

PROBLEM 2-37

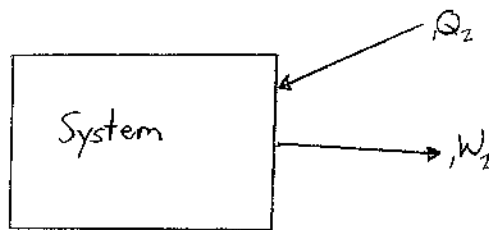
GIVEN: A system of fixed mass at constant pressure and temperature

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

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

substituting into the first law

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

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

$$q_2 = {}_1Q_2/m = h_2 - h_1$$

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

$$\boxed{q = h_p - h_r} \quad \leftarrow \text{same form as Eqn 2.35}$$

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:  $A/F = \dot{m}_A/\dot{m}_F = 18$   
 $T_A = 800 \text{ K}$  (preheated)  
 $T_F = 450 \text{ K}$   
 $P = 1 \text{ atm}$   
 $h_{f,A} = h_{f,F} = 0$

$c_{p,F} = 3500 \text{ J/kg-K}$   
 $c_{p,A} = 1200 \text{ J/kg-K}$   
 $c_{p,Pr} = 1200 \text{ J/kg-K}$   
 $\bar{h}_{f,F} = 1.16 \cdot 10^9 \text{ J/kmol}$

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

ASSUMPTIONS: Air  $\equiv 79\% \text{ N}_2$  /  $21\% \text{ O}_2$ ; properties as given.

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

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

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

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

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

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

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

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

Solve for  $T_{ad}$

PROBLEM 2-38 (continued)

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

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

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

COMMENTS: i) Use of simplified properties focuses attention on energy conservation. ii) The use of a mass-based 1<sup>st</sup> law simplifies the solution ( $h_R = h_P$ ).

PROBLEM 2-39

GIVEN: Adiabatic, const.-P combustion:

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

$$T_F = T_A = 600K, \quad \text{simplified properties}$$

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:



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

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

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

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

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

$$H_{Pr} = 16(-125 \cdot 10^6 + 1500(T_{ad} - 300))$$

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

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)

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

PROBLEM 2-39 (Continued)

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

From part a),  $H_R(600) = 2.645 \cdot 10^7 \text{ J (per kg}_F)$  -

$$H_{Pr}(600) = 16 \left( h_{f,Pr}^{\circ} + C_{p,Pr} (T - T_{ref}) \right)_{T=600}$$

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

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

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

$HV_{600} = 3.925 \cdot 10^7 \text{ J (per kg}_F)$
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COMMENT: This fictitious 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).

PROBLEM 2-40

GIVEN: Steady-flow reactor with  $H_2 - O_2$  @  $\Phi = 0.5$ ,  $P = 5 \text{ atm}$ ,  
 $\dot{Q}/\dot{m} = 187 \text{ kJ/kg}$ ; zero-K reference state

$$\bar{h}_{f,i}^{\circ} : \bar{h}_{f,O_2}^{\circ} = \bar{h}_{f,H_2}^{\circ} = 0$$

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

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

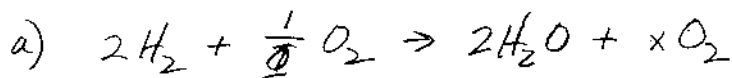
FIND: a)  $MW_{pr}$  (w/o dissociation)

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

c)  $T_{out}$  (w/o dissociation) for  $T_{in,H_2} = 300 \text{ K}$ ,  $T_{in,O_2} = 800 \text{ K}$ ,  
 all  $\bar{c}_{p,i} = 40 \text{ kJ/kmol-K}$

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

SOLUTION:



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

$$MW_{pr} = \frac{\sum N_i MW_i}{\sum N_i}$$

$$= \frac{2(18.016) + 1(31.999)}{3} = 22.68 \text{ kg/kmol}$$

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

$$= 0.470$$

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

PROBLEM 2-40 (continued)

c) 1st law:  $\dot{Q} - \dot{W} = \dot{m} (h_{pr} - h_R)$

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

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

Reactants

	N	$\gamma$	$\bar{h}$ kJ/kmol
H <sub>2</sub>	2	0.5	0 + 40(300-0) = 12,000
O <sub>2</sub>	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	$\gamma$	$\bar{h} (= \bar{h}_f + c_p(T-0))$ kJ/kmol
H <sub>2</sub> O	2	0.666	(-238,000 + 40 T <sub>pr</sub> )
O <sub>2</sub>	1	0.333	(0 + 40 T <sub>pr</sub> )

$$h_{pr} = \frac{\sum \gamma_i \bar{h}_i}{MW_{pr}} = \frac{0.666(-238,000 + 40 T_{pr}) + 0.333(40 T_{pr})}{22.68}$$

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

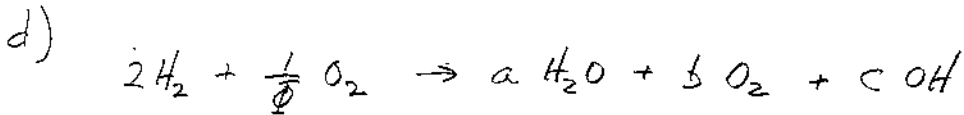
Returning to 1st law:  $\dot{Q}/\dot{m} + h_R = h_{pr}$

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

PROBLEM 2-40 (continued)

Solving for  $T_{Pr}$ :

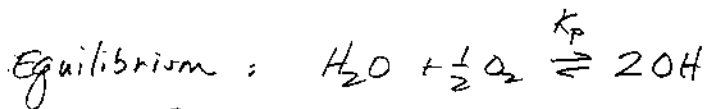
$$T_{Pr} = 4594 \text{ K}$$



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

i) 
$$\frac{\# \text{H atoms}}{\# \text{O atoms}} = \frac{4}{4} = 1 = \frac{2\gamma_{\text{H}_2\text{O}} + \gamma_{\text{OH}}}{\gamma_{\text{H}_2\text{O}} + 2\gamma_{\text{O}_2} + \gamma_{\text{OH}}}$$

ii) 
$$\gamma_{\text{OH}} + \gamma_{\text{O}_2} + \gamma_{\text{H}_2\text{O}} = 1$$



iii) 
$$\frac{\gamma_{\text{OH}}^2 (P/P^0)^2}{\gamma_{\text{H}_2\text{O}} (P/P^0) \cdot \gamma_{\text{O}_2}^{1/2} (P/P^0)^{1/2}} = \frac{\gamma_{\text{OH}}}{\gamma_{\text{H}_2\text{O}} \gamma_{\text{O}_2}^{1/2}} (P/P^0)^{1/2} = K_p$$

where  $K_p = \exp(-\Delta G_T / R_u T)$

$$= \exp\left[ \frac{-(2\bar{g}_{\text{OH}}(T) - \bar{g}_{\text{H}_2\text{O}} - 0.5\bar{g}_{\text{O}_2}(T))}{R_u T} \right]$$

Eqs. i-iii define the product mixture composition,

$\gamma_{\text{H}_2\text{O}}$ ,  $\gamma_{\text{O}_2}$ , &  $\gamma_{\text{OH}}$ . Knowing these, the 1<sup>st</sup> law is formulated as in part c:

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



PROBLEM 2-40 (CONTINUED)

The LHS of Eqn. i-v 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

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

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

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

With the above substitutions into Eqn i-v, our  
eqn. set is complete; Eqn i-v 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 1<sup>st</sup>-law analysis.

PROBLEM 2-41

GIVEN: The equilibrium reaction  $\text{CO}_2 \leftrightarrow \text{CO} + \frac{1}{2}\text{O}_2$

FIND: Verify that the results of table 2.2 satisfy Eqtns 2.64 and 2.65 for the following conditions:

- a)  $T = 2000 \text{ K}$ ,  $P = 0.1 \text{ atm}$
- b)  $T = 2500 \text{ K}$ ,  $P = 100 \text{ atm}$
- c)  $T = 3000 \text{ K}$ ,  $P = 1 \text{ atm}$

ASSUMPTIONS: ideal gas behavior ( $x_i = P_i/P$ )

APPROACH: Calculate  $\Delta G_T^\circ$  using appendix A and compare with table 2.2. Using  $\Delta G_T^\circ$ , calculate  $K_p$ . Compare with the value of  $K_p$  calculated using the mole fractions listed in table 2.2.

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

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

where  $N_i$  represents the stoichiometric coefficients of the equilibrium reaction

$$\Delta G_T^\circ = [N \bar{g}_f^\circ]_{\text{CO}} + [N \bar{g}_f^\circ]_{\text{O}_2} - [N \bar{g}_f^\circ]_{\text{CO}_2} = 1 \bar{g}_{f,\text{CO}}^\circ + \frac{1}{2} \bar{g}_{f,\text{O}_2}^\circ - 1 \bar{g}_{f,\text{CO}_2}^\circ$$

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

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

$$K_p = \frac{x_{\text{CO}} x_{\text{O}_2}^{1/2}}{x_{\text{CO}_2}} \left(\frac{P}{P_0}\right)^{1/2} = \frac{(0.0315)(0.0158)^{1/2}}{(0.9527)} \left(\frac{0.1 \text{ atm}}{1 \text{ atm}}\right)^{1/2} = 1.314 \times 10^{-3}$$

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

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

$$\Delta G_T^\circ = 1 \bar{g}_{f,\text{CO}}^\circ + \frac{1}{2} \bar{g}_{f,\text{O}_2}^\circ - 1 \bar{g}_{f,\text{CO}_2}^\circ = 1(-327245) + \frac{1}{2}(0) - 1(-396152) = 68907 \text{ KJ}$$

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

$$K_p = \frac{x_{\text{CO}} x_{\text{O}_2}^{1/2}}{x_{\text{CO}_2}} \left(\frac{P}{P_0}\right)^{1/2} = \frac{(0.0289)(0.0145)^{1/2}}{(0.9566)} (100)^{1/2} = 0.03638$$

(continued)

PROBLEM 2-41 (CONTINUATION)

b (continued):

The value of  $\Delta G_T^\circ$  calculated here matches  $\Delta G_T^\circ$  in table 2.2 so Eqn. 2.64 is satisfied and the  $K_p$  calculated from  $\Delta G_T^\circ$  matches the  $K_p$  determined from the mole fractions in table 2.2 so Eqn. 2.65 is satisfied

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

$$\Delta G_T^\circ = 1 \bar{g}_{\text{CO}}^\circ + \frac{1}{2} \bar{g}_{\text{O}_2}^\circ - 1 \bar{g}_{\text{CO}_2}^\circ = 1(-367684) + \frac{1}{2}(0) - 1(-395562) = 27878 \text{ kJ}$$

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

$$K_p = \frac{x_{\text{CO}} x_{\text{O}_2}^{1/2}}{x_{\text{CO}_2}} \left(\frac{P}{P_0}\right)^{1/2} = \frac{(0.3581)(0.1790)^{1/2}}{(0.4629)} \left(\frac{1 \text{ atm}}{1 \text{ atm}}\right)^{1/2} = 0.32730$$

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

PROBLEM 2-42

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

FIND: The mole fractions  $X_{O_2}$  and  $X_{O}$  at the following conditions:

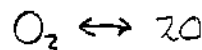
a)  $T = 2500 \text{ K}$ ,  $P = 1 \text{ atm}$

b)  $T = 2500 \text{ K}$ ,  $P = 3 \text{ atm}$

ASSUMPTIONS: Ideal gas, system is in chemical equilibrium

APPROACH: There are two unknowns ( $X_{O_2}$  and  $X_{O}$ ) so 2 equations must be used. The first is the definition of  $K_p$  and the second is  $\sum X_i = 1$

a)  $T = 2500 \text{ K}$



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

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

$$K_p = \frac{X_O^2}{X_{O_2}} \left(\frac{P}{P_0}\right) = 206.3 \times 10^{-6} \quad \leftarrow \text{FIRST EQUATION}$$

From  $\sum X_i = 1 = X_{O_2} + X_{O_2}$

$$X_{O_2} = 1 - X_O \quad \leftarrow \text{SECOND EQUATION}$$

substituting the second equation into the first and rearranging yields

$$\left(\frac{P}{P_0}\right) X_O^2 + K_p X_O - K_p = 0 \quad \text{quadratic equation}$$

solving for  $X_O$  
$$X_O = \frac{-K_p \pm \sqrt{K_p^2 + 4\left(\frac{P}{P_0}\right)(K_p)}}{2\left(\frac{P}{P_0}\right)}$$
 Note: Only + yields physically realistic result

$T = 2500 \text{ K}, P = 1 \text{ atm}: K_p = 206.3 \times 10^{-6}, \frac{P}{P_0} = 1 \rightarrow X_{O_2} = 0.0143, X_{O_2} = 1 - X_O = 0.9857$

$T = 2500 \text{ K}, P = 3 \text{ atm}: K_p = 206.3 \times 10^{-6}, \frac{P}{P_0} = 3 \rightarrow X_{O_2} = 0.00826, X_{O_2} = 1 - X_O = 0.9917$

COMMENTS: Note how this system follows the principle of Le Chatelier.

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  $x_o$  and  $x_{O_2}$ . 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  $\Delta G_T^\circ$  and  $K_p$ . Using the definition of  $K_p$  and conservation of elements, solve for the two unknowns  $x_o$  and  $x_{O_2}$

conservation of elements:	$O_2$	$O$	$Ar$
Initial	$\frac{1}{1}$	$\frac{0}{0}$	$\frac{1}{1}$
equilibrium shift	$-\xi$	$+2\xi$	$0$
final state	$\frac{1-\xi}{1-\xi}$	$\frac{2\xi}{2\xi}$	$\frac{1}{1} \leftarrow \# \text{ OF MOLES}$

$$\text{mole fractions: } x_{O_2} = \frac{N_{O_2}}{N_{TOT}} = \frac{1-\xi}{2+\xi}, \quad x_o = \frac{N_o}{N_{TOT}} = \frac{2\xi}{2+\xi}$$

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

$$\Delta G_T^\circ = [Nq_f^\circ]_o - [Nq_f^\circ]_{O_2} = 2[88203]_o - 1[0] = 176406 \text{ kJ/kmole}$$

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

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

substituting for  $x_o$  and  $x_{O_2}$  in terms of  $\xi$

$$K_p = \frac{\left[\frac{2\xi}{2+\xi}\right]^2}{\left[\frac{1-\xi}{2+\xi}\right]} = 206.6 \times 10^{-6} \text{ for } P = P_o = 1 \text{ atm}$$

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

for physically realistic results

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

(continued)

PROBLEM 2-43 (continued)

Solving for  $z$  :  $z = 0.0101$

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

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

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

$$X_{O_2} = 0.492$$

$$X_O = 0.01$$

$$X_{Ar} = 0.4974$$

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

$$O: N_O = X_O N_{TOT} = 0.014$$

$$O_2: N_{O_2} = X_{O_2} N_{TOT} = 0.9926$$

Problem 2-23

$$N_O = X_O N_{TOT} = X_O (2+z) = 0.01(2.01) = 0.02$$

$$N_{O_2} = X_{O_2} (2+z) = 0.492(2.01) = 0.989$$

COMMENTS: Note that the diluent does not affect  $\Delta G^\circ$  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 Chatelier's principle in that reducing the partial pressures (with the diluent) results in more dissociation.

PROBLEM 2-44

GIVEN: At  $P = 10 \text{ atm}$ ,  $T = 3000 \text{ K}$ :

$$x_{\text{CO}_2} = 0.6783, \quad x_{\text{CO}} = 0.2144, \quad x_{\text{O}_2} = 0.1072$$

FIND:  $K_p$  for  $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2} \text{O}_2$

ASSUMPTIONS: ideal gas mixture

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

$$K_p = \frac{(P_{\text{CO}}/P^0)(P_{\text{O}_2}/P^0)^{1/2}}{(P_{\text{CO}_2}/P^0)} = \frac{x_{\text{CO}} x_{\text{O}_2}^{1/2} (P/P^0)^{1/2}}{x_{\text{CO}_2}}$$

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

$$K_p = 0.3273$$

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:  $\Delta G_{3000} = -367,685 + \frac{1}{2}(0) - (-395,562) = 27,877 \text{ kJ/rmol}$ ;  $K_p = \exp(-27877/8.315(3000)) = 0.327$ , the same result as above.

PROBLEM 2-45

GIVEN: At  $P = 0.8 \text{ atm}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{O}_2$  mixture has the composition:  $\gamma_{\text{H}_2\text{O}} = 0.9$ ,  $\gamma_{\text{H}_2} = 0.03$ ,  $\gamma_{\text{O}_2} = 0.07$ .

FIND:  $K_p$  for  $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2} \text{O}_2$

ASSUMPTIONS: ideal gas mixture

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

$$K_p = \frac{(P_{\text{H}_2}/P^\circ)(P_{\text{O}_2}/P^\circ)^{1/2}}{(P_{\text{H}_2\text{O}}/P^\circ)} = \frac{\gamma_{\text{H}_2} \gamma_{\text{O}_2}^{1/2} (P/P^\circ)^{1/2}}{\gamma_{\text{H}_2\text{O}}}$$

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

$$\boxed{K_p = 0.00789}$$

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



PROBLEM 2-46

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

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

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

ASSUMPTIONS: ideal gas behavior

SOLUTION: a)  $K_p(T) = \frac{\gamma_{CO_2} \gamma_{H_2}}{\gamma_{H_2O} \gamma_{CO}} (P/P^{\circ})^{1+1-1-1}$

The net exponent of  $P/P^{\circ}$  is zero. There is no effect of P.

$$\begin{aligned} \text{b) } \Delta H_R &= \bar{h}_{f, CO_2}^{\circ} + \bar{h}_{f, H_2}^{\circ} - \bar{h}_{f, H_2O}^{\circ} - \bar{h}_{f, CO}^{\circ} \\ &= -396,600 + 0 - (-251,700) - (-118,700) \\ \Delta H_R &= -26,200 \Rightarrow \text{exothermic @ T} \end{aligned}$$

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  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$  and a ratio of moles of elemental H to elemental O equal to one

**FIND:** The equilibrium composition at  $T = 2000 \text{ K}$  and  $P = 1 \text{ atm}$

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

**APPROACH:** Evaluate  $\Delta G_T^\circ$ , determine  $K_p$ , and using the definition of  $K_p$  and conservation of elements, determine  $X_{\text{H}_2}$ ,  $X_{\text{O}_2}$  &  $X_{\text{H}_2\text{O}}$

Evaluation of  $\Delta G_T^\circ$ : 
$$\Delta G_T^\circ = 1(g_{f,T}^\circ)_{\text{H}_2\text{O}} - 1(g_{f,T}^\circ)_{\text{H}_2} - \frac{1}{2}(g_{f,T}^\circ)_{\text{O}_2}$$

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

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

In terms of  $X_i$ :

$$K_p = \frac{X_{\text{H}_2\text{O}}}{X_{\text{H}_2} X_{\text{O}_2}^{1/2}} \left(\frac{P}{P_0}\right)^{-1/2} \quad (1)$$

Conservation of elements:

$$\frac{\#H}{\#O} = 1 = \frac{2X_{\text{H}_2\text{O}} + 2X_{\text{H}_2}}{X_{\text{H}_2\text{O}} + 2X_{\text{O}_2}} \quad (2)$$

and by definition:

$$\sum X_i = 1 = X_{\text{H}_2\text{O}} + X_{\text{H}_2} + X_{\text{O}_2} \quad (3)$$

Solving (2) and (3) for  $X_{\text{H}_2}$  &  $X_{\text{H}_2\text{O}}$  in terms of  $X_{\text{O}_2}$  and substituting into (1):

$$\left. \begin{aligned} X_{\text{H}_2} &= 3X_{\text{O}_2} - 1 \\ X_{\text{H}_2\text{O}} &= 2 - 4X_{\text{O}_2} \end{aligned} \right\} K_p = \frac{2 - 4X_{\text{O}_2}}{(3X_{\text{O}_2} - 1)(X_{\text{O}_2})^{1/2}} \left(\frac{P}{P_0}\right)^{-1/2}$$

Solving for  $X_{\text{O}_2}$  by trial & error with  $P = P_0 = 1 \text{ atm}$

$$\begin{aligned} X_{\text{O}_2} &= 0.3334 \\ X_{\text{H}_2} &= 3X_{\text{O}_2} - 1 = 0.0003 \\ X_{\text{H}_2\text{O}} &= 2 - 4X_{\text{O}_2} = 0.6662 \end{aligned}$$

Comments:

PROBLEM 2-48

GIVEN: Equilibrium:  $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$  @ 2000 K, 1 atm.

FIND:  $\chi_{\text{H}_2}$ ,  $\chi_{\text{O}_2}$ ,  $\chi_{\text{H}_2\text{O}}$  when  $\frac{\# \text{H-atoms}}{\# \text{O-atoms}}$  is 0.5, 1, & 2

ASSUMPTIONS: ideal gas behavior

SOLUTION: Apply element conservation:

$$\frac{\# \text{H-atoms}}{\# \text{O-atoms}} (\equiv z) = \frac{2\chi_{\text{H}_2\text{O}} + 2\chi_{\text{H}_2}}{2\chi_{\text{O}_2} + \chi_{\text{H}_2\text{O}}}$$

Rearranging,

$$z(2\chi_{\text{O}_2} + \chi_{\text{H}_2\text{O}}) = 2\chi_{\text{H}_2\text{O}} + 2\chi_{\text{H}_2}, \text{ or}$$

$$\text{i) } (z-2)\chi_{\text{H}_2\text{O}} + 2z\chi_{\text{O}_2} - 2\chi_{\text{H}_2} = 0$$

$$\text{ii) } \chi_{\text{H}_2\text{O}} + \chi_{\text{O}_2} + \chi_{\text{H}_2} - 1 = 0$$

Apply equilibrium:

$$\text{iii) } \frac{\chi_{\text{H}_2} \chi_{\text{O}_2}^{1/2}}{\chi_{\text{H}_2\text{O}}} \left(\frac{P}{P^0}\right)^{1/2} = K_P = \exp\left(\frac{-\Delta G_r^0}{R_u T}\right)$$

Use i) & ii) to eliminate  $\chi_{\text{H}_2}$  & express  $\chi_{\text{H}_2\text{O}} = f(\chi_{\text{O}_2})$ :

$$\text{iv) } \chi_{\text{H}_2\text{O}} = \frac{z}{z-2} - \frac{2(z-1)}{z-2} \chi_{\text{O}_2}$$

Similarly, use i) & ii) to express  $\chi_{\text{H}_2}$  as function of  $\chi_{\text{O}_2}$ :

$$\text{v) } \chi_{\text{H}_2} = \frac{z-2}{z} + \frac{z+2}{z} \chi_{\text{O}_2}$$

Now substitute iv) & v) into iii):

PROBLEM 2-48 (continued)

$$\left(\frac{z-2}{z}\right)\left(\frac{P}{P_0}\right)^{1/2} \gamma_{O_2}^{1/2} + \left(\frac{z+2}{z}\right)\left(\frac{P}{P_0}\right)^{1/2} \gamma_{O_2}^{3/2} + \frac{2(z+1)K_P}{z} \gamma_{O_2} - \frac{2K_P}{z} = 0 \equiv f(\gamma_{O_2}) \quad \text{vi)}$$

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

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

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

$$\text{viii)} \quad f'(\gamma_{O_2}) = \frac{1}{2} \left(\frac{z-2}{z}\right) \left(\frac{P}{P_0}\right)^{1/2} \gamma_{O_2}^{-1/2} + \frac{3}{2} \left(\frac{z+2}{z}\right) \left(\frac{P}{P_0}\right)^{1/2} \gamma_{O_2}^{1/2} + \frac{2(z+1)K_P}{z}$$

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

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

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

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

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

PROBLEM 2-4B (CONTINUED)

$z$	$\chi_{O_2}$	$\chi_{H_2}$	$\chi_{H_2O}$
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  $\chi_{H_2}$  and  $\chi_{H_2O}$  increase.

For  $z = 2$ ,  $\chi_{H_2O}$  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  $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$  @  $T = 2000\text{ K}$

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

FIND:  $x_{\text{H}_2}$ ,  $x_{\text{O}_2}$ ,  $x_{\text{H}_2\text{O}}$  for a)  $P = 0.5 \text{ atm}$ ,  
 b)  $P = 1 \text{ atm}$ , c)  $P = 2 \text{ atm}$

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.

$P_{\text{atm}}$	$x_{\text{O}_2}$	$x_{\text{H}_2}$	$x_{\text{H}_2\text{O}}$
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  $\text{H}_2\text{O}$  decreases as the pressure increases. At 2000K, we expect that other dissociation species should be included in the analysis, in particular,  $\text{OH}$ ,  $\text{O}$ , and  $\text{H}$ .

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  $\sum X_i = 1$ , and the other four from the definition of equilibrium constants  $K_p$

$$\text{conservation of elements: } \frac{\#H \text{ atoms}}{\#O \text{ atoms}} = \frac{2X_{H_2} + X_{OH} + X_H + 2X_{H_2O}}{2X_{O_2} + X_{OH} + X_O + X_{H_2O}} = 2 \quad (1)$$

$$\text{Summation of } X_i : \quad \sum X_i = X_{H_2} + X_{O_2} + X_{OH} + X_O + X_H + X_{H_2O} = 1 \quad (2)$$

equilibrium reactions:

$$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O \quad K_{p_{H_2O}} = \exp\left[-\frac{\Delta G_T^\circ}{R_u T}\right]_{H_2O} = \frac{X_{H_2O}}{X_{H_2} X_{O_2}^{1/2}} \left(\frac{P}{P_0}\right)^{-1/2} \quad (3)$$

$$H_2 \leftrightarrow 2H \quad (K_p)_H = \exp\left[-\frac{\Delta G_T^\circ}{R_u T}\right]_H = \frac{X_H^2}{X_{H_2}} \left(\frac{P}{P_0}\right) \quad (4)$$

$$O_2 \leftrightarrow 2O \quad (K_p)_O = \exp\left[-\frac{\Delta G_T^\circ}{R_u T}\right]_O = \frac{X_O^2}{X_{O_2}} \left(\frac{P}{P_0}\right) \quad (5)$$

$$H + O \leftrightarrow OH \quad (K_p)_{OH} = \exp\left[-\frac{\Delta G_T^\circ}{R_u T}\right]_{OH} = \frac{X_{OH}}{X_H X_O} \left(\frac{P}{P_0}\right)^{-1} \quad (6)$$

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

$$X_{H_2}, X_{O_2}, X_{OH}, X_O, X_H, X_{H_2O}$$

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 2-5}**

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

FINN: The approximate mole fractions of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{H}$ ,  $\text{OH}$ ,  $\text{O}_2$ ,  $\text{O}$ ,  $\text{N}_2$ ,  $\text{NO}$  and  $\text{N}$  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  $H_{\text{reactants}} = -103,847 \text{ kJ/kmole-fuel}$

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

Species	$\chi$	Species	$\chi$
$\text{N}_2$	0.737	$\text{N}_2$	0.69
$\text{H}_2\text{O}$	0.125	$\text{H}_2\text{O}$	0.155
$\text{CO}_2$	0.094	$\text{CO}_2$	0.079
$\text{O}_2$	0.038	$\text{CO}$	0.054
$\text{NO}$	3500 ppm	$\text{H}_2$	0.020
$\text{OH}$	1800 ppm	$\text{OH}$	860 ppm
$\text{CO}$	890 ppm	$\text{H}$	800 ppm
$\text{H}_2$	250 ppm	$\text{NO}$	240 ppm
$\text{O}$	176 ppm	$\text{O}_2$	77 ppm
$\text{H}$	34 ppm	$\text{O}$	20 ppm
$\text{N}$	0.14 ppb	$\text{N}$	1 ppb

minor species {

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

Problem Title: PROBLEM 2-51 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

C10H22	PHI = 0.75	PHI = 0.75	PHI = 0.75	PHI = 1.0	PHI = 1.0	PHI = 1.0
	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

C10H22	PHI = 1.25	PHI = 1.25	PHI = 1.25
	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, 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.

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

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

Conservation of:

C

O

H

b = will solve for using water-gas shift  $K_p$

$$c = x - b$$

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

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

$$f = 0 \quad \text{since combustion is fuel-rich}$$

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

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

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

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)

PROBLEM 2-54 (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

$$\Delta G_T^\circ = (1) \bar{g}_{f, \text{CO}_2}^\circ + (1) \bar{g}_{f, \text{H}_2}^\circ - (1) \bar{g}_{f, \text{CO}}^\circ - (1) \bar{g}_{f, \text{H}_2\text{O}}^\circ$$

at 2200 K:

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

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

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	$\chi$
CO <sub>2</sub>	5.36	0.079
CO	4.64	0.069
H <sub>2</sub> O	9.44	0.140
H <sub>2</sub>	1.56	0.023
N <sub>2</sub>	46.62	0.690
	67.62	1.0

$$\text{Check: } K_p = \frac{\chi_{\text{CO}_2} \chi_{\text{H}_2}}{\chi_{\text{CO}} \chi_{\text{H}_2\text{O}}} = \frac{(0.0793)(0.0231)}{(0.0686)(0.1396)}$$

$$K_p = 0.191 \quad \checkmark$$

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.

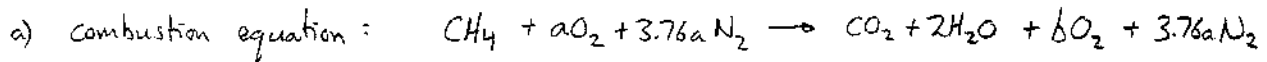
PROBLEM 2-55

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 ( $P=1 \text{ atm}$ )

ASSUMPTIONS: no product dissociation, all energy lost by flue gases in preheater is transferred to air entering boiler,  $\Delta KE \neq \Delta PE$  are negligible, steady-state

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



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

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

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

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

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

$$b = a - 2 = 0.19$$

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

$$\phi = 0.914$$

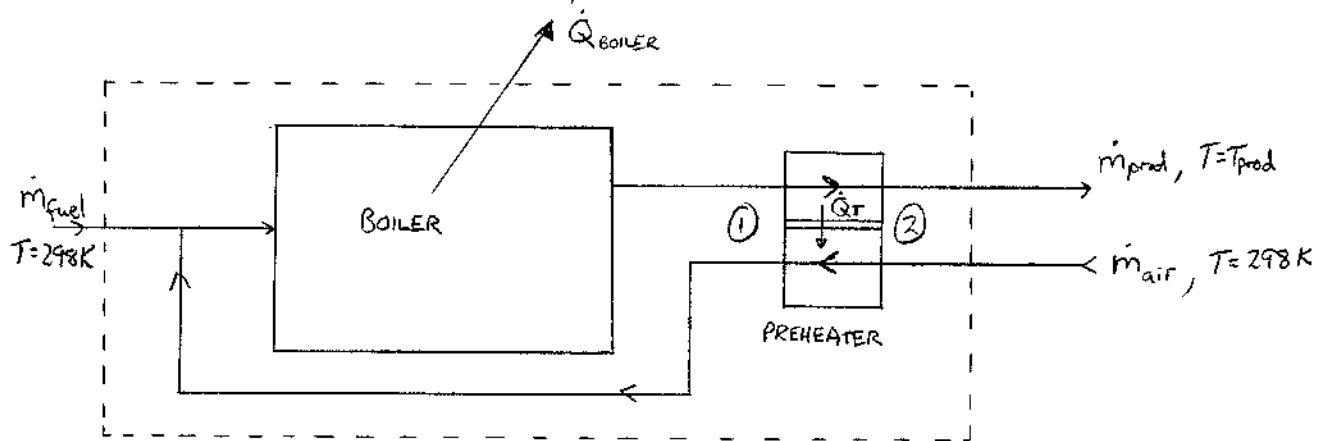
(continued)

PROBLEM 2-55 (continued)

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

where  $\dot{Q}_{\text{BOILER}}$  is the heat transferred by the boiler and  $\dot{Q}_{\text{MAX}}$  represents the maximum possible heat transfer (products at 298 K)

schematic for first law analysis:



first law for control volume:

$$\dot{Q} - \dot{W} = [\sum \dot{N}_i \bar{h}_i]_{\text{prod}} - [\dot{N} \bar{h}]_{\text{fuel}} - [\dot{N} \bar{h}]_{\text{air}}$$

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

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

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

$$\begin{aligned} \sum \frac{\dot{N}_i}{\dot{N}_{\text{fuel}}} \bar{h}_i &= 1 \bar{h}_f^\circ_{\text{CO}_2} + 2 \bar{h}_f^\circ_{\text{H}_2\text{O}} + b \bar{h}_f^\circ_{\text{O}_2} + 3.76a \bar{h}_f^\circ_{\text{N}_2} \leftarrow \text{from combustion equation} \\ &= 1[-393546] + 2[-241847] + 0 + 0 = -877240 \text{ kJ/(kmole-fuel)} \end{aligned}$$

so,  $q_{\text{max}} = -877240 - \left[ \frac{-74831}{\text{fuel}} \right] - 10.42 (0)_{\text{air}} = -802409 \text{ kJ/(kmole-fuel)}$

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

$$\begin{aligned} \sum \frac{\dot{N}_i}{\dot{N}_{\text{fuel}}} \bar{h}_i &= 1[-393546 + 17749]_{\text{CO}_2} + 2[-241847 + 14209] + 0.19[0 + 12503]_{\text{O}_2} + 8.23[0 + 11742]_{\text{N}_2} \\ &= -730415 \text{ kJ/(kmole-fuel)} \end{aligned}$$

(continued)

PROBLEM 2-55 (continued)

$$b(\text{continued}): \dot{q}_{\text{BOILER}} = -730415 - [-74831] - 10.42(0) = -655584 \text{ kJ/kmole-fuel}$$

$$\eta = \frac{\dot{Q}_{\text{BOILER}}}{\dot{Q}_{\text{max}}} = \frac{\dot{q}_{\text{BOILER}}}{\dot{q}_{\text{max}}} = \frac{-655584}{-802409} = 0.82$$

$$\boxed{\eta = 0.82} \quad \text{without preheat}$$

c) with air preheat ( $T_{\text{prod}} = 433\text{K}$ ):  $\bar{h} = \bar{h}_f^\circ + (\bar{h} - \bar{h}_f^\circ)$

$$\dot{q}_{\text{BOILER}} = \sum \frac{\dot{N}_i}{\dot{N}_{\text{fuel}}} \bar{h}_i - \bar{h}_f^\circ - \frac{1}{F} \sum \dot{N}_{\text{AIR}} \bar{h}_{\text{air}}$$

$$\begin{aligned} \sum \frac{\dot{N}_i}{\dot{N}_{\text{fuel}}} &= 1[-393546 + 5421]_{\text{CO}_2} + 2[-241847 + 4609]_{\text{H}_2\text{O}} + 0.19[0 + 4043]_{\text{O}_2} + 8.23[0 + 3746]_{\text{N}_2} \\ &= -829357 \text{ kJ/kmole-fuel} \end{aligned}$$

$$\dot{q}_{\text{BOILER}} = -829357 - [-74831]_{\text{fuel}} - 10.42(0)_{\text{air}} = -754526 \text{ kJ/kmole-fuel}$$

$$\eta = \frac{-754526}{-802409} = 0.94 \quad \boxed{\eta = 0.94} \quad \text{with preheat}$$

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 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:

$$\begin{aligned} \dot{H}_{\text{IN}} &= \dot{H}_{\text{OUT}} \\ \dot{H}_{\text{P}①} + \dot{H}_{\text{air}②} &= \dot{H}_{\text{P}②} + \dot{H}_{\text{air}①} \end{aligned}$$

$$\dot{H}_{\text{air}①} = \dot{H}_{\text{P}①} - \dot{H}_{\text{P}②} + \dot{H}_{\text{air}②}$$

per kmole of fuel burned:

$$a\bar{h}_{\text{O}_2} + 3.76a\bar{h}_{\text{N}_2} = \sum \frac{\dot{N}_i}{\dot{N}_{\text{fuel}}} \bar{h}_i_{700\text{K}} - \sum \frac{\dot{N}_i}{\dot{N}_{\text{fuel}}} \bar{h}_i_{433\text{K}} + [a\bar{h}_{\text{O}_2} + 3.76a\bar{h}_{\text{N}_2}]_{298\text{K}}$$

(CONTINUED)



PROBLEM 2-55 (continued)

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

determine adiabatic flame temperature:

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

$$H_p = [-74831 + 0] + 98942 \text{ KJ/kmole-fuel} = 24111 \text{ KJ/kmol-fuel}$$

$$\begin{aligned} H_p &= 1\bar{h}_{CO_2} + 2\bar{h}_{H_2O} + 0.19\bar{h}_{O_2} + 8.23\bar{h}_{N_2} \\ &= 1[-393546 + \Delta h_{sens}]_{CO_2} + 2[-241847 + \Delta h_{sens}]_{H_2O} + 0.19[0 + \Delta h_{sens}]_{O_2} + 8.23[0 + \Delta h_{sens}]_{N_2} \end{aligned}$$

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

where  $\Delta h_{sens} = \bar{h} - \bar{h}_f^\circ$  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

$T = 2405 \text{ K}$

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.

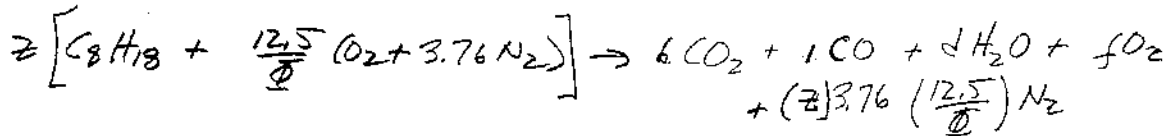
PROBLEM 2-56

GIVEN:  $C_8H_{18}$  products:  $x_{CO_2} = 0.06$  (wet);  $x_{CO} = 0.01$  (wet)

FIND: a)  $\Phi$       b)  $x_{O_2}$

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:  $a = x + y/4 = 8 + 18/4 = 12.5$



C-balance:  $8z = 6 + 1$  (RHS  $\equiv 100$  kmols)  
 $z = 7/8$

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

O-balance:  $\frac{7}{8} \frac{12.5}{\Phi} z = 12 + 1 + \frac{63}{8} + 2f$

i)  $\frac{10.9375}{\Phi} = 10.4375 + f$

Overall:  $\sum N_{pr} = 100 \Rightarrow 6 + 1 + \frac{63}{8} + f + \frac{7}{8} 3.76 \frac{12.5}{\Phi} = 100$

or  $f = 85.125 - \frac{41.125}{\Phi}$  (ii)

Substitute i)  $\rightarrow$  ii)

a)  $\frac{10.9375}{\Phi} - 10.4375 = 85.125 - \frac{41.125}{\Phi}$ ;  $\Phi = \frac{52.0625}{95.5625} = \boxed{0.5448}$

b)  $f = 85.125 - \frac{41.125}{0.5448} = 9.6386$   $x_{O_2} = f/100 = 0.0964$   
 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)

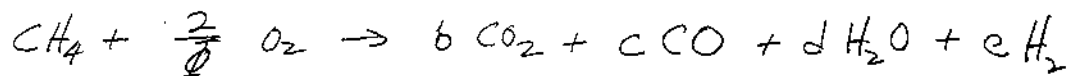
PROBLEM 2-57

GIVEN:  $\text{CH}_4/\text{O}_2$  burned to yield  $\text{CO}, \text{CO}_2, \text{H}_2\text{O}, \text{H}_2$ ;  $\Phi = 1.5$

FIND: a) mixture composition for  $T = 1500\text{K}$   
 b) mixture composition for  $T = 2500\text{K}$

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.



Arbitrarily reference to # H atoms:

$$\text{i) } \frac{\# \text{C atoms}}{\# \text{H atoms}} = \frac{1}{4} = \frac{\gamma_{\text{CO}} + \gamma_{\text{CO}_2}}{2\gamma_{\text{H}_2\text{O}} + 2\gamma_{\text{H}_2}}$$

$$\text{ii) } \frac{\# \text{O atoms}}{\# \text{H atoms}} = \frac{4/\Phi}{4} = \frac{1}{\Phi} = \frac{2}{3} = \frac{\gamma_{\text{CO}} + 2\gamma_{\text{CO}_2} + \gamma_{\text{H}_2\text{O}}}{2\gamma_{\text{H}_2\text{O}} + 2\gamma_{\text{H}_2}}$$

$$\text{iii) } 1 = \gamma_{\text{CO}} + \gamma_{\text{CO}_2} + \gamma_{\text{H}_2\text{O}} + \gamma_{\text{H}_2}$$

Equilibrium:  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$

$$\text{iv) } K_p(T) = \frac{\gamma_{\text{CO}_2} \gamma_{\text{H}_2}}{\gamma_{\text{CO}} \gamma_{\text{H}_2\text{O}}}$$

a) Simultaneously solve Eqs i-iv for  $K_p(T)$  evaluated at  $T = 1500\text{K}$ . 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. ( $\dot{N}_{N_2} = 0$ )

Using spreadsheet software, we obtain the following results:

<u>T (K)</u>	<u><math>K_p</math></u>	<u>% CO<sub>2</sub></u>	<u>% CO</u>	<u>% H<sub>2</sub>O</u>	<u>% H<sub>2</sub></u>
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<sub>2</sub> 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

$$T_{ref} = 300 \text{ K}$$

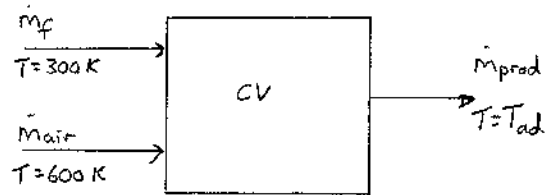
$$MW_f = MW_{air} = MW_{prod} = 29 \text{ kg/kmole}$$

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

$$h_{f,air}^{\circ} = h_{f,prod}^{\circ} = 0$$

$$h_{f,f}^{\circ} = 4 \times 10^7 \text{ J/kg}$$

APPROACH: This is a first law analysis



$$\dot{Q} - \dot{W} = \dot{H}_p - \dot{H}_R \longrightarrow \dot{H}_p = \dot{H}_R$$

for  $A/F_{mass}$

$$\begin{aligned} \dot{m}_{prod} &= \dot{m}_f (1 + A/F) \\ \dot{m}_{air} &= \dot{m}_f (A/F) \\ \dot{m}_f &= \dot{m}_f (1) \end{aligned}$$

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

$$\begin{aligned} \dot{m}_p h_p &= \dot{m}_f h_f + \dot{m}_{air} h_{air} \longrightarrow \dot{m}_f (1 + A/F) [0 + C_p (T_{ad} - T_{ref})]_p = \dot{m}_f (A/F) [0 + C_p (T_{air} - T_{ref})]_{air} \\ &\quad + \dot{m}_f [h_f^{\circ} + C_p (T_f - T_{ref})]_f \\ (1+16)[0 + 1200(T_{ad} - 300)] &= (16)[0 + 1200(600 - 300)] + (1)[4 \times 10^7 + 1200(300 - 300)] \end{aligned}$$

solving for  $T_{ad}$  :

$$T_{ad} = 2543 \text{ K}$$

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 ( $\Delta T_{ad} = 283 \text{ K}$ ). If the fuel were preheated too, then  $\Delta T_{ad} = 300 \text{ K}$ , exactly.

## PROBLEM 2-64

NOTE: This problem can be used as a small project.

GIVEN:  $T_{\text{CH}_4} = 298 \text{ K}$ ;  $T_{\text{air}} = 325 \text{ K}$ ;  $\gamma_{\text{O}_2} = 0.02$

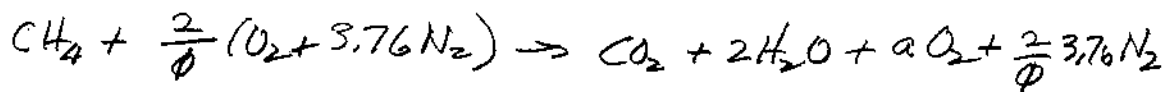
FIND: Combinations of % FGR &  $T_{\text{FGR}}$  that result in  $T_{\text{ad}} = 1950 \text{ K}$ .

ASSUMPTIONS: FGR composition based on no dissociation; natural gas  $\sim \text{CH}_4$ ;  
 $T_{\text{FGR, max}} = 1200 \text{ K}$ .

APPROACH: i) Use  $\gamma_{\text{O}_2}$  to determine stoichiometry  
 ii) Apply 1<sup>st</sup> law (Eqn 2.40) to determine req'd enthalpy of FGR  
 iii) Relate  $H_{\text{FGR}}$  to % FGR &  $T_{\text{FGR}}$

SOLUTION:

For no dissociation, flue gas composition can be obtained:



$$\text{O-balance: } 2\left(\frac{2}{\phi}\right) = 2 + 2 + 2a \quad ; \quad a = \frac{2}{\phi} - 2 \quad (\text{I})$$

$$\text{Given } \gamma_{\text{O}_2}: \quad 0.02 = a / \left(1 + 2 + a + \frac{2}{\phi}(3.76)\right) \quad (\text{II})$$

Simultaneous solution of I & II yields:

$$a = 0.2325$$

$$\phi = 0.8958$$

$$N_{\text{tot}} = N_{\text{CO}_2} + N_{\text{H}_2\text{O}} + N_{\text{O}_2} + N_{\text{N}_2} = 1 + 2 + 0.2325 + \frac{2(3.76)}{0.8958}$$

PROBLEM 2-64 (continued)

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

$$x_{CO_2} = \frac{1}{11.627} = 0.0860 \quad x_{O_2} = \frac{0.2325}{11.627} = 0.0200$$

$$x_{H_2O} = \frac{2}{11.627} = 0.1720 \quad x_{N_2} = \frac{8.395}{11.627} = 0.7220$$

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

or 
$$1 \bar{h}_{CH_4} + N_A \bar{h}_A + N_{FGR} \bar{h}_{FGR}(T_{FGR}) = N_{Pr} \bar{h}_{Pr}(1950 K) \quad (II)$$

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

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

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  $N_{Pr}/N_{FGR} = \frac{11.6357}{11.627} = 1.0007 \sim 1$

Substitute IV into III & solve for  $N_{FGR}/N_F$ :

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

where

See TPEQUIL  
output

$$\begin{aligned} (N_{Pr}/N_F) \bar{h}_{Pr}(1950K) &= (N_{Pr}/N_F) h_{Pr} M U_{Pr} \\ &= 11.6357 (-532.8 \frac{kJ}{kg}) 27.7295 \frac{kg}{kmol} \\ &= -1.71909 \cdot 10^5 \text{ kJ/kmol} \end{aligned}$$

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

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

(Tables A.11 & A.7)

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

$$N_A/N_F = \frac{2(4.76)}{\phi} = \frac{2(4.76)}{0.8958} = 10.627$$

Substituting numerical values from above into V:

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

PROBLEM 2-64 (CONTINUED)

To complete our solution, we calculate  $\bar{h}_{FGR}$  for a range of temperatures (330-1200K); solve eqn VII for  $N_{FGR}/N_F$ ; and apply the definition of %FGR:

$$\begin{aligned} \%FGR &= \frac{N_{FGR} \cdot 100\%}{N_A + N_F} = \frac{N_{FGR}/N_F}{N_A/N_F + 1} \cdot 100\% \\ &= (N_{FGR}/N_F) \frac{100}{11.627} = 8.6(N_{FGR}/N_F) \end{aligned}$$

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

For example, at 1200K,

$$\begin{aligned} \bar{h}_{FGR}(1200K) &= 0.0860(-393,546 + 44,488) + \\ &\quad 0.1720(-241,845 + 34,518) + \\ &\quad 0.020(0 + 29,715) + \\ &\quad 0.7220(0 + 28,118) \\ &= -44,782 \text{ kJ/kmol} \end{aligned}$$

$T_{FGR}$ (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.