13.62 Determine the lower heating value, in kJ per kmol of fuel and in kJ per kg of fuel, at 25°C, 1 atm for
(a) gaseous ethane (C\textsubscript{2}H\textsubscript{6})
(b) liquid ethanol (C\textsubscript{3}H\textsubscript{7}OH)
(c) gaseous propane (C\textsubscript{3}H\textsubscript{8})
(d) liquid octane (C\textsubscript{8}H\textsubscript{18})

**KNOWN:** Specified fuels react completely with the theoretical amount of air. The reactants and products are both at 25°C, 1 atm.

**FIND:** The lower heating value for (a) gaseous ethane (C\textsubscript{2}H\textsubscript{6}), (b) liquid ethanol (C\textsubscript{3}H\textsubscript{7}OH), (c) gaseous propane (C\textsubscript{3}H\textsubscript{8}), and (d) liquid octane (C\textsubscript{8}H\textsubscript{18}). Compare with Table A-25 data.

**ENGINEERING MODEL:**
1. Combustion is with the theoretical amount of air.
2. Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen, which is inert.
3. The combustion air and the products of combustion each form ideal gas mixtures.
4. The water formed during combustion is in the vapor phase in the products.

**ANALYSIS:** The lower heating value (LHV) is a positive number equal to the magnitude of the enthalpy of combustion at 298 K, 1 atm, when all the water formed by combustion is a vapor.

(a) **Gaseous Ethane (C\textsubscript{2}H\textsubscript{6}):** The balanced chemical equation for complete combustion of ethane with the theoretical amount of air is

\[ \text{C}_2\text{H}_6 + 3.5(\text{O}_2 + 3.76\text{N}_2) \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O(g)} + 13.16\text{N}_2 \]

The enthalpy of combustion per kmol of C\textsubscript{2}H\textsubscript{6} at 25°C, 1 atm is

\[ \bar{h}_{\text{cp}} = 2(\bar{h}_f^\circ)_{\text{CO}_2} + 3(\bar{h}_f^\circ)_{\text{H}_2\text{O(g)}} - (\bar{h}_f^\circ)_{\text{C}_2\text{H}_6} \]

\[ \bar{h}_{\text{cp}} = \left( \frac{2 \text{ kmol CO}_2}{\text{kmol C}_2\text{H}_6} \right) \left( -393,520 \frac{\text{kJ}}{\text{kmol CO}_2} \right) + \left( \frac{3 \text{ kmol H}_2\text{O}}{\text{kmol C}_2\text{H}_6} \right) \left( -241,820 \frac{\text{kJ}}{\text{kmol H}_2\text{O}} \right) - \left( \frac{84,680 \text{kJ}}{\text{kmol C}_2\text{H}_6} \right) = -1,427,820 \text{kJ/kmol(C}_2\text{H}_6) \]

Accordingly

\[ \text{LHV} = 1,427,820 \text{ kJ/kmol C}_2\text{H}_6 \]

Dividing molar lower heating value by molecular weight of ethane, lower heating value on a mass basis is

1
Problem 13.62 (Continued) – Page 2

\[
1,427,820 \frac{\text{kJ}}{\text{kmol } C_2H_6} = \text{47,483 kJ/kg } C_2H_6
\]

This value compares favorably with that in Table A-25.

(b) Liquid Ethanol (C\textsubscript{2}H\textsubscript{5}OH): The balanced chemical equation for complete combustion of liquid ethanol with the theoretical amount of air is

\[
C_2H_5OH(l) + 3(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O(g) + 11.28N_2
\]

The enthalpy of combustion per kmol of C\textsubscript{2}H\textsubscript{5}OH at 25°C, 1 atm is

\[
\bar{h}_R^o = 2\bar{h}_p^{o} \text{CO}_2 + 3\bar{h}_p^{o} \text{H}_2\text{O} - (\bar{h}_p^{o} \text{C}_2\text{H}_5\text{OH}(l))
\]

\[
\bar{h}_R^o = \left(2 \frac{\text{kmol } \text{CO}_2}{\text{kmol } C_2H_5OH} \times -393,520 \frac{\text{kJ}}{\text{kmol CO}_2}\right) + \left(3 \frac{\text{kmol } \text{H}_2\text{O}}{\text{kmol } C_2H_5OH} \times -241,820 \frac{\text{kJ}}{\text{kmol H}_2\text{O}}\right)
\]

\[
- \left(-277,690 \frac{\text{kJ}}{\text{kmol } C_2H_5OH}\right) = -1,234,810 \frac{\text{kJ}}{\text{kmol } (C_2H_5OH)}
\]

Accordingly

\[
\text{LHV} = 1,234,810 \frac{\text{kJ}}{\text{kmol } C_2H_5OH}
\]

Dividing molar lower heating value by molecular weight of ethanol, the lower heating value on a mass basis is

\[
\frac{1,234,810}{46.07} \frac{\text{kJ}}{\text{kg } C_2H_5OH} = 26,803 \frac{\text{kJ}}{\text{kg } C_2H_5OH}
\]

This value compares favorably with that in Table A-25.

(c) Gaseous Propane (C\textsubscript{3}H\textsubscript{8}): The balanced chemical equation for complete combustion of propane with the theoretical amount of air is

\[
C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O(g) + 18.8N_2
\]

The enthalpy of combustion per kmol of C\textsubscript{3}H\textsubscript{8} at 25°C, 1 atm is
Problem 13.62 (Continued) – Page 3

\[ \bar{h}_{\text{LP}} = 3(\bar{h}^o_{\text{CO}_2}) + 4(\bar{h}^o_{\text{H}_2\text{O}}) - (\bar{h}^o_{\text{C}_3\text{H}_8}) \]

\[ \bar{h}_{\text{LP}} = \left( 3 \text{ kmol CO}_2 \text{ } \frac{\text{kJ}}{\text{kmol C}_4\text{H}_8} \right) \left( -393,520 \frac{\text{kJ}}{\text{kmol CO}_2} \right) + \left( 4 \text{ kmol H}_2\text{O} \text{ } \frac{\text{kJ}}{\text{kmol C}_4\text{H}_8} \right) \left( -241,820 \frac{\text{kJ}}{\text{kmol H}_2\text{O}} \right) \]

\[ \text{Accordingly} \]

\[ \text{LHV} = 2,043,990 \frac{\text{kJ}}{\text{kmol C}_4\text{H}_8} \]

Dividing molar lower heating value by molecular weight of ethane, lower heating value on a mass basis is

\[ \text{LHV} = \frac{2,043,990}{44.09 \frac{\text{kg C}_4\text{H}_8}{\text{kmol C}_4\text{H}_8}} = 46,359 \frac{\text{kJ}}{\text{kg C}_4\text{H}_8} \]

This value compares favorably with that in Table A-25.

(d) Liquid Octane (C\text{\textsubscript{8}H\textsubscript{18}}): The balanced chemical equation for complete combustion of octane with the theoretical amount of air is

\[ \text{C}_8\text{H}_{18} + 12.5(\text{O}_2 + 3.76\text{N}_2) \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O(g)} + 47\text{N}_2 \]

The enthalpy of combustion per kmol of C\text{\textsubscript{8}H\textsubscript{18}} at 25°C, 1 atm is

\[ \bar{h}_{\text{DP}} = 8(\bar{h}^o_{\text{CO}_2}) + 9(\bar{h}^o_{\text{H}_2\text{O}}) - (\bar{h}^o_{\text{C}_8\text{H}_{18}}) \]

\[ \bar{h}_{\text{DP}} = \left( 8 \text{ kmol CO}_2 \text{ } \frac{\text{kJ}}{\text{kmol C}_4\text{H}_8} \right) \left( -393,520 \frac{\text{kJ}}{\text{kmol CO}_2} \right) + \left( 9 \text{ kmol H}_2\text{O} \text{ } \frac{\text{kJ}}{\text{kmol C}_4\text{H}_8} \right) \left( -241,820 \frac{\text{kJ}}{\text{kmol H}_2\text{O}} \right) \]

\[ \text{Accordingly} \]

\[ \text{LHV} = 5,074,630 \frac{\text{kJ}}{\text{kmol C}_8\text{H}_{18}} \]

Dividing molar lower heating value by molecular weight of ethane, lower heating value on a mass basis is

\[ \text{LHV} = \frac{5,074,630}{114.22 \frac{\text{kg C}_8\text{H}_{18}}{\text{kmol C}_8\text{H}_{18}}} = 44,429 \frac{\text{kJ}}{\text{kg C}_8\text{H}_{18}} \]

This value compares favorably with that in Table A-25.
PROBLEM 13.65

Liquid octane (C₈H₁₈) at 25°C, 1 atm enters an insulated reactor operating at steady state and burns with 90% of theoretical air at 25°C, 1 atm to form products consisting of CO₂, CO₂, H₂O, and N₂ only. Determine the temperature of the exiting products, in K. Compare with the results of Example 13.8 and comment.

**KNOWN:** Operating data are provided for an insulated reactor in which C₈H₁₈(g) is burned with 90% of theoretical air.

**FIND:** Determine the temperature of the exiting products.

**SCHEMATIC & GIVEN DATA:**

- C₈H₁₈(g)
- 25°C, 1 atm
- 90% Theo. air
- \{ CO₂, CO₂, H₂O, N₂ \}
- \( T_p \) ?

**ENGINEERING MODEL:** (1) The control volume shown in the figure is at steady state.
(2) For the control volume \( Q_W + W_L = 0 \) and kinetic/potential energy effects can be ignored. (3) The ideal gas model is applicable to the combustion air and the combustion products. (4) 576 moles of inert N₂ accompany each mole of O₂ in the combustion air; N₂ is inert.

**ANALYSIS:** The balanced reaction equation for complete combustion with the theoretical amount of air is:

\[
\text{C}_8\text{H}_{18} + 12.5 \left( \text{O}_2 + 3.76 \text{N}_2 \right) \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O} + 47\text{N}_2
\]

For combustion with 90% of theoretical air:

\[
\text{C}_8\text{H}_{18} + 11.25 \text{O}_2 + 42.3 \text{N}_2 \rightarrow 5.5 \text{CO}_2 + 2.5 \text{CO} + 49\text{H}_2\text{O} + 42.3 \text{N}_2
\]

An energy balance reduces to:

\[
\overline{h}_p = \overline{h}_R \quad \text{With} \quad \overline{h}_R = \overline{h}_f^{\text{C}_8\text{H}_{18}} + \overline{h}_f^{\text{O}_2} \Delta n
\]

Or:

\[
5.5 \left( \overline{h}_f^{\text{CO}_2} + 2.5 \left( \overline{h}_f^{\text{CO}} + \overline{h}_f^{\text{H}_2\text{O}} \right) \right) + 9 \left( \overline{h}_f^{\text{H}_2\text{O}} + 42.3 \left( \overline{h}_f^{\text{N}_2} \right) \right) = \left( \overline{h}_f^{\text{C}_8\text{H}_{18}} \right)_{\text{gas} \text{(1)}} - 2.5 \left( \overline{h}_f^{\text{CO}} \right) - 9 \left( \overline{h}_f^{\text{H}_2\text{O}} \right)_{\text{Liq}}
\]

With data from the ideal gas tables:

\[
5.5 \left( \overline{h}_f^{\text{CO}_2} \right)_{\text{Liq}} - 9064 \overline{h}_f^{\text{CO}_2} + 2.5 \left( \overline{h}_f^{\text{CO}} \right)_{\text{Liq}} - 1866 \overline{h}_f^{\text{CO}} + 9 \left( \overline{h}_f^{\text{H}_2\text{O}} \right)_{\text{Liq}} - 393,520 \overline{h}_f^{\text{H}_2\text{O}} + 42.3 \left( \overline{h}_f^{\text{N}_2} \right) - 4664 \overline{h}_f^{\text{N}_2} = 0
\]

= \[ -2799.93 \times 10^3 - 5.5 \times \{ -393,520 \} - 2.5 \times \{ -1866 \} + 9 \times \{ -393,520 \} - 42.3 \times \{ -4664 \} \]

\[
= 4,367,155 \text{ kJ/kg mol}
\]

\[
T_p = 2285 \text{ K}
\]

**Discussion:** In Example 13.8, for the case of complete combustion with the theoretical amount of air, \( T_p = 2395 \text{ K} \), and for complete combustion with 100% theoretical air, \( T_p = 2422 \text{ K} \). Accordingly, in accordance with the discussion of Sec. 13.3b.3.

1. Iteration using table data can be avoided by using IT. Still, when using table data a first trial can be obtained assuming the products consist only of \( \text{CO}_2 \).

Then Eq. (a) reads:

\[
59.3 \overline{h}_{\text{NE}} = 4,367,155
\]

Solving gives \( \overline{h}_{\text{NE}} = 73,645 \text{ kJ/kg mol} \). Inspection of Table 12.28 then gives \( T_p = 2200 \text{ K} \).
1.3.74 Methane (CH₄) at 77°F enters the combustor of a gas turbine power plant operating at steady state and burns completely with air entering at 400°F. The temperature of the products of combustion flowing from the combustor to the turbine depends on the percent excess air for combustion. Plot the percent excess air versus combustion product temperatures ranging from 1400 to 1800°F. There is no significant heat transfer between the combustor and its surroundings, and kinetic and potential energy effects can be ignored.

**Known:** Steady state operating data are provided for the combustor of a gas turbine power plant.

**Find:** Plot the percent excess air versus the combustion product temperature for 1400°F ≤ T ≤ 1800°F.

**Schematic & Given Data:**

![Combustion process](image)

**Engineering Model:** (1) The control volume shown in the accompanying figure operates at steady state with GCH₄ = 0 and negligible effects of kinetic and potential energy. (2) Complete combustion with excess air occurs. (3) 7.76 mol of N₂ accompany each mole of CH₄ in air. N₂ is inert. (4) The combustion air and combustion products can be modeled as ideal gases.

**Analysis:** Complete combustion of CH₄ with excess air is described by

\[
	ext{CH}_4 + 2x \left( O_2 + 1.24 \right) \rightarrow \text{CO}_2 + 2 \text{H}_2 \text{O} + 2 \text{CO} + 7.5x \text{N}_2
\]

For combustion with the theoretical amount of air, x = 1.

An energy rate balance at steady state reduces to

\[
0 = \text{\Delta} h_{\text{in}} = \text{\Delta} h_{\text{out}} + \text{\Delta} h_{\text{comb}} = (\text{\Delta} h_{\text{comb}})_{\text{comb}} - (\text{\Delta} h_{\text{comb}})_{\text{comb}}
\]

With \( T = T_{\text{comb}} \), and noting that \( \text{\Delta} h_{\text{comb}} \) for \( \text{O}_2 \) and \( \text{N}_2 \), this becomes

\[
0 = \left( \frac{\partial h}{\partial h} \right)_{\text{comb}} + 2x \left[ T_{\text{comb}}(\text{comb})_{\text{comb}} + 7.5x \left( \frac{\partial h}{\partial h} \right)_{\text{comb}} \right]_{\text{comb}} - \left( \frac{\partial h}{\partial h} \right)_{\text{comb}}_{\text{comb}} - 2 \left( \frac{\partial h}{\partial h} \right)_{\text{comb}}_{\text{comb}}_{\text{comb}} - 7.5x \left( \frac{\partial h}{\partial h} \right)_{\text{comb}}_{\text{comb}}_{\text{comb}}
\]

Introducing data from Table 6.18(b) and Table A-2, and solving for x

\[
x = \frac{\left[ \frac{\partial h}{\partial h} \right]_{\text{comb}}_{\text{comb}} - \left[ \frac{\partial h}{\partial h} \right]_{\text{comb}}_{\text{comb}}_{\text{comb}}}{2 \left[ \frac{\partial h}{\partial h} \right]_{\text{comb}}_{\text{comb}}_{\text{comb}} + 7.5x \left[ \frac{\partial h}{\partial h} \right]_{\text{comb}}_{\text{comb}}_{\text{comb}}}
\]

\[
x = -32.210 \left[ -419.330 + (T_{\text{comb}})_{\text{comb}} + 402.2 \text{CO}_2 \right] - 2 \left[ 419.330 + (T_{\text{comb}})_{\text{comb}} + 402.2 \right]_{\text{comb}}_{\text{comb}} + 2 \left[ (T_{\text{comb}})_{\text{comb}} + 402.2 \right]_{\text{comb}}_{\text{comb}}
\]

\[
x = \frac{-419.330 + 7.5 \text{H}_2 \text{O} + (T_{\text{comb}})_{\text{comb}} - 570.99}{2 \text{H}_2 \text{O} + 402.2 + 7.5 \text{H}_2 \text{O} + (T_{\text{comb}})_{\text{comb}} - 570.99}
\]

Sample Calculation: \( T = 1860°F \) (1400°F)

\[
x = \frac{-19.173 - 2(16028) + 2(1987) + 350.264}{2(1987) + 7.5(13427) - 570.99} = 4.55\text{\% excess air}
\]

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PROBLEM 13.74  (Cont'd.)-Page 2

The data for the required plot are obtained using IT, as follows:

// Code
T1 = 77 // °F
T2 = 400 // °F
T = 1400 // °F

\[ 0 = h_{CH_4} + 2 \times (h_{O_2} - 3.76 \times h_{N_2}) - \\
(3.76 \times h_{H_2O} + 2 \times (x - 1) \times h_{O_2} + 7.52 \times h_{N_2}) \]

\[ h_{CH_4} = h_{T}(CH_4, T1) \]
\[ h_{O_2} = h_{T}(O_2, T2) \]
\[ h_{N_2} = h_{T}(N_2, T2) \]
\[ h_{H_2O} = h_{T}(H_2O, T) \]
\[ h_{O_2} = h_{T}(O_2, T) \]
\[ h_{N_2} = h_{T}(N_2, T) \]
\[ PC_{excess} = (x - 1) \times 100 \]

// Results for T = 1400°F
% Excess = 354.7%

Plot:

\[ \text{% Excess Air} \]
\[ \text{1400} \quad \text{1500} \quad \text{1600} \quad \text{1700} \quad \text{1800} \]
\[ \text{T (°F)} \]

Notice that excess air leads to a decrease in the temperature of the combustion products, as expected.
Liquid ethanol (C₆H₁₂O₆) at 25°C, 1 atm enters a reactor operating at steady state and burns completely with 130% of theoretical air entering in a separate stream at 25°C, 1 atm. Combustion products exit at 227°C, 1 atm. Heat transfer from the reactor takes place at an average surface temperature of 127°C. Determine

(a) the rate of entropy production within the reactor, in kJ/K per kmol of fuel,
(b) the rate of exergy destruction within the reactor, in kJ per kmol of fuel. Kinetic and potential energy effects are negligible. Let T₀ = 25°C.

**Known:** Data are provided for a liquid ethanol-fueled reactor.

**Given Data:**

**Schematic:**

**Engineering Model:**

1. The control volume shown in the accompanying figure operates at steady state with W = 0; negligible kinetic and potential energy effects, and heat transfer occurring at temperature T₀. (a) Combustion is complete; 3.76 moles of H₂ accompany each mole of O₂ in the air. N₂ is inert. (d) The combustion air and products of combustion can be modeled as ideal gases. (f) For the exergy reference environment, T₀ = 25°C (298 K).

**Analysis:**

Complete combustion of C₆H₁₂O₆ with theoretical amount of air is described by

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 3(\text{O}_2 + 3.76\text{N}_2) \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O} + 11.28\text{N}_2 \]

Complete combustion with 120% of the theoretical amount of air is thus

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 3.9(\text{O}_2 + 3.76\text{N}_2) \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O} + 0.31\text{O}_2 + 14.66\text{N}_2 \]

(a) With assumption 1, an entropy rate balance at steady state reduces to

\[ \dot{S} = \frac{\dot{S}_\text{fuel}}{T_0} + (\dot{S}_\text{prod}) - (\dot{S}_\text{fuel}) - (3.9\dot{S}_\text{O}_2 + 14.66\dot{S}_\text{N}_2) \quad (1) \]

Accordingly

\[ \dot{S}_\text{fuel} = \frac{\dot{S}_\text{fuel}}{T_0} + (2.3\dot{S}_\text{CO}_2 + 0.7\dot{S}_\text{H}_2\text{O} + 1.88\dot{S}_\text{N}_2) - (\dot{S}_\text{fuel}) - (3.9\dot{S}_\text{O}_2 + 14.66\dot{S}_\text{N}_2) \]

The term \( \dot{S}_\text{fuel} / T_0 \) can be obtained from an energy rate balance which reduces with assumption 1 to give

\[ \dot{S}_\text{fuel} = 2[\dot{S}_\text{CO}_2 + \dot{S}_\text{H}_2\text{O} + 0.9\dot{S}_\text{N}_2 + 14.66\dot{S}_\text{N}_2] - (\dot{S}_\text{fuel}) - (3.9\dot{S}_\text{O}_2 + 14.66\dot{S}_\text{N}_2) \]

\[ = 2[\dot{S}_\text{CO}_2 + \dot{S}_\text{H}_2\text{O} - 0.9\dot{S}_\text{N}_2 + 14.66\dot{S}_\text{N}_2] + (3.9\dot{S}_\text{O}_2 + 14.66\dot{S}_\text{N}_2) - (\dot{S}_\text{fuel}) \]

With data from the ideal gas tables and Table A-25

\[ \dot{S}_\text{fuel} = 2[-392,310 + 17,428 - 934] + 3[-341,820 + 14,718 - 934] + 0.9[14,770 - 266] + 14.66[14,581 - 866] - (-277,690) \]

\[ = -1,052,337 \text{ KJ/kmol of fuel} \]
PROBLEM 13.84 (Continued)

Next, the specific entropies appearing in Eq. (1) are evaluated. Since the fuel enters at 27°C, lab., \( S_{\text{fuel}} \) is obtained from Table A-25: \( E^{\text{fuel}} = 166.7 \text{ KJ/kmol-K} \). The combustion air enters at a mixture with \( Y_{O_2} = 0.21 \), \( Y_{N_2} = 0.79 \). Thus, with \( p = 10^5 \) bar and \( T_b = 298 \text{ K} \),

\[
S_{\text{O}_2} = S^0_{\text{O}_2} (298) - R \ln \frac{Y_{\text{O}_2}}{p} = 205.90 - 8.314 \ln 0.21 = 218.01 \text{ KJ/kmol-K}
\]

\[
S_{\text{N}_2} = S^0_{\text{N}_2} (298) - R \ln \frac{Y_{\text{N}_2}}{p} = 113.78 - 8.314 \ln 0.21 = 193.46 \text{ KJ/kmol-K}
\]

The combustion products exit as a mixture at 500 K, lab., with the composition \( Y_{O_2} = 76.05\% \), \( Y_{CO_2} = 20.58\% \), \( Y_{CO} = 3.48\% \), \( Y_{H_2} = 1\% \), \( Y_{N_2} = 11.94\% \). Thus, with \( \Delta H_{\text{fuel}} \) data from the ideal gas table,

\[
S_{\text{O}_2} = S^0_{\text{O}_2} (500) - R \ln \frac{Y_{\text{O}_2}}{p} = 234.81 - 8.314 \ln 0.21 = 254.18 \text{ KJ/kmol-K}
\]

\[
S_{\text{CO}_2} = S^0_{\text{CO}_2} (500) - R \ln \frac{Y_{\text{CO}_2}}{p} = 206.43 - 8.314 \ln 0.21 = 222.47 \text{ KJ/kmol-K}
\]

\[
S_{\text{CO}} = S^0_{\text{CO}} (500) - R \ln \frac{Y_{\text{CO}}}{p} = 220.08 - 8.314 \ln 0.21 = 214.56 \text{ KJ/kmol-K}
\]

\[
S_{\text{H}_2} = S^0_{\text{H}_2} (500) - R \ln \frac{Y_{\text{H}_2}}{p} = 206.63 - 8.314 \ln 0.21 = 209.44 \text{ KJ/kmol-K}
\]

Collecting results,

\[
\frac{\Delta S}{\text{KJ}} = \left( -1.105, 227 \right) + 2 \left( 218.01 + 3 \left( 218.41 \right) \right) = 3384 \text{ KJ/kmol(fuel)-K}
\]

\[\text{With } T_b = 400 \text{ K, we get}\]

\[
\frac{\Delta S}{\text{KJ}} = \left( 2763.1 + 620.9 \right) \frac{\text{KJ}}{\text{KJ/kmol(fuel)-K}} = 3384 \frac{\text{KJ}}{\text{KJ/kmol(fuel)-K}}
\]

\[
\frac{\Delta S}{\text{KJ}} = \left( 248 \text{ K} \right) \left( 3384 \frac{\text{KJ}}{\text{KJ/kmol(fuel)-K}} \right) = 1.01 \times 10^6 \frac{\text{KJ}}{\text{KJ/kmol(fuel)}}
\]

1. The following plot gives the energy destruction versus temperature \( T_b \) in °C.

\[
E, \text{ J/kmol}\]

\[
1.5 \times 10^6
\]

\[
0
\]

\[
25 50 75 100 125 150 175 200
\]

\[T_b \, (\text{°C})\]

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PROBLEM 14.2

KNOWN: The reaction is
\[ \text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2} \text{O}_2 \]

FIND: Determine \( \log_{10} K \) at (a) 500 K (b) 1800°C

ENGINEERING MODEL: Ideal gas mixture principles apply.

ANALYSIS: From Eq. 14.31 \( \ln K = -\Delta G^\circ / RT \) where

\[ \Delta G^\circ = \sum h^\circ - \sum h^\circ \]

with \( h^\circ = h^0 + h^\circ \) where \( h^\circ = h^0 + \Delta h^\circ \)

\[ \Delta G^\circ = \left[ (\Delta h^0 + \Delta h^\circ)_{\text{CO}} + \frac{1}{2} (\Delta h^0 + \Delta h^\circ)_{\text{O}_2} - (\Delta h^0 + \Delta h^\circ)_{\text{CO}_2} \right] - T \left[ (\Delta h^0 + \frac{1}{2} \Delta h^\circ)_{\text{CO}} - (\Delta h^0 + \frac{1}{2} \Delta h^\circ)_{\text{O}_2} - \Delta h^\circ_{\text{O}_2} \right] \] (1)

(a) \( T = 500 \text{K} \) with data from ideal gas tables

\[ \Delta G^\circ = \left[ (-110,580) + 14,600 - 8669 \right] + \frac{1}{2} \left[ 0 + 14,770 - 8682 \right] - \left[ (-393,520) + 17,678 - 9364 \right] - 500 \left[ 212.719 + \frac{1}{2} (220.589) - 254.814 \right] = 239.551 \text{ kJ/kmol} \]

Then \( \ln K = -2.39551 \) \( \Rightarrow \) \( \log_{10} K = -2.57, 027 \) Table Value: \( \log_{10} K = 25.025 \)

(b) \( T = 1800 \text{°C} = 1000 \text{K} \) with data from ideal gas tables

\[ \Delta G^\circ = \left[ (-110,580) + 30,355 - 7649 \right] + \frac{1}{2} \left[ 0 + 21,889 - 8682 \right] - \left[ (-393,520) + 42,769 - 9364 \right] - 1000 \left[ 242.427 + \frac{1}{2} (243.471) - 269.215 \right] \approx 195,688 \text{ kJ/kmol} \]

Then \( \ln K = \frac{-195,688}{(3.314)(1000)} \) \( \Rightarrow \) \( \log_{10} K = -10.222 \) Table Value: \( \log_{10} K = -10.221 \).
PROBLEM 14.8

KNOWN: Reactions are specified as
1. \( \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2 \)
2. \( 2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2 \)
3. \( 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2 \)

FIND: Show that the equilibrium constants are related by the expression \( K_1 = (K_3/K_2)^{1/2} \).

ENGINEERING MODEL: (1) Ideal gas principles apply. (2) The temperature is \( T \).

ANALYSIS: Using Eq. 14.31 the equilibrium constants corresponding to the three reactions have the forms
\[
\ln K_1 = -\frac{(\Delta G^o)_1}{RT}, \quad \ln K_2 = -\frac{(\Delta G^o)_2}{RT}, \quad \ln K_3 = -\frac{(\Delta G^o)_3}{RT}
\]

Where
\[
\begin{align*}
(\Delta G^o)_1 &= \bar{g}_\text{H}_2 + \bar{g}_\text{CO}_2 - \bar{g}_\text{CO} - \bar{g}_\text{H}_2\text{O} \\
(\Delta G^o)_2 &= 2\bar{g}_\text{CO} + \bar{g}_\text{O}_2 - 2\bar{g}_\text{O}_2 \\
(\Delta G^o)_3 &= 2\bar{g}_\text{H}_2 + \bar{g}_\text{O}_2 - 2\bar{g}_\text{H}_2\text{O}
\end{align*}
\]

From Eqs. (1) it follows that
\[
(\Delta G^o)_1 = \frac{1}{2} \left[ (\Delta G^o)_3 - (\Delta G^o)_2 \right]
\]

Accordingly
\[
\frac{(\Delta G^o)_1}{RT} = \frac{1}{2} \left[ \frac{(\Delta G^o)_3}{RT} - \frac{(\Delta G^o)_2}{RT} \right]
\]

or
\[
\ln K_1 = \frac{1}{2} \left[ \ln K_3 - \ln K_2 \right]
\]

Finally
\[
K_1 = \left( \frac{K_3}{K_2} \right)^{1/2}
\]