for each species.

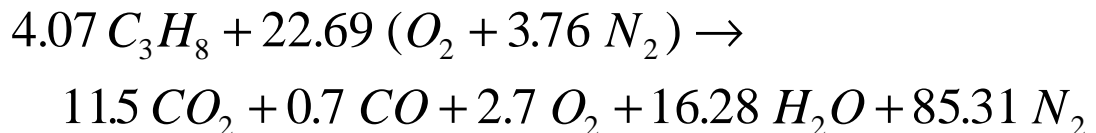
$$C: X(3) = 11.5(1) + 0.7(1) \quad X = 4.07$$

$$H: X(8) = B(2) \quad B = 16.28$$

$$O: A(2) = 11.5(2) + 0.7(1) + 2.7(2) + B(1) \quad A = 22.69$$

$$N_2: A(3.76) = 85.31$$

The balanced equation is



Second method to find  $A$ :

Assume the remainder of the 100 kmol of dry product gases is  $N_2$ .

$$kmol N_2 = 100 - (11.5 + 0.7 + 2.7) = 85.1$$

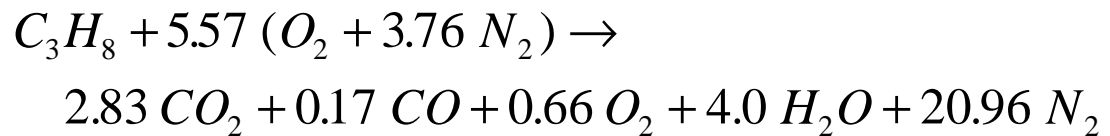
Then A is

$$A = \frac{85.1}{3.76} = 22.65 \quad (\text{fairly good check})$$

These two methods don't give the same results for A, but they are close.

What would be the units on the coefficients in the balanced combustion equation?

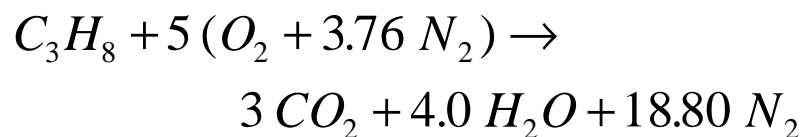
Generally we should write the combustion equation per kmol of fuel. To write the combustion equation per unit kmol of fuel, divide by 4.07:



The actual air-fuel ratio is

$$AF_{actual} = \frac{(5.57)(1 + 3.76) \text{ kmol air } 28.97 \frac{\text{kg air}}{\text{kmol air}}}{1 \text{ kmol fuel } [3(12) + 8(1)] \frac{\text{kg fuel}}{\text{kmol fuel}}} \\ = 17.45 \frac{\text{kg air}}{\text{kg fuel}}$$

The theoretical combustion equation is



The theoretical air-fuel ratio is



$$\begin{aligned}
 AF_{th} &= \frac{(5)(1 + 3.76) \text{ kmol air } 28.97 \frac{\text{kg air}}{\text{kmol air}}}{1 \text{ kmol fuel } [3(12) + 8(1)] \frac{\text{kg fuel}}{\text{kmol fuel}}} \\
 &= 15.66 \frac{\text{kg air}}{\text{kg fuel}}
 \end{aligned}$$

The percent theoretical air is

$$\begin{aligned}
 \text{Percent theoretical air} &= \frac{AF_{actual}}{AF_{th}} 100\% \\
 &= \frac{17.45}{15.66} 100 = 111\%
 \end{aligned}$$

or

$$\begin{aligned}
 \text{Percent theoretical air} &= \frac{N_{O_2 actual}}{N_{O_2 th}} 100\% \\
 &= \frac{5.57}{5} 100 = 111\%
 \end{aligned}$$

The percent excess air is

$$\begin{aligned}\text{Percent excess air} &= \frac{AF_{actual} - AF_{th}}{AF_{th}} 100\% \\ &= \frac{17.45 - 15.66}{15.66} 100 = 11\%\end{aligned}$$

### **Dew Point Temperature**

The dew point temperature for the product gases is the temperature at which the water in the product gases would begin to condense when the products are cooled at constant pressure. The dew point temperature is equal to the saturation temperature of the water at its partial pressure in the products.

$$T_{dp} = T_{sat} \text{ at } P_v = y_v P_{\text{products}}$$

$$y_v = \frac{N_{\text{water}}}{\sum_{\text{products}} N_e}$$

$$y_v = \frac{4}{2.83 + 0.17 + 0.66 + 4 + 20.96} = 0.1398$$

$$P_v = y_v P_{\text{products}} = 0.1398(100 \text{ kPa})$$

$$= 13.98 \text{ kPa}$$

$$T_{\text{dp}} = T_{\text{sat}} \text{ at } 13.98 \text{ kPa}$$

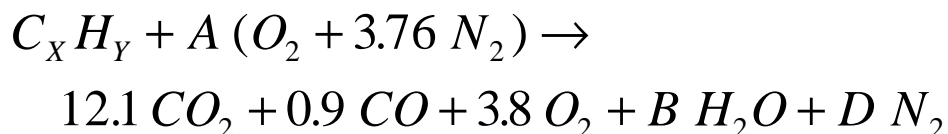
$$= 52.44^\circ \text{ C}$$

What would happen if the product gases are cooled to 100°C or to 30°C?

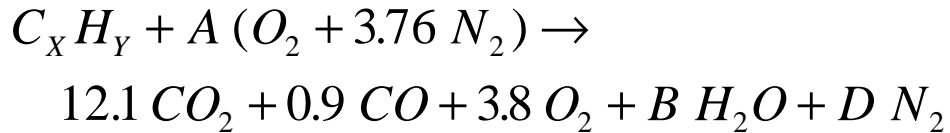
### Example 14-11

An unknown hydrocarbon fuel,  $C_xH_y$  is reacted with air such that the dry product gases are 12.1 percent  $\text{CO}_2$ , 3.8 percent  $\text{O}_2$ , and 0.9 percent  $\text{CO}$  by volume. What is the average makeup of the fuel?

We assume 100 kmol (do you have to always assume 100 kmol?) of dry product gases; then the percent by volume can be interpreted to be mole numbers. We do not know how much air was supplied or water formed to get the 100 kmol of dry product gases, but we assume 1 kmol of unknown fuel.



The five unknown coefficients  $A$ ,  $B$ ,  $D$ ,  $x$ , and  $y$  are found by conservation of mass for each species,  $C$ ,  $H$ ,  $O$ , and  $N$  plus one other equation. Here we use the subtraction method for the nitrogen to generate the fifth independent equation for the unknowns.



The unknown coefficients  $A$ ,  $B$ ,  $D$ ,  $X$ , and  $Y$  are found by conservation of mass for each species. Here we assume the remainder of the dry product gases is nitrogen.

$$N_2: D = 100 - (12.1 + 0.9 + 3.8) = 83.2$$

$$O_2: A = \frac{D}{3.76} = \frac{83.2}{3.76} = 22.13$$

$$O: A(2) = (12.1)(2) + (0.9)(1) + (3.8)(2) + B(1)$$

$$B = 11.54$$

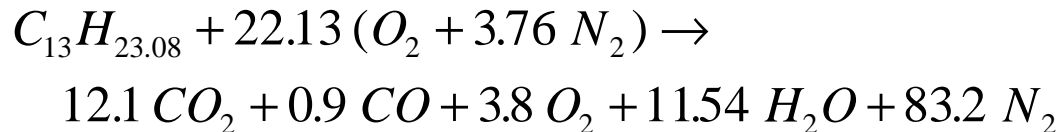
$$C: 1(X) = 12.1(1) + (0.9)(1)$$

$$X = 13.0$$

$$H: 1(Y) = B(2)$$

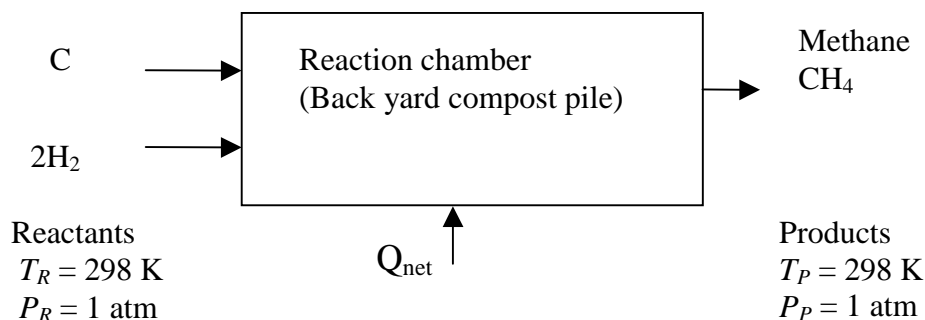
$$Y = 23.08$$

The balanced equation is

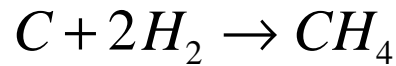


## Enthalpy of Formation

When a compound is formed from its elements (e.g., methane,  $CH_4$ , from C and  $H_2$ ), heat transfer occurs. When heat is given off, the reaction is called **exothermic**. When heat is required, the reaction is called **endothermic**. Consider the following.



The reaction equation is



The conservation of energy for a steady-flow combustion process is

$$E_{in} = E_{out}$$
$$Q_{net} + H_{\text{Reactants}} = H_{\text{Products}}$$

$$Q_{net} = H_{\text{Products}} - H_{\text{Reactants}}$$
$$Q_{net} = \sum_{\text{Products}} N_e \bar{h}_e - \sum_{\text{Reactants}} N_i \bar{h}_i$$
$$Q_{net} = 1\bar{h}_{CH_4} - (1\bar{h}_C + 2\bar{h}_{H_2})$$

A common reference state for the enthalpies of all reacting components is established as

**The enthalpy of the elements or their stable compounds is defined to be ZERO at 25°C (298 K) and 1 atm (or 0.1 MPa).**

$$Q_{net} = 1\bar{h}_{CH_4} - (1(0) + 2(0))$$
$$= \bar{h}_{CH_4}$$

This heat transfer is called the **enthalpy of formation** for methane,  $\bar{h}_f^o$ . The superscript (o) implies the 1 atm pressure value and the subscript (f) implies 25°C data,  $\bar{h}_f^o$  is given in Table A-26.

During the formation of methane from the elements at 298 K, 0.1 MPa, heat is given off (an exothermic reaction) such that

$$Q_{net} = \bar{h}_{f, CH_4}^o = -74,850 \frac{kJ}{kmol_{CH_4}}$$

The enthalpy of formation  $\bar{h}_f^o$  is tabulated for typical compounds. The enthalpy of formation of the elements in their stable form is taken as zero. The enthalpy of formation of the elements found naturally as diatomic elements, such as nitrogen, oxygen, and hydrogen, is defined to be zero. The enthalpies of formation for several combustion components are given in the following table.

Substance	Formula	$M$	$\bar{h}_f^o$ kJ/kmol
Air		28.97	0
Oxygen	O <sub>2</sub>	32	0
Nitrogen	N <sub>2</sub>	28	0
Carbon dioxide	CO <sub>2</sub>	44	-393,520
Carbon monoxide	CO	28	-110,530
Water (vapor)	H <sub>2</sub> O <sub>vap</sub>	18	-241,820
Water (liquid)	H <sub>2</sub> O <sub>liq</sub>	18	-285,830
Methane	CH <sub>4</sub>	16	-74,850
Acetylene	C <sub>2</sub> H <sub>2</sub>	26	+226,730
Ethane	C <sub>2</sub> H <sub>6</sub>	30	-84,680
Propane	C <sub>3</sub> H <sub>8</sub>	44	-103,850
Butane	C <sub>4</sub> H <sub>10</sub>	58	-126,150
Octane (vapor)	C <sub>8</sub> H <sub>18</sub>	114	-208,450
Dodecane	C <sub>12</sub> H <sub>26</sub>	170	-291,010

The enthalpies are calculated relative to a common base or reference called the enthalpy of formation. The enthalpy of formation is the heat transfer required to form the compound from its elements at 25°C (77 °F) or 298 K (537 R), 1 atm. The enthalpy at any other temperature is given as

$$\bar{h} = \bar{h}_f^o + (\bar{h}_T - \bar{h}^o)$$

Here the term  $\bar{h}^o$  is the enthalpy of any component at 298 K. The enthalpies at the temperatures  $T$  and 298 K can be found in Tables A-18 through A-25. If tables are not available, the enthalpy difference due to the temperature difference can be calculated from

$$(\bar{h}_T - \bar{h}^o) = \int_{298K}^T \bar{C}_P dT' = \bar{C}_{P,ave} (T - 298)$$

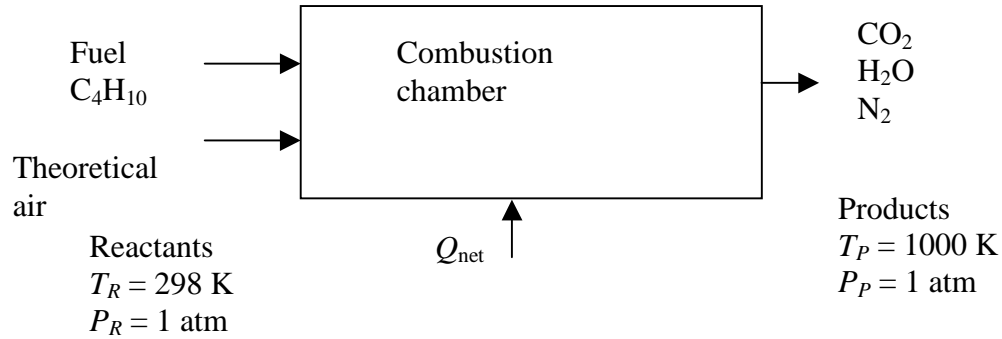
The net heat transfer to the reacting system is

$$\begin{aligned} Q_{net} &= H_P - H_R \\ &= \sum_{\text{Products}} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{\text{Reactants}} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i \end{aligned}$$

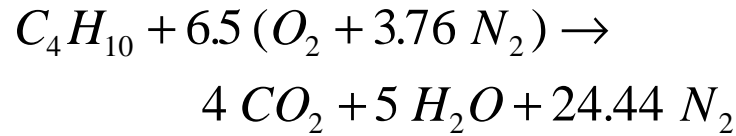
In an actual combustion process, is the value of  $Q_{net}$  positive or negative?

### Example 14-3

Butane gas  $C_4H_{10}$  is burned in theoretical air as shown below. Find the net heat transfer per kmol of fuel.



Balanced combustion equation:



The steady-flow heat transfer is

$$\begin{aligned} Q_{net} &= H_P - H_R \\ &= \sum_{\text{Products}} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{\text{Reactants}} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i \end{aligned}$$

Reactants:  $T_R = 298 \text{ K}$

Comp	$N_i$ kmol/kmol fuel	$\bar{h}_f^o$ kJ/kmol	$\bar{h}_T$ kJ/kmol	$\bar{h}^o$ kJ/kmol	$N_i[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i$ kJ/kmol fuel
$C_4H_{10}$	1	-126,150	--	--	-126,150
$O_2$	6.5	0	8,682	8,682	0
$N_2$	24.44	0	8,669	8,669	0



$$\begin{aligned}
 H_R &= \sum_{\text{Reactants}} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i \\
 &= -126,150 \frac{kJ}{kmol C_4H_{10}}
 \end{aligned}$$

Products:  $T_P = 1000 \text{ K}$

Comp	$N_e$ kmol/kmol fuel	$\bar{h}_f^o$ kJ/kmol	$\bar{h}_T$ kJ/kmol	$\bar{h}^o$ kJ/kmol	$N_e[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e$ kJ/kmol fuel
CO <sub>2</sub>	4	-393,520	42,769	9,364	-1,440,460
H <sub>2</sub> O	5	-241,820	35,882	9,904	-1,079,210
N <sub>2</sub>	24.44	0	30,129	8,669	+524,482

$$\begin{aligned}
 H_P &= \sum_{\text{Products}} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e \\
 &= -1,995,188 \frac{kJ}{kmol C_4H_{10}}
 \end{aligned}$$

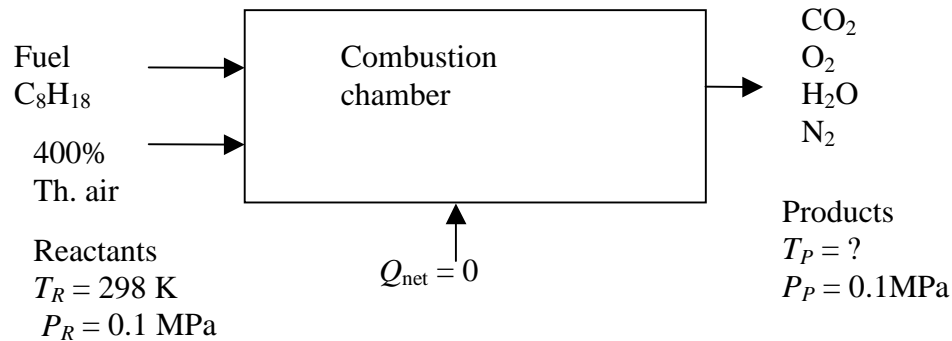
$$\begin{aligned}
 Q_{net} &= H_P - H_R \\
 &= -1,869,038 \frac{kJ}{kmol C_4H_{10}}
 \end{aligned}$$

## Adiabatic Flame Temperature

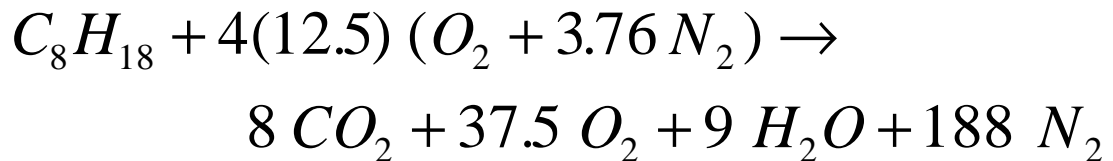
The temperature the products have when a combustion process takes place adiabatically is called the **adiabatic flame temperature**.

### Example 14-4

Liquid octane  $C_8H_{18}(liq)$  is burned with 400 percent theoretical air. Find the adiabatic flame temperature when the reactants enter at 298 K, 0.1 MPa, and the products leave at 0.1MPa.



The combustion equation is



The steady-flow heat transfer is

$$\begin{aligned} Q_{net} &= H_P - H_R \\ &= \sum_{\text{Products}} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{\text{Reactants}} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i \\ &= 0 \quad (\text{Adiabatic Combustion}) \end{aligned}$$

Thus,  $H_P = H_R$  for adiabatic combustion. We need to solve this equation for  $T_P$ .

Since the temperature of the reactants is 298 K,  $(\bar{h}_T - \bar{h}^\circ)_i = 0$ ,

$$\begin{aligned} H_R &= \sum_{\text{Reactants}} N_i \bar{h}_{f,i}^\circ \\ &= 1(-249,950) + 4(12.5)(0) + 4(12.5)(3.76)(0) \\ &= -249,950 \frac{kJ}{kmol C_4H_{10}} \end{aligned}$$

Since the products are at the adiabatic flame temperature,  $T_P > 298$  K

$$\begin{aligned} H_P &= \sum_{\text{Products}} N_e [\bar{h}_{f,e}^\circ - (\bar{h}_{T_P} - \bar{h}^\circ)]_e \\ &= 8(-393,520 + \bar{h}_{T_P} - 9364)_{CO_2} \\ &\quad + 9(-241,820 + \bar{h}_{T_P} - 9904)_{H_2O} \\ &\quad + 37.5(0 + \bar{h}_{T_P} - 8682)_{O_2} \\ &\quad + 188(0 + \bar{h}_{T_P} - 8669)_{N_2} \\ &= (-7,443,845 + 8\bar{h}_{T_P,CO_2} + 9\bar{h}_{T_P,H_2O} \\ &\quad + 37.5\bar{h}_{T_P,O_2} + 188\bar{h}_{T_P,N_2}) \frac{kJ}{kmol C_4H_{10}} \end{aligned}$$

Thus, setting  $H_P = H_R$  yields

$$\begin{aligned} \sum_{\text{Products}} N_e \bar{h}_{T_P,e} &= 8\bar{h}_{T_P,CO_2} + 9\bar{h}_{T_P,H_2O} + 37.5\bar{h}_{T_P,O_2} + 188\bar{h}_{T_P,N_2} \\ &= 7,193,895 \end{aligned}$$

To estimate  $T_P$ , assume all products behave like  $N_2$  and estimate the adiabatic flame temperature from the nitrogen data, Table A-18.

$$242.5 \bar{h}_{T_p, N_2} = 7,193,895$$

$$\bar{h}_{T_p, N_2} = 29,665.5 \frac{kJ}{kmol N_2}$$

$$T_p \cong 985 K$$

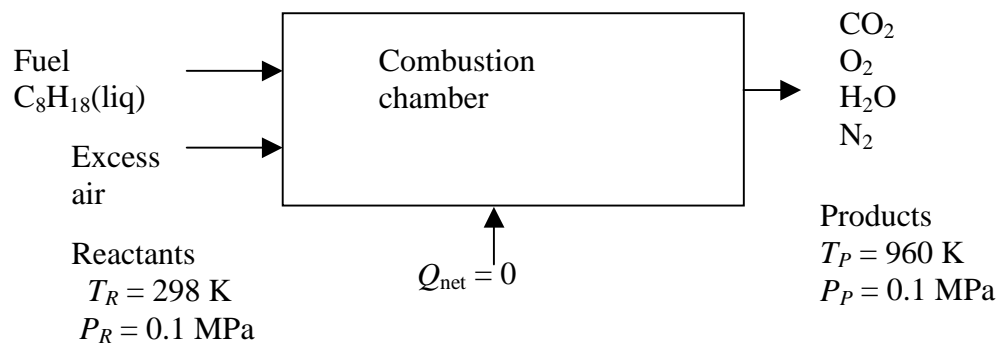
Because of the tri-atomic CO<sub>2</sub> and H<sub>2</sub>O, the actual temperature will be somewhat less than 985 K. Try  $T_p = 960 K$  and 970K.

	$N_e$	$\bar{h}_{960 K}$	$\bar{h}_{970 K}$
CO <sub>2</sub>	8	40,607	41,145
H <sub>2</sub> O	9	34,274	34,653
O <sub>2</sub>	37.5	29,991	30,345
N <sub>2</sub>	188	28,826	29,151
	$\sum_{\text{Products}} N_e \bar{h}_{T_p, e}$	7,177,572	7,259,362

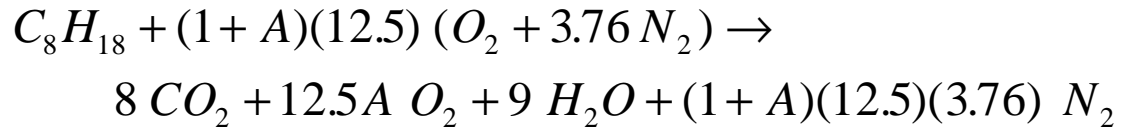
Interpolation gives:  $T_p = 962 K$ .

### Example 14-5

Liquid octane C<sub>8</sub>H<sub>18</sub>(liq) is burned with excess air. The adiabatic flame temperature is 960 K when the reactants enter at 298 K, 0.1 Mpa, and the products leave at 0.1MPa. What percent excess air is supplied?



Let A be the excess air; then combustion equation is



The steady-flow heat transfer is

$$\begin{aligned} Q_{net} &= H_P - H_R \\ &= \sum_{\text{Products}} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{\text{Reactants}} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i \\ &= 0 \quad (\text{Adiabatic combustion}) \end{aligned}$$

Here, since the temperatures are known, the  $\bar{h}_{T_p}$  is known. The product gas mole numbers are unknown but are functions of the amount of excess air, A. The energy balance can be solved for A.

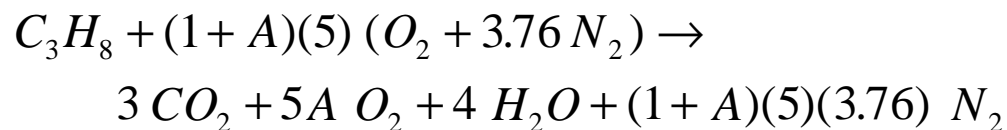
$$A = 3$$

Thus, 300 percent excess, or 400 percent theoretical, air is supplied.

### Example 14-6

Tabulate the adiabatic flame temperature as a function of excess air for the complete combustion of  $C_3H_8$  when the fuel enters the steady-flow reaction chamber at 298 K and the air enters at 400 K.

The combustion equation is



where A is the value of excess air in decimal form.

The steady-flow heat transfer is

$$\begin{aligned}
 Q_{net} &= H_P - H_R \\
 &= \sum_{\text{Products}} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{\text{Reactants}} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i \\
 &= 0 \quad (\text{Adiabatic combustion})
 \end{aligned}$$

Percent Excess Air	Adiabatic Flame Temp. K
0	2459.3
20	2191.9
50	1902.5
100	1587.1
217	1200

## Enthalpy of Reaction and Enthalpy of Combustion

When the products and reactants are at the same temperature, the **enthalpy of reaction**  $h_R$ , is the difference in their enthalpies. When the combustion is assumed to be complete with theoretical air supplied the enthalpy of reaction is called the **enthalpy of combustion**  $h_C$ . The enthalpy of combustion can be calculated at any value of the temperature, but it is usually determined at 25°C or 298 K. See Table A-27 for the enthalpy of combustion at 25°C.

$$\begin{aligned}
 \bar{h}_C &= H_P - H_R \quad \text{when } T_P = T_R = 25^\circ \text{C} = 298 \text{ K} \\
 &= \sum_{\text{Products}} N_e \bar{h}_{f_e}^o - \sum_{\text{Reactants}} N_i \bar{h}_{f_i}^o
 \end{aligned}$$

## Heating Value

The **heating value, HV**, of a fuel is the absolute value of the enthalpy of combustion or just the negative of the enthalpy of combustion.

$$HV = \left| \bar{h}_C \right|$$

The **lower heating value, LHV**, is the heating value when water appears as a gas in the products.

$$LHV = \left| \bar{h}_C \right| = -\bar{h}_C \text{ with } H_2O_{gas} \text{ in products}$$

The lower heating value is often used as the amount of energy per kmol of fuel supplied to the gas turbine engine.

The **higher heating value, HHV**, is the heating value when water appears as a liquid in the products.

$$HHV = \left| \bar{h}_C \right| = -\bar{h}_C \text{ with } H_2O_{liquid} \text{ in products}$$

The higher heating value is often used as the amount of energy per kmol of fuel supplied to the steam power cycle.

The higher and lower heating values are related by the amount of water formed during the combustion process and the enthalpy of vaporization of water at the temperature.

$$HHV = LHV + N_{H_2O} \bar{h}_{fg, H_2O}$$

### Example 14-7

The enthalpy of combustion of gaseous  $C_8H_{18}$  at  $25^\circ C$  with liquid water in the products is  $-5,512,200$  kJ/kmol (see Table A-27). Find the lower heating value of liquid octane.

$$\begin{aligned} LHV_{C_8H_{18} \text{ gas}} &= HHV_{C_8H_{18} \text{ gas}} - N_{H_2O} \bar{h}_{fg H_2O} \\ &= 5,512,200 \frac{\text{kJ}}{\text{kmol } C_8H_{18}} - 9 \frac{\text{kmol } H_2O}{\text{kmol } C_8H_{18}} (44,010) \frac{\text{kJ}}{\text{kmol } H_2O} \\ &= 5,116,110 \frac{\text{kJ}}{\text{kmol } C_8H_{18}} \end{aligned}$$

$$\begin{aligned} LHV_{C_8H_{18} \text{ liq}} &= LHV_{C_8H_{18} \text{ gas}} - \bar{h}_{fg C_8H_{18}} \\ &= (5,116,110 - 41,460) \frac{\text{kJ}}{\text{kmol } C_8H_{18}} \\ &= 5,074,650 \frac{\text{kJ}}{\text{kmol } C_8H_{18} \text{ liq}} \end{aligned}$$

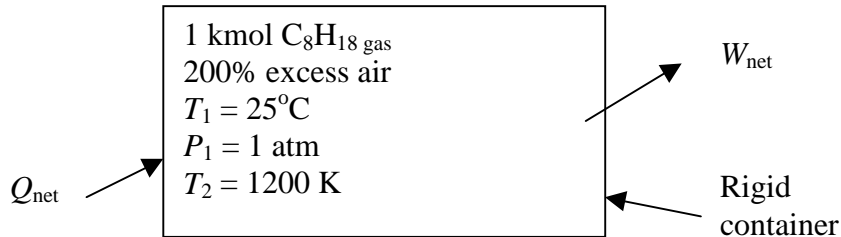
Can you explain why  $LHV_{\text{liq}} < LHV_{\text{gas}}$ ?



## Closed System Analysis

### Example 14-8

A mixture of 1 kmol  $\text{C}_8\text{H}_{18 \text{ gas}}$  and 200 percent excess air at  $25^\circ\text{C}$ , 1 atm, is burned completely in a closed system (a bomb) and is cooled to 1200 K. Find the heat transfer from the system and the system final pressure.



Apply the first law closed system:

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

$$Q_{net} - W_{net} = U_P - U_R$$

$$W_{net} = 0 \quad (\text{Rigid container})$$

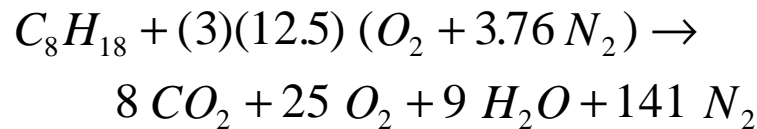
$$\begin{aligned} Q_{net} &= U_P - U_R = H_P - (PV)_P - (H_R - (PV)_R) \\ &= H_P - H_R - ((PV)_P - (PV)_R) \end{aligned}$$

Assume that the reactants and products are ideal gases; then

$$PV = NR_u T$$

$$\begin{aligned}
Q_{net} &= H_P - H_R - \left[ \sum_{\text{Products}} N_e R_u T_e - \sum_{\text{Reactants}} N_i R_u T_i \right] \\
&= \sum_{\text{Products}} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o) - R_u T]_e \\
&\quad - \sum_{\text{Reactants}} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o) - R_u T]_i
\end{aligned}$$

The balanced combustion equation for 200 percent excess (300 percent theoretical) air is



$$\begin{aligned}
Q_{net} &= 8(-393,520 + 53,848 - 9364 - 8.314(1200))_{CO_2} \\
&\quad + 9(-241,820 + 44,380 - 9904 - 8.314(1200))_{H_2O} \\
&\quad + 25(0 + 38,447 - 8682 - 8.314(1200))_{O_2} \\
&\quad + 141(0 + 36,777 - 8669 - 8.314(1200))_{N_2} \\
&\quad - 1(-208,450 + \bar{h}_{298K} - \bar{h}^o - 8.314(298))_{C_8H_{18}} \\
&\quad - 37.5(0 + 8682 - 8682 - 8.314(298))_{O_2} \\
&\quad - 141(0 + 8669 - 8669 - 8.314(298))_{N_2} \\
&= -1.12 \cdot 10^6 \frac{kJ}{kmol C_8H_{18}}
\end{aligned}$$

To find the final pressure, we assume that the reactants and the products are ideal-gas mixtures.

$$P_1 V_1 = N_1 R_u T_1$$

$$P_2 V_2 = N_2 R_u T_2$$

where state 1 is the state of the mixture of the reactants before the combustion process and state 2 is the state of the mixture of the products after the combustion process takes place. Note that the total moles of reactants are not equal to the total moles of products.

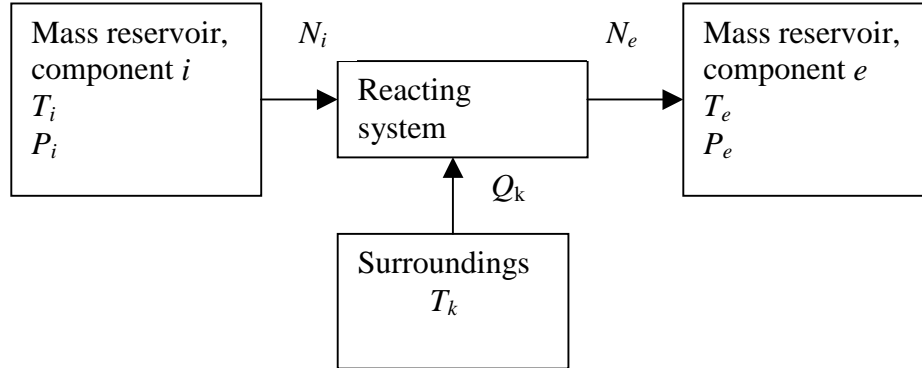
$$\frac{P_2 V_2}{P_1 V_1} = \frac{N_2 R_u T_2}{N_1 R_u T_1}$$

but  $V_2 = V_1$ .

$$\begin{aligned} P_2 &= P_1 \frac{N_2}{N_1} \frac{T_2}{T_1} \\ &= 1 \text{ atm} \left( \frac{183 \text{ kmol products}}{179.5 \text{ kmol reactants}} \right) \left( \frac{1200 \text{ K}}{298 \text{ K}} \right) \\ &= 4.11 \text{ atm} \end{aligned}$$

## Second Law Analysis of Reacting Systems

### Second law for the open system



The entropy balance relations developed in Chapter 6 are equally applicable to both reacting and nonreacting systems provided that the entropies of individual constituents are evaluated properly using a common basis.

Taking the positive direction of heat transfer to be *to* the system, the entropy balance relation can be expressed for a *steady-flow combustion chamber* as

$$\sum \frac{Q_k}{T_k} + S_{\text{React}} - S_{\text{Prod}} + S_{\text{gen}} \geq \Delta S_{\text{CV}} \quad (\text{kJ} / \text{k})$$

For an *adiabatic, steady-flow process*, the entropy balance relation reduces to

$$S_{\text{gen, adiabatic}} = S_{\text{Prod}} - S_{\text{React}} \geq 0$$

The *third law of thermodynamics* states that the entropy of a pure crystalline substance at absolute zero temperature is zero. The third law provides a common base for the entropy of all substances, and the entropy values relative to this base are called the *absolute entropy*.

The ideal-gas tables list the absolute entropy values over a wide range of temperatures but at a fixed pressure of  $P_o = 1$  atm. Absolute entropy values at other pressures  $P$  for any temperature  $T$  are determined from

$$\bar{s}(T, P) = \bar{s}^o(T, P_o) - R_u \ln \frac{P}{P_o} \quad [kJ / (kmol \cdot K)]$$

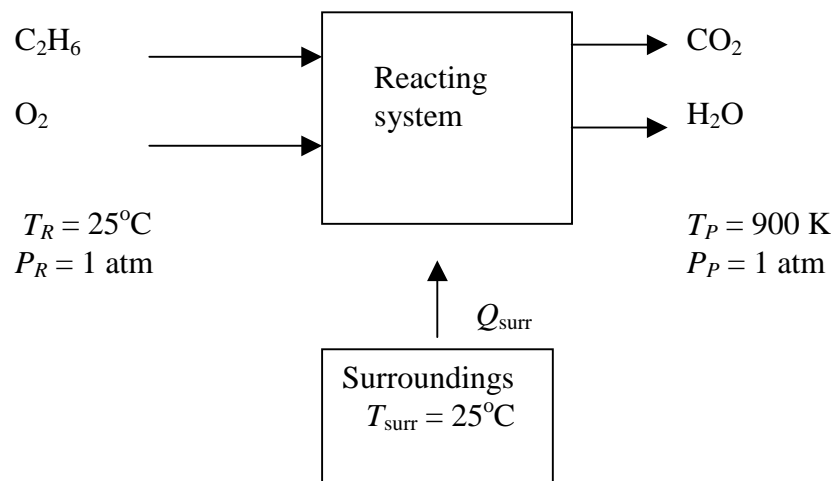
For component  $i$  of an ideal-gas mixture, the absolute entropy can be written as

$$\bar{s}_i(T, P_i) = \bar{s}_i^o(T, P_o) - R_u \ln \frac{y_i P_m}{P_o} \quad [kJ / (kmol \cdot K)]$$

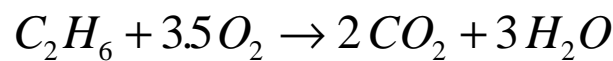
where  $P_i$  is the partial pressure,  $y_i$  is the mole fraction of the component, and  $P_m$  is the total pressure of the mixture in atmospheres.

### Example 14-8

A mixture of ethane gas  $C_2H_6$  and oxygen enters a combustion chamber at 1 atm,  $25^\circ\text{C}$ . The products leave at 1 atm, 900 K. Assuming complete combustion, does the process violate the second law?



The balanced combustion equation is



The mole fractions for the reactants and the products are

$$y_{C_2H_6} = \frac{1}{1+3.5} = \frac{1}{4.5}$$

$$y_{O_2} = \frac{3.5}{1+3.5} = \frac{3.5}{4.5}$$

$$y_{CO_2} = \frac{2}{2+3} = \frac{2}{5}$$

$$y_{H_2O} = \frac{3}{2+3} = \frac{3}{5}$$

Now to calculate the individual component entropies.

For the reactant gases:

$$\begin{aligned}\bar{s}_{C_2H_6}(T, P_{C_2H_6}) &= \bar{s}_{C_2H_6}^o(T, P_o) - R_u \ln \frac{y_{C_2H_6} P_m}{P_o} \\ &= \left[ 229.49 - 8.314 \ln \left( \frac{\frac{1}{4.5} 1 \text{ Atm}}{1 \text{ Atm}} \right) \right] \frac{kJ}{kmol_{C_2H_6} \cdot K} \\ &= 242.0 \frac{kJ}{kmol_{C_2H_6} \cdot K}\end{aligned}$$

$$\begin{aligned}
 \bar{s}_{O_2}(T, P_{O_2}) &= \bar{s}_{O_2}^o(T, P_o) - R_u \ln \frac{y_{O_2} P_m}{P_o} \\
 &= \left[ 205.03 - 8.314 \ln \left( \frac{\frac{3.5}{4.5} 1 \text{ Atm}}{1 \text{ Atm}} \right) \right] \frac{kJ}{kmol_{O_2} \cdot K} \\
 &= 207.1 \frac{kJ}{kmol_{O_2} \cdot K}
 \end{aligned}$$

$$\begin{aligned}
 S_{\text{React}} &= \sum_{\text{Reactants}} N_i \bar{s}_i \\
 &= 1(242.0) + 3.5(207.1) \\
 &= 966.9 \frac{kJ}{kmol_{C_2H_6} \cdot K}
 \end{aligned}$$

For the product gases:

$$\begin{aligned}
 \bar{s}_{CO_2}(T, P_{CO_2}) &= \bar{s}_{CO_2}^o(T, P_o) - R_u \ln \frac{y_{CO_2} P_m}{P_o} \\
 &= \left[ 263.56 - 8.314 \ln \left( \frac{\frac{2}{5} 1 \text{ Atm}}{1 \text{ Atm}} \right) \right] \frac{kJ}{kmol_{CO_2} \cdot K} \\
 &= 271.2 \frac{kJ}{kmol_{CO_2} \cdot K}
 \end{aligned}$$

$$\begin{aligned}
\bar{s}_{H_2O}(T, P_{H_2O}) &= \bar{s}_{H_2O}^o(T, P_o) - R_u \ln \frac{y_{H_2O} P_m}{P_o} \\
&= \left[ 228.32 - 8.314 \ln \left( \frac{\frac{3}{5} 1 \text{ Atm}}{1 \text{ Atm}} \right) \right] \frac{kJ}{\text{kmol}_{H_2O} \cdot K} \\
&= 232.6 \frac{kJ}{\text{kmol}_{H_2O} \cdot K} \\
S_{\text{Prod}} &= \sum_{\text{Products}} N_e \bar{s}_e \\
&= 2(271.2) + 3(232.6) \\
&= 1240.2 \frac{kJ}{\text{kmol}_{C_2H_6} \cdot K}
\end{aligned}$$

The entropy change for the combustion process is

$$\begin{aligned}
S_{\text{Prod}} - S_{\text{React}} &= (1240.2 - 966.9) \frac{kJ}{\text{kmol}_{C_2H_6} \cdot K} \\
&= 273.3 \frac{kJ}{\text{kmol}_{C_2H_6} \cdot K}
\end{aligned}$$

Now to find the entropy change due to heat transfer with the surroundings.  
The steady-flow conservation of energy for the control volume is

$$\begin{aligned}
Q_{\text{net sys}} &= H_P - H_R \\
&= \sum_{\text{Products}} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{\text{Reactants}} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i
\end{aligned}$$



$$\begin{aligned}
Q_{net\ sys} &= 2(-393,520 + 37,405 - 9364)_{CO_2} \\
&\quad + 3(-241,820 + 31,828 - 9904)_{H_2O} \\
&\quad - 1(-214,820 + \bar{h}_{298K} - \bar{h}^o)_{C_2H_6} \\
&\quad - 3.5(0 + 8682 - 8682)_{O_2} \\
&= -1.306 \cdot 10^6 \frac{kJ}{kmol\ C_2H_6} \\
\sum \frac{Q_k}{T_k} &= \frac{Q_{net\ sys}}{T_o} \\
&= \frac{-1.306 \cdot 10^6 \frac{kJ}{kmol\ C_2H_6}}{(25 + 273)K} \\
&= -4,383 \frac{kJ}{kmol\ C_2H_6 \cdot K}
\end{aligned}$$

The entropy generated by this combustion process is

$$\begin{aligned}
S_{gen} &= S_{Prod} - S_{React} - \sum \frac{Q_k}{T_k} \geq 0 \\
&= (273.3 - (-4383)) \frac{kJ}{kmol\ C_2H_6 \cdot K} \\
&= 4656.3 \frac{kJ}{kmol\ C_2H_6 \cdot K}
\end{aligned}$$

Since  $S_{gen}$ , or  $\Delta S_{net}$ , is  $\geq 0$ , the second law is not violated.