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PROBLEM 2-1

Determine the mass fraction of O_2 and N_2 in air, assuming the molar composition is 21 percent O_2 and 79 percent N_2.

GIVEN: Air with a molar composition of 79% N_2 and 21% O_2

FIND: The mass fraction of O_2 and N_2 in the air

APPROACH: This is a simple conversion problem using:

$$MW_{mix} = \sum \chi_i MW_i \quad \text{and} \quad Y_i = \chi_i \frac{MW_i}{MW_{mix}}$$

Given the molar composition: $\chi_{N_2} = 0.79$ and $\chi_{O_2} = 0.29$

mixture molecular weight:

$$MW_{mix} = \Sigma \chi_i MW_i = \chi_{N_2} MW_{N_2} + \chi_{O_2} MW_{O_2}$$
$$= 0.79(28.013) + (0.21)(32) = 28.85 \text{ kg/kmol}$$

mass fraction of O_2 and N_2

$$Y_{O_2} = \chi_{O_2} \left(\frac{MW_{O_2}}{MW_{mix}} \right) = 0.21 \left(\frac{32}{28.85} \right) = 0.233$$

$$Y_{N_2} = \chi_{N_2} \left(\frac{MW_{N_2}}{MW_{mix}} \right) = 0.79 \left(\frac{28.013}{28.85} \right) = 0.767$$

COMMENT: Note that $Y_{O_2} > \chi_{O_2}$ since $MW_{O_2} > MW_{mix}$ and that $\sum Y_i = 1$ as would be expected.

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PROBLEM 2-2

A mixture is composed of the following number of moles of various species:

Species	*No. of moles*
CO	0.095
CO_2	6
H_2O	7
N_2	34
NO	0.005

A. Determine the mole fraction of nitric oxide (NO) in the mixture. Also, express your result as mole percent, and as parts-per-million.
B. Determine the molecular weight of the mixture.
C. Determine the mass fraction of each constituent.

GIVEN: The following mixture:

Species	# Moles	χ_i	Y_i	MW_i
CO	0.095	0.002	0.002	28.010
CO_2	6	0.127	0.195	44.011
H_2O	7	0.149	0.094	18.016
N_2	34	0.722	0.707	28.013
NO	0.005	106×10^{-6}	111×10^{-6}	30.006
TOTAL	47.1	1.0	1.0	

FIND:

a) The mole fraction, mole %, and ppm of NO in the mixture
b) Determine the MW of the mixture
c) Determine the mass fraction of each constituent

a) $$\chi_i = \frac{N_i}{\sum N_i} = \frac{N_{NO}}{N_{CO} + N_{CO_2} + N_{H_2O} + N_{N_2} + N_{NO}} = \frac{0.005}{0.095 + 6 + 7 + 34 + 0.005}$$

$$\boxed{\chi_{NO} = 106 \times 10^{-6} \text{ kmol/kmol-mix}}$$

$$\boxed{\text{MOLE}\,\% = \chi_i \cdot 100 = 0.0106\ \%}$$

$$\text{PPM} = \frac{\#\,\text{NO}}{\text{TOT}\,\#}\left(1 \times 10^6\right) = \frac{N_{NO} \cdot A}{\sum N_i \cdot A}\left(1 \times 10^6\right) = \chi_{NO}\left(1 \times 10^6\right) = \boxed{106\,\text{ppm}}$$

where A ≡ Avogadro's Number

b) $$MW_{mix} = \sum \chi_i MW_i = \chi_{CO} MW_{CO} + \chi_{CO_2} MW_{CO_2} + \chi_{H_2O} MW_{H_2O} + \chi_{N_2} MW_{N_2} + \chi_{NO} MW_{NO}$$

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where $\chi_{CO}, \chi_{CO_2}, \chi_{H_2O}$, and χ_{N_2} are found in the same manner as χ_{NO} was found

$$MW_{mix} = (0.002)(28.010) + (0.127)(44.011) + (0.149)(18.016) + 0.722(28.013) + (106\times10^{-6})(33.006)$$

$$\boxed{MW_{mix} = 28.6\,\text{kg/kmol-mix}}$$

c) $Y_i = \chi_i \dfrac{MW_i}{MW_{mix}}$ $\left(kg_i/kg_{mix}\right)$ ⟶

CO: $Y = (0.002)(28.01/28.6) = 0.002$

CO_2: $Y = (0.127)(44.011/28.6) = 0.195$

H_2O: $Y = (0.149)(18.016/28.6) = 0.094$

N_2: $Y = (0.722)(28.013/28.6) = 0.707$

NO: $Y = (106\times10^{-6})(30.006/28.6) = 111\times10^{-6}$

COMMENT: Note that $ppm_i = \chi_i (1\times10^6)$ and that $\sum\chi_i = 1$ and $\sum Y_i = 1$ can often be used to check your calculations

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PROBLEM 2-3

Consider a gaseous mixture consisting of 5 kmol of H_2 and 3 kmol of O_2. Determine the H_2 and O_2 mole fractions, the molecular weight of the mixture, and the H_2 and O_2 mass fractions.

GIVEN: Mixture with 5 kmole H_2 and 3 kmole O_2

FIND: $\chi_{H_2}, \chi_{O_2}, MW_{mix}, Y_{H_2}, Y_{O_2}$

SOLUTION:

a) $\chi_i = \dfrac{N_i}{N_{tot}}; \chi_{H_2} = \dfrac{5}{5+3} = \boxed{0.625}$

$\chi_{O_2} = 1 - \chi_{H_2} = 1 - 0.625 = \boxed{0.375}$

b) $MW_{mix} = \sum \chi_i MW_i = \chi_{H_2} MW_{H_2} + \chi_{O_2} MW_{O_2}$

$= 0.625(2.016) + .375(31.999)$

$\boxed{MW_{mix} = 13.260}$

c) $Y_i = \chi_i \dfrac{MW_i}{MW_{mix}}; Y_{H_2} = 0.625 \dfrac{2.016}{13.260} = \boxed{0.095}$

$Y_{O_2} = 1 - Y_{H_2} = 1 - 0.095 = \boxed{0.905}$

COMMENT: Even though the mole fraction of H_2 is large, its low molecular weight results in its having a small mass fraction.

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PROBLEM 2-4

Consider a binary mixture of oxygen and methane. The methane mole fraction is 0.2. The mixture is at 300 K and 100 kPa. Determine the methane mass fraction in the mixture and the methane molar concentration in kmol of methane per m^3 of mixture.

GIVEN: O_2–CH_4 mixture @ 300 K & 100 kPa; $\chi_{O_2} = 0.2$

FIND: Y_{CH_4}, $N_{CH_4}/\forall$

ASSUMPTIONS: ideal gas mixture

SOLUTION:

a) $$Y_{CH_4} = \chi_{CH_4}\frac{MW_{CH_4}}{MW_{mix}}$$

$$= \chi_{CH_4}\frac{MW_{CH_4}}{\chi_{CH_4}MW_{CH_4} + \left(1-\chi_{CH_4}\right)MW_{O_2}}$$

$$= 0.2\frac{16.043}{0.2\left(16.043\right)+0.8\left(31.999\right)} = \frac{0.2\left(16.043\right)}{28.808}$$

$$\boxed{Y_{CH_4} = 0.111}$$

b) $$P_{CH_4}\forall = N_{CH_4}R_uT; P_{CH_4} = \chi_{CH_4}P$$

$$N_{CH_4}/\forall = \frac{\chi_{CH_4}P}{R_uT}$$

$$= \frac{\left(0.2\right)100.10^3}{8315\left(300\right)} = \boxed{8.018.10^{-3}\,\frac{kmol}{m^3}}$$

COMMENT: Careful treatment of units is required in part b.

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PROBLEM 2-5

Consider a mixture of N_2 and Ar in which there are three times as many moles of N_2 as there are moles of Ar. Determine the mole fractions of N_2 and Ar, the molecular weight of the mixture, the mass fractions of N_2 and Ar, and the molar concentration of N_2 in kmol/m^3 for a temperature of 500 K and a pressure of 250 kPa.

GIVEN: N_2-A_r mixture with $N_{N_2} = 3N_{Ar}$;

T = 500 K; P = 250 kPa

FIND: $\chi_i, MW_{mix}, Y_i, N_{N_2}/\forall$

ASSUMPTION: ideal gas mixture

SOLUTION:

a) $$\chi_{N_2} = \frac{N_{N_2}}{N_{mix}} = \frac{3N_{Ar}}{3N_{Ar} + N_{Ar}} = \frac{3}{4} = \boxed{0.75}$$

$$\chi_{Ar} = 1 - 0.75 = \boxed{0.25}$$

b) $$MW_{mix} = \sum \chi_i MW_i$$

$$= 0.75(28.014) + 0.25(39.948)$$

$$\boxed{MW_{mix} = 30.998}$$

c) $$Y_{N_2} = \chi_{N_2} \frac{MW_{N_2}}{MW_{mix}} = 0.75 \frac{28.014}{30.998} = \boxed{0.678}$$

$$\boxed{Y_{Ar} = 1 - Y_{N_2} = 0.322}$$

d) $$P_{N_2} \forall = N_{N_2} R_u T; \; P_{N_2} = \chi_{N_2} P_{tot}$$

$$N_{N_2}/\forall = \frac{\chi_{N_2} P_{tot}}{R_u T} = \frac{(0.75)250 \cdot 10^3}{8315(500)} = \boxed{0.0451 \text{ kmol}_{N_2}/\text{m}^3}$$

COMMENT: Careful treatment of units is required in part d.

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PROBLEM 2-6

Determine the standardized enthalpy in J/ $kmol_{mix}$ of a mixture of CO_2 and O_2 where $\chi_{CO_2} = 0.10$ and $\chi_{CO_2} = 0.90$ at a temperature of 400 K.

GIVEN: CO_2-O_2 mixture with $\chi_{CO_2} = 0.1; \chi_{O_2} = 0.9$; T = 400 K

FIND: Standardized enthalpy of mixture

ASSUMPTION: Ideal-gas behavior

SOLUTION: This is a straightforward application of Eqn. 2.15a combined with the definition of standardized enthalpy (Eqn. 2.34).

$$\bar{h}_{CO_2} = \bar{h}^{o}_{f,CO_2} + \Delta\bar{h}_{S,CO_2} = -393,546 + 4003 \left(\text{Table A.2}\right)$$

$$= -389,543 \,\text{kJ/kmol}$$

$$\bar{h}_{O_2} = \bar{h}^{o}_{f,O_2} + \Delta\bar{h}_{S,O_2} = 0 + 3031 = 3031 \text{ kJ/kmole} \left(\text{Table A.11}\right)$$

$$\bar{h}_{mix} = \sum \chi_i \bar{h}_i = \chi_{CO_2} \bar{h}_{CO_2} + \chi_{O_2} \bar{h}_{O_2} \quad \left(\text{Eqn. 2.15a}\right)$$

$$= 0.1\left(-389,543\right) + 0.9\left(3031\right)$$

$$\boxed{\bar{h}_{mix} = -36,226 \text{ kJ/kmol}_{mix}}$$

COMMENTS: The use of Appendix A tables made this problem simple. Note that the same information is available as curvefit equations in Table A-13.

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PROBLEM 2-7

Determine the molecular weight of a stoichiometric ($\Phi = 1.0$) methane–air mixture.

GIVEN: A stoichiometric mixture of methane and air

FIND: The mixture molecular weight

ASSUMPTIONS: Air consists of N_2 and O_2 and has the following composition: 21% O_2 and 79% N_2 by volume

APPROACH: Determine the stoichiometric ratio of air and fuel and then find the constituent mole fractions and MW_{mix}

Stoichiometric relation: $C_xH_y + aO_2 + 3.76aN_2 \rightarrow xCO_2 + y/2\,H_2O + 3.76aN_2$

methane: $x = 1, y = 4 \rightarrow a = x + y/4 = 2$

so the air-fuel stoichiometric mixture is

$$1CH_4 + 2O_2 + 7.52N_2$$

$$N_{CH_4} = 1 \qquad \chi_{CH_4} = \frac{N_{CH_4}}{N_{TOT}} = \frac{N_{CH_4}}{N_{CH_4} + N_{O_2} + N_{N_2}} = \frac{1}{10.52} = 0.095$$

$$N_{O_2} = 2 \qquad \chi_{O_2} = \frac{N_{O_2}}{N_{TOT}} = \frac{2}{10.52} = 0.190$$

$$N_{N_2} = 7.52 \qquad \chi_{N_2} = \frac{N_{N_2}}{N_{TOT}} = \frac{7.52}{10.52} = 0.715$$

$$MW_{mix} = \sum \chi_i MW_i = \chi_{CH_4} MW_{CH_4} + \chi_{O_2} MW_{O_2} + \chi_{N_2} MW_{N_2}$$

$$= (0.095)(16.043) + (0.190)(32) + (0.715)(28.013)$$

$$\boxed{MW_{mix} = 27.6 \text{ kg/kmole}}$$

COMMENT: If this was a fuel-rich or fuel-lean mixture,

$a = \dfrac{x + y/4}{\phi}$ where $\phi =$ equivalence ratio

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PROBLEM 2-8

Determine the stoichiometric air–fuel ratio (mass) for propane (C_3H_8).

GIVEN: A stoichiometric air-propane (C_3H_8) mixture

FIND: The stoichiometric A/F ratio (mass)

ASSUMPTIONS: Air is comprised of 79% N_2 and 21% O_2 by volume

APPROACH: Determine the molar A/F ratio and convert to mass A/F ratio
Stoichiometric relation: $C_3H_8 + aO_2 + 3.76aN_2 \rightarrow 3CO_2 + 4H_2O + 3.76aN_2$

$$a = \frac{x + y/4}{\phi} \qquad x = 3, y = 8, \phi = 1$$

$$a = 5$$

$$\text{Molar A/F ratio: } A/F = \frac{a + 3.76a}{1} = \frac{4.76a}{1}$$

$$\text{Mass A/F ratio} = (A/F)_{molar}\left(\frac{MW_{air}}{MW_{fuel}}\right) = 4.76a\left(\frac{MW_{air}}{MW_{fuel}}\right)$$

$$\left(\frac{A}{F}\right)_{MASS} = 4.76(5)\left(\frac{28.85}{44.096}\right)$$

$$\boxed{(A/F)_{MASS} = 15.6}$$

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PROBLEM 2-9

Propane burns in a premixed flame at an air–fuel ratio (mass) of 18:1. Determine the equivalence ratio Φ.

GIVEN: Propane (C_3H_8) burning at an air-fuel ratio (mass) of 18:1

FIND: The equivalence ratio, ϕ

ASSUMPTIONS: Air is comprised of 79% N_2 and 21% O_2 by volume

APPROACH: Determine the stoichiometric A/F ratio and then the equivalence ratio
Stoichiometric relation: $C_3H_8 + aO_2 + 3.76aN_2 \rightarrow 3CO_2 + 4H_2O + 3.76aN_2$

$$a = \frac{x + y/4}{\phi} \qquad x = 3, y = 8, \phi = 1 \qquad a = 5$$

$$A/F)_{STOICH} = 4.76a\left(\frac{MW_{air}}{MW_{fuel}}\right) = 4.76(5)\left(\frac{28.85}{44.096}\right) = 15.6$$

Equivalence ratio:

$$\phi = \frac{(A/F)_{STOICH}}{(A/F)_{ACTUAL}} = \frac{15.6}{18.0} = 0.87$$

$$\boxed{\phi = 0.87}$$

COMMENTS: Since $\phi < 1$ this combustion process is fuel-lean. Also note that ϕ does not depend on whether the A/F ratios are expressed in terms of moles or mass since ϕ is also a ratio.

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PROBLEM 2-10

For an equivalence ratio of $\Phi = 0.6$, determine the associated air–fuel ratios (mass) for methane, propane, and decane ($C_{10}H_{22}$).

GIVEN: An equivalence ratio of 0.6

FIND: The corresponding A/F ratios (mass) for methane (CH_4), propane (C_3H_8) and decane ($C_{10}H_{22}$)

ASSUMPTIONS: Air is comprised of 79% N_2 and 21% O_2 by volume

APPROACH: Use the relationships:

$$a = \frac{x + y/4}{\phi} \quad \text{and} \quad A/F)_{mass} = 4.76a \frac{MW_{air}}{MW_{fuel}}$$

methane (CH_4) $x = 1,\ y = 4,\ MW = 16.043$ kg/kmole

$$a = \frac{1+4/4}{0.6} = 3.33 \rightarrow A/F)_{mass} = 4.76(3.33)\left(\frac{28.85}{16.043}\right)$$

$$\boxed{A/F)_{mass} = 28.50 \text{ kg-air/kg-fuel}}$$

propane (C_3H_8) $x = 3,\ y = 8,\ MW = 44.096$ kg/kmole

$$a = \frac{3+8/4}{0.6} = 8.33 \rightarrow A/F)_{mass} = 4.76(8.33)\left(\frac{28.85}{44.096}\right)$$

$$\boxed{A/F)_{mass} = 25.94 \text{ kg-air/kg-fuel}}$$

decane ($C_{10}H_{22}$)

$$a = \frac{10+22/4}{0.6} = 25.83 \rightarrow A/F)_{mass} = 4.76(25.83)\left(\frac{28.85}{142.284}\right)$$

$$\boxed{A/F)_{mass} = 24.93 \text{ kg-air/kg-fuel}}$$

COMMENTS: Note how the A/F ratio (mass) changes only slightly from one hydrocarbon fuel to another, while the A/F ratio (molar) varies from 15.9 (methane) to 123 (decane).
The difference in behavior is due to the MW_{fuel} increasing as the molar A/F ratio increases.

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PROBLEM 2-11

In a propane-fueled truck, 3 percent (by volume) oxygen is measured in the exhaust stream of the running engine. Assuming complete combustion without dissociation, determine the air–fuel ratio (mass) supplied to the engine.

GIVEN: 3% (by volume) O_2 measured in the exhaust of a propane (C_3H_8)-fueled truck

FIND: The air-fuel ratio (mass) supplied to the engine

ASSUMPTIONS: Complete combustion with no dissociation

APPROACH: Use conservation of O atoms to determine the A/F ratio from the exhaust oxygen mole fraction

assumed combustion reaction: $C_3H_8 + aO_2 + 3.76aN_2 \rightarrow 3CO_2 + 4H_2O + bO_2 + 3.76aN_2$

conservation of O atoms: $2a = 3(2) + 4 + b(2)$

$$a = 5 + b$$

$$b = a - 5$$

exhaust O_2 mole fraction:

$$\chi_{O_2} = \frac{N_{O_2}}{N_{CO_2} + N_{H_2O} + N_{O_2} + N_{N_2}} = \frac{b}{3 + 4 + b + 3.76a}$$

using b = a – 5

$$\chi_{O_2} = \frac{a-5}{4.76a + 2} \rightarrow a = \frac{5 + 2\chi_{O_2}}{1 - 4.76\chi_{O_2}}$$

exhaust O_2 3% (by volume) $\rightarrow \chi_{O_2} = 0.03$

$$a = \frac{5 + 2(0.03)}{1 - 4.76(0.03)} = 5.90$$

$$A/F)_{mass} = 4.76a\left(\frac{MW_{air}}{MW_{fuel}}\right) = 4.76(5.90)\left(\frac{28.85}{44.096}\right)$$

$$\boxed{A/F)_{mass} = 18.37}$$

COMMENT: This engine is running at a fuel-lean condition

$$a = \frac{x + y/4}{\phi} \rightarrow \phi = \frac{x + y/4}{a} = \frac{5}{5.9} = 0.85$$

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PROBLEM 2-12

Assuming complete combustion, write out a stoichiometric balance equation, like Eqn. 2.30, for 1 mol of an arbitrary alcohol $C_xH_yO_z$. Determine the number of moles of air required to burn 1 mol of fuel.

GIVEN: 1 mole of alcohol ($C_xH_yO_z$) undergoing complete combustion.

FIND: Stoichiometric balance equation and number of moles of air to burn 1 mole of alcohol

ASSUMPTIONS: no dissociation and air that is 79% N_2 and 21% O_2 (vol)

APPROACH: Use conservation of elements for the combustion of one mole of alcohol
Stoichiometric balance:

$$C_xH_yO_z + aO_2 + 3.76aN_2 \rightarrow bCO_2 + cH_2O + 3.76aN_2$$

conservation of carbon: $x = b \rightarrow \boxed{b = x}$

conservation of H: $y = 2c \rightarrow \boxed{c = y/2}$

conservation of O: $z + 2a = 2b + C = 2x + y/2$

$$\boxed{a = x + y/4 - z/2}$$

numbers of moles of air to burn 1 mole of alcohol:

$$\frac{N_{air}}{N_{fuel}} = \frac{a + 3.76a}{1} = 4.76a$$

$$\boxed{\frac{N_{air}}{N_{fuel}} = 4.76\left[x + {}^{y}\!/_{4} - {}^{z}\!/_{2}\right]}$$

COMMENT: Note that stoichiometric combustion of an alcohol ($C_xH_yO_z$) requires less oxygen than the combustion of a comparable hydrocarbon fuel (C_xH_y) due to the presence of oxygen in the fuel.

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PROBLEM 2-13

Using the results of problem 2.12, determine the stoichiometric air–fuel ratio (mass) for methanol (CH_3OH). Compare your result with the stoichiometric ratio for methane (CH_4). What implications does this comparison have?

GIVEN: Methanol (CH_3OH) and the results of the problem 2-8

FIND: The stoichiometric A/F ratio (mass) and compare with that of methane.

APPROACH: Use the relationship developed in problem 2-8 for both methanol and methane

Methanol (CH_3OH): $C_xH_yO_z$ $x = 1, y = 4, z = 1$

$MW = 32\,\text{kg/kmole}$

$$(A/F)_{mass} = 4.76[x + y/4 - z/2]\left(\frac{MW_{air}}{MW_{fuel}}\right)$$

$$= 4.76[1 + 4/4 - 1/2]\left(\frac{28.85}{32}\right) = 6.4$$

$$\boxed{(A/F)_{mass} = 6.4}$$

$\text{methane}(CH_4): C_xH_yO_z \quad x = 1, y = 4, z = 0$

$MW = 16\ \text{kg/kmole}$

$$(A/F)_{mass} = 4.76[x + y/4 - z/2]\left(\frac{MW_{air}}{MW_{fuel}}\right)$$

$$= 4.76[1 + 4/4 - 0]\left(\frac{28.85}{16}\right)$$

$$\boxed{(A/F)_{mass} = 17.2}$$

COMMENTS: The large difference in the A/F ratios for the methanol and methane is primarily due to the differences in fuel MW. On a molar basis the A/F ratio for methanol is 7.14 and 9.52 for methane.

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PROBLEM 2-14

Consider a stoichiometric mixture of isooctane and air. Calculate the enthalpy of the mixture at the standard-state temperature (298.15 K) on a per-kmol-offuel basis ($kJ/kmol_{fuel}$), on a per-kmol-of-mixture basis ($kJ/kmol_{mix}$), and on a per-mass-of-mixture basis (kJ/kg_{mix}).

GIVEN: Stoichiometric mixture of isooctane & air

FIND: H per kmol of C_8H_{18}; $\bar{h}_{mix}$; h_{mix}.

ASSUMPTIONS: Air is 79% N_2 & 21% O_2: ideal gas

APPROACH: We start by finding the stoichiometric proportions of each component:

$$C_8H_{18} + a\left(O_2 + 3.76N_2\right) \rightarrow \text{products}\left(\text{Eqn. 2.30}\right)$$

$$a = x + y/4 = 8 + 18/4 = 12.5 \quad \left(\text{Eqn. 2.31}\right)$$

So (1) $C_8H_{18} + 12.5O_2 + 47\,N_2 \rightarrow \text{Products}$

As the above is written for 1 kmol of C_8H_{18},

a) $H = (1)\bar{h}_{C_8H_{18}} + 12.5\bar{h}_{O_2} + 47\bar{h}_{N_2}\,[=]\,\text{J/kmol-}C_8H_{18}$

At 298 K, $\bar{h}_{isooctane} = -224{,}109\,\text{kJ/kmol}$ (Evaluated from curvefit coefficients in Table B.2)

$$\bar{h}_{O_2} = \bar{h}^{o}_{f,O_2} = 0$$

$$\bar{h}_{N_2} = \bar{h}_{f,O_2} = 0$$

$$\boxed{H\left(\text{kJ/kmol} - C_8H_{18}\right)} = (1)(-224{,}109) + 12.5(0) + 47(0)$$

$$= \boxed{-224{,}109}$$

b) $\bar{h}_{mix} = \sum \chi_i \bar{h}_i ; \chi_i = N_i/N_{tot}$

$$\chi_{C_8H_{18}} = 1/(1 + 12.5 + 47) = 1/60.5 = 0.0165$$

$$\chi_{O_2} = 12.5(1 + 12.5 + 47) = 0.2066$$

$$\chi_{N_2} = 1 - \chi_{C_8H_{18}} - \chi_{O_2} = 0.7769$$

$$\bar{h}_{mix} = 0.0165(-224{,}109) + 0.2066(0) + 0.7769(0)$$

$$\boxed{\bar{h}_{mix} = -3700 \ \text{kJ/kmol-mix}}$$

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c) $h_{mix} = \sum Y_i h_i = \bar{h}_{mix} / MW_{mix}$

$$MW_{mix} = \sum \chi_i MW_i$$
$$= 0.0165(114.230) + 0.2066(31.999) +$$
$$0.7769(28.014) = 30.260$$

$$\boxed{h_{mix}} = \frac{-3698}{30.260} = \boxed{-122.2 \text{ kJ/kg-mix}}$$

COMMENTS: We note that although both n-octane and isooctane are represented as C_8H_{18}, they have different molecular structures as discussed in the Chapter 2 Appendix. Because of these structural differences, the enthalpy-of-formations of the two compounds have different values. Table B.2 was used to calculate $\bar{h}_f^o$ for isooctane as the value given in Table B.1 is for n-octane. Spreadsheet software simplifies calculating properties from the Table B.2 curvefit coefficients.

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PROBLEM 2-15

Repeat problem 2.14 for a temperature of 500 K.

GIVEN: Isooctane-air, $\Phi = 1$, T = 500 K

FIND: H (per kmol C_3H_8), $\bar{h}_{mix}, h_{mix}$

ASSUMPTIONS: Air is 79% N_2 & 21% O_2; ideal gas.

APPROACH: We need only evaluate the enthalpies of the constituents at 500K and then follow the solution to problem 2-14.

	$\bar{h}_f$	$\Delta\bar{h}_s$ @ 500K	$\bar{h}(500K)$	
Isooctane	–	–	− 175,807	Table B.2*
O_2	0	6097	6097	Table A.11
N_2	0	5920	5920	Table A.7

* Evaluated using spreadsheet software

a) $H\left(\text{kJ/kmol}_{C_8H_{18}}\right) = (1)(-175,807) + 12.5(6097) + 47(5920)$

$\boxed{H = +178,646\,\text{kJ}}\,(\text{for 1 mole } C_8H_{18})$

b) $\bar{h}_{mix} = \dfrac{H}{N_{mix}} = \dfrac{178,646}{1+12.5+47} = \boxed{2953\ \text{kJ/kmol-mix}}$

c) $h_{mix} = \bar{h}_{mix}/MW_{mix} = \dfrac{2953}{30.260} = \boxed{97.59\ \text{kJ/kg-mix}}$

COMMENT: Note the use of Table B.2 in combination with Tables A.7 & A.11.

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PROBLEM 2-16

Repeat problem 2.15, but now let the equivalence ratio $\Phi = 0.7$. How do these results compare with those of problem 2.15?

GIVEN: Isooctane-air, $\Phi = 0.7$, T = 500 K

FIND: $H(\text{per kmol } C_3H_8), \bar{h}_{mix}, h_{mix}$

ASSUMPTIONS: See problem 2-14

APPROACH: After calculating the proportions of the constituents for $\Phi = 0.7$, we follow the same solution as for problem 2-17.

$$(1)C_8H_{18} + \frac{12.5}{\Phi}(O_2 + 3.76\,N_2) \rightarrow \text{Products}$$

	N	χ	$\bar{h}(500K)$	
C_8H_{18}	1	0.0116	−175,807	see problem 2-15
O_2	17.86	0.2077	6097	
N_2	67.14	0.7807	5920	
$\sum N_i = 86.00$				

a) $H = 1(-175{,}807) + 17.86(6097) + 67.14(5920)$

$\boxed{H = +330{,}554\,\text{kJ}}$ (for 1 kmol C_8H_{18})

b) $\bar{h}_{mix} = \dfrac{H}{N_{mix}} = \dfrac{330{,}554}{86} = \boxed{3844\,\text{kJ/kmol-mix}}$

c) $MW_{mix} = \sum \chi_i MW_i = 0.0116(114.230) + 0.2077(31.999) + 0.7807(28.014) = 29.842$

$$h_{mix} = \frac{\bar{h}_{mix}}{MW_{mix}} = \frac{3844}{29.842} = \boxed{128.8\ \text{kJ/kg-mix}}$$

COMMENT: Note how for non-stoichiometric combustion "a/Φ" is substituted for "a" in Eqn. 2.30. As expected, the mixture enthalpy increases with the addition of excess air.

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PROBLEM 2-17

Consider a fuel which is an equimolar mixture of propane (C_3H_8) and natural gas (CH_4). Write out the complete stoichiometric combustion reaction for this fuel burning with air and determine the stoichiometric fuel–air ratio on a molar basis. Also, determine the molar air–fuel ratio for combustion at an equivalence ratio, Φ, of 0.8.

GIVEN: Equimolar mixture of C_3H_8 & CH_4 burning with air

FIND: N_F/N_A for $\Phi = 1$ and $\Phi = 0.8$

ASSUMPTIONS: Air is 79% N_2 & 21% O_2

APPROACH: C, H, & O element balances are required to determine the coefficient "a".

$$C_3H_8 + CH_4 + a\left(O_2 + 3.76N_2\right) \rightarrow$$
$$b\ CO_2 + c\ H_2O + 3.76aN_2$$

$$\text{C}: \quad 3+1 = b \quad (b = 4)$$
$$\text{H}: \quad 8+4 = 2C \quad (C = 6)$$
$$\text{O}: \quad 2a = 2b + c = 2(4) + 6 = 14$$
$$a = 7$$

a) For $\Phi = 1$,

$$\frac{N_F}{N_A} = \frac{1+1}{7(4.76)} = \boxed{0.0600 \frac{\text{kmol}_{\text{fuel}}}{\text{kmol}_{\text{air}}}}$$

b) For $\Phi = 0.8$

$$\frac{N_F}{N_A} = \Phi\left(N_F/N_A\right)_{\Phi=1} = 0.8(0.060) = \boxed{0.048 \frac{\text{kmol}_F}{\text{kmol}_{\text{air}}}}$$

COMMENT: An alternative approach would be to define a composite fuel ($C_3H_8 + CH_4 \equiv C_4H_{12}$) and calculate "a" from Eqn. 2.31 $(a = x + y/4 = 4 + 12/4 = 7)$.

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PROBLEM 2-18

Determine the enthalpy of the products of "ideal" combustion, i.e., no dissociation, resulting from the combustion of an isooctane–air mixture for an equivalence ratio of 0.7. The products are at 1000 K and 1 atm. Express your result using the following three bases: per kmol-of-fuel, per kg-of-fuel, and per kg-of-mixture. *Hint:* You may find Eqns. 2.68 and 2.69 useful; however, you should be able to derive these from atom-conservation considerations.

GIVEN: Ideal (no dissociation) combustion products of C_8H_{18}-air for

$$\Phi = 0.7, T = 1000\ \text{K}, P = 1\ \text{atm}$$

FIND: $H_{prod}\left(\text{per kmole } C_8H_{18}\right)$

$H_{prod}\left(\text{per kg } C_3H_{18}\right)$

h_{prod}

ASSUMPTIONS: No dissociation (given), ideal gas mixture

APPROACH: We first find the mixture composition & then calculate the mixture enthalpy.

Employing Eqn. 2.68, $a = \left(x + y/4\right)/\Phi$,

$$a = \frac{8 + 18/4}{0.7} = \frac{12.5}{0.7}\cdot \text{ Thus,}$$

$$C_8H_{18} + \frac{12.5}{0.7}\left(O_2 + 3.76N_2\right) \rightarrow$$

$$b\,CO_2 + d\,H_2O + f\,O_2 + \frac{12.5}{0.7}3.76\,N_2$$

$$\text{C}: \quad 8 = b \quad (b = 8)$$

$$\text{H}: \quad 18 = 2d \quad (d = 9)$$

$$\text{O}: \quad \left(\frac{12.5}{0.7}\right)2 = 2b + d + 2f$$

$$= 16 + 9 + 2f$$

$$f = \frac{1}{2}\left(\frac{12.5}{0.7}2 - 16 - 9\right) = 5.357$$

$$N_{tot} = b + d + f + 3.76a$$

$$= 8 + 9 + 5.357 + 3.76\frac{12.5}{0.7}$$

$$= 89.50$$

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Mole fractions, $\chi_i = N_i / N_{tot}$:

$$\begin{aligned}
\chi_{CO_2} &= 8/89.5 &&= 0.0894 \\
\chi_{H_2O} &= 9/89.5 &&= 0.1006 \\
\chi_{O_2} &= 5.357/89.5 &&= 0.0599 \\
\chi_{N_2} &= 67.14/89.5 &&= \underline{0.7502} \\
& && \sum = 1.000
\end{aligned}$$

Species i	N_i	$\bar{h}^o_{f,i}$	$\Delta\bar{h}^o_{s,i}\,(1000K)$	$N_i\bar{h}_i\,(1000K)$
CO_2	8	− 393,546	33,425	−2,880,968
H_2O	9	− 241,845	25,993	−1,942,668
O_2	5.357	0	22,721	121,716
N_2	67.14	0	21,468	1,441,362

$\sum N_i = 89,497$ $\qquad\qquad$ $\sum N_i\bar{h}_i = -3,260,558$

$$\boxed{H\left(\text{per kmole}\right)_{C_8H_{18}}} = \sum N_i\bar{h}_i = \boxed{-3,260,558\,\text{kJ}}$$

$$\boxed{H\left(\text{per kg}\right)_{C_8H_{18}}} = \frac{\sum N_i\bar{h}_i}{MW_{C_8H_{18}}} = \frac{-3,260,558}{114,230} = \boxed{-28,544\,\text{kJ}}$$

$$h_{prod} = \frac{\sum N_i\bar{h}_i / \sum N_i}{MW_{prod}}$$

$$\begin{aligned}
MW_{prod} &= \sum \chi_i MW_i \\
&= 0.0894(44.011) + 0.1006(18.016) \\
&\quad + 0.0599(31.999) + 0.7502(28.014) \\
&= 28.68
\end{aligned}$$

$$\boxed{h_{prod}} = \frac{-3,260,558}{89.497(28.68)} = \boxed{-1270\ \text{kJ/kg-prod}}$$

COMMENT: This problem illustrates calculation of product properties on a “fuel basis”, i.e., per mole of fuel or mass of fuel.

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PROBLEM 2-19

Butane (C_4H_{10}) burns with air at an equivalence ratio of 0.75. Determine the number of **moles** of air required per mole of fuel.

GIVEN: C_4H_{10}-air, $\Phi = 0.75$

FIND: N_A/N_F

SOLUTION:

$$C_4H_{10} + a\left(O_2 + 3.76N_2\right) \rightarrow \text{products}$$

For $\Phi = 1$, $a = x + y/4 = 4 + 10/4 = 6.5$

$$\frac{N_A}{N_F} = \frac{4.76a}{\Phi} = \frac{4.76(6.5)}{0.75} = \boxed{41.25}$$

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PROBLEM 2-20

A glass melting furnace is burning ethene (C_2H_4) in pure oxygen (not air). The furnace operates at an equivalence ratio of 0.9 and consumes 30 kmol/hr of ethene.

A. Determine the energy input rate based on the LHV of the fuel. Express your result in both kW and Btu/ hr.
B. Determine the O_2 consumption rate in kmol/ hr and kg/s.

GIVEN: $C_2H_4\text{-}O_2, \Phi = 0.9, \dot{N}_{C_2H_4} = 30\,\text{kmol/hr}$

FIND: a) $\dot{E}\left(= \dot{m}_{C_2H_4} \text{LHV}\right)$

b) $\dot{N}_{O_2}$, $\dot{m}_{O_2}$

SOLUTION:

a) $\dot{E} = \dot{m}_{C_2H_4} \text{LHV} = \dot{N}_{C_2H_4} \text{MW}_{C_2H_4} \text{LHV}$

$$= 30 \frac{\text{kmol}}{\text{hr}} \frac{1\text{hr}}{3600\text{s}} 28,054 \frac{\text{kg}}{\text{kmol}} 47,161 \frac{\text{kJ}}{\text{kg}} \text{Table B.1}$$

$$= 11025 \frac{\text{kJ}}{\text{s}}$$

$$\boxed{\dot{E} = 11025\,\text{kW}}$$

$$\dot{E} = 11025\,\text{kW} \frac{1000\text{W}}{\text{kW}} \frac{3.412\,\text{BTU/hr}}{\text{W}}$$

$$\boxed{\dot{E} = 37.62 \cdot 10^6 \frac{\text{BTU}}{\text{hr}}} = 37.62\,\text{mm BTU/hr}$$

b) For stoichiometric conditions,

$$C_2H_4 + aO_2 \rightarrow 2CO_2 + 2H_2O$$

$$\text{O-balance: } 2a = 4 + 2;\ a = 3$$

$$\dot{N}_{O_2} = \dot{N}_{C_2H_4} \frac{N_{O_2}}{N_{C_2H_4}} = \dot{N}_{C_2H_4} \frac{a}{\Phi}$$

$$\boxed{\dot{N}_{O_2}} = 30 \frac{\text{kmol}}{\text{hr}} \frac{3}{0.9} = \boxed{100 \frac{\text{kmol}}{\text{hr}}}$$

$$\boxed{\dot{m}_{O_2}} = \dot{N}_{O_2} \text{MW}_{O_2} = 100 \frac{\text{kmol}}{\text{hr}} \frac{1\text{hr}}{3600\text{s}} 31.999 \frac{\text{kg}}{\text{kmol}} = \boxed{0.889 \frac{\text{kg}}{\text{s}}}$$

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PROBLEM 2-21

Methyl alcohol (CH_3OH) burns with excess air at an air–fuel ratio (mass) of 8.0. Determine the equivalence ratio, Φ, and the mole fraction of CO_2 in the product mixture assuming complete combustion, i.e., no dissociation.

GIVEN: CH_3OH-air ($\Phi < 1$); A/F = 8 kg_f/kg_{air}

FIND: Φ, χ_{CO_2}

ASSUMPTIONS: no dissociation; air is 79% N_2, 21% O_2.

SOLUTION: For $\Phi = 1$

a) $$CH_3OH + a\left(O_2 + 3.76\right)N_2 \rightarrow CO_2 + \tfrac{3}{2}H_2O + 3.76aN_2$$

O-balance: $1 + 2a = 2 + 1.5$; $a = 2.5/2 = 1.25$

$$\left(A/F\right)_{\Phi=1} = \frac{4.76a\ MW_{air}}{MW_{CH_3OH}} \qquad \text{(Eqn. 2.32)}$$

$$= \frac{4.76\left(1.25\right)28.85}{32.040} = 5.358$$

$$\boxed{\Phi} = \frac{\left(A/F\right)_{\phi=1}}{\left(A/F\right)} = \frac{5.358}{8} = \boxed{0.670} \qquad \text{Eqn. 2.33a}$$

b) $$CH_3OH + \frac{a}{\Phi}\left(O_2 + 3.76N_2\right) \rightarrow CO_2 + \frac{3}{2}H_2O + bO_2 + 3.76\frac{a}{\Phi}N_2$$

O-balance: $$1 + \frac{2a}{\Phi} = 2 + 1.5 + 2b$$

$$b = \frac{1}{2}\left(\frac{2a}{\Phi} - 2.5\right) = \frac{a}{\Phi} - 1.25 = \frac{1.25}{0.67} - 1.25$$

$$b = 0.6157$$

$$\chi_{CO_2} = \frac{N_{CO_2}}{N_{tot}} = \frac{1}{1 + 1.5 + 0.6157 + 3.76(1.25)/0.67} = \frac{1}{10.131}$$

$$\boxed{\chi_{CO_2} = 0.0987}$$

COMMENT: O-element balances must account for oxygen content in the fuel.

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PROBLEM 2-22

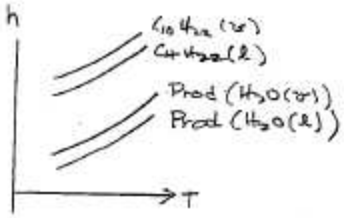
The lower heating value of vapor *n*-decane is 44,597 kJ/ kg at T = 298 K. The enthalpy of vaporization of *n*-decane is 276.8 kJ/ kg of *n*-decane. The enthalpy of vaporization of water at 298 K is 2442.2 kJ/ kg of water.

A. Determine the lower heating value of liquid *n*-decane. Use units of kJ/ kg *n*-decane to express your result.
B. Determine the higher heating value of vapor *n*-decane at 298 K.

GIVEN: n-decane LHV = 44,597 kJ/kg (vapor)

n-decane h_{fg} = 276.8 kJ/kg

water h_{fg} = 2442.2 kJ/kg



FIND: a) LHV n-decane (liq.)

b) HHV n-decane (vap.)

SOLUTION:

a) $\text{LHV(liq.)} = \text{LHV(vap.)} - h_{fgC_{10}H_{22}}$

(see graph)

$$\boxed{\text{LHV(l)}} = 44597 - 276.8 = \boxed{44,320 \text{ kJ/kg}}$$

b) $$\text{HHV(vap)} = \text{LHV(vap)} + \left(\frac{N_{H_2O}}{N_{C_{10}H_{22}}} \frac{MW_{H_2O}}{MW_{C_{10}H_{22}}} \right) h_{fg,H_2O}$$

where the term in brackets is mass of H_2O per mass of $C_{10}H_{22}$. To find $N_{H_2O}/N_{C_{10}H_{22}}$, we write:

$$C_{10}H_{22} + 15.5\left(O_2 + 3.76N_2\right) \rightarrow 10CO_2 + 11H_2O + 15.5(3.76)N_2$$

$$\boxed{\text{HHV(vap)}} = 44,597 + \frac{11}{1}\frac{18.016}{142.284}2442.2 = \boxed{47,999 \text{ kJ/kg}}$$

COMMENTS: Visualizing LHV, HHV graphically greatly aids in performing these computations. Note how the conversion from LHV $\leftrightarrow$ HHV involves the mass ratio of water formed to fuel burned. The HHV-value of 47,999 kJ/kg is for practical purposes the same as the value given in Table B.1 (HHV = 48,002 kJ/kg).

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PROBLEM 2-23

Determine the enthalpy of formation in kJ/kmol for methane, given the lower heating value of 50,016 kJ/kg at 298 K.

GIVEN: The lower heating value for methane, LHV = 50,016 kJ/kg @ 298 K

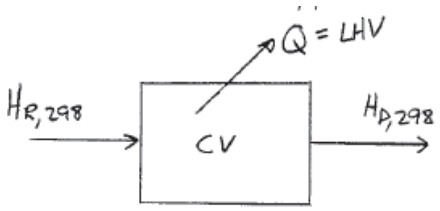
FIND: The enthalpy of formation of methane at 298 K

ASSUMPTIONS: Complete combustion of methane to form CO_2, H_2O and N_2

APPROACH: Use the stoichiometric relation to determine the proper A/F ratio and combustion products for 1 kmole of methane. Then use the first law of thermodynamics to evaluate the reactant enthalpy.

Stoichiometric relation

$$CH_4 + aO_2 + 3.76aN_2 \rightarrow CO_2 + 2H_2O + 3.76aN_2$$
$$a = x + y/4 = 2$$



BASED ON FIRST LAW ANALYSIS OF CONTROL VOLUME (CV) at steady-state

$$H_{R,298} = H_{P,298} + LHV_{298}$$

$$H_{P,298} = 1\left[\bar{h}^o_{f,298} + \left(\bar{h} - \bar{h}^o_{f,298}\right)\right]_{CO_2} + 2\left[\bar{h}^o_f + \left(\bar{h} - \bar{h}^o_{f,298}\right)\right]_{H_2O} + 7.52\left[\bar{h}^o_{f_{298}} + \left(\bar{h} - \bar{h}^o_{f,298}\right)\right]_{N_2}$$

using Appendix A – T = 298 K

$$H_{P,298} = 1[-393546 + 0] + 2[-241847 + 0] + 7.52[0 + 0] = -877240\,kJ$$

$$H_{R,298} = 1\left[\bar{h}^o_{f,298} + \left(\bar{h} - \bar{h}^o_{f,298}\right)\right]_{CH_4} + 2\left[\bar{h}^o_f + \left(\bar{h} - \bar{h}^o_{f,298}\right)\right]_{O_2} + 7.52\left[\bar{h}^o_{f,298} + \left(\bar{h} - \bar{h}^o_{f,298}\right)\right]_{N_2}$$

again using Appendix A – T = 298 K

$$H_{R,298} = 1\left[\bar{h}^o_{f,298} + O\right]_{CH_4} + 2\left[0 + 0\right]_{O_2} + 7.52\left[0 + 0\right]_{N_2} = 1\left[\bar{h}^o_{f,298}\right]_{CH_4}$$

$$H_R = 1\left[\bar{h}^o_{f,298}\right]_{CH_4} = H_{P,298} + LHV_{298} = -877240\,kJ + (50,016\,kJ/kg)\left(\frac{16\,kg}{kmole}\right)(1\,kmole)$$

$$\boxed{\left[\bar{h}^o_{f,298}\right]_{CH_4} = -76984\,kJ/kmole}$$

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PROBLEM 2-24

Determine the standardized enthalpy of the mixture given in problem 2.2 for a temperature of 1000 K. Express your result in kJ/kmol of mixture.

GIVEN: The mixture composition in problem 2-2 at T = 1000 K

FIND: The absolute enthalpy of the mixture (kJ/kmol-mix)

APPROACH: Determine the absolute enthalpy of each species in the mixture using Appendix A and then calculate the mixture absolute enthalpy from:

$$\bar{h}_{mix} = \Sigma \chi_i \bar{h}_i$$

mixture composition (from problem 2-2) and species enthalpies (Appendix A)

Species	# Moles	χ	$\bar{h}^o_{f,298}$ (kJ/kmol)	$\left(\bar{h}_{1000} - \bar{h}^o_{f,298}\right)$ (kJ/kmol)
CO	0.095	0.002	–110541	21697
CO_2	6	0.127	–393546	33425
H_2O	7	0.149	–241847	25993
N_2	34	0.722	0	21468
NO	0.005	106×10^{-6}	90297	22241

$$\bar{h}_{mix} = \Sigma \chi_i \bar{h}_i \quad \text{where} \quad \bar{h}_i = \left[\bar{h}^o_{f,298} + \left(\bar{h}_{1060} - \bar{h}^o_{f,298}\right)\right]_i$$

$$\bar{h}_{mix} = \left(\chi \bar{h}_i\right)_{CO} + \left(\chi \bar{h}_i\right)_{CO_2} + \left(\chi \bar{h}_i\right)_{H_2O} + \left(\chi \bar{h}_i\right)_{N_2} + \left(\chi \bar{h}_i\right)_{NO}$$

$$\bar{h}_{mix} = 0.002[-110541 + 21697] + 0.127[-393546 + 33425] + 0.149[-241847 + 25993]$$
$$+ 0.722[0 + 21468] + 106 \times 10^{-6}[90297 + 22241]$$

$$\boxed{\bar{h}_{mix} = -62563 \text{ kJ/kmole}}$$

COMMENTS: Note how much the N_2 contributes to the mixture specific enthalpy (15500 kJ/kmole-mix) despite having a relatively small absolute enthalpy itself (21468 kJ/kmole-N_2). This is due to the large mole fraction of N_2 present in the mixture.

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PROBLEM 2-25

The lower heating value of methane is 50,016 kJ/kg (of methane). Determine the heating value:

A. per mass of mixture.
B. per mole of air–fuel mixture.
C. per cubic meter of air–fuel mixture.

GIVEN: Methane lower heating value, LHV = 50,016 kJ/kg-fuel at 298 K

FIND: The lower heating value per: a) mass of fuel-air mixture
b) kmole of fuel-air mixture
c) cubic meter of fuel-air mixture

ASSUMPTIONS: fuel-air mixture behaves as an ideal gas and P = 1 atm

APPROACH: Determine the stoichiometric A/F ratio for methane and using this mixture ratio perform a units conversion

Stoichiometric relation: $CH_4 + aO_2 + 3.76aN_2 \rightarrow CO_2 + 2H_2O + 3.76aN_2$
for $\phi = 1$ $a = x + y/4$ $x = 1$ $y = 4$
$a = 2$

a) $$\left(A/F\right)_{MASS} = 4.76a\frac{MW_{air}}{MW_{fuel}} = 4.76(2)\frac{28.85}{16.043} = 17.12\frac{\text{kg-air}}{\text{kg-fuel}}$$

$$LHV\left[\text{kJ/kg-mix}\right] = LHV\left[\text{kJ/kg-fuel}\right]\left(\frac{1}{1+A/F}\right)\left[\frac{\text{kg-fuel}}{\text{kg-mix}}\right]$$

$$LHV\left[\text{kJ/kg-mix}\right] = \left(50016\,\text{kJ/kg-f}\right)\left(\frac{1}{1+17.12}\frac{\text{kg-fuel}}{\text{kg-mix}}\right)$$

$$\boxed{LHV = 2760\ \text{kJ/kg-mix}}$$

b) $$\left(A/F\right)_{MOLAR} = 4.76a = 4.76(2) = 9.52\frac{\text{kmol-air}}{\text{kmol-fuel}}$$

$$LHV\left[\text{kJ/kmol-mix}\right] = LHV\left[\text{kJ/kg-fuel}\right]\cdot MW_f\left[\frac{\text{kg-fuel}}{\text{kmole-fuel}}\right]\cdot\frac{1}{1+A/F}\left[\frac{\text{kmol-fuel}}{\text{kmol-mix}}\right]$$

$$LHV\left[\text{kJ/kmol-mix}\right] = (50016)(16.043)\left(\frac{1}{1+9.52}\right) = 76274\,\text{kJ/kmole-mix}$$

$$\boxed{LHV\left[\text{kJ/kmol-mix}\right] = 76274\ \text{kJ/kmole-mix}}$$

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c) $\mathrm{LHV}\left[\mathrm{kJ/m^3\text{-}mix}\right] = \mathrm{LHV}\left[\mathrm{kJ/kmol\text{-}mix}\right] \cdot \frac{\mathrm{N}}{\mathrm{V}}\left(\frac{\mathrm{kmol\text{-}mix}}{\mathrm{m^3}}\right)$

Assuming ideal gas $\frac{\mathrm{N}}{\mathrm{V}} = \frac{\mathrm{P}}{\mathrm{R_u T}} = \frac{101.325}{(8.315)(298)} = 0.0409 \frac{\mathrm{kmols}}{\mathrm{m^3}}$

$\mathrm{LHV}\left[\mathrm{kJ/m^3\text{-}mix}\right] = \left(76274\,\mathrm{kJ/kmol}\right)\left(0.0409\,\mathrm{kmols/m^3}\right) = 3119\,\mathrm{kJ/m^3\text{-}mix}$

$\boxed{\mathrm{LHV}\left[\mathrm{kJ/m^3\text{-}mix}\right] = 3119\,\mathrm{kJ/m^3\text{-}mix}}$

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PROBLEM 2-26

The higher heating value for liquid octane (C_8H_{18}) at 298 K is 47,893 kJ/kg and the heat of vaporization is 363 kJ/kg. Determine the enthalpy of formation at 298 K for octane vapor.

GIVEN: The higher heating value of liquid octane (C_8H_{18}) at 298 K is 47893 kJ/kg-f and the enthalpy of vaporization is 363 kJ/kg-fuel

FIND: The enthalpy of formation of octane vapor at 298 K

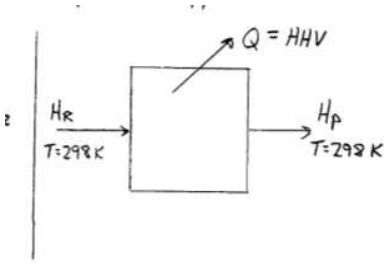
ASSUMPTIONS: Complete combustion, all H_2O exists in liquid form, and no dissociation

APPROACH: Determine the product composition for stoichiometric combustion of octane. Then use a first-law analysis to calculate the enthalpy of formation for liquid octane, from which the vapor enthalpy can be found.

Stoichiometric relation:

$$C_8H_{18} + aO_2 + 3.76aN_2 \rightarrow 8\,CO_2 + 9\,H_2O_{(l)} + 3.76aN_2$$

Since the reactants and products are at 298 K, the sensible enthalpies of all species are zero and the O_2 and N_2 heats of formation are zero. Consequently O_2 and N_2 can be neglected in this calculation.



First-law analysis: $H_{R,298} = H_P + HHV$ at steady-state

$$H_{P,298} = 8\,[\bar{h}_f^o]_{CO_2} + 9\,[\bar{h}_{fH_2O(v)}^o - \bar{h}_{fg,H_2O}]_{H_2O(l)} = 8\,[-393546]_{CO_2} + 9\,[-241847 - 44011]_{H_2O(l)}$$

$$H_{P,298} = -5.7211\times10^6 \text{ kJ} \quad \text{(enthalpies from Appendix A)}$$

$$H_{R,298} = (1)\,[\bar{h}_f^o]_{C_8H_{18}(l)}$$

$$\text{HHV[kJ/kmol-fuel]} = \text{HHV [kJ/kg-f]}\,MW_{fuel}\left[\frac{\text{kg.f}}{\text{kmol-f}}\right] = 47893\,(114.23) = 5.471\times10^6 \text{kJ / kmol-f}$$

$$H_{R,298} = H_{P,298} + \text{HHV}(1\text{ kmol-fuel}) \rightarrow \bar{h}_{fC_8H_{18}(l)}^o = -5.7211\times10^6 + 5.471\times10^6 \text{ kJ/kmol}$$

$$= -250273 \text{ kJ/kmol-fuel}$$

$$\bar{h}_{fC_8H_{18}(v)}^o = \bar{h}_{fC_8H_{18}(l)}^o + h_{fgC_8H_{18}} = -250273 \text{ kJ/kmol-f} + 363 \text{ kJ/kg-f}\left[114.23\frac{\text{kgf}}{\text{kmol}}\right]$$

$$\boxed{\bar{h}_{fC_8H_{18}(v)}^o = -208807 \text{ kJ/kmol}}$$

COMMENTS: The absolute enthalpy of a species in the vapor-phase can be found from the liquid-phase enthalpy:

$$h_{(v)} = h_{(l)} + h_{fg}$$

Results agree well with Appendix B.1

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PROBLEM 2-27

Verify the information in Table 2.1 under the headings Δh_R (kJ/kg of fuel), Δh_R (kJ/kg of mix), and $(O/F)_{stoic}$ for the following:

A. CH_4–air
B. H_2–O_2.
C. C(s)–air.

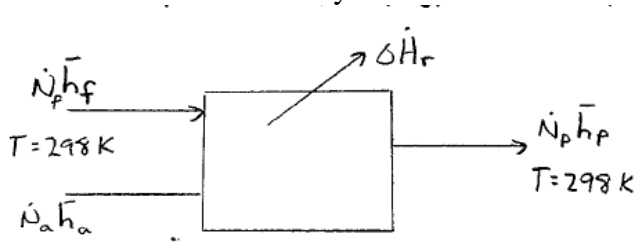
Note that any H_2O in the product is assumed to be in the liquid state.

GIVEN: The following reactions: CH_4-air, H_2-O_2, and C(s)-air

FIND: the heat of reaction Δh_r in kJ/kg-fuel, kJ/kg-mix and the A/F (mass) ratio. Compare the results with Table 2.1.

ASSUMPTIONS: complete combustion, no species dissociation

APPROACH: Calculate the A/F ratio using conservation of elements and then determine Δh_r from the first law of thermodynamics.



$$\Delta\dot{H}_r = \dot{N}_P\bar{h}_P - \dot{N}_f\bar{h}_f - \dot{N}_a\bar{h}_a$$

a) methane-air: $CH_4 + aO_2 + 3.76aN_2 \rightarrow CO_2 + 2H_2O_{(l)} + 3.76aN_2$

$$a = \frac{x + y/4}{\phi} = 2 \quad \text{for} \quad x = 1,\ y = 4,\ \phi = 1$$

$$\boxed{A/F : 4.76a\left(\frac{MW_a}{MW_f}\right) = 4.76(2)\left(\frac{28.85}{16.043}\right) = 17.12}$$

first law: $\Delta\bar{h}_r = \dfrac{\Delta\dot{H}_r}{\dot{N}_f} = \sum \dfrac{\dot{N}_i}{\dot{N}_f}\bar{h}_{i,p} - \bar{h}_f - a\bar{h}_{O_2} - 3.76a\bar{h}_{\dot{N}_2}$

$$\Delta\bar{h}_r = 1[-393546]_{CO_2} + 2[-285856]_{H_2O(l)} - [-74831] - 2[0]_{O_2} - 7.52[0]_{O_2}$$

for products and reactants at 298 K (i.e., $\bar{h} = \bar{h}_f^o$)

$$\Delta\bar{h}_r = -890427 \ \text{kJ/kmol-f} \rightarrow \Delta h_r\left[\text{kJ/kg-f}\right] = \Delta\bar{h}_r\left[\text{kJ/kmole-f}\right] \cdot \frac{1}{MW_f}\left[\frac{\text{kmole-f}}{\text{kg-f}}\right]$$

$$\boxed{\Delta h_r = -890427\left(\frac{1}{16.043}\right) = -55503 \ \text{kJ/kg-f}}$$

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$$\Delta h_r\left[\text{kJ/kg-mix}\right] = \Delta h_r\left[\text{kJ/kg-f}\right]\cdot\frac{1}{1+\text{A/F}}\left[\frac{\text{kg-f}}{\text{kg-mix}}\right]$$

$$\Delta h_r\left[\text{kJ/kg-mix}\right] = -55503\cdot\frac{1}{1+17.12}$$

$$\boxed{\Delta h_r = -3063\ \text{kJ/kg-mix}}$$

b) H_2-O_2: $\quad H_2 + aO_2 \rightarrow H_2O_{(l)}$

$$a = \frac{x + y/4}{\phi} = \frac{1}{2} \qquad \text{for } x = 0,\ y = 2,\ \phi = 1$$

$$\text{A/F} = a\frac{MW_{O_2}}{MW_{H_2}} = \frac{1}{2}\left(\frac{32}{2}\right) = 8 \quad \boxed{\text{A/F} = 8}$$

$$\Delta\bar{h}_r = \sum\frac{\dot{N}_i}{\dot{N}_f}\bar{h}_{P,i} - a\bar{h}_{O_2} - \bar{h}_f = 1\bar{h}_{H_2O(l)} - 2\bar{h}_{O_2} - \bar{h}_{H_2}$$

$$= 1\left[-285856\right] - 2\left[0\right] - 1\left[0\right]$$

$$\Delta\bar{h}_r = -285856\ \text{kJ/kmole-f}$$

$$\Delta h_r = \Delta\bar{h}_r\cdot\frac{1}{MW_f} = \frac{-285856}{2} \rightarrow \boxed{\Delta h_r = -142928\ \text{kJ/kg-f}}$$

$$\Delta h_r\left[\text{kJ/kg-mix}\right] = \Delta h_r\left[\text{kJ/kg-f}\right]\cdot\frac{1}{1+\text{A/F}} = -142928\left(\frac{1}{1+8}\right)$$

$$\boxed{\Delta h_r\left[\text{kJ/kg-mix}\right] = -15880\ \text{kJ/kg-mix}}$$

c) $C_{(s)} + aO_2 + 3.76aN_2 \rightarrow CO_2 + 3.76aN_2$

$$a = \frac{x + y/4}{\phi} = 1 \quad \text{for } x = 1,\ y = 0,\ \phi = 1 \quad \text{A/F} = 4.76a\left(\frac{MW_a}{MW_f}\right) = 4.76(1)\left(\frac{28.85}{12}\right)$$

$$\boxed{\text{A/F} = 11.44}$$

$$\Delta\bar{h}_r = \sum\frac{\dot{N}_i}{\dot{N}_f}\bar{h}_{p,i} - a\bar{h}_{O_2} - 3.76a\bar{h}_{N_2} - \bar{h}_f = 1\left[-393546\right]_{CO_2} - 1\left[0\right]_{O_2} - 3.76\left[0\right]_{N_2} - 1\left[0\right]_{C(s)}$$

$$\Delta\bar{h}_r = -393546\ \text{kJ/kmole-f}$$

$$\Delta h_r\left[\text{kJ/kg-f}\right] = \Delta\bar{h}_r\cdot\frac{1}{MW_f} = -393546\cdot\frac{1}{12} = -32796\ \text{kJ/kg-f}$$

$$\Delta h_r\left[\text{kJ/kg-mix}\right] = \Delta h_r\left[\text{kJ/kg-f}\right]\frac{1}{1+\text{A/F}} = -32796\left(\frac{1}{1+11.44}\right) = -2636\ \text{kJ/kg-mix}$$

$$\boxed{\begin{array}{l}\Delta h_r = -32796\ \text{kJ/kg-f}\\ \\ \Delta h_r = -2636\ \text{kJ/kg-mix}\end{array}}$$

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PROBLEM 2-28

Generate the same information requested in problem 2.27 for a stoichiometric mixture of C_3H_8 (propane) and air.

GIVEN: A stoichiometric mixture of propane (C_3H_8) and air

FIND: Δh_r (kJ/kg-f), Δh_r (kJ/kg-mix), and A/F (mass) ratio

ASSUMPTIONS: Complete combustion with no dissociation, water in combustion products exists in liquid-phase since T = 298 K

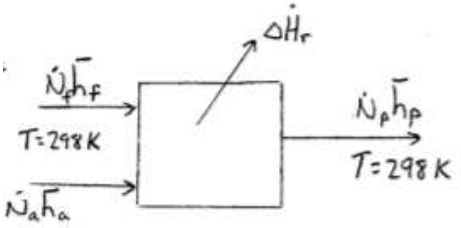
APPROACH: Calculate the A/F ratio using elemental conservation and then determine Δh_r from the first law of thermodynamics

Combustion equation: $C_3H_8 + aO_2 + 3.76\,aN_2 \rightarrow 3CO_2 + 4\,H_2O + 3.76\,aN_2$

$$a = \frac{x + y/4}{\phi} = \frac{3+2}{1} = 5 \rightarrow A/F = 4.76a\,\frac{MW_{air}}{MW_{fuel}}$$

$$\boxed{A/F = 4.76(5)\left(\frac{28.85}{44}\right) = 15.57}$$

First-law analysis:



$$\Delta\dot{H}_r = \dot{H}_p - \dot{H}_R = \dot{N}_p\bar{h}_p - \dot{N}_{ia}\bar{h}_a - \dot{N}_f\bar{h}_f \qquad \text{Note: at 298 K } \bar{h} = \bar{h}_f^\circ + (\bar{h} - \bar{h}_f^\circ)$$

$$\Delta\bar{h}_r = \frac{\Delta\dot{H}_r}{\dot{N}_f} = \Sigma\frac{\dot{N}_i}{N_f}\bar{h}_{P,i} - a\bar{h}_{O_2}^\circ - 3.76a\bar{h}_{N_2}^\circ - \bar{h}_f$$

$$\Delta\bar{h}_r = 3\,\bar{h}^\circ_{fCO_2} + 4\,\bar{h}^\circ_{f,H_2O(l)} - \bar{h}^\circ_{f,f} = 3[-393546] + 4[-285856] - [-103847]$$

$$\Delta\bar{h}_r = -2.2202\times10^6 \text{ kJ/kmole-f}$$

$$\Delta h[\text{kJ/kg-fuel}] = \Delta\bar{h}_r[\text{kJ/kmole}].\frac{1}{MW_f}\left[\frac{\text{kmole}}{\text{kg-f}}\right] = -2.2202\times10^6\left[\frac{1}{44.096}\right]$$

$$\boxed{\Delta h_r = -50349 \text{ kJ/kg-f}}$$

$$\Delta h_r[\text{kJ/kg-mix}] = \Delta h_r[\text{kJ/kg-f}].\frac{1}{1+A/F}\left[\frac{\text{kg-f}}{\text{kg-mix}}\right] = -50459\left[\frac{1}{1+15.57}\right]$$

$$\boxed{\Delta h_r = -3039 \text{ kJ/kg-mix}}$$

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COMMENTS: Note that this Δh_r is based on condensed H_2O in the product mixture. Also, $\Delta h_r(\text{kJ/kg-f}) = -\text{HHV}$ from Appendix B.1 as would be expected.

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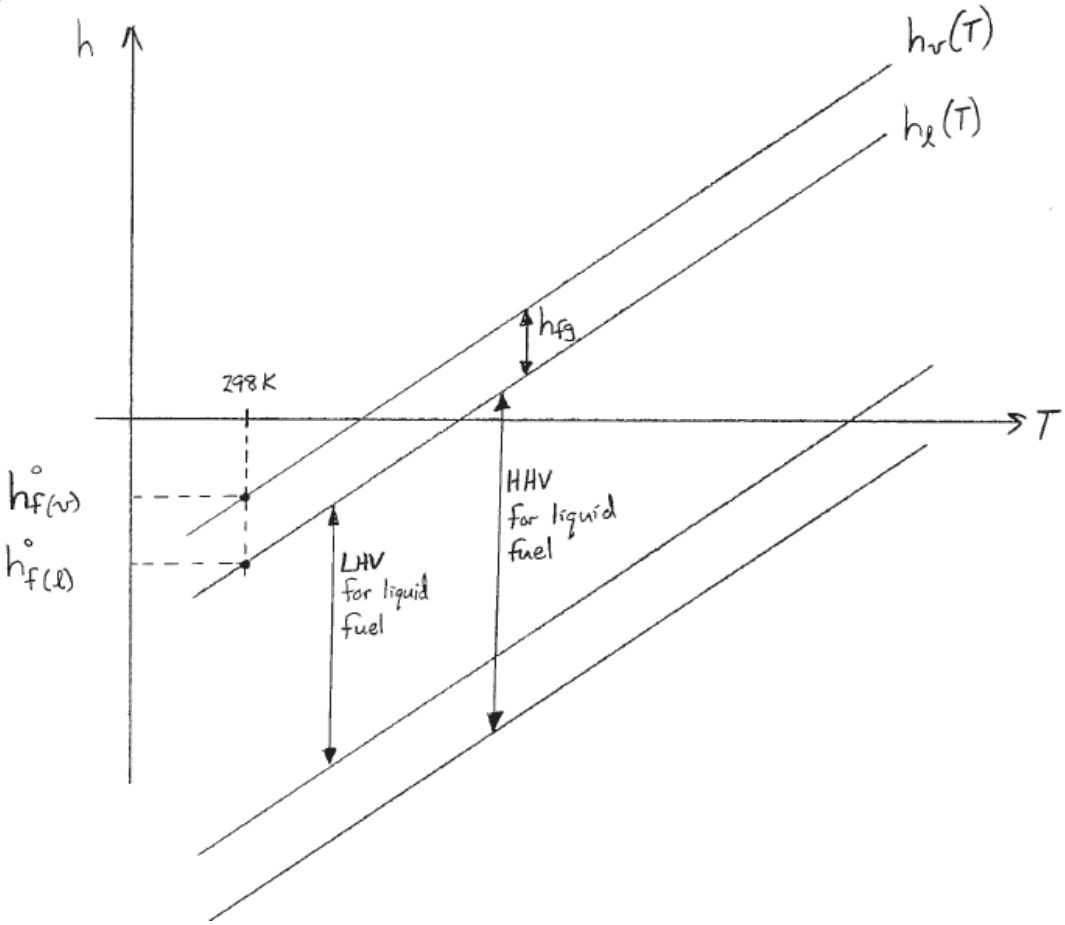
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PROBLEM 2-29

Consider a liquid fuel. Draw a sketch on *h–T* coordinates illustrating the following quantities: $h_l(T)$; $h_v(T)$; heat of vaporization, h_{fg}; heat of formation for fuel vapor; enthalpy of formation for fuel liquid; lower heating value; higher heating value.

GIVEN: A liquid fuel undergoing combustion

FIND: On an h-T sketch illustrate the following quantities; $h_l(T)$, $h_v(T)$, enthalpy of vaporization, h_{fg}, enthalpy of formation for fuel vapor, enthalpy of formation for fuel liquid, lower heating value, and higher heating value



COMMENTS: Note that the greatest enthalpy change at T = const (or greatest temperature change for h = const) occurs when fuel vapor is burned and the products contain liquid H_2O. Also, the lower and higher heating values for fuel vapor can be found by adding the enthalpy of vaporization to the fuel liquid lower and higher heating values.

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PROBLEM 2-30

Determine the adiabatic flame temperature for constant-pressure combustion of a stoichiometric propane–air mixture assuming reactants at 298 K, no dissociation of the products, and constant specific heats evaluated at 298 K.

GIVEN: A stoichiometric propane (C_3H_8)-air mixture at 298 K

FIND: The adiabatic flame temperature, T_{ad}

ASSUMPTIONS: no dissociation, constant specific heats evaluated at 298 K

APPROACH: Use element conservation to determine the correct fuel-air mix and product composition. Then use a first-law analysis to evaluate T_{ad}

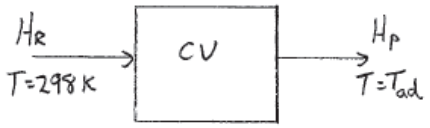
Stoichiometric relation:

$$C_3H_8 + aO_2 + 3.76aN_2 \rightarrow 3CO_2 + 4H_2O + 3.76aN_2$$

$$\text{at } \phi = 1 \quad a = x + y/4 = 5$$

$$C_3H_8 + 5O_2 + 18.8N_2 \rightarrow 3CO_2 + 4H_2O + 18.8N_2$$

(Since the reactants are at T = 298 K the O_2 and N_2 contributions to the reactant enthalpy are zero)



First law for adiabatic conditions: $H_{R_{298}} = H_{P_{T_{ad}}}$

$$[N\bar{h}]_{C_3H_8} + [N\bar{h}]_{O_2} + [N\bar{h}]_{N_2} = [N\bar{h}]_{CO_2} + [N\bar{h}]_{H_2O} + [N\bar{h}]_{N_2}$$

where $\bar{h} = \bar{h}_f^\circ + (\bar{h} - \bar{h}_{f,298}^\circ) = \bar{h}_f^\circ + \bar{c}_p(T - 298)$ ← properties from appendix A

$$(1)[-103847 + 0]_{C_3H_8} = 3[-393546 + 37.198(T_{ad} - 298)]_{CO_2} + 4[-241847 + 33.448(T_{ad} - 298)]_{H_2O} + 18.8[0 + 29.071(T_{ad} - 298)]_{N_2}$$

Solving for T_{ad}: $\boxed{T_{ad} = 2879\,\text{K}}$

COMMENTS: Note that this flame temperature is much greater than the adiabatic flame temperature in Appendix B.1. This is due to the assumption of no species dissociation and the assumption of constant specific heats evaluated at 298 K. An examination of Appendix A shows that the specific heats can vary significantly from 298 K to 2879 K.

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PROBLEM 2-31

Repeat problem 2.30, but using constant specific heats evaluated at 2000 K. Compare your result with that of problem 2.30 and discuss.

GIVEN: A stoichiometric propane (C_3H_8)-air mixture at 298 K

FIND: The adiabatic flame temperature, T_{ad}

ASSUMPTIONS: no dissociation, constant specific heats evaluated at 2000 K

APPROACH: Use element conservation to determine the correct fuel-air mixture and product composition. Then use a first-law analysis to evaluate T_{ad}

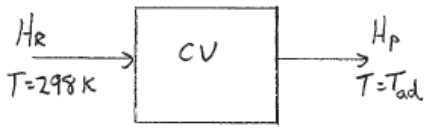
Stoichiometric relation:

$$C_3H_8 + aO_2 + 3.76aN_2 \rightarrow 3CO_2 + 4H_2O + 3.76aN_2$$

$$\text{at } \phi = 1 \quad a = x + y/4 = 5$$

$$C_3H_8 + 5O_2 + 18.8N_2 \rightarrow 3CO_2 + 4H_2O + 18.8N_2$$

(Since the reactants are at T = 298 K the O_2 and N_2 contributions to the reactant enthalpy are zero)



First law for adiabatic conditions: $H_{R_{298}} = H_{P_{T_{ad}}}$

$$[N\bar{h}]_{C_3H_8} + [N\bar{h}]^{0}_{O_2} + [N\bar{h}]^{0}_{N_2} = [N\bar{h}]_{CO_2} + [N\bar{h}]_{H_2O} + [N\bar{h}]_{N_2}$$

where $\bar{h} = \bar{h}^{\circ}_{f,298} + (\bar{h} - \bar{h}^{\circ}_{f,298}) = \bar{h}^{\circ}_{f} + \bar{c}_p (T - 298)$ ← $\bar{h}^{\circ}_{f}$ and $\bar{c}_p$ from appendix A

$$(1)[-103847 + 0]_{C_3H_8} = 3[-393546 + 60.433(T_{ad} - 298)]_{CO_2} + 4[-241847 + 51.143(T_{ad} - 298)]_{H_2O}$$
$$+18.8[0 + 35.988(T_{ad} - 298)]_{N_2}$$

Solving for T_{ad} : $\boxed{T_{ad} = 2222 \text{ K}}$

COMMENTS: Note that this flame temperature is much closer to the value listed in Appendix B.1 than the temperature calculated in problem 2-17. This is due to a more appropriate estimate of the constant specific heats. The effects of dissociation on the flame temperature are still unaccounted for.

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PROBLEM 2-32

Repeat problem 2.30, but now use property tables (Appendix A) to evaluate the sensible enthalpies.

GIVEN: A stoichiometric propane (C_3H_8)-air mixture

FIND: The adiabatic flame temperature, T_{ad}

ASSUMPTIONS: no dissociation, species thermophysical properties equal to those in Appendix A

APPROACH: Use element conservation to determine the correct fuel-air mixture and product composition. Then use Appendix A to evaluate the species thermophysical properties and a first-law analysis to determine the flame temperature. This is an iterative process in which a flame temperature is guessed, the first law is checked, and if necessary a new flame temperature is chosen.

See problems 2-17 and 2-18 for correct fuel-air mixture and product composition. A control volume sketch for the energy conservation is also shown first law for adiabatic conditions:

$H_{R,298} = H_{P,T_{ad}} \rightarrow HP - HR = 0$

$$[N\bar{h}]_{C_3H_8} + [N\bar{h}]^{\circ}_{O_2} + [N\bar{h}]^{\circ}_{N_2} = [N\bar{h}]_{CO_2} + [N\bar{h}]_{H_2O} + [N\bar{h}]_{N_2}$$

where $\bar{h} = \bar{h}^{\circ}_{f_{298}} + (\bar{h} - \bar{h}^{\circ}_{f,298}) = \bar{h}^{\circ}_{f} + \Delta\bar{h}_s$ ← values from appendix A

$$(1)[-103847 = 3[-393546 + \Delta h_s]_{CO_2} + 4[-241847 + \Delta h_s]_{H_2O} + 18.8[0 + \Delta h_s]_{N_2}$$

$$\text{Rearranging in form } H_p - H_R = 0 : 3\Delta h_{s,CO_2} + 4\Delta h_{s,H_2O} + 18.8\Delta h_{sN_2} - 2.0442\times10^6 = 0$$

T(K)	$\Delta h_{s,CO_2}$ (kJ/kmol)	$\Delta h_{s,H_2O}$ (kJ/kmole)	$\Delta h_{s,N_2}$ (kJ/kmole)	$H_P - H_R$	
2000	91420	72805	56130	–423476	
2100	97477	77952	59738	–316887	
2200	103562	83160	63360	–209706	ΛΙΝΕΑΡ ΙΝΤΕΡΠΟΛΑΤΙΟΝ ΥΣΙΝΓ $H_Π - H_P = 0$
2300	109670	88426	66997	–101942	
2400	115798	93744	70645	6296	

$\boxed{T_{ad} = 2394 \text{ K}}$

COMMENTS: Note that this flame temperature is slightly greater than that listed in Appendix B.1 despite using accurate thermophysical properties from Appendix A. This is due to neglecting species dissociation.

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PROBLEM 2-33

Once more, repeat problem 2.30, but eliminate the unrealistic assumptions, i.e., allow for dissociation of the products and variable specific heats. Use HPFLAME (Appendix F), or other appropriate software. Compare and contrast the results of problems 2.30–2.33. Explain why they differ.

GIVEN: A stoichiometric propane (C_3H_8)-mixture at 298 K

FIND: The adiabatic flame temperature using the computer code HPFLAME or other software. Compare and contrast the results of problems 2-17 to 2-20

Using HPFLAME: $\boxed{T_{ad} = 2267K}$ which matches Appendix B.1

The adiabatic flame temperatures calculated in problems 2-17 through 2-20 differ for two main reasons; the method of evaluating the thermophysical properties and whether dissociation of the product species is considered. In problem 2-17 the species sensible enthalpies were estimated using constant specific heats at 298 K. Thus, $\Delta h_{sens} = \int_{298}^{T_{ad}} C_P dt \rightarrow \Delta h_{sens} = C_{P,298}(T_{ad} - 298)$.

Since specific heat increases with temperature, we were effectively using too low of a specific heat, resulting in too high of an adiabatic flame temperature for a given Δh_{sens}.

In problem 2-18 the adiabatic flame temperature was calculated using constant specific heats evaluated at 2000 K. While using these specific heats yields an adiabatic flame temperature close to that listed in Appendix B.1, the thermophysical properties are wrong. This can be seen by comparing the adiabatic flame temperature calculated in problem 2-18 (above) with that calculated in problem 2-19. In problem 2-19, tabulated values of sensible enthalpies (Appendix A) were used but the calculated flame temperature is much greater than that calculated using HPFLAME or listed in Appendix B.1. This difference cannot be attributed to incorrect thermophysical properties and must therefore be due to dissociation of the product species.

From the results of problems 2-17 through 2-20 it becomes apparent that accurate evaluation of mixture thermophysical properties and product dissociation are required to obtain a close calculation of adiabatic flame temperature.

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PROBLEM 2-34

Using the data in Appendix A, calculate the adiabatic constant-pressure flame temperature for a boiler operating with the fuel blend and equivalence ratio given in problem 2.17. Assume complete combustion to CO_2 and H_2O and neglect any dissociation. Also, assume the heat capacity of the combustion products is constant evaluated at 1200 K. The boiler operates at 1 atm, and both the air and fuel enter at 298 K.

GIVEN: Equimolar fuel blend of C_3H_8 & CH_4 burns in air ($\Phi = 0.8$)

$T_{air} = T_F = 298$ K

P = 1 atm = constant

FIND: T_{ad}

ASSUMPTIONS: No dissociation (given)

Constant $\bar{C}_P$ @ 1200 K (given)

Air $\equiv$ 79% N_2, 21% O_2

SOLUTION: Apply first law, Eqn. 2.40a:

$H_R(T_i, P) = H_{Pr}(T_{ad}, P)$

To evaluate the above, we need to determine the composition of the reactants and products:

$$C_3H_8 + CH_4 + \frac{7}{\Phi}(O_2 + 3.76\,N_2) \rightarrow$$

$$4CO_2 + 6H_2O + 7\left(\frac{1-\Phi}{\Phi}\right)O_2 + \frac{7}{\Phi}3.76\,N_2$$

Reactants:

	N	$\bar{h}(=\bar{h}_f^o)$	$N\bar{h}$	Table
C_3H_8	1	–103,847	–103,847	B.1
CH_4	1	–74,831	–74,831	B.1
O_2	8.75	0	0	–
N_2	32.90	0	0	–
			$H_R = \Sigma N_i \bar{h}_i = -178,678$	[=] kJ

Products:

	N	$\bar{h}_f^o$	$\bar{C}_P$ @ 1200 K	$N\bar{h}_f^o$	$N\bar{C}_P$	Table
CO_2	4	–393,546	54.360	–1,574,184	217.440	A.2
H_2O	6	–241,845	43.874	–1,451,070	263.244	A.6
O_2	1.75	0	34.936	0	61.138	A.11
N_2	32.90	0	32.762	0	1077.870	A.7
				–3,025,254	1619.692	

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$$H_{Pr} = \Sigma N_i \bar{h}_i = \Sigma N_i \left[\bar{h}^{o}_{fi} + \bar{C}_{Pi} (T_{ad} - 298.15) \right]$$

$$= \Sigma N_i \bar{h}_{fi} + \Sigma N_i \bar{C}_{Pi} (T_{ad} - 298.15)$$

$$H_{Pr} = -3,025,254 + 1619.692 (T_{ad} - 298.15) [=] kJ$$

$$H_R = H_P \quad \text{(Eqn. 2.40a)}$$

$$-178,678 = -3,025,254 + 1619.692 \ (T_{ad} - 298.15)$$

$$T_{ad} - 298.15 = \frac{-178,678 + 3,025,254}{1619.692} = 1978.1$$

$$\boxed{T_{ad}} = 1978.1 + 298.15 = \boxed{2276\,K}$$

COMMENTS: Tabulating needed information for reactants & products helps to organize calculations of this type.

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PROBLEM 2-35

Repeat problem 2.30, but for constant-volume combustion. Also, determine the final pressure.

GIVEN: C_3H_8-air

$\Phi = 1$, $T_i = 298$, $P_i = 1$ atm

Constant-volume combustion

FIND: T_{ad}, P_{final}

ASSUMPTIONS: No dissociation (given)

Constant $\bar{C}_{P,i}$ @ 298 K

Air $\equiv 79\%\ N_2,\ 21\%\ O_2$

SOLUTION: Apply first law, Eqn. 2.41:

$$\bar{U}_R(T_i, P_i) = U_{Pr}(T_{ad}, P_f)$$

or

$$H_R - H_{pr} - R_u(N_R T_i - N_{pr} T_{ad}) = 0 \qquad \text{Eqn. 2.43}$$

To evaluate Eqn. 2.43, we need the composition of both the reactants & products:

$$C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 5(3.76)N_2$$

Reactants:

	N	$\bar{h}\left(=\bar{h}_f^o\right)$	$N\bar{h}$	Table
C_3H_8	1	−103,847	−103,847	B.1
O_2	5	0	0	–
N_2	18.8	0	0	–
$\sum_R$	24.8 kmol		−103,847 kJ	

$$H_R = \sum_R N_i h_i = -103{,}847 \text{ kJ}$$

Products:

	N	$\bar{h}_f^o$	$\bar{C}_P$ @ 298 K	$N\bar{h}_f^o$	$N\bar{C}_P$	Table
CO_2	3	−393,546	37.198	−1,180,638	111.594	A.2
H_2O	4	−241,845	33.448	−967,380	133.792	A.6
N_2	18.8	0	29.071	0	546.535	A.7
$\sum_{Pr}$	25.8			−2,148,018	791.921	

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$$H_{Pr} = \sum_{Pr} N_i \bar{h}_i = \sum N_i \left[\bar{h}_{fi} + \bar{C}_{P,i} \left(T_{ad} - T_{ref} \right) \right]$$

$$= \sum N_i \bar{h}_{fi} + \sum N_i \bar{C}_{Pi} \left(T_{ad} - T_{ref} \right)$$

$$H_{Pr} = -2{,}148{,}018 + 791.921 \left(T_{ad} - T_{ref} \right)$$

Substituting into Eqn. 2.43 with $T_{ref} = T_i$,

$H_R - H_{Pr} - R_u N_R T_i + R_u N_{Pr} T_{ad} = 0$

$-103.847 - [-2{,}148{,}018 + 791.921\ (T_{ad} - T_i)]$

$-8.3145\ (24.8)\ 298.15 + 8.3145(25.8) T_{ad} = 0$

Simplifying:

$2{,}218{,}804 - 577.407\ T_{ad} = 0$

$$\boxed{T_{ad} = 3843 \text{ K}}$$

$$\forall = \frac{N_R R_u T_i}{P_i} = \frac{N_{pr} R_u T_{ad}}{P_f} \Rightarrow P_f = P_i \frac{N_{Pr}}{N_r} \frac{T_{ad}}{T_i}$$

$$\boxed{P_f} = 1 \text{ atm } \frac{25.8}{24.8} \frac{3843}{298.15} = \boxed{13.4 \text{ atm}}$$

COMMENT: As expected, the constant-vol. adia.flame temperature is significantly greater than the const.-P value of 2879 K from problem 2.30.

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PROBLEM 2-36

Use the condition given in problem 2.33, but calculate the constant-volume adiabatic flame temperature using UVFLAME (Appendix F), or other appropriate software. Also, determine the final pressure. Compare your results with those of problem 2.35 and discuss.

GIVEN: C_3H_8-air; ™ = 1; T_i = 298 K; P_i = 1 atm.

FIND: T_{ad} @ constant volume, P_{final}

ASSUMPTIONS: Ideal gas; product dissociation.

SOLUTION: To use UVFLAME, we need to determine H_R(per kmol of fuel), N_R, and MW_R:

$C_3H_8 + 5(O_2 + 3.76\ N_2) \rightarrow$ Products

$$H_R = (1)\left[\bar{h}^\circ_{f,C_3H_8} + \Delta h^{\,0}_{s,C_3H_8}\right] + 5\left[\bar{h}^\circ_{f,O_2} + \Delta h^{\,0}_{s,O_2}\right] + 5(3.76)\left[\bar{h}^\circ_{f,N_2} + \Delta h^{\,0}_{s,N_2}\right]$$

$$H_R = -103{,}848\ \text{kJ/kmol}_{C_3H_8}\ (\text{Table B.1})$$

$N_R = 1 + 5(4.76) = 24.8$ kmole

$$MW_R = \frac{(1)44.096 + 23.8(28.85)}{24.8} = 29.465$$

OUTPUT FROM UVFLAME:

Constant-Volume Adiabatic Flame Calculation for Specified Fuel, Phi⁻, & Reactant Properties Using Olikara & Borman Equilibrium Routines

Problem Title: PROBLEM 2.36 (2nd Ed.)

Data below are as read from the input file. Compare with INPUT.UV. If they do not agree, your input data have not been entered correctly.

CARBON ATOMS	3.0
HYDROGEN ATOMS	8.0
OXYGEN ATOMS	0.0
NITROGEN ATOMS	0.0
EQUIVALENCE RATIO	1.000
FINAL TEMPERATURE (K) guess	2500.0
REACTANT TEMPERATURE (K)	298.1
REACTANT PRESSURE (Pa)	101325.0
ENTHALPY OF REACTANTS (kJ/kmol of fuel)	−103848.0
MOLES OF REACTANTS (kmol/kmol of fuel)	24.800

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MOLEC WT OF REACTANTS (kg/kmol)	29.465

FLAME TEMP. & COMBUSTION PRODUCTS PROPERTIES

Const-vol Flame Temperature [K] =	2631.53
Pressure [Pa] =	0.946107E+06
Mixture Enthalpy [J/kg] =	0.5593E+06
Mixture Specific Heat, Cp [J/kg-K] =	0.255109E+04
Specific Heat Ratio, Cp/Cv =	1.1531
Mixture Molecular Weight [kg/kmol] =	27.8520
Moles of Fuel per Mole of Products =	0.03809654

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The mole fractions of the product species are:

H:	0.00104322	O:	0.00083162	N: 0.00000026
H2:	0.00538231	OH:	0.00664940	CO: 0.02220778
NO:	0.00594248	O2:	0.00910174	H2O 0.14315753
CO2:	0.09208184	N2:	0.71360183	

From above:

$\boxed{T_{ad} = 2631.5 \text{ K}}$

$\boxed{P_{final}} = 9.46107.10^5 \text{ P}_a = \boxed{9.337 \text{ atm}}$

Compared with results using $C_{p's}$ evaluated at 298 K and ignoring dissociation (problem 2-35), these values are much lower (T_{ad} = 2632 K vs. 3843 K). This is as expected, since $C_{p's}$ @ 298 K are much too low and dissociation is important.

COMMENT: Note the minimal computation required to use UVFLAME to calculate constant-volume adiabatic flame temperatures.

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PROBLEM 2-37

Derive the equivalent system (fixed mass) form of the first law corresponding to Eqn. 2.35, which is used to define the heat of reaction. Treat the system as constant pressure with initial and final temperatures equal.

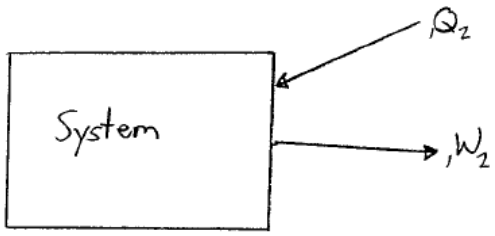
GIVEN: A system of fixed mass at constant pressure and temperature

FIND: Equivalent system form of Eqn. 2.35 (First Law) which is used to define the heat of reaction.

ASSUMPTIONS: expansion/contraction of the system boundary is a reversible process, only work done by system is boundary expansion/contraction

APPROACH: Write the first law for the system. Substitute the appropriate expression for constant pressure work and solve for the specific heat transfer.

sketch of system:



First law for a system:

$$_1Q_2 - {}_1W_2 = m(u_2 - u_1)$$

For a system at constant pressure the reversible work can be expressed as

$$_1W_2 = \int_1^2 Pdv = P(V_2 - V_1) = mP(v_2 - v_1) \qquad v \equiv \text{specific volume}$$

substituting into the first law

$$_1Q_2 - mP(v_2 - v_1) = m(u_2 - u_1)$$
$$_1Q_2 = m[(u_2 + P_{v_2}) - (u_1 + P_{v_1})] = m(h_2 - h_1)$$
$$_1q_2 = {}_1Q_2/m = h_2 - h_1$$

if state 1 is the reactants and state 2 is the products then

$$\boxed{q = h_P - h_R} \leftarrow \text{same form as Eqn. 2.35}$$

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COMMENTS: Note that the first law for a constant pressure system has the same form as for a control volume. This is only true for constant pressure. Also, the internal energies u_1 and u_2 are mixture internal energies. Even assuming ideal gas behavior, $u_1 \neq u_2$ at constant temperature if the composition changes. (See Joule's experiment with gases and internal energy)

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PROBLEM 2-38

A furnace, operating at 1 atm, uses preheated air to improve its fuel efficiency. Determine the adiabatic flame temperature when the furnace is run at a mass air–fuel ratio of 18 for air preheated to 800 K. The fuel enters at 450 K. Assume the following simplified thermodynamic properties:

$$T_{\text{ref}} = 300 \text{ K},$$
$$MW_{\text{fuel}} = MW_{\text{air}} = MW_{\text{prpd}} = 29 \text{ kg/kmol},$$
$$c_{p,\text{fuel}} = 3500 \text{ J/kg-K}; \; c_{p,\text{air}} = c_{p,\text{prod}} = 1200 \text{ J/kg-K},$$
$$\bar{h}^{o}_{f,\text{air}} = \bar{h}^{o}_{f,\text{prod}} = 0,$$
$$\bar{h}^{o}_{f,\text{fuel}} = 1.16 \cdot 10^{9} \text{ J/kmol}.$$

GIVEN:

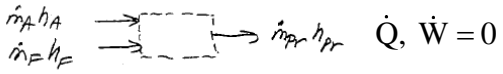
$A/F = \dot{m}_A / \dot{m}_F = 18$	$C_{P,F} = 3500$ J/kg-K
$T_A = 800$ K (preheated)	$C_{P,A} = 1200$ J/kg-K
$T_F = 450$ K	$C_{P,Pr} = 1200$ J/kg-K
$P = 1$ atm	
$h_{f,A} = h_{f,Pr} = 0$	$\bar{h}_{f,F} = 1.16 \cdot 10^{9}$ J/kmol

FIND: T_{ad} for P = 1 atm

ASSUMPTIONS: Air ≡ 79% N_2/21% O_2; properties as given.

SOLUTION: Write first law (mass basis) recognizing that

$$\dot{m}_{P_r} = \dot{m}_A + \dot{m}_F$$



$$\dot{m}_A h_A + \dot{m}_F h_F = (\dot{m}_A + \dot{m}_F) h_{Pr}$$

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Divide by $\dot{m}_F$ & substitute properties ($h_i = h_{fi} + c_{pi}\,(T_i - T_{ref})$):

$$\left(\frac{\dot{m}_A}{\dot{m}_F}\right)\left(0 + C_{P,A}(T_A - T_{ref})\right) + (1)\left[\frac{\bar{h}_F}{MW_F} + C_{P,F}(T_F - T_{ref})\right]$$

$$= \left(\frac{\dot{m}_A}{\dot{m}_F} + 1\right)\left[0 + C_{P,Pr}(T_{ad} - T_{ref}\right]$$

$$18\left(1200(800-300)\right) + \left(\frac{1.16\cdot 10^9}{29} + 3500(450-300)\right)$$

$$= (18+1)\left(1200(T_{ad} - 300)\right)$$

Solve for T_{ad}

$$1.080\cdot 10^7 + 4.0525\cdot 10^7 = 2.28\cdot 10^4\ (T_{ad} - 300)$$

$$T_{ad} = 2251 + 300$$

$$\boxed{T_{ad} = 2551\ \text{K}}$$

COMMENTS: i) Use of simplified properties focuses attention on energy conservation. ii) The use of a mass-based first law simplifies the solution ($H_R = H_{Pr}$).

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PROBLEM 2-39

Consider the constant-pressure, adiabatic combustion of a stoichiometric ($\Phi = 1$) fuel–air mixture where $(A/F)_{stoic} = 15$. Assume the following simplified properties for the fuel, air, and products, with $T_{ref} = 300$ K:

	Fuel	*Air*	*Products*
c_p(J/kg-K)	3500	1200	1500
$h^o_{f,300}$(J/kg)	$2 \cdot 10^7$	0	$-1.25 \cdot 10^6$

A. Determine the adiabatic flame temperature for a mixture initially at 600 K.
B. Determine the heating value of the fuel at 600 K. Give units.

GIVEN: Adiabatic, const.-P combustion: $(A/F)_{\phi=1} = 15$, $\Phi = 1$, $T_{ref} = 300$, $T_F = T_A = 600$ K, simplified properties

FIND: a) T_{ad} b) HV @ 600 K

ASSUMPTIONS: Air is 79% N_2, 21% O_2

SOLUTION: a) $H_R = H_{Pr}$ or $h_R = h_{Pr}$

Stoichiometry:

$1\ kg_F + 15\ kg_A \rightarrow 16\ kg_{Pr}$

$$H_R = m_A h_A + m_F h_F = m_A\left(h^o_{f,A} + c_{P,A}(T_A - T_{ref})\right) + m_F\left(h^o_{f,F} + c_{P,F}(T_F - T_{ref})\right)$$

$$H_{Pr} = (m_A + m_F)h_{Pr} = (m_A + m_F)\left(h^o_{f,Pr} + C_{P,Pr}(T_{ad} - T_{ref})\right)$$

Substitute property values & let $m_F = 1,\ m_A = 15$:

$$H_R = 15\left(0 + 1200(600 - 300)\right) + 1\left(2 \cdot 10^7 + 3500(600 - 300)\right)$$

$$H_R = 5.4 \cdot 10^6 + 2.105 \cdot 10^7 = 2.645 \cdot 10^7\ J$$

$$H_{Pr} = 16\left(-1.25 \cdot 10^6 + 1500(T_{ad} - 300)\right)$$

$$H_{Pr} = -2 \cdot 10^7 + 2.4 \cdot 10^4 (T_{ad} - 300)$$

Set $H_R = H_{Pr}$ & solve for T_{ad}:

$$2.645 \cdot 10^7 = -2 \cdot 10^7 + 2.4 \cdot 10^4 (T_{ad} - 300)$$

a) $\boxed{T_{ad} = 2235\ K}$

b) HV = $H_R - H_{Pr}$ for 1 kg Fuel @ 600 K
From part a), $H_R(600) = 2.645 \cdot 10^7$ J (per kg_F).

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$$H_{Pr}(600) = 16\left(h^{o}_{f,Pr} + C_{P,Pr}(T - T_{ref})\right)_{T=600}$$

$$= 16\left(-1.25\cdot10^{6} + 1500(600 - 300)\right)$$

$$H_{Pr} = -1.28\cdot10^{7}\ \text{J (per kg}_{F}\text{)}$$

$$HV = H_{R} - H_{Pr} = 2.645\cdot10^{7} - (-1.28\cdot10^{7})$$

$$\boxed{HV_{600} = 3.925\cdot10^{7}\ \text{J (per kg}_{F}\text{)}}$$

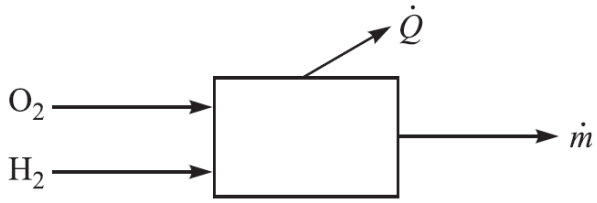
COMMENT: This ficticious fuel with simplified properties has a low HV (240,000 kJ/kg) compared to most real fuels (HV ~ 45,000 kJ/kg, cf. Table B.1).

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PROBLEM 2-40

Consider the combustion of hydrogen (H_2) with oxygen (O_2) in a steadyflow reactor as shown in the sketch. The heat loss through the reactor walls per unit mass flow $\left(\dot{Q}/\dot{m}\right)$ is 187 kJ/kg. The equivalence ratio is 0.5 and the pressure is 5 atm.



For a zero-Kelvin reference state, approximate enthalpies-of-formation are

$$\bar{h}^o_{f,H_2}(0) = \bar{h}^o_{f,O_2}(0) = 0 \text{ KJ/mol},$$
$$\bar{h}^o_{f,H_2O}(0) = -238{,}000 \text{ KJ/mol},$$
$$\bar{h}^o_{f,OH}(0) = -38{,}600 \text{ KJ/mol},$$

A. Determine the mean molecular weight of the combustion product gases in the outlet stream, assuming no dissociation.
B. For the same assumption as in part A, determine the mass fractions of the species in the outlet stream.
C. Determine the temperature in the product stream at the reactor outlet, again assuming no dissociation. Furthermore, assume that all species have the same constant molar specific heats, $\bar{c}_{p,i}$, equal to 40 kJ/kmol-K. The H_2 enters at 300 K and the O_2 at 800 K.
D. Now assume that dissociation occurs, but that the only minor product is OH. Write out all of the equations necessary to calculate the outlet temperature. List the unknowns in your equation set.

GIVEN: Steady-flow reactor with $H_2 - O_2$ @ $\Phi = 0.5$, P = 5 atm,

$\dot{Q}/\dot{m} = 187$ kJ/kg; zero-K reference state

$\bar{h}^o_{f,i}$s: $\bar{h}^o_{f,O_2} = \bar{h}^o_{f,H_2} = 0$

$\bar{h}^o_{f,H_2O} = -238{,}000$ kJ/kmol

$\bar{h}^o_{f,OH} = -38{,}600$ kJ/kmol

FIND: a) MW_{Pr} (w/o dissociation)

b) $Y_{i,Pr}$ (w/o dissociation)

c) T_{out} (w/o dissoc.) for $T_{in,H_2} = 300$ K, $T_{in,O_2} = 800$ K, all $\bar{C}_{Pi} = 40$ kJ/kmol-K

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d) Add OH to products & write equations needed to find $T_{ad.}$

SOLUTION:

a) $2H_2 + \frac{1}{\Phi} O_2 \rightarrow 2H_2O + xO_2$

O-balance: $\frac{2}{\Phi} = 2 + 2x;\ x = \frac{1}{\Phi} - 1 = \frac{1}{0.5} - 1 = 1$

$MW_{Pr} = \sum N_i\, MW_i / \sum N_i$

$= \frac{2(18.016) + 1(31.999)}{3}$ $\boxed{= 22,68 \text{ kg/kmol}}$

b) $Y_{O_2} = \chi_{O_2} \frac{MW_{O_2}}{MW_{Pr}} = \frac{N_{O_2}}{N_{Pr}} \frac{MW_{O_2}}{MW_{Pr}} = \frac{1}{3} \frac{31.999}{22.68}$

$\boxed{= 0.470}$

$\boxed{Y_{H_2O} = 1 - Y_{O_2} = 0.530}$

c) First law: $\dot{Q} - \dot{W}^{\circ} = \dot{m}(h_{Pr} - h_R)$

$\dot{Q}/\dot{m} + h_R = h_{Pr}$

$h_R = Y_{H_2} h_{H_2} + Y_{O_2} h_{O_2}$ or $h_R = \frac{\bar{h}_R}{MW_R} = \frac{\chi_{H_2} \bar{h}_{H_2} + \chi_{O_2} \bar{h}_{O_2}}{\chi_{H_2} MW_{H_2} + \chi_{O_2} MW_{O_2}}$

Reactants

	$\frac{\dot{N}}{2}$	χ	$\bar{h}$ kJ/kmol
H_2	2	0.5	$0 + 40\,(300 - 0) = 12,000$
O_2	2	0.5	$0 + 40\,(800 - 0) = 32,000$

$MW_R = 0.5\,(2.016) + 0.5\,(31.999) = 17.008$

$\bar{h}_R = 0.5(12000) + 0.5(32000) = 22,000$ kJ/kmol

$h_R = \frac{22,000}{17.0} = 1294$ kJ/kg

Products

	$\frac{N}{2}$	χ	$\bar{h}\ (=\bar{h}_f + C_P(T\text{-}0))$ kJ/kmol
H_2O	1	$0.66\overline{6}$	$(-238,000 + 40\ T_{Pr})$
O_2	1	0.333	$(0 + 40\ T_{Pr})$

$h_{Pr} = \frac{\sum \chi_i \bar{h}_i}{MW_{Pr}} = \frac{0.66\overline{6}(-238,000 + 40\ T_{Pr}) + 0.33\overline{3}\ (40\ T_{Pr})}{22.68}$

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$h_{Pr} = -6995.88 + 1.7637\ T_{Pr}$ ([=] kJ/kg)

Returning to first law: $\dot{Q}/\dot{m} + h_R = h_{Pr}$

$-187 + 1294 = -6995.88 + 1.7637\ T_{Pr}$

Solving for T_{Pr}:

$$\boxed{T_{Pr} = 4594\ \text{K}}$$

d) $$2H_2 + \frac{1}{\Phi} O_2 \rightarrow a\ H_2O + b\ O_2 + c\ OH$$

Element conservation: ratio of H-to-Q atoms in reactants equals H-to-O ratio in products, i.e.,

i) $$\frac{\#\text{H atoms}}{\#\text{O atoms}} = \frac{4}{4} = 1 = \frac{2\chi_{H_2O} + \chi_{OH}}{\chi_{H_2O} + 2\chi_{O_2} + \chi_{OH}}$$

ii) $$\chi_{OH} + \chi_{O_2} + \chi_{H_2O} = 1$$

Equilibrium: $H_2O + \frac{1}{2} O_2 \rightleftharpoons 2OH$

iii) $$\frac{\chi_{OH}^2\ (p/p^O)^2}{\chi_{H_2O}\ (p/p^O)\ \chi_{O_2}^{1/2}\ (p/p^O)^{1/2}} = \frac{\chi_{OH}}{\chi_{H_2O}\ \chi_{O_2}^{1/2}}\ (p/p^O)^{1/2} = K_P$$

where $$K_P = \exp(-\Delta G_T / R_u T)$$
$$= \exp\left[\frac{-(2\bar{g}_{OH}(T) - \bar{g}_{H_2O} - 0.5\ \bar{g}_{O_2}(T))}{R_u T}\right]$$

Eqns. i–iii define the product mixture composition, χ_{H_2O}, χ_{O_2}, & χ_{OH}. Knowing these, the first law is formulated as in part C:

iv) $$\dot{Q}/\dot{m} + h_R = h_{Pr}$$

The LHS of Eqn. iv is unchanged from part c. The RHS becomes

$$h_R = \frac{\bar{h}_{Pr}}{MW_{Pr}} = \frac{\chi_{H_2O}\bar{h}_{H_2O}(T) + \chi_{O_2}\bar{h}_{O_2}(T) + \chi_{OH}\bar{h}_{OH}(T)}{\chi_{H_2O}MW_{H_2O} + \chi_{O_2}MW_{O_2} + \chi_{OH}MW_{OH}}$$

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where

$$\bar{h}_{H_2O}(T) = \bar{h}^{o}_{f,H_2O} + \bar{c}_P(T - T_{ref})$$
$$\bar{h}_{O_2}(T) = \bar{h}^{o}_{f,O_2} + \bar{c}_P(T - T_{ref})$$
$$\bar{h}_{OH}(T) = \bar{h}^{o}_{f,OH} + \bar{c}_P(T - T_{ref}).$$

with the above substitutions into Eqn. iv, our equation set is complete: Eqns. i–iv with unknowns $\chi_{H_2O}, \chi_{O_2}, \chi_{OH}$, & T.

COMMENTS: Part d shows, in a simple manner, how dissociation of products is coupled to a first-law analysis.

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PROBLEM 2-41

Verify that the results given in Table 2.2 satisfy Eqns. 2.64 and 2.65 for the following conditions:

A. $T = 2000$ K, $P = 0.1$ atm.
B. $T = 2500$ K, $P = 100$ atm.
C. $T = 3000$ K, $P = 1$ atm.

GIVEN: The equilibrium reaction $CO_2 \leftrightarrow CO + \frac{1}{2}O_2$

FIND: Verify that the results of Table 2.2 satisfy Eqns. 2.64 and 2.65 for the following conditions:

a) T = 2000 K, P = 0.1 atm
b) T = 2500 K, P = 100 atm
c) T = 3000 K, P = 1 atm

ASSUMPTIONS: ideal gas behavior $(\chi_i = Pi/P)$

APPROACH: Calculate ΔG_T^o using Appendix A and compare with Table 2.2. Using ΔG_T^o, calculate K_P. Compare with the value of K_P calculated using the mole fractions listed in Table 2.2.

a) T = 2000 K, P = 0.1 atm

$$\Delta G_T^o = \left[\sum N_i \bar{g}_{f,i}^o\right]_P - \left[\sum N_i \bar{g}_{f,i}^o\right]_R$$

where N_i represents the stoichiometric coefficients of the equilibrium reaction

$$\Delta G_T^o = \left[N\bar{g}_f^o\right]_{CO} + \left[N\bar{g}_f^o\right]_{O_2} - \left[N\bar{g}_f^o\right]_{CO_2} = 1\bar{g}_{f_{CO}}^o + \frac{1}{2}\bar{g}_{f_{O_2}}^o - 1\bar{g}_{f_{CO_2}}^o$$

$$\Delta G_T^o = 1(-285948) + \tfrac{1}{2}(0) - 1(-396410) = \boxed{110462 \text{ kJ}} \text{ agrees with Table 2.2}$$

$$K_P = \exp\left[-\frac{\Delta G_T^o}{R_u T}\right] = \exp\left[\frac{-110462}{(8.315)(2000)}\right] = 1.304 \times 10^{-3}$$

$$K_P = \frac{\chi_{CO}\chi_{O_2}^{1/2}}{\chi_{CO_2}}\left(\frac{P}{P_O}\right)^{1/2} = \frac{(0.0315)(0.0158)^{1/2}}{(0.9527)}\left(\frac{0.1 \text{ atm}}{1 \text{ atm}}\right)^{1/2} = 1.314 \times 10^{-3}$$

2 methods of determining K_P match so the data in Table 2.2 satisfy Eqn. 2.65

b) T = 2500 K, P = 1 atm

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$$\Delta G_T^o = 1\bar{g}_{f_{CO}}^o + \tfrac{1}{2}\bar{g}_{f_{O_2}}^o - 1\bar{g}_{f_{CO_2}}^o = 1(-327245) + \tfrac{1}{2}(0) - 1(-396152) = 68907 \text{ kJ}$$

$$K_P = \exp\left[\frac{-\Delta G_T^o}{R_u T}\right] = \exp\left[\frac{-68907}{(8.315)(2500)}\right] = 0.03634$$

$$K_P = \frac{\chi_{CO}\chi_{O_2}^{1/2}}{\chi_{CO_2}}\left(\frac{P}{P_O}\right)^{1/2} = \frac{(0.0289)(0.0145)^{1/2}}{(0.9566)}(100)^{1/2} = 0.03638$$

The value of ΔG_T^o calculated here matches ΔG_T^o in Table 2.2 so Eqn. 2.64 is satisfied and the K_P calculated from ΔG_T^o matches the K_P determined from the mole fractions in Table 2.2 so Eqn. 2.65 is satisfied

c) T = 3000 K, P = 1 atm

$$\Delta G_T^o = 1\bar{g}_{f_{CO}}^o + \tfrac{1}{2}\bar{g}_{f_{O_2}}^o - 1\bar{g}_{f_{OCO_2}} = 1(-367684) + \tfrac{1}{2}(0) - 1(-395562) = 27878 \text{ kJ}$$

$$K_P = \exp\left[-\frac{\Delta G_T^o}{R_u T}\right] = \exp\left[-\frac{27878}{(8.315)(3000)}\right] = 0.32707$$

$$K_P = \frac{\chi_{CO}\chi_{O_2}^{1/2}}{\chi_{CO_2}}\left(\frac{P}{P_O}\right)^{1/2} = \frac{(0.3581)(0.1790)^{1/2}}{(0.4629)}\left(\frac{1 \text{ atm}}{1 \text{ atm}}\right)^{1/2} = 0.32730$$

Again, these calculations show that the results in Table 2.2 satisfy Eqns. 2.64 and 2.65

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PROBLEM 2-42

Consider the equilibrium reaction $O_2 \Leftrightarrow 2O$ in a closed vessel. Assume the vessel contains 1 mol of O_2 when there is no dissociation. Calculate the mole fractions of O_2 and O for the following conditions:

A. $T = 2500$ K, $P = 1$ atm.
B. $T = 2500$ K, $P = 3$ atm.

GIVEN: A closed vessel containing 1 kmole of O_2 when there is no dissociation

FIND: The mole fractions χ_O and χ_{O_2} at the following conditions:

a) T = 2500 K, P = 1 atm
b) T = 2500 K, P = 3 atm

ASSUMPTIONS: Ideal gas, system is in chemical equilibrium

APPROACH: There are two unknowns (χ_O and χ_{O_2}) so 2 equations must be used. The first is the definition of K_P and the second is $\sum \chi_i = 1$

a) T = 2500 K $\quad O_2 \leftrightarrow 2O$

$$\Delta G_T^o = \left[\overline{Ng}_{f,T}^o\right]_O - \left[\overline{Ng}_{F,T}^o\right]_{O_2} = 2(88203) - 0 = 176406 \text{ kJ/kmole}$$

$$K_P = \exp\left[\frac{-\Delta G}{R_u T}\right] = \exp\left[-\frac{(176406)}{(8.315)(2500)}\right] = 206.3\times10^{-6}$$

$$K_P = \frac{\chi_O^2}{\chi_{O_2}}\left(P/P_O\right) = 206.3\times10^{-6} \leftarrow \text{FIRST EQUATION}$$

From $\sum \chi_i = 1 = \chi_O + \chi_{O_2}$

$$\chi_{O_2} = 1 - \chi_O \leftarrow \text{SECOND EQUATION}$$

substituting the second equation into the first and rearranging yields

$$\left(P/P_O\right)\chi_O^2 + K_P\chi_O - K_P = 0 \qquad \text{quadratic equation}$$

solving for χ_o $\quad \chi_o = \dfrac{-K_P \pm \sqrt{K_P^2 + 4\left(P/P_O\right)(K_P)}}{2\left(P/P_O\right)}$ Note: Only + yields physically realistic result

$$\text{T} = 2500 \text{ K, P} = 1 \text{ atm: } K_P = 206.3\times10^{-6},\ P/P_O = 1 \rightarrow \boxed{\chi_O = 0.0143,\ \chi_{O_2} = 1 - \chi_O = 0.9857}$$
$$\text{T} = 2500 \text{ K, P} = 3 \text{ atm: } K_P = 206.3\times10^{-6},\ P/P_O = 3 \rightarrow \boxed{\chi_O = 0.00826,\ \chi_{O_2} = 1 - \chi_O = 0.9917}$$

COMMENTS: Note how this system follows the principle of Le Châtelier. Increasing the system pressure causes the system to shift towards more O_2, thereby reducing the number of moles in the system $\left(N_O + N_{O_2}\right)$

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PROBLEM 2-43

Repeat problem 2.42A, but add 1 mol of an inert diluent to the mixture, e.g., argon. What is the influence of the diluent? Discuss.

GIVEN: The equilibrium reaction $O_2 \leftrightarrow 2O$ in a closed vessel containing 1 kmole of inert diluent and 1 kmole of O_2 with no dissociation

FIND: The mole fractions χ_O and χ_{O_2}. Compare these results with those found in problem 2.22. Discuss.

ASSUMPTIONS: ideal gas behavior, system is in chemical equilibrium, inert diluent (Ar) does not play a role in the equilibrium reaction

APPROACH: Calculate ΔG_T^o and K_P. Using the definition of K_P and conservation of elements, solve for the two unknowns χ_O and χ_{O_2}

conservation of elements:	O_2	O	Ar
	1	0	1
Initial equilibrium shift	$-Z$	$+2Z$	0
final state	$1-Z$	$2Z$	1 ← # of moles

mole fractions: $\chi_{O_2} = \dfrac{N_{O_2}}{N_{TOT}} = \dfrac{1-Z}{2+Z}, \qquad \chi_O = \dfrac{N_O}{N_{TOT}} = \dfrac{2Z}{2+Z}$

at T = 2500 K: Note: Ar is not part of the equilibrium reaction

$$\Delta G_T^o = \left[N\bar{g}_f^o\right]_O - \left[N\bar{g}_f^o\right]_{O_2} = 2[88203]_O - 1[0] = 176406 \text{ kJ/kmole}$$

$$K_P = \exp\left[-\frac{\Delta G_T^o}{R_u T}\right] = \exp\left[-\frac{176406}{(8.315)(2500)}\right] = 206.3 \times 10^{-6}$$

$$K_P = \frac{\chi_o^2}{\chi_{o_2}}\left(\frac{P}{P_o}\right) = 206.3 \times 10^{-6}$$

substituting f χ_O and χ_{O_2} in terms of Z

$$K_P = \frac{[2Z/(2+Z)]^2}{[(1-Z)/2+Z]} = 206.6 \times 10^{-6} \text{ for } P = P_o = 1 \text{ atm}$$

$$(4+K_P)Z^2 + K_P Z - 2K_P = 0 \rightarrow Z = \frac{-K_P \pm \sqrt{K_P^2 - 4(4+K_P)(-2K_P)}}{2(4+K_P)}$$

for physically realistic results

$$Z = \frac{-K_P \oplus \sqrt{}}{2(4+K_P)}$$

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Solving for Z: $Z = 0.0101$

$$\chi_{O_2} = \frac{1-Z}{2+Z} = \frac{1-0.0101}{2+0.0101} = 0.492 \qquad \boxed{\chi_{O_2} = 0.492}$$

$$\chi_{O} = \frac{2Z}{2+Z} = \frac{2(0.0101)}{2+0.0101} = 0.01 \qquad \boxed{\chi_{o} = 0.01}$$

$$\chi_{Ar} = \frac{1}{2+Z} = \frac{1}{2+0.0101} = 0.4974 \qquad \boxed{\chi_{Ar} = 0.4794}$$

To compare the results of problem 2-22 with the above results, we must look at number of moles instead of mole fractions since there is argon present in this problem (i.e., even with no dissociation of O_2 to form O, the mole fractions would be different despite the fact that there would be 1 kmole of O_2 present in both problems)

	Problem 2-22	Problem 2-23
O:	$N_o = \chi_o N_{TOT} = 0.014$	$N_o = \chi_o N_{TOT} = \chi_o(2+Z) = 0.01(2.01) = 0.02$
O:	$N_{o_2} = \chi_{o_2} N_{TOT} = 0.9926$	$N_{o_2} = \chi_{o_2}(2+Z) = 0.492(2.01) = 0.989$

COMMENTS: Note that the diluent does not affect ΔG_T^o or the formulation of K_P in terms of mole fractions since it does not participate in the equilibrium reaction. The diluent does, however, affect the system by altering how the mole fractions are defined. For example, the total number of moles in problem 2-22 could be written as $1 + Z$ while in this problem $N_{TOT} = 2 + Z$ due to the diluent. This result is consistent with Le Châtelier's principle in that reducing the partial pressures (with the diluent) results in more dissociation.

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PROBLEM 2-44

Consider the equilibrium reaction $CO_2 \Leftrightarrow CO + \frac{1}{2}O_2$. At 10 atm and 3000 K, the equilibrium mole fractions of a particular mixture of CO_2, CO, and O_2 are 0.6783, 0.2144, and 0.1072, respectively. Determine the equilibrium constant K_p for this situation.

GIVEN: At P = 10 atm, T = 300 K:

$\chi_{CO_2} = 0.6783, \chi_{CO} = 0.2144, \chi_{O_2} = 0.1072$

FIND: K_P for $CO_2 \; f \;\; CO + 1/2\, O_2$

ASSUMPTIONS: ideal gas mixture

SOLUTION: This is a straightforward application of the definition of K_P (Eqn. 2.65):

$$K_P = \frac{(P_{co}/P^O)(P_{O_2}/P^O)^{1/2}}{(P_{CO_2}/P^O)} = \frac{\chi_{CO}\,\chi_{O_2}{}^{1/2}}{\chi_{CO_2}}(P/P^O)^{1/2}$$

$$K_P = \frac{0.2144\,(0.1072)^{1/2}}{0.6783}\left(\frac{10}{1}\right)^{1/2} = 0.1035\,(3.1623)$$

$$\boxed{K_P = 0.3273}$$

COMMENT: Note the influence of the total pressure on the result. Note also that, since the temperature is given, we could have calculated K_p from $\exp(-\Delta G_T/R_u T)$, a more complicated approach. From Appendix A Tables 1, 2, & 11: $\Delta G_{3000} = -367,685 + \frac{1}{2}(0) - (-395,562) = 27,877$ kJ/kmol; $Kp = \exp(-27877/8.315(3000)) = 0.327$, the same result as above.

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PROBLEM 2-45

Consider the equilibrium reaction $H_2O \Leftrightarrow H_2 + \frac{1}{2}O_2$. At 0.8 atm, the mole fractions are $\chi_{H_2O} = 0.9,\ \chi_{H_2} = 0.03, \text{and}\ \chi_{O_2} = 0.07$. Determine the equilibrium constant K_p for this situation.

GIVEN: At P = 0.8 atm, H_2O, H_2, O_2 mixture has the composition:
$\chi_{H_2O} = 0.9, \chi_{H_2} = 0.03, \text{and} \chi_{O_2} = 0.07$.

FIND: K_P for H_2O *f* $H_2 + ½O_2$

ASSUMPTIONS: ideal gas mixture

SOLUTION: This is a straightforward application of the definition of K_P (Eqn. 2.65):

$$K_p = \frac{(P_{H_2}/P^o)(P_{o_2}/P^o)^{1/2}}{(P_{H_2O}/P^o)} = \frac{\chi_{H_2}\,\chi_{O_2}{}^{1/2}}{\chi_{H_2O}}(P/P^o)^{1/2}$$

$$= \frac{0.03(0.07)^{1/2}}{0.9}\left(\frac{0.8}{1}\right)^{1/2} = 0.008819\,(0.8944)$$

$$\boxed{K_P = 0.00789}$$

COMMENT: Note how the total pressure enters into this calculation.

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PROBLEM 2-46

Consider the equilibrium reaction $H_2O + CO \Leftrightarrow CO_2 + H_2$ at a particular temperature *T*. At *T*, the enthalpies-of-formation of each species are as follows:

$\bar{h}^o_{H_2O} = -251,7000$ kJ/kmol, $\bar{h}^o_{f,CO_2} = -396,000$ kJ/kmol,

$\bar{h}^o_{f,CO} = -118,700$ kJ/kmol, $\bar{h}^o_{f,H_2} = 0.$

A. What is the effect of pressure on the equilibrium? Explain.

B. What is the effect of temperature on the equilibrium? Explain (calculation required).

GIVEN: Water-gas shift reaction @ T & enthalpies-of-formation at T:

$$\left.\begin{aligned} \bar{h}^0_{f,H_2O} &= -251,700 \\ \bar{h}^0_{f,CO} &= -118,700 \\ \bar{h}^0_{f,CO_2} &= -396,600 \\ \bar{h}^0_{f,H_2} &= 0 \end{aligned}\right\} \text{ kJ/kmol}$$

FIND: a) Effect of P on equilibrium?

b) Effect of T on equilibrium?

ASSUMPTIONS: ideal gas behavior

SOLUTION: a) $K_P(T) = \dfrac{\chi_{CO_2}\chi_{H_2}}{\chi_{H_2O}\,\chi_{CO}}(P/P^O)^{1+1-1-1}$

The net exponent of P/P^O is zero. There is *no* effect of P.

b) $\Delta H_R = \bar{h}^o_{f,CO_2} + \bar{h}^o_{f,H_2} - \bar{h}^o_{f,H_2O} - \bar{h}^o_{f,CO}$

$= -396,600 + 0 - (-251,700) - (-118,700)$

$\Delta H_R = -26,200 \Rightarrow$ exothermic @ T

Le Châtelier's law thus indicates that the reaction will shift to the reactants side with increasing T: $H_2O + CO \leftarrow CO_2 + H_2$

COMMENT: This problem demonstrates the application of Le Châtelier's principle.

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PROBLEM 2-47

Calculate the equilibrium composition for the reaction $H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O$ when the ratio of the number of moles of elemental hydrogen to elemental oxygen is unity. The temperature is 2000 K, and the pressure is 1 atm.

GIVEN: The reaction $H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$ and a ratio of moles of elemental H to elemental O equal to one

FIND: The equilibrium composition at T = 2000 K and P = 1 atm

ASSUMPTIONS: The above reaction is the only reaction involving H & O

APPROACH: Evaluate ΔG_T^o, determine K_P, and using the definition of K_P and conservation of elements, determine χ_{H_2} χ_{O_2} & χ_{H_2O}

Evaluation of ΔG_T^o : $\Delta G_T^o = 1\,(g_{f,T}^o)_{H_2O} - 1\,(g_{f,T}^o)_{H_2} - \frac{1}{2}(g_{f,T}^o)_{O_2}$

Using Appendix A $\Delta G_{2000}^o = 1\,(-135643) - 1\,(0) - \frac{1}{2}(0) = -135643$ kJ/kmol

$$K_P = \exp\left[-\frac{\Delta G_T^o}{R\,T}\right] = \exp\left[\frac{135643}{(8.315)(2000)}\right] = 3.486\times10^3$$

In terms of χ_i :

$$K_P = \frac{\chi_{H_2O}}{\chi_{H_2}\,\chi_{O_2}^{\frac{1}{2}}}\left(\frac{P}{P^o}\right)^{-\frac{1}{2}} \qquad (1)$$

Conservation of elements:

$$\frac{\#H}{\#O} = 1 = \frac{2\chi_{H_2O} + 2\chi_{H_2}}{\chi_{H_2O} + 2\chi_{O_2}} \qquad (2)$$

and by definition:

$$\Sigma\chi_i = 1 = \chi_{H_2o} + \chi_{H_2} + \chi_{O_2} \qquad (3)$$

Solving (2) and (3) for χ_{H_2} & χ_{H_2O} in terms of χ_{O_2} and substituting into (1):

$$\left.\begin{aligned}\chi_{H_2} &= 3\chi_{O_2} - 1\\ \chi_{H_2O} &= 2 - 4\chi_{O_2}\end{aligned}\right\} \quad K_P = \frac{2 - 4\chi_{O2}}{(3\chi_{O_2} - 1)(\chi_{O_2})^{1/2}}\left(\frac{P}{P_O}\right)^{-1/2}$$

Solving for χ_{O_2} by trial & error:

with $P = P_o = 1$ atm

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$$\chi_{O_2} = 0.3334$$
$$\chi_{H_2} = 3\chi_{O_2} - 1 = 0.0003$$
$$\chi_{H_2O} = 2 - 4\chi_{O_2} = 0.6662$$

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PROBLEM 2-48

Calculate the equilibrium composition for the reaction $H_2O \Leftrightarrow H_2 + \frac{1}{2}O_2$ when the ratio of the number of moles of elemental hydrogen to elemental oxygen, *Z*, is varied. Let $Z = 0.5$, 1.0, and 2.0. The temperature is 2000 K, and the pressure is 1 atm. Plot your results and discuss. *Hint:* Use spreadsheet software to perform your calculations.

GIVEN: Equilibrium: H_2O *f* $H_2 + \frac{1}{2}O_2$ @ 2000 K, 1 atm

FIND: $\chi_{H_2}, \chi_{O_2}, \chi_{H_2O}$ when $\frac{\#\text{H-atoms}}{\#\text{O-atoms}}$ is 0.5, 1 & 2

ASSUMPTIONS: ideal gas behavior

SOLUTION: Apply element conservation:

$$\frac{\#\text{H-atoms}}{\#\text{O-atoms}} (\equiv Z) = \frac{2\chi_{H_2O} + 2\chi_{H_2}}{2\chi_{O_2} + \chi_{H_2O}}$$

Rearranging,

$Z\left(2\chi_{O_2} + \chi_{H_2O}\right) - 2\chi_{H_2O} - 2\chi_{H_2}$, or

i) $$(Z-2)\chi_{H_2O} + 2Z\chi_{O_2} - 2\chi_{H_2} = 0$$

ii) $$\chi_{H_2O} + \chi_{O_2} + \chi_{H_2} - 1 = 0$$

Apply equilibrium:

iii) $$\frac{\chi_{H_2}\ \chi_{O_2}^{1/2}}{\chi_{H_2O}} \left(\frac{P}{P^o}\right)^{1/2} = K_P = \exp\left(\frac{-\Delta G_T^o}{R_u T}\right)$$

use i) & ii) to eliminate χ_{H_2} & express $\chi_{H_2O} = f\left(\chi_{O_2}\right)$.

iv) $$\chi_{H_2O} = \frac{2}{Z} - \frac{2(Z+1)}{Z}\chi_{O_2}$$

Similarly, use i) & ii) to express χ_{H_2} as function of χ_{O_2}:

v) $$\chi_{H_2} = \frac{Z-2}{Z} + \frac{Z+2}{Z}\chi_{O_2}$$

Now substitute iv) & v) into iii):

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$$\left(\frac{Z-2}{Z}\right)\left(\frac{P}{P^o}\right)^{1/2}\chi_{O_2}{}^{1/2}+\left(\frac{Z+2}{Z}\right)\left(\frac{P}{P^o}\right)^{1/2}\chi_{O_2}^{3/2}+\frac{2(Z+1)}{Z}K_P\ \chi_{O_2}$$

$$-\frac{2K_P}{Z}=0\equiv f(O_2) \qquad \text{vi)}$$

To solve the above transcendental equation for χ_{O_2}, we apply the Newton-Raphson iteration method:

$$\text{vii)} \qquad \chi_{O_2}^{new}=\chi_{O_2}^{old}-\frac{f(\chi_{O_2}^{old})}{f'(\chi_{O_2}^{old})}$$

where the derivative $f'\left(=df/d\chi_{O_2}\right)$ is

$$\text{viii)} \qquad f'\left(\chi_{O_2}\right)=\frac{1}{2}\left(\frac{Z-2}{Z}\right)\left(\frac{P}{P^o}\right)^{1/2}\chi_{O_2}{}^{-1/2}+\frac{3}{2}\left(\frac{Z+2}{Z}\right)\left(\frac{P}{P^o}\right)^{1/2}\chi_{O_2}^{1/2}+\frac{2(Z+1)}{Z}K_P$$

We evaluate $\Delta G_T^o=\left[\overline{g}_{f,H_2}^o+\frac{1}{2}\overline{g}_{f,O_2}^o-\overline{g}_{f,H_2O}^o\right]_{T=2000}$

$$=0+\tfrac{1}{2}(0)-(-135{,}643)=+135{,}643\ \text{kJ/kmol}$$

$$K_P=\exp\left[\frac{-\Delta G_T^o}{R_uT}\right]=\exp\left[\frac{-135{,}643}{8.315(2000)}\right]$$

$$K_P=2.86857\cdot10^{-4}$$

Eqn. vii) was applied iteratively in a spreadsheet to obtain the following results:

Z	χ_{O_2}	χ_{H_2}	χ_{H_2O}
0.5	0.6000	0.000148	0.39982
1.0	0.3334	0.00033	0.6662
2.0	0.00273	0.00545	0.99182

COMMENT: As the #H-atoms to #O-atoms increases, both χ_{H_2} and χ_{H_2O} increase. For Z = 2, χ_{H_2O} is nearly unity, i.e., nearly all of the H and O atoms, in a 2:1 ratio, are contained in the water.

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PROBLEM 2-49

Calculate the equilibrium composition for the reaction $H_2O \Leftrightarrow H_2 + \frac{1}{2}O_2$ when the ratio of the number of moles of elemental hydrogen to elemental oxygen, Z, is fixed at $Z = 2.0$, while the pressure is varied. Let $P = 0.5$, 1.0, and 2.0 atm. The temperature is 2000 K. Plot your results and discuss. *Hint:* Use spreadsheet software to perform your calculations.

GIVEN: Equilibrium reaction $H_2O\ f\ \ H_2 + \frac{1}{2}O_2$ @ T = 2000 K

$$\frac{\#\text{mol H}}{\#\text{mol O}} = 2\ (\equiv Z)$$

FIND: χ_{H_2}, χ_{O_2}, χ_{H_2O} for a) P = 0.5 atm, b) P = 1 atm, c) P = 2 atm

ASSUMPTIONS: ideal gas behavior

SOLUTION: The spreadsheet developed in problem 2-48 is used here w/o any changes other than, now, P is varied, while Z is fixed.

P_{atm}	χ_{O_2}	χ_{H_2}	χ_{H_2O}
0.5	0.00343	0.00686	0.98971
1.0	0.00273	0.00545	0.99182
2.0	0.00217	0.00433	0.99350

COMMENTS: As expected, the dissociation of H_2O decreases as the pressure increases. At 2000 K, we expect that other dissociation species should be included in the analysis, in particular, OH, O, and H.

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PROBLEM 2-50

Reformulate problem 2.47 to include the species OH, O, and H. Identify the number of equations and the number of unknowns. They should, of course, be equal. Do not solve your system.

GIVEN: The species H_2, O_2, OH, O, H and H_2O

FIND: The solution formulation, indicating the number of unknowns and the equations that will be used to find the unknowns.

ASSUMPTIONS: ideal gas behavior, system in chemical equilibrium

APPROACH: There are 6 species and consequently 6 unknowns. Therefore there must be 6 equations to find a solution. One equation comes from conservation of elements, one from $\sum \chi_i = 1$, and the other four from the definition of equilibrium constants K_P

Conservation of elements: $$\frac{\#\,H_{atoms}}{\#\,O_{atoms}} = \frac{2\,\chi_{H_2} + \chi_{OH} + \chi_H + 2\,\chi_{H_2O}}{2\,\chi_{O_2} + \chi_{OH} + \chi_O + \chi_{H_2O}} = Z \qquad (1)$$

Summation of χ_i: $$\sum \chi_i = \chi_{H_2} + \chi_{O_2} + \chi_{OH} + \chi_O + \chi_{H_2O} = 1 \qquad (2)$$

Equilibrium reactions:

$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$ $$K_{PH_2O} = \exp\left[-\frac{\Delta G_T^O}{R_u T}\right]_{H_2O} = \frac{\chi_{H_2O}}{\chi_{H_2}\,\chi_{O_2}^{1/2}}\left(\frac{P}{P_O}\right)^{-1/2} \qquad (3)$$

$H_2 \leftrightarrow 2H$ $$(K_P)_H = \exp\left[-\frac{\Delta G_T^O}{R_u T}\right]_H = \frac{\chi_H^{\,2}}{\chi_{H_2}}\left(\frac{P}{P_O}\right) \qquad (4)$$

$O_2 \leftrightarrow 2O$ $$(K_P)_O = \exp\left[-\frac{\Delta G_T^O}{R_u T}\right]_O = \frac{\chi_O^{\,2}}{\chi_{O_2}}\left(\frac{P}{P_O}\right) \qquad (5)$$

$H + O \leftrightarrow OH$ $$(K_P)_{OH} = \exp\left[-\frac{\Delta G_T^O}{R_u T}\right]_{OH} = \frac{\chi_{OH}}{\chi_H\,\chi_O}\left(\frac{P}{P_O}\right)^{-1} \qquad (6)$$

Equations 1–6 can be solved to find the six unknowns:

$\chi_{H_2}, \chi_{O_2}, \chi_{OH}, \chi_O, \chi_H, \chi_{H_2O}$

COMMENTS: Note that other equilibrium reactions involving the species of interest could have been chosen for equations 3–6. For example, the equilibrium reactions $OH + H \leftrightarrow H_2O$ or $\frac{1}{2}H_2 + OH \leftrightarrow H_2O$ would have been equally valid choices.

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PROBLEM 2-51

Use STANJAN or other appropriate software to calculate the complete equilibrium for the H–O system using the conditions and atom constraints given in problem 2.47.

GIVEN: An H-O system containing one mole each of elemental hydrogen and oxygen at a temperature of 2000 K and pressure of 1 atm

FIND: The complete equilibrium of the system

APPROACH: Using STANJAN with the appropriate inputs

```
Computed properties

Independent atom       population       element potential

       H             1.00000000E+00          -13.7382

       O             1.00000000E+00          -14.9286
Products at T = 2000.00 K P = 1.000E+00 atmospheres

     species       mol fraction    mol fraction    mass fraction       mols*
                   in the phase     in mixture      in mixture

phase 1: molal mass = 22.635 kg/kmol

 H               .29482E-04       .29482E-04  .13129E-05       2.21525E-05
 HO              .58544E-02       .58544E-02  .43988E-02       4.39892E-03
 H2              .33139E-03       .33139E-03  .29515E-04       2.48999E-04
 H2O             .66217E+00       .66217E+00  .52704E+00       4.97540E-01
 O               .38202E-03       .38202E-03  .27003E-03       2.87042E-04
 O2              .33124E+00       .33124E+00  .46826E+00       2.48887E-01

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 22.635 kg/kmol

 T = 2000.00 K             P = 1.0133E+05 Pa         V = 7.2503E+00 m**3/kg
 U =-4.7862E+06 J/kg       H =-4.0516E+06 J/kg       S = 1.1988E+04 J/kg-K


Made  0  (T,P) iterations;  4 equilibrium iterations; v 3.95 IBM-PC
```

COMMENTS: Compare these results with those obtained in problem 2-24 to see the effects of incorporating the additional species H, O, and OH.

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PROBLEM 2-52

For the conditions given below, list from highest to lowest the mole fractions of CO_2, CO, H_2O, H_2, OH, H, O_2, O, N_2, NO, and N. Also, give approximate values.

A. Propane–air constant-pressure combustion products at their adiabatic flame temperature for $\Phi = 0.8$.
B. As in part A, but for $\Phi = 1.2$.
C. Indicate which species may be considered major and which minor in parts A and B.

GIVEN: Propane-air combustion products at 1 atm

FIND: The approximate mole fractions of CO_2, CO, H_2O, H_2, H, OH, O_2, O, N_2, NO and N for the following conditions. List the species from highest to lowest mole fraction.

a) $\phi = 0.8$, $T = T_{ad}$

b) $\phi = 1.2$, $T = T_{ad}$

ASSUMPTIONS: The products are in chemical equilibrium

APPROACH: Use HPFLAME code with $H_{Reactants} = -103{,}847$ kJ/kmole-fuel

SOLUTION: $\phi = 0.8$ $T_{ad} =$ K $\phi = 1.2$, $T_{ad} =$ K

	Species	χ	Species	χ
	N_2	0.737	N_2	0.69
	H_2O	0.125	H_2O	0.155
	CO_2	0.094	CO_2	0.079
	O_2	0.038	CO	0.054
			H_2	0.020
minor species	NO	3500 ppm		
	OH	1800 ppm	OH	860 ppm
	CO	890 ppm	H	800 ppm
	H_2	250 ppm	NO	240 ppm
	O	176 ppm	O_2	77 ppm
	H	34 ppm	O	20 ppm
	N	0.14 ppb	N	1 ppb

COMMENT: Note the relatively large concentration of CO for $\phi = 1.2$ and NO for $\phi = 0.8$.

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Problem Title: PROBLEM 2-52 PART A

Data below are as read from the input file. Compare with INPUT.HP. If they do not agree, your input data have not been entered correctly.

CARBON ATOMS	3.0
HYDROGEN ATOMS	8.0
OXYGEN ATOMS	0.0
NITROGEN ATOMS	0.0
EQUIVALENCE RATIO	0.800
TEMPERATURE (K) guess	2000.0
PRESSURE (Pa)	101325.0
ENTHALPY OF REACTANTS (kJ/kmol fuel)	-103847.0

FLAME TEMP. & COMBUSTION PRODUCTS PROPERTIES

Flame Temperature [K] =	2042.03
Mixture Enthalpy [J/kg] =	-0.1151E+06
Mixture Specific Heat, Cp [J/kg-K] =	0.160011E+04
Specific Heat Ratio, Cp/Cv =	1.2282
Mixture Molecular Weight [kg/kmol] =	28.3900
Moles of Fuel per Mole of Products =	0.03146029

The mole fractions of the product species are:

H:	0.00003419	O:	0.00017639	N:	0.00000000
H2:	0.00025351	OH:	0.00180270	CO:	0.00088887
NO:	0.00372180	O2:	0.03750533	H2O:	0.12466922
CO2:	0.09349201	N2:	0.73745598		

Problem Title: PROBLEM 2-52 PART B

Data below are as read from the input file. Compare with INPUT.HP. If they do not agree, your input data have not been entered correctly.

CARBON ATOMS	3.0
HYDROGEN ATOMS	8.0
OXYGEN ATOMS	0.0
NITROGEN ATOMS	0.0
EQUIVALENCE RATIO	1.200
TEMPERATURE (K) guess	2000.0
PRESSURE (Pa)	101325.0
ENTHALPY OF REACTANTS (kJ/kmol fuel)	-103847.0

FLAME TEMP. & COMBUSTION PRODUCTS PROPERTIES

Flame Temperature [K] =	2201.09
Mixture Enthalpy [J/kg] =	-0.1685E+06
Mixture Specific Heat, Cp [J/kg-K] =	0.166262E+04
Specific Heat Ratio, Cp/Cv =	1.2304
Mixture Molecular Weight [kg/kmol] =	27.1613
Moles of Fuel per Mole of Products =	0.04407123

The mole fractions of the product species are:

H:	0.00080465	O:	0.00002376	N:	0.00000001
H2:	0.02031565	OH:	0.00085746	CO:	0.05358114
NO:	0.00024014	O2:	0.00007722	H2O:	0.15513821
CO2:	0.07863255	N2:	0.69032921		

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PROBLEM 2-53

Consider the adiabatic, constant-pressure combustion of *n*-decane ($C_{10}H_{22}$) with air for reactants at 298.15 K. Use HPFLAME (Appendix F) to calculate T_{ad} and species mole fractions for O_2, H_2O, CO_2, N_2, CO, H_2, OH, and NO. Use equivalence ratios of 0.75, 1.00, and 1.25 and evaluate each condition for three pressure levels: 1, 10, and 100 atm. Construct a table showing your results and discuss the effects of equivalence ratio and pressure on T_{ad} and the product mixture composition.

PROBLEM 2.53

Cl0H22	PHI = 0.75 P = 1 atm	PHI = 0.75 P = 10 atm	PHI = 0.75 P = 100 atm	PHI = 1.0 P = 1 atm	PHI = 1.0 P = 10 atm	PHI = 1.0 P = 100 atm
Tad(K)	1973.2	1978.5	1980.8	2276.6	2330.1	2365.6
h(J/kg)	-8.38E+04	-8.38E+04	-8.38E+04	-1.10E+05	-1.10E+05	-1.10E+05
Cp(J/kg-K)	1514	1462	1441	2287	1941	1728
Cp/Cv	1.239	1.248	1.252	1.163	1.188	1.210
MWmix	28.67	28.68	28.69	28.37	28.48	28.55
NF/Nprod mix	0.00962	0.00962	0.00963	0.01248	0.01253	0.01257
X H	1.43E-05	2.70E-06	4.93E-07	4.69E-04	1.49E-04	4.14E-05
X O	1.18E-04	3.89E-05	1.25E-05	3.42E-04	1.11E-04	3.08E-05
X N	5.25E-10	1.80E-10	5.87E-11	2.57E-08	1.46E-08	6.70E-09
X H2	1.13E-04	3.73E-05	1.20E-05	3.02E-03	1.75E-03	9.52E-04
X OH	1.26E-03	7.28E-04	4.15E-04	0.00320	0.00193	0.00105
X CO	4.55E-04	1.51E-04	4.88E-05	0.01380	0.00850	0.00481
X NO	3.51E-03	3.56E-03	3.59E-03	0.00263	0.00222	0.00171
X O2	0.04787	0.04784	0.04786	0.00634	0.00361	0.00186
X H2O	0.1051	0.1055	0.1057	0.1325	0.1351	0.1367
X CO2	0.0958	0.0961	0.0962	0.1111	0.1168	0.1209
X N2	0.7458	0.7461	0.7462	0.7267	0.7298	0.7319

Cl0H22	PHI = 1.25 P = 1 atm	PHI = 1.25 P = 10 atm	PHI = 1.25 P = 100 atm
Tad(K)	2179.0	2186.2	2188.5
h(J/kg)	-1.35E+05	-1.35E+05	-1.35E+05
Cp(J/kg-K)	1604	1525	1500
Cp/Cv	1.238	1.251	1.255
MWmix	27.26	27.28	27.28
NF/Nprod mix	0.0148	0.0148	0.0148
X H	7.60E-04	2.50E-04	8.02E-05
X O	1.40E-05	1.54E-06	1.59E-07
X N	8.01E-09	2.77E-09	9.00E-10
X H2	0.02331	0.02326	0.02325
X OH	6.09E-04	2.04E-04	6.57E-05
X CO	0.06847	0.06844	0.06844
X NO	1.54E-04	5.23E-05	1.69E-05
X O2	3.54E-05	3.93E-06	4.06E-07
X H2O	0.1385	0.1391	0.1393
X CO2	0.0793	0.0794	0.0794
X N2	0.6888	0.6893	0.6894

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COMMENTS:

1. At lean, stoichiometric, & rich conditions, the effect of increasing P is to suppress dissociation and, as a result, flame temperatures increase slightly. This effect on Tad is greatest at phi = 1, where temperatures are highest. We note that pressure has a negligible influence on the major species [CO2, H2O, N2, O2 (lean), and H2 (rich)], while the minor species mole fractions decrease greatly with pressure.

2. The most significant effect of equivalence ratio is the lower flame temperatures at rich & lean conditions. The CO2 mole fraction exhibits the same behavior as Tad, while the H2O mole fraction falls at lean conditions only, & shows a small increase at the rich condition. For the lean condition, H2 & CO are minor species & O2 a major species; at the rich condition, O2 is a minor species & H2 & CO are major species.

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PROBLEM 2-54

Consider the combustion products of decane ($C_{10}H_{22}$) with air at an equivalence ratio of 1.25, pressure of 1 atm, and temperature of 2200 K. Estimate the mixture composition assuming no dissociation except for the water-gas shift equilibrium. Compare with results of TPEQUIL.

GIVEN: The products of decane ($C_{10}H_{22}$)-air combustion at an equivalence ratio of 1.25

FIND: The mixture composition

ASSUMPTIONS: ideal gas behavior, only dissociation is the water-gas equilibrium shift, K_p is not a strong function of temperature in temperature range of interest

APPROACH: write the overall combustion equation, determine the A/F ratio, and solve for the species concentrations using conservation of elements and the equilibrium water-gas shift
$CO + H_2O \leftrightarrow CO_2 + H_2$

combustion equation: $C_x H_y + aO_2 + 3.76aN_2 \rightarrow bCO_2 + cCO + dH_2O + eH_2 + fO_2 + 3.76aN_2$

$$a = \frac{x + y/4}{\phi} = \frac{10 + 22/4}{1.25} = 12.4$$

Conservation of: b = will solve for using water-gas shift K_P

C $c = x - b$

O $d = 2a - 2b - c = 2a - b - x$

H $e = y/2 - d = y/2 - 2a + b + x$

$f = 0$ since combustion is fuel-rich

looking at water-gas equilibrium: $CO + H_2O \leftrightarrow CO_2 + H_2$

$$K_P = \frac{\chi_{CO_2}\,\chi_{H2}}{\chi_{CO}\,\chi_{H_2O}} = \frac{b \cdot e}{c \cdot d} \cdot \left(\frac{1/N_{TOT}}{1/N_{TOT}} \right)^2 = \frac{b \cdot e}{c \cdot d}$$

$$K_P = \frac{b(y/2 - a + b + x)}{(x - b)(2a - b - x)}$$

rearranging: $(1 - K_P)b^2 + (y/2 - 2a + 2aK_P + x)b + (x^2K_p - 2axK_P) = 0$

solving this quadratic equation for b:

$$b = \frac{(2a\,(K_P - 1) + x + y/2) \pm \sqrt{[2a\,(K_P - 1) + x + y/2]^2 - 4(K_P - 1)\,K_P(2ax - x^2)}}{2\,(K_P - 1)}$$

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where only the negative root yields a physically realistic value of b (i.e. b must be positive) the preceding equation can be solved by substituting for a, x, y and K_P (which must still be determined)

$$K_P = \exp\left[-\frac{\Delta G_T^O}{R_u T}\right]$$

guessing an approximate flame temperature of 2200 K and assuming that K_P doesn't vary much over a few hundred degrees K

$$\Delta G_T^O = (1)\bar{g}^o_{f\,CO_2} + (1)\bar{g}^o_{f\,H_2} - (1)\bar{g}^o_{f\,CO} - (1)\bar{g}^o_{f\,H_2O}$$

at 2200 K:

$$\Delta G_T^O = (-396346) + 0 - (-302576) - (-124030) = 30260$$

$$K_P = \exp\left[-\frac{\Delta G}{R_u T}\right] = \exp\left[-\frac{30260}{(8.315)(2200)}\right] = 0.19125$$

solving for b: a = 12.4, x = 10, y = 22, $K_P = 0.19125$

b = 5.361

c = x − b = 10 − 5.361 = 4.638

d = 2a − b − x = 2(12.4) − 5.361 − 10 = 9.439

e = y/2 − 2a + b + x = 11 − 2(12.4) + 5.361 + 10 = 1.561

Species	#Moles	χ
CO_2	5.36	0.079
CO	4.64	0.069
H_2O	9.44	0.140
H_2	1.56	0.023
N_2	46.62	0.690
	67.62	1.0

Check: $$K_P = \frac{\chi_{CO_2}\,\chi_{H_2}}{\chi_{CO}\,\chi_{H_2O}} = \frac{(0.0793)(0.0231)}{(0.0686)(0.1396)}$$

$K_P = 0.191$

COMMENTS: From this problem we see that dissociation plays an important role in determining the combustion products, and therefore, adiabatic flame temperature in a fuel-rich process. Compare these results to problems 2-19 and 2-20 where only slight dissociation decreased the adiabatic flame temperature by approximately 130 K.

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PROBLEM 2.55

A natural gas–fired industrial boiler operates with excess air such that the O_2 concentration in the flue gases is 2 percent (vol.), measured after removal of the moisture in the combustion products. The flue gas temperature is 700 K without air preheat.

A. Determine the equivalence ratio for the system assuming that the properties of natural gas are the same as methane.
B. Determine the thermal efficiency of the boiler, assuming that both the air and fuel enter at 298 K.
C. With air preheat, the flue gases are at 433 K (320°F) after passing through the air preheater. Again, determine the thermal efficiency of the boiler for both air and fuel entering at the preheater and burner, respectively, at 298 K.
D. Assuming premixed operation of the burners, estimate the maximum temperature in the combustion space (P = 1 atm) with air preheat.

GIVEN: A natural gas-fired industrial boiler operates with excess air such that the O_2 concentration in the flue gases is 2% (vol) after removal of the moisture in the combustion products. The flue gas temperature without air preheat is 700 K.

FIND: a) equivalence ratio of system assuming natural gas is CH_4

b) thermal efficiency of the boiler if air and fuel enter at 298 K (no air preheat)

c) with air preheat, the flue gases exit the preheater at 433 K. Determine the thermal efficiency if fuel enters at 298 K and air enters the preheater at 298 K

d) assuming premixed burner operation, estimate the maximum temperature in the combustion space with air preheat (P = 1 atm)

ASSUMPTIONS: no product dissociation, all energy lost by flue gases in preheater is transferred to air entering boiler, $\Delta KE \,\&\, \Delta PE$ are negligible, steady-state

APPROACH: Determine the A/F ratio from element conservation then use conservation of energy to determine the boiler efficiency

a) combustion equation: $CH_4 + aO_2 + 3.76aN_2 \rightarrow CO_2 + 2H_2O + bO_2 + 3.76aN_2$

in products: $\chi_{O_2} = 0.02 = \dfrac{N_{O_2}}{N_{CO_2} + \cancel{N_{H_2O}} + N_{O_2} + N_{N_2}} = \dfrac{b}{1 + b + 3.76a}$ (N_{H_2O} removed)

O atom conservation: $b = a - 1 \quad - \quad 1 = a - 2$

$\uparrow \quad \uparrow$

$CO_2 \quad H_2O$

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Note that the water is still included in the O-atom conservation even though it is not included in the measured O_2 mole fraction

Substituting b = a – 2 into the definition of the O_2 mole fraction

$$\chi_{O_2} = \frac{a-2}{1+(a-2)+3.76a} = \frac{a-2}{4.76a-1} = 0.02$$

$$a = 2.19 \rightarrow a = \frac{x + y/4}{\phi} \quad x = 1,\ y = 4$$

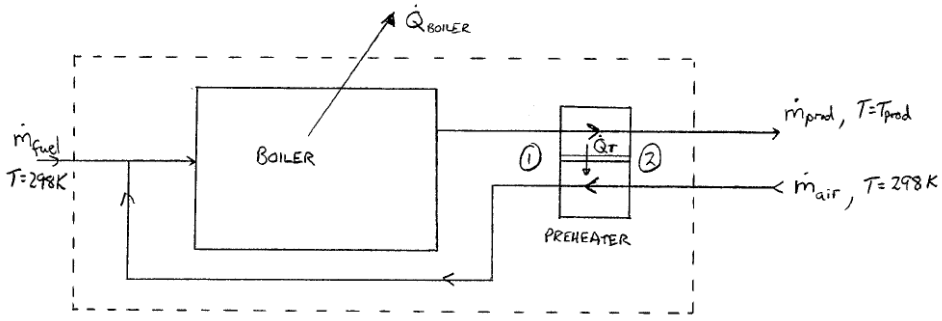
$$b = a - 2 = 0.19$$

$$A/F)_{molar} = 4.76a = 10.42 \qquad \boxed{\phi = 0.914}$$

b) defining the boiler thermal efficiency: $\eta = \dfrac{\dot{Q}_{BOILER}}{\dot{Q}_{MAX}}$

where $\dot{Q}_{BOILER}$ is the heat transferred by the boiler and $\dot{Q}_{max}$ represents the maximum possible heat transfer (products at 298 K)

schematic for first-law analysis:



first law for control volume:

$$\dot{Q} - \dot{W}_{cv} = [\Sigma \dot{N}_i \bar{h}_i]_{prod} - [\dot{N}\bar{h}]_{fuel} - [\dot{N}\bar{h}]_{air}$$

$$q = \frac{\dot{Q}}{\dot{N}_{fuel}} = \frac{1}{\dot{N}_{fuel}}\left[\sum \dot{N}_i \bar{h}_i\right]_{prod} - \bar{h}_{fuel} - \left(\frac{A}{F}\right)_{MOLAR} \bar{h}_{air}$$

$$q = \left[\sum \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_i\right]_{prod} - \bar{h}_{fuel} - \left(\frac{A}{F}\right)_{MOLAR} \bar{h}_{air}$$

$$\text{for } q_{max}\ (T_{prod} = 298\ k):\ \bar{h} = \bar{h}_f^o + (\bar{h} - \bar{h}_f^o) = \bar{h}_f^o$$

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$$\sum \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_i = 1\bar{h}^o_{f_{CO_2}} + 2\bar{h}^o_{f_{H_2O}} + b\bar{h}^o_{fO_2} + 3.76a\bar{h}^o_{fN_2} \leftarrow \text{from combustion equation}$$

$$= 1[-393546] + 2[-241847] + 0 + 0 = -877240 \text{ kJ/(kmole-fuel)}$$

so, $q_{max} = -877240 - [-74831]_{fuel} - 10.42(0)_{air} = -802409$ kJ/(kmole-fuel)

for no preheat $\left(T_{prod} = 700 \text{ K}\right) = \bar{h} = \bar{h}^o_f + \left(\bar{h} - \bar{h}^o_f\right)$

$$\sum \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_i = 1[-393546 + 17749]_{CO_2} + 2[-241847 + 14209] + 0.19[0 + 12503]_{O_2} + 8.23[0 + 11942]_{N_2}$$

$$= -730415 \text{ kJ/(kmole-fuel)}$$

$$q_{BOILER} = -730415 - [-74831] - 10.42(0) = -655584 \text{ kJ/kmole-fuel}$$

$$\eta = \frac{\dot{Q}_{BOILER}}{\dot{Q}_{max}} = \frac{q_{BOILER}}{q_{max}} = \frac{-655584}{-802409} = 0.82$$

$\boxed{\eta = 0.82}$ without preheat

c) with air preheat (T_{prod} = 433 K): $\bar{h} = \bar{h}^o_f + (\bar{h} - \bar{h}^o_f)$

$$q_{BOILER} = \sum \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_i - \bar{h}^o_f - A/F)_{MOLAR} \bar{h}_{air}$$

$$\sum \frac{\dot{N}_i}{\dot{N}_{fuel}} = 1[-393546 + 5421]_{CO_2} + 2[-241847 + 4609]_{H_2O} + 0.19[0 + 4043]_{O_2} + 8.23[0 + 3946]_{N_2}$$

$$= -829357 \text{ kJ/(kmole-fuel)}$$

$$q_{BOILER} = -829357 - [-74831]_{fuel} - 10.42(0)_{air} = -754526 \text{ kJ/kmole-fuel}$$

$$\eta = \frac{-754526}{-802409} = 0.94 \quad \boxed{\eta = 0.94} \text{ with preheat}$$

d) Estimate the maximum gas temperature in the combustion space with air preheat.

Assume that this temperature is the adiabatic flame temperature and that the flue gas temperature before entering the preheater is 700 K (i.e., the temperature of the flue gas exiting the boiler remains constant, regardless of whether air preheat is used)

first law for the preheater:

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$$\dot{H}_{in} = \dot{H}_{out}$$

$$\dot{H}_{P①} + \dot{H}_{air②} = \dot{H}_{P②} + \dot{H}_{air①}$$

$$H_{air①} = H_{P①} - H_{P②} + H_{air②}$$

per kmole of fuel burned:

$$a\bar{h}_{O_2} + 3.76a\bar{h}_{N_2} = \sum \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_{i\ 700K} - \sum \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_{i\ 433K} + \left[a\bar{h}^{\circ}_{O_2} + 3.76a\bar{h}^{\circ}_{N_2}\right]_{298K}$$

$$\underbrace{a\bar{h}_{O_2} + 3.76a\bar{h}_{N_2}}_{H_{air}\ \text{(kJ/kmole-fuel)}} = -730415 - \left[-829357\right] = 98942 \text{ kJ/(kmole-fuel)}$$

determine adiabatic flame temperature:

$H_P = H_R = H_{fuel} + H_{air}$

$H_P = [-74831 + 0] + 98942 \text{ kJ/kmole-fuel} = 24111 \text{ kJ/kmol-fuel}$

$$H_P = 1\bar{h}_{CO_2} + 2\bar{h}_{H_2O} + 0.19\bar{h}_{O_2} + 8.23\bar{h}_{N_2}$$
$$= 1\left[-393546 + \Delta h_{sens}\right]_{CO_2} + 2\left[-241847 + \Delta h_{sens}\right]_{H_2O} + 0.19\left[0 + \Delta h_{sens}\right]_{O_2} + 8.23\left[0 + \Delta h_{sens}\right]_{N_2}$$

$$\Delta h_{sens,CO_2} + 2\Delta h_{sens,H_2O} + 0.19\Delta h_{sens,O_2} + 8.23\Delta h_{sens,N_2} - 901351 \text{ kJ/kmol-fuel} = R$$

where $\Delta h_{sens} = \bar{h} - \bar{h}^{o}_{f}$ and $R = 0$ for correct solution

using Appendix A:

T (K)	R (kJ/kmole-fuel)	
2200	–97329	
2300	–50028	
2400	–2508	} Linear interpolation for R = 0 yields
2500	45233	$\boxed{T = 2405 \text{ k}}$

COMMENTS: Measured combustion product mole fractions are typically based on a "dry" mixture since H_2O is usually condensed out of the mixture before the mixture enters the measuring instruments. This prevents H_2O from condensing in the instruments and damaging them. Also note that the temperature in part d is the upper limit since dissociation is neglected and the combustion process is assumed to be adiabatic.

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PROBLEM 2-56

The equivalence ratio of a combustion process is often determined by extracting a sample of the exhaust gas and measuring the concentrations of major species. In a combustion experiment using isooctane (C_8H_{18}), continuous gas analyzers monitor the exhaust gas and measure a CO_2 concentration of 6 percent by volume and a CO concentration of 1 percent by volume. The sample gas is not dried before the measurements are made.

A. What is the equivalence ratio associated with this combustion process? Assume the process is overall lean.
B. If an O_2 analyzer was monitoring the exhaust gas, what would it be reading?

GIVEN: C_8H_{18} products: $\chi_{CO_2} = 0.06(\text{wet}); \chi_{CO} = 0.01(\text{wet})$

FIND: a) Φ b) χ_{O_2}

ASSUMPTIONS: All of the carbon in the fuel is converted to CO & CO_2 and all of the hydrogen to H_2O. $\Phi < 1$.

SOLUTION: $a = x + y/4 = 8 + 18/4 = 12.5$

$$z\left[C_8H_{18} + \frac{12.5}{\Phi}\left(O_2 + 3.76N_2\right)\right] \rightarrow 6CO_2 + 1CO + dH_2O + fO_2 + (z)3.76\left(\frac{12.5}{\Phi}\right)N_2$$

C-balance: $8Z = 6 + 1$ (RHS $\equiv$ 100 kmoles)

$$Z = 7/8$$

H-balance: $\frac{7}{8}/8 = 2d \Rightarrow d = \frac{63}{8} = 7.875$

O-balance: $\frac{7}{8}\frac{12.5}{\phi}\ 2 = 12 + 1 + \frac{63}{8} = 2f$

i) $\frac{10.9375}{\phi} = +10.4375 + f$

Overall: $\Sigma N_{pr} = 100 \Rightarrow 6 + 1 + \frac{63}{8} + f + \frac{7}{8}3.76\frac{12.5}{\phi} = 100$

or $f = 85.125 - \frac{41.125}{\Phi}$ ii)

Substitute i) → ii)

a) $\frac{10.9375}{\phi} - 10.4375 = 85.125 - \frac{41.125}{\phi}; \boxed{\phi} = \frac{52.0625}{95.5625} = \boxed{0.5448}$

b) $f = 85.125 - \frac{41.125}{0.5448} = 9.6386$ $\boxed{\chi_{O_2} = f/100 = 0.0964 \text{ or } 9.64\%}$

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COMMENT: What is the source of CO in a lean product mixture? Perhaps incomplete mixing or insufficient residence time to convert CO → CO_2 (see Chapter 5)

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PROBLEM 2-57

An inventor has devised an atmospheric-pressure process to manufacture methanol. The inventor claims he has developed a catalyst that promotes the economical reaction of CO and H_2 to yield methanol; however, a cheap supply of CO and H_2 is needed. The inventor proposes burning natural gas (CH_4) in oxygen under fuel-rich conditions to yield a gas mixture of CO, CO_2, H_2O, and H_2.

A. If methane burns in oxygen at an equivalence ratio $\Phi = 1.5$, and the combustion reactions go to equilibrium, what will be the resulting gas composition? Assume the combustion temperature is controlled to 1500 K.
B. What would be the composition if the temperature were controlled to 2500 K?

GIVEN: CH_4/O_2 burned to yield CO, CO_2, H_2O, H_2; $\Phi = 1.5$

FIND: a) mixture composition for T = 1500 K

b) mixture composition for T = 2500 K

ASSUMPTIONS: ideal gas mixture

APPROACH: "Water-gas shift" equilibrium will control the composition together with the relative proportions of C, H, & O in the reactant stream.

$$CH_4 + \frac{2}{\Phi} O_2 \rightarrow b\ CO_2 + c\ CO + d\ H_2O + e\ H_2$$

Arbitrarily reference to # H atoms:

i) $$\frac{\#\text{C atoms}}{\#\text{H atoms}} = \frac{1}{4} = \frac{\chi_{CO} + \chi_{CO_2}}{2\chi_{H_2O} + 2\chi_{H_2}}$$

ii) $$\frac{\#\text{O atoms}}{\#\text{H atoms}} = \frac{4/\Phi}{4} = \frac{1}{\Phi} = \frac{2}{3} = \frac{\chi_{CO} + 2\chi_{CO_2} + \chi_{H_2O}}{2\chi_{H_2O} + 2\chi_{H_2}}$$

iii) $$1 = \chi_{CO} + \chi_{CO_2} + \chi_{H_2O} + \chi_{H_2}$$

Equilibrium: $CO + H_2O\ f\ CO_2 + H_2$

iv) $$K_p(T) = \frac{\chi_{CO_2}\chi_{H_2}}{\chi_{CO}\chi_{H_2O}}$$

a) Simultaneously solve Eqns. i–iv for $K_p(T)$ evaluated at T = 1500 K. From Table 2.3, $K_p(1500) = 0.3887$.

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Alternatively, Eqns. 2.72, 2.73, 2.74, 2.75, 2.76 can be employed to solve this problem. $\left(\chi_{N_2} \equiv 0\right)$ using spreadsheet software, we obtain the following results:

T (K)	K_p	% CO_2	% CO	%H_2O	% H_2
1500	0.3887	13.4	20.0	42.2	24.5
2500	0.1622	9.1	24.3	46.5	20.2

COMMENTS: Relatively large amounts of CO and H_2 are produced at these conditions. The effect of temperature is not particularly strong.

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PROBLEMS 2-58 to 2-62

Consider the combustion of 1 kmol of propane with air at 1 atm. Construct a single graph using *H–T* coordinates that shows the following:

A. Reactants' enthalpy, *H*, in kJ versus temperature, over the range of 298–800 K for $\Phi = 1.0$.
B. Repeat part A for $\Phi = 0.75$.
C. Repeat part A for $\Phi = 1.25$.
D. Products' enthalpy, *H*, for ideal combustion (no dissociation) versus temperature, over the range of 298–3500 K for $\Phi = 1.0$.
E. Repeat part D for $\Phi = 0.75$.
F. Repeat part D for $\Phi = 1.25$, using the water-gas equilibrium to account for incomplete combustion.

Using the graph constructed in problem 2.58, estimate the constant-pressure adiabatic flame temperatures for the following conditions:

A. For reactants at 298 K with $\Phi = 0.75$, 1.0, and 1.25.
B. For $\Phi = 1.0$ with reactants' temperatures of 298 K, 600 K, and 800 K.
C. Discuss your results from parts A and B.

Repeat problem 2.58, but use the code TPEQUIL (Appendix F) to calculate the products' *H* versus *T* curves. Use the same scales as you did in problem 2.58 so that the results can be overlaid for comparison. Discuss the differences associated with the product enthalpy curves for the ideal combustion case compared with the equilibrium case. *Hint:* Make sure the basis for all the enthalpies is per mole of methane. You will have to convert the results from TPEQUIL to this basis.

Repeat parts A and B of problem 2.59 using the graph obtained in problem 2.60. Compare your results with those of problem 2.59 and discuss.

Use the code HPFLAME (Appendix F) to determine the adiabatic flame temperature for the conditions given in parts A and B of problem 2.59. Compare your results with those of problems 2.59 and 2.61. Discuss.

THIS SERIES OF PROBLEMS CAN BE USED AS A SINGLE PROJECT.

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PROBLEM 2-63

A furnace uses preheated air to improve its fuel efficiency. Determine the adiabatic flame temperature when the furnace is operating at a mass air–fuel ratio of 16 for air preheated to 600 K. The fuel enters at 300 K. Assume the following simplified thermodynamic properties:

$$\begin{aligned} T_{\text{ref}} &= 300 \text{ K}, \\ MW_{\text{fuel}} &= MW_{\text{air}} = MW_{\text{prod}} = 29 \text{ kg/kmol}, \\ c_{p,\text{fuel}} &= c_{p,\text{air}} = c_{p,\text{prod}} = 1200 \text{ J/kg-K}, \\ h^o_{f,\text{fuel}} &= h^o_{f,\text{prod}} = 0, \\ h^o_{f,\text{fuel}} &= 4 \cdot 10^7 \text{ J/kg}. \end{aligned}$$

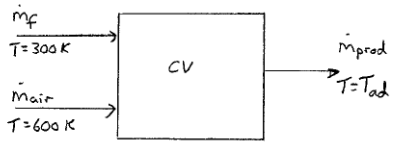
GIVEN: A furnace utilizing preheated air and operating at a mass air-fuel ratio of 16. The air is preheated to 600 K and the fuel enters at 300 K.

FIND: the adiabatic flame temperature

ASSUMPTIONS: The following simplified thermodynamic properties apply

$$\begin{aligned} &\text{T}_{\text{ref}} = 300 \text{ K} \\ &\text{MW}_{\text{f}} = \text{MW}_{\text{air}} = \text{MW}_{\text{prod}} = 29 \text{ kg/kmole} \\ &\text{C}_{\text{p,f}} = \text{C}_{\text{p,air}} = \text{C}_{\text{p,prod}} = 1200 \text{ J/kg} \cdot \text{K} \\ &\text{h}^{\text{o}}_{\text{f,air}} = \text{h}^{\text{o}}_{\text{f,prod}} = 0 \\ &\text{h}^{\text{o}}_{\text{f,f}} = 4 \times 10^7 \text{ J/kg} \end{aligned}$$

APPROACH: This a first law analysis



$$\dot{\cancel{Q}}^{\text{o}} - \dot{\cancel{W}}^{\text{o}} = \dot{\text{H}}_{\text{P}} - \dot{\text{H}}_{\text{R}} \rightarrow \dot{\text{H}}_{\text{P}} = \dot{\text{H}}_{\text{R}}$$

for $\text{A/F})_{\text{mass}}$

$$\begin{aligned} \dot{m}_{\text{prod}} &= \dot{m}_{\text{F}} \left(1 + \text{A/F}\right) \\ \dot{m}_{\text{air}} &= \dot{m}_{\text{F}} \left(\text{A/F}\right) \\ \dot{m}_{\text{f}} &= \dot{m}_{\text{f}} \left(1\right) \end{aligned}$$

$$\dot{\text{H}}_{\text{p}} = \dot{\text{H}}_{\text{R}}$$

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$$\dot{m}_p h_p = \dot{m}_f h_f + \dot{m}_{air} h_{air} \rightarrow \dot{m}_f \left(1 + A/F\right)\left[0 + C_P\left(T_{ad} - T_{ref}\right)\right]_P = \dot{m}_f \left(A/F\right)\left[0 + C_P\left(T_{air} - T_{ref}\right)\right]_{air} + \dot{m}_f \left[h_f^o + C_p\left(T_f - T_{ref}\right)\right]_f$$

$(1 + 16)[0 + 1200(T_{ad} - 300)] = (16)[0 + 1200(600 - 300)] + (1)\ [4 \times 10^7 + 1200(300 - 300)]$

solving for T_{ad}: $\boxed{T_{ad} = 2543 \text{ K}}$

COMMENTS: Because of the simplified thermodynamic properties and the fact that implicitly there is no dissociation, preheating the air ($\Delta T = 300$) results in T_{ad} being nearly 300 K higher ($\Delta T_{ad} = 283$ K). If the fuel were preheated too, then $\Delta T_{ad} = 300$ K, exactly.

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PROBLEM 2-64

In one strategy to decrease the amount of oxides of nitrogen (NO_x) formed and emitted from boilers, a portion of the flue gases is recirculated and introduced with the air and fuel. The effect of the recirculated gases is to decrease the maximum temperatures in the flame zone. Decreased flame temperatures result in less NO_x being formed. To increase the effectiveness of a given amount of recycled gases, the gases may be cooled. Your job is to determine what combinations of percent FGR and T_{FGR} result in maximum (adiabatic) flame temperatures of approximately 1950 K.

Your design should be based on the following constraints and assumptions: the fuel enters the burner at 298 K and 1 atm; the air enters the burner at 325 K and 1 atm; the oxygen (O_2) mole fraction in the cold, i.e., undissociated, flue gases is $\chi_{O_2} = 0.02$; the flue gas composition can be approximated as complete combustion products for all conditions, with the equivalence ratio determined from the flue-gas O_2 content; the percent FGR is defined as the molar percentage of fuel and air supplied; the natural gas can be treated as methane; and the maximum flue-gas temperature is 1200 K.

Use graphs and tables as appropriate to present your results. Also, discuss the practical ramifications of adding FGR (pumping requirements, capital equipment costs, etc.). How might these considerations affect the choice of operating conditions (%FGR, T_{EGR})?

NOTE: This problem can be used as a small project.

GIVEN: $T_{CH_4} = 298$ K; $T_{air} = 325$ K; $\chi_{O_2} = 0.02$

FIND: Combinations of % FGR & T_{FGR} that result in $T_{ad} = 1950$ K.

ASSUMPTIONS: FGR composition based on no dissociation; natural gas NCH_4; $T_{FGR,\,max} = 1200$ K.

APPROACH: i) Use χ_{O_2} to determine stoichiometry
ii) Apply 1st law (Eqn. 2.40) to determine required enthalpy of FGR
iii) Relate H_{FGR} to % FGR & T_{FGR}

SOLUTION:

For no dissociation, flue gas composition can be obtained:

$$CH_4 + \frac{2}{\phi}\left(O_2 + 3.76N_2\right) \rightarrow CO_2 + 2H_2O + aO_2 + \frac{2}{\phi}3.76N_2$$

O-balance: $2\left(\frac{2}{\phi}\right) = 2 + 2 + 2a;\ a = \frac{2}{\phi} - 2$ (I)

Given % O_2: $0.02 = a/\left(1 + 2 + a + \frac{2}{\phi}(3.76)\right)$ (II)

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Simultaneous solution of I & II yields:

a = 0.2325

$\phi = 0.8958$

$$N_{tot} = N_{CO_2} + N_{H_2O} + N_{O_2} + N_{N_2} = 1 + 2 + 0.2325 + \frac{2(3.76)}{0.8958}$$

$N_{tot} = 11.627 \Rightarrow$ FGR composition:

$$\chi_{CO_2} = \frac{1}{11.627} = 0.0860 \qquad \chi_{O_2} = \frac{0.2325}{11.627} = 0.0200$$

$$\chi_{H_2O} = \frac{2}{11.627} = 0.1720 \qquad \chi_{N_2} = \frac{8.395}{11.627} = 0.7220$$

First law: $H_R = H_{pr}(1950\ K)$

or

$$1\bar{h}_{CH_4} + N_A\bar{h}_A + N_{FGR}\bar{h}_{FGR}(T_{FGR}) = N_{pr}\bar{h}_{pr}(1950\ K) \quad \text{(III)}$$

Now N_{pr} depends on both the combustion of the fuel and N_{FGR}, i.e.,

$$N_{pr} = N_F\left(\frac{N_{pr}}{N_F}\right) + N_{FGR}\left(\frac{N_{pr}}{N_{FGR}}\right);\ F \equiv CH_4 \qquad \text{(IV)}$$

We use TPEQUIL to determine N_{pr}/N_F:

```
Output from TPEQUIL

Equil. Calc. for Specified Fuel, Phi, T, & P Using
Olikara/Borman Code

   Data below are as read from the input file.
   Compare with INPUT.TP. If they do not agree, your
   input data have not been entered correctly.

   CARBON ATOMS                      1.0
   HYDROGEN ATOMS                    4.0
   OXYGEN ATOMS                      0.0
   NITROGEN ATOMS                    0.0
   EQUIVALENCE RATIO                 0.8958
   TEMPERATURE (K)                1950.0
   PRESSURE (Pa)                101325.0
```

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```
CALCULATED COMBUSTION PRODUCTS PROPERTIES
Mixture Enthalpy [J/kg] =                -0.5328E+06
Mixture Specific Heat, Cp [J/kg-K] =      0.158621E+04
Specific Heat Ratio, Cp/Cv =              1.2360
Mixture Molecular Weight [kg/kmol] =     27.7295
Moles of Fuel per Mole of Products =      0.08594273 = NF/Npr
```

or $N_{pr}/N_F = 11.6357$

and $N_{pr}/N_{FGR} = \dfrac{11.6357}{11.627} = 1.0007 \sim 1$

Substitute IV into III & solve for N_{FGR}/N_F:

$$\frac{N_{FGR}}{N_F} = \frac{\left(N_{pr}/N_F\right)\bar{h}_{pr} - \bar{h}_F(298\text{ K}) - \left(N_A/N_F\right)\bar{h}_{air}(325\text{ K})}{\bar{h}_{FGR} - \left(N_{pr}/N_{FGR}\right)\bar{h}_{pr}} \qquad \text{(V)}$$

where

See TPEQUIL Output

$$\left(N_{pr}/N_F\right)\bar{h}_{pr}(1950\text{ K}) = \left(N_{pr}/N_F\right)h_{pr}\,MW_{pr}$$

$$= 11.6357\left(-532.8\frac{\text{kJ}}{\text{kg}}\right)27.7295\frac{\text{kg}}{\text{kmol}}$$

$$= -1.71909\cdot 10^5\,\text{kJ/kmol},$$

$\bar{h}_F = \bar{h}_{CH_4}(298) = -74{,}831$ kJ/kmol (Table B.1),

$\bar{h}_{air} = 0.21(789) + 0.79(783) = 784.3\dfrac{\text{kJ}}{\text{kmol}}$,

(Tables A.11 & A.7)

$\left(N_{pr}/N_{FGR}\right)\bar{h}_{pr} = (1)(-532.8)27.7295 = -14{,}774$ kJ/kmol

$N_A/N_F = \dfrac{2(4.76)}{\phi} = \dfrac{2(4.76)}{0.8958} = 10.627$

Substituting numerical values from above into V:

$$\frac{N_{FGR}}{N_F} = \frac{-1.71909\cdot 10^5 - (-74{,}831) - 10.627(784.3)}{\bar{h}_{FGR} - (-14{,}774)} = \frac{-105{,}413}{\bar{h}_{FGR} + 14{,}774} \qquad \text{(VI)}$$

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To complete our solution, we calculate $\bar{h}_{FGR}$ for a range of temperatures (330–1200 K); solve Eqn. VI for N_{FGR}/N_F; and apply the definition of % FGR:

$$\%\ \text{FGR} = \frac{N_{FGR} \cdot 100\%}{N_A + N_F} = \frac{N_{FGR}/N_F}{N_A/N_F + 1} \cdot 100\%$$

$$= (N_{FGR}/N_F)\frac{100}{11.627} = 8.6(N_{FGR}/N_F)$$

$$\bar{h}_{FGR}(T_{FGR}) = \sum_{FGR} \chi_i \, \bar{h}_i(T_{FGR})$$

For Example, at 1200 K,

$$\begin{aligned}\bar{h}_{FGR}(1200\ \text{K}) &= 0.0860(-393,546 + 44,488) \\ &\quad + 0.1720(-241,845 + 34,518) \\ &\quad + 0.020(0 + 29,775) \\ &\quad + 0.7220(0 + 28,118) \\ &= -44,782\ \text{kJ/kmol}\end{aligned}$$

T_{FGR} (K)	$\bar{h}_{FGR}(T_{FGR})$ kJ/kmol	N_{FGR}/N_F	% FGR
330	–74,409	1.768	15.2
600	–65,858	2.064	17.7
900	–55,669	2.578	22.2
1200	–44,782	3.513	30.2

COMMENT: As expected, less % FGR is required for cooler recycled gases.

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