PROBLEM 2-37

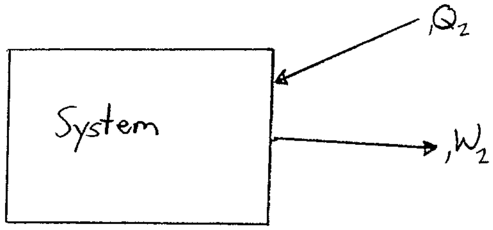
GIVEN: A system of fixed mass at constant pressure and temperature

FIND: Equivalent system form of Eqtn. 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

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

substituting into the first law

$${}_1Q_2 - mP(v_2 - v_1) = m(u_2 - u_1)$$

$${}_1Q_2 = m[(u_2 + Pv_2) - (u_1 + Pv_1)] = m(h_2 - h_1)$$

$${}_1q_2 = {}_1Q_2/m = h_2 - h_1$$

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

$$\boxed{q = h_P - h_R} \longleftarrow \text{same form as Eqtn 2.35}$$

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)

PROBLEM 2-38

GIVEN:

$A/F = \dot{m}_A/\dot{m}_F = 18$

$T_A = 800\ K$ (preheated)

$T_F = 450\ K$

$P = 1\ atm$

$h_{f,A} = h_{f,Pr} = 0$

$c_{p,F} = 3500\ J/kg\text{-}K$

$c_{p,A} = 1200\ J/kg\text{-}K$

$c_{p,Pr} = 1200\ J/kg\text{-}K$

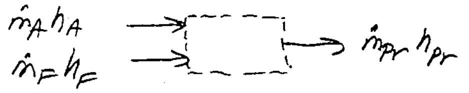
$\bar{h}_{f,F} = 1.16 \cdot 10^9\ J/kmol$

FIND: T_{ad} for $P = 1\ atm$

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

SOLUTION: Write 1st law (mass basis) recognizing that

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



$\dot{Q}, \dot{W} = 0$

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

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

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

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

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

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

Solve for T_{ad}

PROBLEM 2-38 (continued)

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

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

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

COMMENTS: i) Use of simplified properties focuses attention on energy conservation. ii) The use of a mass-based 1st law simplifies the solution ($H_R = H_{Pr}$).

PROBLEM 2-39

GIVEN: Adiabatic, const.-P combustion:

$(A/F)_{\phi=1} = 15$, $\Phi = 1$, $T_{ref} = 300$,

$T_F = T_A = 600K$, simplified properties

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

ASSUMPTIONS: Air is 79% N_2, 21% O_2

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

Stoichiometry:

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

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

$$H_{Pr} = (m_A + m_F) h_{Pr} = (m_A + m_F)(h^o_{f,Pr} + c_{p,Pr}(T_{ad} - T_{ref}))$$

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

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

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

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

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

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

b) $HV = H_R - H_{Pr}$ for 1 kg FUEL @ 600K

From part a), $H_R(600) = 2.645 \cdot 10^7 J$ (per kg_F).

$$H_{Pr}(600) = 16\left(h^\circ_{f,Pr} + c_{p,Pr}(T - T_{ref})\right)_{T=600}$$

$$= 16(-1.25 \cdot 10^6 + 1500(600-300))$$

$$H_{Pr} = -1.28 \cdot 10^7 \text{ J (per } kg_F)$$

$$HV = H_R - H_{Pr} = 2.645 \cdot 10^7 - (-1.28 \cdot 10^7)$$

$$\boxed{HV_{600} = 3.925 \cdot 10^7 \text{ J (per } kg_F)}$$

COMMENT: This ficticious fuel with simplified properties has a low HV (≈ 40,000 kJ/kg) compared to most real fuels (HV ~ 45,000 kJ/kg, cf. Table B.1).

PROBLEM 2-40

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 $\bar{c}_{p,i} = 40$ kJ/kmol-K
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) 1st law: $\dot{Q} - \cancel{\dot{W}}^{0} = \dot{m}(h_{pr} - h_R)$

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

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

Reactants

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

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

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

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

Products

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

$$h_{pr} = \frac{\sum \chi_i \bar{h}_i}{MW_{pr}} = \frac{0.66\bar{6}(-238{,}000 + 40T_{pr}) + .33\bar{3}(40T_{pr})}{22.68}$$

$$h_{pr} = -6995.88 + 1.7637\,T_{pr} \quad ([=]\ \text{kJ/kg})$$

Returning to 1st law: $\dot{Q}/\dot{m} + h_R = h_{pr}$

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

PROBLEM 2-40 (Continued)

Solving for T_{Pr}:

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

d)

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

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

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

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

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

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

Eqns. i–iii define the product mixture composition, χ_{H_2O}, χ_{O_2}, & χ_{OH}. Knowing these, the 1st 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

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

where

$$\bar{h}_{H_2O}(T) = \bar{h}^{\circ}_{f,H_2O} + \bar{c}_p\,(T - T_{ref})$$

$$\bar{h}_{O_2}(T) = \bar{h}^{\circ}_{f,O_2} + \bar{c}_p\,(T - T_{ref})$$

$$\bar{h}_{OH}(T) = \bar{h}^{\circ}_{f,OH} + \bar{c}_p\,(T - T_{ref}).$$

With the above substitutions into Eqn iv, our eqn. set is complete: Eqn i - iv with unknowns χ_{H_2O}, χ_{O_2}, χ_{OH}, & T.

COMMENTS: Part d shows, in a simple manner, how dissociation of products is coupled to a 1st-law analysis.

PROBLEM 2-41

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

FIND: Verify that the results of table 2.2 satisfy Eqtns 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 $(\chi_i = P_i/P)$

APPROACH: Calculate ΔG_T° using appendix A and compare with table 2.2. Using ΔG_T°, calculate K_p. Compare with the value of K_p calculated using the mole fractions listed in table 2.2.

a) $T = 2000\ K$, $P = 0.1\ atm$

$$\Delta G_T^\circ = [\Sigma N_i \bar{g}_{f,i}^\circ]_P - [\Sigma N_i \bar{g}_{f,i}^\circ]_R$$

where N_i represents the stoichiometric coefficients of the equilibrium reaction

$$\Delta G_T^\circ = [N\bar{g}_f^\circ]_{CO} + [N\bar{g}_f^\circ]_{O_2} - [N\bar{g}_f^\circ]_{CO_2} = 1\bar{g}_{f_{CO}}^\circ + \tfrac{1}{2}\bar{g}_{f_{O_2}}^\circ - 1\bar{g}_{f_{CO_2}}^\circ$$

$$\Delta G_T^\circ = 1(-285948) + \tfrac{1}{2}(0) - 1(-396410) = \boxed{110462\ KJ}$$ agrees with table 2.2

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

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

2 methods of determining K_p match so the data in table 2.2 satisfy Eqtn. 2.65

b) $T = 2500\ K$, $P = 1\ atm$

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

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

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

(continued)

PROBLEM 2-41 (CONTINUATION)

b (continued):

The value of ΔG_T° calculated here matches ΔG_T° in table 2.2 so Eqtn. 2.64 is satisfied and the K_p calculated from ΔG_T° matches the K_p determined from the mole fractions in table 2.2 so Eqtn. 2.65 is satisfied

c) $T = 3000\ K$, $P = 1\ atm$

$$\Delta G_T^\circ = 1\,\bar{g}^\circ_{f\,CO} + \tfrac{1}{2}\,\bar{g}^\circ_{f\,O_2} - 1\,\bar{g}^\circ_{f\,CO_2} = 1(-367684) + \tfrac{1}{2}(0) - 1(-395562) = 27878\ KJ$$

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

$$K_p = \frac{X_{CO}\,X_{O_2}^{1/2}}{X_{CO_2}}\left(\frac{P}{P_o}\right)^{1/2} = \frac{(0.3581)(0.1790)^{1/2}}{(0.4629)}\left(\frac{1atm}{1atm}\right)^{1/2} = 0.32730$$

Again, these calculations show that the results in table 2.2 satisfy Eqtns. 2.64 and 2.65

PROBLEM 2-42

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

FIND: The mole fractions X_o and X_{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 (X_o and X_{O_2}) so 2 equations must be used. The first is the definition of K_p and the second is $\Sigma X_i = 1$

a) $T = 2500\ K$

$$O_2 \leftrightarrow 2O$$

$$\Delta G_T^\circ = [N\bar{g}^\circ_{f,T}]_O - [N\bar{g}^\circ_{f,T}]_{O_2} = 2(88203) - 0 = 176406\ KJ/Kmole$$

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

$$K_p = \frac{X_o^2}{X_{O_2}}\left(P/P_o\right) = 206.3\times 10^{-6} \longleftarrow \text{FIRST EQUATION}$$

from $\Sigma X_i = 1 = X_o + X_{O_2}$

$$X_{O_2} = 1 - X_o \longleftarrow \text{SECOND EQUATION}$$

substituting the second equation into the first and rearranging yields

$$(P/P_o)X_o^2 + K_p X_o - K_p = 0 \qquad \text{quadratic equation}$$

solving for X_o

$$X_o = \frac{-K_p \pm\sqrt{K_p^2 + 4(P/P_o)(K_p)}}{2(P/P_o)}$$

Note: Only + yields physically realistic result

$T = 2500K, P = 1atm$: $K_p = 206.3\times10^{-6}$, $P/P_o = 1 \longrightarrow$ $\boxed{X_o = 0.0143,\ X_{O_2} = 1 - X_o = 0.9857}$

$T = 2500K, P = 3atm$: $K_p = 206.3\times10^{-6}$, $P/P_o = 3 \longrightarrow$ $\boxed{X_o = 0.00826,\ X_{O_2} = 1 - X_o = 0.9917}$

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 ($N_o + N_{O_2}$)

PROBLEM 2-43

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° 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	
Initial	1	0	1	
equilibrium shift	$-z$	$+2z$	0	
final state	$1-z$	$2z$	1	← # OF MOLES

mole fractions: $\chi_{O_2} = \frac{N_{O_2}}{N_{TOT}} = \frac{1-z}{2+z}$, $\chi_o = \frac{N_o}{N_{TOT}} = \frac{2z}{2+z}$

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

$$\Delta G_T^\circ = [N\bar{g}_f^\circ]_O - [N\bar{g}_f^\circ]_{O_2} = 2[88203]_O - 1[0] = 176406 \text{ KJ/Kmole}$$

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

$$K_p = \frac{\chi_o^2}{\chi_{O_2}}\left(\frac{P}{P_o}\right) = 206.3 \times 10^{-6}$$

substituting f χ_o and χ_{O_2} in terms of z

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

$$(4+K_p)z^2 + K_p z - 2K_p = 0 \longrightarrow z = \frac{-K_p \pm \sqrt{K_p^2 - 4(4+K_p)(-2K_p)}}{2(4+K_p)}$$

for physically realistic results

$$z = \frac{-K_p \oplus \sqrt{\quad}}{2(4+K_p)}$$

(continued)

PROBLEM 2-43 (continued)

Solving for z : $z = 0.0101$

$$\chi_{O_2} = \frac{1-z}{2+z} = \frac{1-0.0101}{2+0.0101} = 0.492$$

$$\chi_{O} = \frac{2z}{2+z} = \frac{2(0.0101)}{2+0.0101} = 0.01$$

$$\chi_{Ar} = \frac{1}{2+z} = \frac{1}{2+0.0101} = 0.4974$$

$$\boxed{\begin{array}{l} \chi_{O_2} = 0.492 \\ \chi_{O} = 0.01 \\ \chi_{Ar} = 0.4974 \end{array}}$$

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_2: $N_{O_2} = \chi_{O_2} N_{TOT} = 0.9926$	$N_{O_2} = \chi_{O_2}(2+z) = 0.492(2.01) = 0.989$

COMMENTS: Note that the diluent does not affect ΔG_r° 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.

PROBLEM 2-44

GIVEN: At $P = 10$ atm, $T = 3000$ K:

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

FIND: K_p for $CO_2 \rightleftarrows CO + \frac{1}{2}O_2$

ASSUMPTIONS: ideal gas mixture

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

$$K_p \equiv \frac{(P_{CO}/P^\circ)(P_{O_2}/P^\circ)^{1/2}}{(P_{CO_2}/P^\circ)} = \frac{\chi_{CO}\,\chi_{O_2}^{1/2}}{\chi_{CO_2}}(P/P^\circ)^{1/2}$$

$$K_p = \frac{0.2144\,(0.1072)^{1/2}}{0.6783}\left(\frac{10}{1}\right)^{1/2} = 0.1635(3.1623)$$

$$\boxed{K_p = 0.3273}$$

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; $K_p = \exp(-27877/8.315(3000)) = 0.327$, the same result as above.

PROBLEM 2-45

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

FIND: K_p for $H_2O \rightleftarrows H_2 + \frac{1}{2} O_2$

ASSUMPTIONS: ideal gas mixture

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

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

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

$$\boxed{K_p = 0.00789}$$

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

PROBLEM 2-46

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

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

FIND: a) Effect of P on equilibrium?
b) Effect of T on equilibrium?

ASSUMPTIONS: ideal gas behavior

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

The net exponent of P/P^o is zero. There is <u>no</u> 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 Chatelier'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 Chatelier's Principle.

PROBLEM 2-47

GIVEN: The reaction $H_2 + \frac{1}{2}O_2 \longleftrightarrow H_2O$ and 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°, 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° : $\Delta G_T^\circ = 1(g^\circ_{f,T})_{H_2O} - 1(g^\circ_{f,T})_{H_2} - \frac{1}{2}(g^\circ_{f,T})_{O_2}$

Using Appendix A $\quad \Delta G^\circ_{2000} = 1(-135643) - 1(0) - \frac{1}{2}(0) = -135643\ kJ/kmol$

$$K_p = \exp\left[-\frac{\Delta G_T^\circ}{R\,T}\right] = \exp\left[\frac{135643}{(8.315)(2000)}\right] = 3.486 \times 10^3$$

In terms of χ_i :

$$K_p = \frac{\chi_{H_2O}}{\chi_{H_2}\ \chi_{O_2}^{1/2}}\left(\frac{P}{P_o}\right)^{-\frac{1}{2}} \qquad (1)$$

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) :

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

Solving for χ_{O_2} by trial & error with $P = P_o = 1\,atm$:

$$\boxed{\begin{aligned}\chi_{O_2} &= 0.3334\\ \chi_{H_2} &= 3\chi_{O_2} - 1 = 0.0003\\ \chi_{H_2O} &= 2 - 4\chi_{O_2} = 0.6662\end{aligned}}$$

Comments :

PROBLEM 2-48

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

FIND: χ_{H_2}, χ_{O_2}, χ_{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,

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

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

Use i) & ii) to eliminate χ_{H_2} & express $\chi_{H_2O} = f(\chi_{O_2})$:

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):

PROBLEM 2-48 (continued)

$$\left(\frac{Z-2}{Z}\right)\left(\frac{P}{P^0}\right)^{1/2}\chi_{O_2}^{1/2} + \left(\frac{Z+2}{Z}\right)\left(\frac{P}{P^0}\right)^{1/2}\chi_{O_2}^{3/2} + \frac{2(Z+1)}{Z}K_p\,\chi_{O_2}$$

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

To solve the above transcendental eqn. for χ_{O_2}, we apply the Newton-Raphson iteration method;

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

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

$$viii) \quad f'(\chi_{O_2}) = \frac{1}{2}\left(\frac{Z-2}{Z}\right)\left(\frac{P}{P^0}\right)^{1/2}\chi_{O_2}^{-1/2} + \frac{3}{2}\left(\frac{Z+2}{Z}\right)\left(\frac{P}{P^0}\right)^{1/2}\chi_{O_2}^{1/2}$$

$$+ \frac{2(Z+1)}{Z}K_p$$

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

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

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

$$K_p = 2.86857 \cdot 10^{-4}$$

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

PROBLEM 2-48 (continued)

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.

PROBLEM 2-49

GIVEN: Equil. reactn $H_2O \rightleftarrows H_2 + \frac{1}{2}O_2$ @ $T = 2000\,K$

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

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 2000K, we expect that other dissociation species should be included in the analysis, in particular, OH, O, and H.

PROBLEM 2-50

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 $\Sigma \chi_i = 1$, and the other four from the definition of equilibrium constants K_p

conservation of elements:

$$\frac{\#H \text{ atoms}}{\#O \text{ atoms}} = \frac{2\chi_{H_2} + \chi_{OH} + \chi_H + 2\chi_{H_2O}}{2\chi_{O_2} + \chi_{OH} + \chi_O + \chi_{H_2O}} = Z \quad ①$$

Summation of χ_i:

$$\Sigma \chi_i = \chi_{H_2} + \chi_{O_2} + \chi_{OH} + \chi_O + \chi_H + \chi_{H_2O} = 1 \quad ②$$

equilibrium reactions:

$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$

$$K_{P\,H_2O} = \exp\left[-\frac{\Delta G_T^\circ}{R_u T}\right]_{H_2O} = \frac{\chi_{H_2O}}{\chi_{H_2}\,\chi_{O_2}^{1/2}}\left(\frac{P}{P_o}\right)^{-1/2} \quad ③$$

$H_2 \leftrightarrow 2H$

$$(K_P)_H = \exp\left[-\frac{\Delta G_T^\circ}{R_u T}\right]_H = \frac{\chi_H^2}{\chi_{H_2}}\left(\frac{P}{P_o}\right) \quad ④$$

$O_2 \leftrightarrow 2O$

$$(K_P)_O = \exp\left[-\frac{\Delta G_T^\circ}{R_u T}\right]_O = \frac{\chi_O^2}{\chi_{O_2}}\left(\frac{P}{P_o}\right) \quad ⑤$$

$H + O \leftrightarrow OH$

$$(K_P)_{OH} = \exp\left[-\frac{\Delta G_T^\circ}{R_u T}\right]_{OH} = \frac{\chi_{OH}}{\chi_H\,\chi_O}\left(\frac{P}{P_o}\right)^{-1} \quad ⑥$$

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.

PROBLEM 2-51

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       population          element
    atom                              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.

PROBLEM 2-52

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	x
	N_2	0.737
	H_2O	0.125
	CO_2	0.094
	O_2	0.038
minor species	NO	3500 ppm
	OH	1800 ppm
	CO	890 ppm
	H_2	250 ppm
	O	176 ppm
	H	34 ppm
	N	0.14 ppb

Species	x
N_2	0.69
H_2O	0.155
CO_2	0.079
CO	0.054
H_2	0.020
OH	860 ppm
H	800 ppm
NO	240 ppm
O_2	77 ppm
O	20 ppm
N	1 ppb

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

```
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
```

Problem 2.53

PROBLEM 2.53	PHI = 0.75	PHI = 0.75	PHI = 0.75	PHI = 1.0	PHI = 1.0	PHI = 1.0
C10H22	P = 1 atm	P = 10 atm	P = 100 atm	P = 1 atm	P = 10 atm	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

	PHI = 1.25	PHI = 1.25	PHI = 1.25
C10H22	P = 1 atm	P = 10 atm	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

COMMENTS:

1. At lean, stoiciometric, & rich conditions, the effect of increasing P is to suppress dissociation and, as a result, flame temperatures increse 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.

PROBLEM 2-54

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 : $C_xH_y + aO_2 + 3.76aN_2 \rightarrow bCO_2 + cCO + dH_2O + eH_2 + fO_2 + 3.76aN_2$

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

b = will solve for using water-gas shift K_p

Conservation of:

C $\quad c = x - b$

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

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

$f = 0$ since combustion is fuel-rich

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

$$K_p = \frac{X_{CO_2} X_{H_2}}{X_{CO} X_{H_2O}} = \frac{b \cdot e}{c \cdot d} \cdot \left(\frac{1/N_{TOT}}{1/N_{TOT}}\right)^2 = \frac{b \cdot e}{c \cdot d}$$

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

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:

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

where only the negative root yields a physically realistic value of b (ie b must be positive)

(continued)

the preceding equation can be solved by substituting for a, x, y and K_p (which must still be determined

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

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

$$\Delta G_T^\circ = (1)\,\bar{g}^\circ_{f\,CO_2} + (1)\,\bar{g}^\circ_{f\,H_2} - (1)\,\bar{g}^\circ_{f\,CO} - (1)\,\bar{g}^\circ_{f\,H_2O}$$

at 2200 K:

$$\Delta G_T^\circ = (-396346) + 0 - (-302576) - (-124030) = 30260$$

$$K_p = \exp\left[-\frac{\Delta G}{R_u T}\right] = \exp\left[-\frac{30260}{(8.315)(2200)}\right] = 0.19125$$

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.

PROBLEM 2-55

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 transfered to air entering boiler, ΔKE & ΔPE are neglibible, steady-state

APPROACH: Determine the A/F ratio from element conservation then use conservation of energy to determine the boiler efficiency

a) combustion equation: $CH_4 + aO_2 + 3.76a\,N_2 \longrightarrow CO_2 + 2H_2O + bO_2 + 3.76a\,N_2$

in products:
$$\chi_{O_2} = 0.02 = \frac{N_{O_2}}{N_{CO_2} + \underset{\text{removed}}{\cancel{N_{H_2O}}} + N_{O_2} + N_{N_2}} = \frac{b}{1 + b + 3.76a}$$

O atom conservation:
$$b = a - \underset{\overset{\uparrow}{CO_2}}{1} - \underset{\overset{\uparrow}{H_2O}}{1} = a - 2$$

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

$$\chi_{O_2} = \frac{a-2}{1 + (a-2) + 3.76a} = \frac{a-2}{4.76a - 1} = 0.02$$

$a = 2.19 \longrightarrow a = \dfrac{x + y/4}{\Phi}$ $\quad x = 1,\ y = 4$

$b = a - 2 = 0.19$

$A/F)_{molar} = 4.76a = 10.42$

$$\boxed{\Phi = 0.914}$$

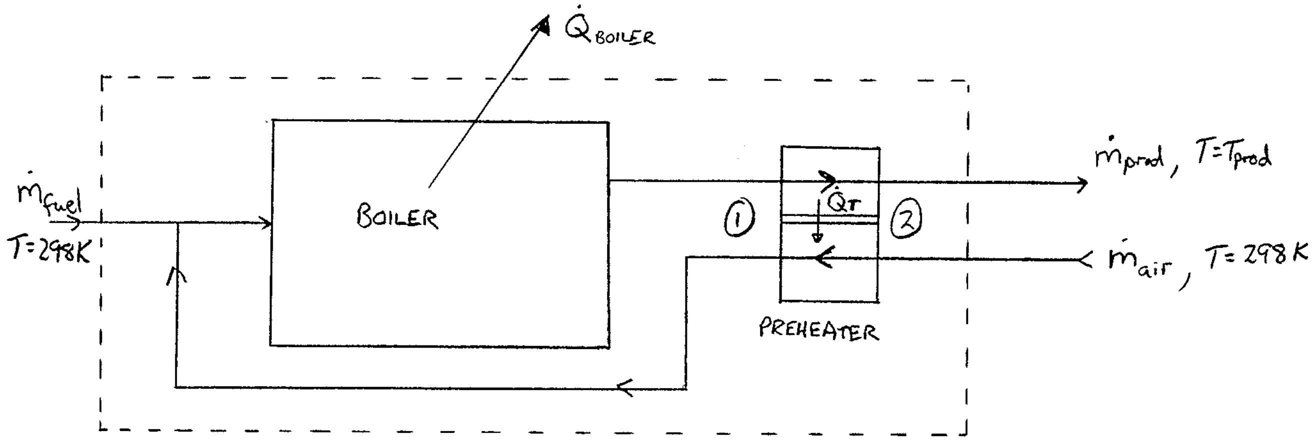
(continued)

PROBLEM 2-55 (continued)

b) defining the boiler thermal efficiency : $\eta = \dfrac{\dot{Q}_{BOILER}}{\dot{Q}_{MAX}}$

where $\dot{Q}_{BOILER}$ is the heat transfered 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 :

$$\dot{Q} - \cancel{\dot{W}}_0 = \left[\Sigma \dot{N}_i \bar{h}_i\right]_{prod} - \left[\dot{N}\bar{h}\right]_{fuel} - \left[\dot{N}\bar{h}\right]_{air}$$

$$q = \frac{\dot{Q}}{\dot{N}_{fuel}} = \frac{1}{\dot{N}_{fuel}}\left[\Sigma \dot{N}_i \bar{h}_i\right]_{prod} - \bar{h}_{fuel} - \left.\frac{A}{F}\right)_{MOLAR} \bar{h}_{air}$$

$$q = \left[\Sigma \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_i\right]_{prod} - \bar{h}_{fuel} - \left.\frac{A}{F}\right)_{MOLAR} \bar{h}_{air}$$

for q_{max} ($T_{prod} = 298\,K$) : $\bar{h} = \bar{h}_f^\circ + (\bar{h} - \bar{h}_f^\circ) = \bar{h}_f^\circ$

$$\Sigma \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_i = 1\bar{h}^\circ_{f_{CO_2}} + 2\bar{h}^\circ_{f_{H_2O}} + b\bar{h}^\circ_{f_{O_2}} + 3.76a\,\bar{h}^\circ_{f_{N_2}} \leftarrow \text{from combustion equation}$$

$$= 1[-393546] + 2[-241847] + 0 + 0 = -877240 \text{ KJ/(Kmole-fuel)}$$

so, $q_{max} = -877240 - [-74831]_{fuel} - 10.42\,(0)_{air} = -802409$ KJ/(Kmole-fuel)

for no preheat ($T_{prod} = 700\,K$) : $\bar{h} = \bar{h}_f^\circ + (\bar{h} - \bar{h}_f^\circ)$

$$\Sigma \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_i = 1[-393546 + 17749]_{CO_2} + 2[-241847 + 14209] + 0.19[0 + 12503]_{O_2} + 8.23[0 + 11942]_{N_2}$$

$$= -730415 \text{ KJ/(Kmole-fuel)}$$

(continued)

PROBLEM 2-55 (continued)

b(continued): $q_{BOILER} = -730415 - [-74831] - 10.42(0) = -655584$ 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 $(T_{prod} = 433K)$: $\bar{h} = \bar{h}_f^\circ + (\bar{h} - \bar{h}_f^\circ)$

$$q_{BOILER} = \sum \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_i - \bar{h}_f^\circ - A/F)_{MAAR} \bar{h}_{air}$$

$$\sum \frac{\dot{N}_i}{\dot{N}_{fuel}} = 1[-393546 + 5421]_{CO_2} + 2[-241847 + 4609]_{H_2O} + 0.19[0 + 4043]_{O_2} + 8.23[0 + 3946]_{N_2}$$

$$= -829357 \text{ KJ/(Kmole-fuel)}$$

$$q_{BOILER} = -829357 - [-74831]_{fuel} - 10.42(0)_{air} = -754526 \text{ KJ/Kmole-fuel}$$

$$\eta = \frac{-754526}{-802409} = 0.94$$

$$\boxed{\eta = 0.94}$$ 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 entering the pre-heater is 700K (i.e., the temperature of the flue gas exiting the boiler remains constant, regardless of whether air pre-heat is used)

First law for the preheater :

$$\dot{H}_{IN} = \dot{H}_{OUT}$$

$$\dot{H}_{P①} + \dot{H}_{air②} = \dot{H}_{P②} + \dot{H}_{air①}$$

$$H_{air①} = H_{P①} - H_{P②} + H_{air②}$$

per Kmole of fuel burned :

$$a\bar{h}_{O_2} + 3.76a\bar{h}_{N_2} = \sum \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_{i\,700K} - \sum \frac{\dot{N}_i}{\dot{N}_{fuel}} \bar{h}_{i\,433K} + \left[\cancelto{0}{a\bar{h}_{O_2}} + \cancelto{0}{3.76a\bar{h}_{N_2}}\right]_{298K}$$

(CONTINUED)

PROBLEM 2-55 (continued)

$$\underbrace{a\bar{h}_{O_2} + 3.76a\bar{h}_{N_2}}_{H_{air}\ (KJ/Kmole\text{-}fuel)} = -730415 - [-829357] = 98942\ KJ/(Kmole\text{-}fuel)$$

determine adiabatic flame temperature:

$$H_P = H_R = H_{fuel} + H_{air}$$

$$H_P = [-74831 + 0] + 98942\ KJ/Kmole\text{-}fuel = 24111\ KJ/Kmol\text{-}fuel$$

$$H_P = 1\bar{h}_{CO_2} + 2\bar{h}_{H_2O} + 0.19\bar{h}_{O_2} + 8.23\bar{h}_{N_2}$$

$$= 1[-393546 + \Delta h_{sens}]_{CO_2} + 2[-241847 + \Delta h_{sens}]_{H_2O} + 0.19[0 + \Delta h_{sens}]_{O_2} + 8.23[0 + \Delta h_{sens}]_{N_2}$$

$$\Delta h_{sens,CO_2} + 2\Delta h_{sens,H_2O} + 0.19\Delta h_{sens,O_2} + 8.23\Delta h_{sens,N_2} - 901351\ KJ/KMOL\text{-}fuel = R$$

where $\Delta h_{sens} = \bar{h} - \bar{h}_f^\circ$ and $R = 0$ for correct solution

using appendix A:

T (K)	R (KJ/Kmole-fuel)
2200	-97329
2300	-50028
2400	-2508
2500	45233

Linear interpolation for $R = 0$ yields

$$\boxed{T = 2405\ K}$$

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.

PROBLEM 2-56

GIVEN: C_8H_{18} products : $\chi_{CO_2} = 0.06$ (wet) ; $\chi_{CO} = 0.01$ (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: $a = x + y/4 = 8 + 18/4 = 12.5$

$$z\left[C_8H_{18} + \frac{12.5}{\Phi}(O_2 + 3.76N_2)\right] \rightarrow 6CO_2 + 1CO + dH_2O + fO_2 + (z)3.76\left(\frac{12.5}{\Phi}\right)N_2$$

(RHS ≡ 100 kmoles)

C-balance: $8z = 6 + 1$

$z = 7/8$

H-balance: $\frac{7}{8}18 = 2d \Rightarrow d = \frac{63}{8} = 7.875$

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) $f = 85.125 - \frac{41.125}{0.5448} = 9.6386$ $\boxed{\chi_{O_2} = f/100 = 0.0964 \text{ or } 9.64\%}$

COMMENT: What is the source of CO in a lean product mixture? Perhaps incomplete mixing or insufficient residence time to convert $CO \rightarrow CO_2$ (See Ch. 5)

PROBLEM 2-57

GIVEN: CH_4/O_2 burned to yield CO, CO_2, H_2O, H_2 ; $\Phi = 1.5$

FIND: a) Mixture composition for $T = 1500K$
b) mixture composition for $T = 2500K$

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) $$\frac{\#C\,atoms}{\#H\,atoms} = \frac{1}{4} = \frac{\chi_{CO} + \chi_{CO_2}}{2\chi_{H_2O} + 2\chi_{H_2}}$$

ii) $$\frac{\#O\,atoms}{\#H\,atoms} = \frac{4/\Phi}{4} = \frac{1}{\Phi} = \frac{2}{3} = \frac{\chi_{CO} + 2\chi_{CO_2} + \chi_{H_2O}}{2\chi_{H_2O} + 2\chi_{H_2}}$$

iii) $$1 = \chi_{CO} + \chi_{CO_2} + \chi_{H_2O} + \chi_{H_2}$$

Equilibrium: $CO + H_2O \rightleftarrows CO_2 + H_2$

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 $T = 1500K$. From Table 2.3, $K_P(1500) = 0.3887$.

PROBLEM 2-57 (Continued)

Alternatively, Eqns. 2.72, 2.73, 2.74, 2.75, 2.76 can be employed to solve this problem. ($\chi_{N_2} \equiv 0$)

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.

PROBLEMS 2.58 – 2.62

THIS SERIES OF PROBLEMS CAN BE USED AS A SINGLE PROJECT.

PROBLEM 2-63

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

$T_{ref} = 300\ K$

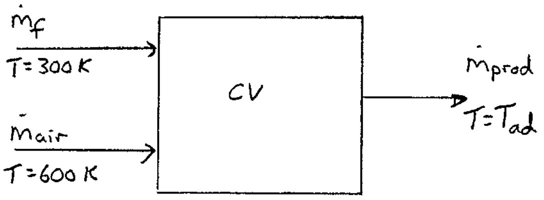
$MW_f = MW_{air} = MW_{prod} = 29\ kg/kmole$

$c_{p,f} = c_{p,air} = c_{p,prod} = 1200\ J/kg\cdot K$

$h^\circ_{f,air} = h^\circ_{f,prod} = 0$

$h^\circ_{f,f} = 4 \times 10^7\ J/kg$

APPROACH: This a first law analysis



$$\overset{0}{\cancel{\dot{Q}}} - \overset{0}{\cancel{\dot{W}}} = \dot{H}_P - \dot{H}_R \longrightarrow \dot{H}_P = \dot{H}_R$$

for $A/F)_{mass}$

$\dot{m}_{prod} = \dot{m}_f\,(1 + A/F)$

$\dot{m}_{air} = \dot{m}_f\,(A/F)$

$\dot{m}_f = \dot{m}_f\,(1)$

$\dot{H}_P = \dot{H}_R$

$$\dot{m}_P h_P = \dot{m}_f h_f + \dot{m}_{air} h_{air} \longrightarrow \dot{m}_f (1 + A/F)\left[0 + c_p (T_{ad} - T_{ref})\right]_P = \dot{m}_f (A/F)\left[0 + c_p (T_{air} - T_{ref})\right]_{air} + \dot{m}_f\left[h^\circ_f + c_p (T_f - T_{ref})\right]_f$$

$$(1+16)\left[0 + 1200(T_{ad} - 300)\right] = (16)\left[0 + 1200(600 - 300)\right] + (1)\left[4\times10^7 + 1200(300 - 300)\right]$$

solving for T_{ad} : $\boxed{T_{ad} = 2543\ K}$

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.

PROBLEM 2-64

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 ~ CH_4; $T_{FGR,max} = 1200\ K$.

APPROACH:
- i) Use χ_{O_2} to determine stoichiometry
- ii) Apply 1st law (Eqn 2.40) to determine req'd enthalpy of FGR
- iii) Relate H_{FGR} to % FGR & T_{FGR}

SOLUTION:

For no dissociation, flue gas composition can be obtained:

$$CH_4 + \frac{2}{\phi}(O_2 + 3.76 N_2) \rightarrow CO_2 + 2H_2O + aO_2 + \frac{2}{\phi}3.76 N_2$$

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)

Simultaneous solution of I & II yields:

$a = 0.2325$

$\phi = 0.8958$

$$N_{tot} = N_{CO_2} + N_{H_2O} + N_{O_2} + N_{N_2} = 1 + 2 + 0.2325 + \frac{2(3.76)}{0.8958}$$

PROBLEM 2-64 (continued)

$N_{tot} = 11.627 \Rightarrow$ FGR composition:

$$\chi_{CO_2} = \frac{1}{11.627} = 0.0860 \qquad \chi_{O_2} = \frac{0.2325}{11.627} = 0.0200$$

$$\chi_{H_2O} = \frac{2}{11.627} = 0.1720 \qquad \chi_{N_2} = \frac{8.395}{11.627} = 0.7220$$

1st Law: $H_R = H_{Pr}(1950\,K)$

or

$$1\,\bar{h}_{CH_4} + N_A \bar{h}_A + N_{FGR}\,\bar{h}_{FGR}(T_{FGR}) = N_{Pr}\,\bar{h}_{Pr}(1950\,K) \qquad \text{(III)}$$

Now N_{Pr} depends on both the combustion of the fuel and N_{FGR}, i.e.,

$$N_{Pr} = N_F\left(\frac{N_{Pr}}{N_F}\right) + N_{FGR}\left(\frac{N_{Pr}}{N_{FGR}}\right) \qquad \text{(IV)} \quad ; F \equiv CH_4$$

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

 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
```

$= N_F / N_{Pr}$

PROBLEM 2-64 (continued)

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 :

$$\frac{N_{FGR}}{N_F} = \frac{(N_{Pr}/N_F)\,\bar{h}_{Pr} - \bar{h}_F(298\,K) - (N_A/N_F)\,\bar{h}_{air}(325\,K)}{\bar{h}_{FGR} - (N_{Pr}/N_{FGR})\,\bar{h}_{Pr}} \qquad (V)$$

where

See TPEQUIL output

$$(N_{Pr}/N_F)\,\bar{h}_{Pr}(1950\,K) = (N_{Pr}/N_F)\,h_{Pr}\,MW_{Pr}$$
$$= 11.6357\left(-532.8\ \frac{kJ}{kg}\right) 27.7295\ \frac{kg}{kmol}$$
$$= -1.71909\cdot 10^5\ kJ/kmol\,,$$

$\bar{h}_F = \bar{h}_{CH_4}(298) = -74{,}831$ kJ/kmol (Table B.1),

$\bar{h}_{air} = 0.21(789\ \ ) + 0.79(783\ \ ) = 784.3\ \frac{kJ}{kmol}$,

(Tables A.11 & A.7)

$(N_{Pr}/N_{FGR})\,\bar{h}_{Pr} = (1)(-532.8)\,27.7295 = -14{,}774$ 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 :

$$\frac{N_{FGR}}{N_F} = \frac{-1.71909\cdot 10^5 - (-74{,}831) - 10.627(784.3)}{\bar{h}_{FGR} - (-14{,}774)} = \frac{-105{,}413}{\bar{h}_{FGR} + 14{,}774}$$

(VI)

PROBLEM 2-64 (continued)

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:

$$\%FGR = \frac{N_{FGR}\cdot 100\%}{N_A + N_F} = \frac{N_{FGR}/N_F}{N_A/N_F + 1}\cdot 100\%$$

$$= (N_{FGR}/N_F)\frac{100}{11.627} = 8.6(N_{FGR}/N_F)$$

$$\bar{h}_{FGR}(T_{FGR}) = \sum_{FGR} \chi_i\, \bar{h}_i(T_{FGR})$$

For example, at 1200 K,

$$\bar{h}_{FGR}(1200\,K) = 0.0860(-393{,}546 + 44{,}488) + 0.1720(-241{,}845 + 34{,}518) + 0.020(0 + 29{,}775) + 0.7220(0 + 28{,}118)$$

$$= -44{,}782 \text{ kJ/kmol}$$

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.