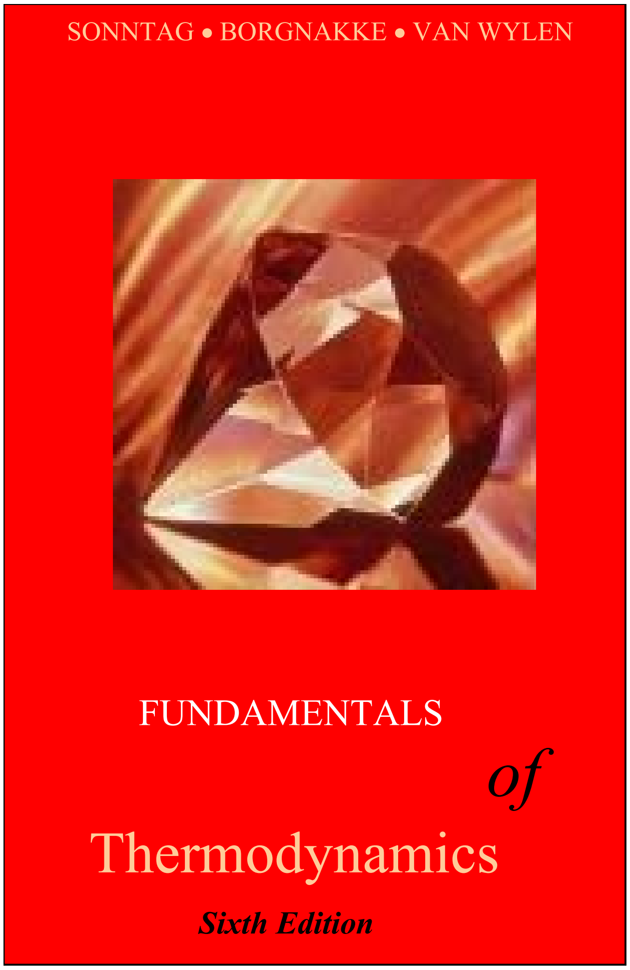
# SOLUTION MANUAL
# ENGLISH UNIT PROBLEMS
# CHAPTER 15



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FUNDAMENTALS

*of*

Thermodynamics

***Sixth Edition***

# CHAPTER 15

## CONTENT CHAPTER 15

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|---|---|---|---|---|---|---|---|---|
| 89 | 53 | 21 | 95 | 62 | 45 | 101 | 67 | 71 |
| 90 | new | 25 | 96 | 63 | 54 | 102 | 68 | 72 |
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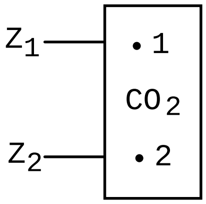
## Equilibrium

**15.89E**

Carbon dioxide at 2200 lbf/in.$^2$ is injected into the top of a 3-mi deep well in connection with an enhanced oil recovery process. The fluid column standing in the well is at a uniform temperature of 100 F. What is the pressure at the bottom of the well assuming ideal gas behavior?



$(Z_1 - Z_2)$ = 3 miles = 15 840 ft

$P_1$ = 2200 lbf/in$^2$, T = 100 F = const

Equilibrium and ideal gas beahvior

$$-w_{REV} = 0 = \Delta g + \Delta PE = RT \ln (P_2/P_1) + g(Z_2 - Z_1) = 0$$

$$\ln (P_2/P_1) = \frac{32.2 \times 15\,840}{32.2 \times 35.1 \times 559.7} = 0.8063$$

$$P_2 = 2200 \exp(0.8063) = 4927 \text{ lbf/in}^2$$

## Chemical equilibrium, Equilibrium Constant

### 15.90E

Calculate the equilibrium constant for the reaction $O_2 <=> 2O$ at temperatures of 537 R and 10 000 R.

Find the change in Gibbs function at the two T's from Table F.6:

537 R: $\Delta H^0 = 2\bar{h}^0_{f\,O} - 1\bar{h}^0_{f\,O2} = 2 \times 107\,124 = 214\,248$ Btu/lbmol;

$\Delta S^0 = 2\bar{s}^0_O - 1\bar{s}^0_{O2} = 2 \times 38.442 - 48.973 = 27.911$ Btu/lbmol R

$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 214\,248 - 537 \times 27.911 = 199\,260$ Btu/lbmol

$$\ln K = -\frac{\Delta G^0}{\bar{R}T} = -\frac{+199\,260}{1.98589 \times 537} = \mathbf{-185.85}$$

10 000 R: $\Delta H^0 = 2\bar{h}^0_{f\,O} - 1\bar{h}^0_{f\,O2} = 2\,(107\,124 + 47\,897) - 87\,997$

$= 222\,045$ Btu/lbmol;

$\Delta S^0 = 2\bar{s}^0_O - 1\bar{s}^0_{O2} = 2 \times 53.210 - 74.034 = 32.386$ Btu/lbmol R

$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 222\,045 - 10\,000 \times 32.386 = -101\,815$

$\ln K = -\Delta G^0/RT = 101\,815 / (1.98589 \times 10\,000) = \mathbf{+5.127}$

**15.91E**

Pure oxygen is heated from 77 F to 5300 F in a steady flow process at a constant pressure of 30 lbf/in.$^2$. Find the exit composition and the heat transfer.

The only reaction will be the dissociation of the oxygen

$$O_2 \Leftrightarrow 2O \ ; \quad K(5300\ F) = K(3200\ K) = 0.046467$$

Look at initially 1 mol Oxygen and shift the above reaction with x

$$n_{O2} = 1 - x; \quad n_O = 2x; \quad n_{tot} = 1 + x; \quad y_i = n_i/n_{tot}$$

$$K = \frac{y_O^2}{y_{02}}\left(\frac{P}{P_o}\right)^{2-1} = \frac{4x^2}{(1+x)^2}\,\frac{1+x}{1-x}\,2 = \frac{8x^2}{1-x^2}$$

$$x^2 = \frac{K/8}{1+K/8} \Rightarrow x = 0.07599; \quad y_{02} = \mathbf{0.859}; \quad y_0 = \mathbf{0.141}$$

$$\bar{q} = n_{02ex}\bar{h}_{02ex} + n_{0ex}\bar{h}_{Oex} - \bar{h}_{02in} = (1+x)(y_{02}\bar{h}_{02} + y_0\bar{h}_O) - 0$$

$$\bar{h}_{02} = 45\ 581; \quad \bar{h}_O = 107124 + 26125 = 133\ 249$$

$$\bar{q} = 1.076(0.859 \times 45581 + 0.141 \times 133249) = 62345 \text{ Btu/lbmol } O_2$$

$$q = \bar{q}/32 = 1948 \text{ Btu/lbm} \ \ (=1424 \text{ if no dissociation})$$

**15.92E**

Air (assumed to be 79% nitrogen and 21% oxygen) is heated in a steady flow process at a constant pressure of 14.7 lbf/in.$^2$, and some NO is formed. At what temperature will the mole fraction of NO be 0.001?

$0.79N_2 + 0.21O_2$ heated at 14.7 lbf/in$^2$, forms NO

At exit, $y_{NO} = 0.001$

$$\begin{array}{llll} N_2 + O_2 \Leftrightarrow & 2\,NO & \qquad & n_{N2} = 0.79 - x \\ -x \quad -x & +2x & & n_{O2} = 0.21 - x \\ & & & n_{NO} = 0 \quad + 2x \\ \hline & & & n \;= 1.0 \end{array}$$

$$y_{NO} = 0.001 = \frac{2x}{1.0} \Rightarrow \quad x = 0.0005 \quad \Rightarrow \quad n_{N2} = 0.7895, \quad n_{O2} = 0.2095$$

$$K = \frac{y_{NO}^2}{y_{N2}y_{O2}}\left(\frac{P}{P^0}\right)^0 = \frac{10^{-6}}{0.7895\times0.2095} = 6.046\times10^{-6} \qquad \text{or} \quad \ln K = -12.016$$

From Table A.11, T = 1444 K = **2600 R**

**15.93E**

The combustion products from burning pentane, $C_5H_{12}$, with pure oxygen in a stoichiometric ratio exists at 4400 R. Consider the dissociation of only $CO_2$ and find the equilibrium mole fraction of CO.

$$C_5H_{12} + 8\ O_2 \rightarrow 5\ CO_2 + 6\ H_2O$$

At 4400 R,

$\ln K = -7.226$

$K = 7.272\text{x}10^{-4}$

|  | $2\ CO_2$ | $\Leftrightarrow 2\ CO$ | $+ 1\ O_2$ |
|---|---|---|---|
| Initial | 5 | 0 | 0 |
| Change | -2z | +2z | +z |
| Equil. | 5-2z | 2z | z |

Assuming $P = P^o = 0.1$ MPa,

$$K = \frac{y_{CO}^2 y_{O_2}}{y_{CO_2}^2}\left(\frac{P}{P^0}\right) = \left(\frac{2z}{5 - 2z}\right)^2\left(\frac{z}{5 + z}\right)(1) = 7.272\text{x}10^{-4};$$

Trial & error on z: $z = 0.2673$

$n_{CO_2} = 4.4654$; $n_{CO} = 0.5346$; $n_{O_2} = 0.2673$

$y_{CO} =$ **0.1015**

**15.94E**

Pure oxygen is heated from 77 F, 14.7 lbf/in.$^2$ to 5300 F in a constant volume container. Find the final pressure, composition, and the heat transfer

As oxygen is heated it dissociates

$O_2 \Leftrightarrow 2O \qquad \ln K_{eq} = -3.069$

C. V. Heater: $U_2 - U_1 = {}_1Q_2 = H_2 - H_1 - P_2v + P_1v$

Per mole $O_2$: ${}_1\bar{q}_2 = \bar{h}_2 - \bar{h}_1 + \bar{R}(T_1 - (n_2/n_1)T_2)$

Shift x in reaction final composition: $(1 - x)O_2 + 2xO$

$n_1 = 1 \qquad n_2 = 1 - x + 2x = 1 + x$

$y_{O2} = (1 - x)/(1 + x)\ ; \quad y_O = 2x/(1 + x)$

Ideal gas and $V_2 = V_1 \Rightarrow P_2 = P_1n_2T_2/n_1T_1 \Rightarrow P_2/P_o = (1 + x)T_2/T_1$

Substitute the molefractions and the pressure into the equilibrium equation

$$K_{eq} = e^{-3.069} = \frac{y_O^2}{y_{02}}\left(\frac{P_2}{P_o}\right) = \left(\frac{2x}{1 + x}\right)^2 \left(\frac{1 + x}{1 - x}\right) \left(\frac{1 + x}{1}\right) \left(\frac{T_2}{T_1}\right)$$

$$\Rightarrow \frac{4x^2}{1 - x} = \frac{T_1}{T_2}e^{-3.069} = 0.00433 \Rightarrow \quad x = 0.0324$$

$(n_{O2})_2 = 0.9676, \quad (n_O)_2 = 0.0648, \quad n_2 = 1.0324$

$${}_1\bar{q}_2 = 0.9676(45\ 581) + 0.0648(107\ 124 + 26\ 125) - 0$$

$$+ 1.98589(536.67 - 1.0324 \times 5760) = \mathbf{41\ 996\ Btu/lbmol\ O_2}$$

$y_{O2} = 0.9676 / 1.0324 = \mathbf{0.937}; \qquad y_O = 0.0648/1.0324 = \mathbf{0.0628}$

**15.95E**

The equilibrium reaction with methane as $CH_4 \Leftrightarrow C + 2H_2$ has ln K = -0.3362 at 1440 R and ln K = -4.607 at 1080 R. By noting the relation of K to temperature, show how you would interpolate lnK in (1/T) to find K at 1260 R and compare that to a linear interpolation.

ln K = -0.3362 at 1440 R  ln K = -4.607 at 1080 R

$$\ln K_{1260} = \ln K_{1440} + \frac{\frac{1}{1260} - \frac{1}{1440}}{\frac{1}{1080} - \frac{1}{1440}} \times (-4.607 + 0.3362)$$

$$= -0.3362 + \frac{\frac{1440}{1260} - 1}{\frac{1440}{1080} - 1} \times (-4.2708) \;\; = -2.1665$$

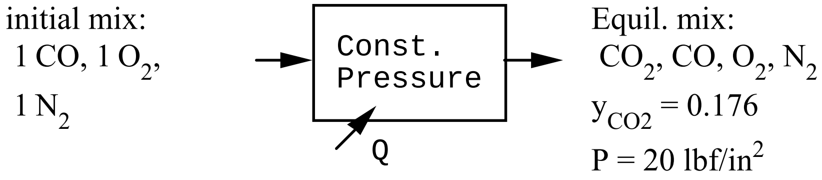
Linear interpolation:

$$\ln K_{1260} = \ln K_{1080} + \frac{1260 - 1080}{1440 - 1080} (\ln K_{1440} - \ln K_{1080})$$

$$= -4.607 + \frac{1}{2} (-0.3362 + 4.607) = \mathbf{-2.4716}$$

**15.96E**

A gas mixture of 1 pound mol carbon monoxide, 1 pound mol nitrogen, and 1 pound mol oxygen at 77 F, 20 lbf/in.$^2$, is heated in a constant pressure steady flow process. The exit mixture can be assumed to be in chemical equilibrium with $CO_2$, CO, $O_2$, and $N_2$ present. The mole fraction of $CO_2$ at this point is 0.176. Calculate the heat transfer for the process.



| reaction | $2\,CO_2$ | ⇔ | 2 CO | + | $O_2$ | also, | $N_2$ |
|---|---|---|---|---|---|---|---|
| initial | 0 | | 1 | | 1 | | 1 |
| change | +2x | | -2x | | -x | | 0 |
| equil. | 2x | | (1-2x) | | (1-x) | | 1 |

$$y_{CO2} = 0.176 = \frac{2x}{3-x} \quad \Rightarrow \quad x = 0.242\,65$$

$$\left.\begin{array}{ll} n_{CO2} = 0.4853 & n_{O2} = 0.757\,35 \\ n_{CO} = 0.5147 & n_{N2} = 1 \end{array}\right\} \left\{\begin{array}{l} y_{CO2} = 0.176 \\ y_{CO} = 0.186\,67 \\ y_{O2} = 0.274\,67 \end{array}\right.$$

$$K = \frac{y_{CO}^2 y_{O2}}{y_{CO2}^2}\left(\frac{P}{P^0}\right)^1 = \frac{0.186\,67^2 \times 0.274\,67}{0.176^2}\left(\frac{20}{14.504}\right) = 0.426\,07$$

Since Table A.11 corresponds to a pressure $P_0$ of 100 kPa, which is 14.504 lbf/in$^2$. Then, from A.11, $T_{PROD}$ = 3200 K = 5760 R

$H_R$ = -47 518 Btu

$H_P$ = 0.4853(-169 184 + 71 075) + 0.5147(-47 518 + 43 406)

+ 0.757 35(0 + 45 581) + 1(0 + 43 050) = +27 842 Btu

$Q_{CV} = H_P - H_R$ = 27 842 - (-47 518) = **+75 360 Btu**

**15.97E**

Use the information in problem 15.95E to estimate the enthalpy of reaction, $\Delta H^{o}$, at 1260 R using the van't Hoff equation (see problem 15.48) with finite differences for the derivatives.

$$d\ln K = [\Delta H°/\bar{R}T^2]dT \quad \text{or} \quad \text{solve for } \Delta H°$$

$$\Delta H° = \bar{R}T^2 \frac{d\ln K}{dT} = \bar{R}T^2 \frac{\Delta \ln K}{\Delta T}$$

$$= 1.98589 \times 1260^2 \times \frac{-0.3362 + 4.607}{1440 - 1080} = 37403 \text{ Btu/lb mol}$$

[Remark: compare this to F.6 values + F.4, F.11,

$$\Delta H° = H_C + 2H_{H_2} - H_{CH_4} = 0.146 \times 12 \times (1260\text{-}537) + 2 \times 5044$$

$$- 0.538 \times 16.043 \times (1260\text{-}537) \ -(-32190) \ = \mathbf{37304}\ ]$$

**15.98E**

Acetylene gas at 77 F is burned with 140% theoretical air, which enters the burner at 77 F, 14.7 lbf/in.$^2$, 80% relative humidity. The combustion products form a mixture of $CO_2$, $H_2O$, $N_2$, $O_2$, and NO in chemical equilibrium at 3500 F, 14.7 lbf/in.$^2$. This mixture is then cooled to 1340 F very rapidly, so that the composition does not change. Determine the mole fraction of NO in the products and the heat transfer for the overall process.

$$C_2H_2 + 3.5\ O_2 + 13.16\ N_2 + \text{water} \rightarrow$$

$$2\ CO_2 + 1\ H_2O + 1\ O_2 + 13.16\ N_2 + \text{water}$$

Water: $P_V = 0.8 \times 0.46 = 0.368\ \text{lbf/in}^2$

$$n_V = n_A \times \frac{P_V}{P_A} = (3.5+13.16) \times \frac{0.368}{14.332} = 0.428$$

So, total $H_2O$ in products is : $1 + n_V = 1.428$.

a) reaction: $N_2 + O_2 \Leftrightarrow 2\ NO$

change : -x -x +2x

at 3500 F = 3960 R (=2200 K), from A.11: K = 0.001 074

Equilibrium products:

$n_{CO2} = 2$, $n_{H2O} = 1.428$, $n_{O2} = 1\text{-}x$,

$n_{N2} = 13.16\text{-}x$, $n_{NO} = 0+2x$, $n_{TOT} = 17.588$

$$K = \frac{(2x)^2}{(1\text{-}x)(13.16\text{-}x)} = 0.001\ 074$$

By trial and error, x = 0.0576

$$y_{NO} = \frac{2 \times 0.0576}{17.588} = \mathbf{0.006\ 55}$$

b) Final products (same composition) at 1340 F = 1800 R

$H_R = 1(97\ 476) + 0.428(-103\ 966) = 52\ 979$ Btu

$H_P = 2(-169\ 184+14\ 358) + 1.428(-103\ 966+11\ 178)$

$+ 0.9424(0+9761) + 13.1024(0+9227) + 0.1152(38\ 818+9557)$

$= -306\ 486$ Btu

$Q_{CV} = H_P - H_R = \mathbf{-359\ 465\ Btu}$

**15.99E**

An important step in the manufacture of chemical fertilizer is the production of ammonia, according to the reaction: $N_2 + 3H_2 \Leftrightarrow 2NH_3$

a. Calculate the equilibrium constant for this reaction at 300 F.

b. For an initial composition of 25% nitrogen, 75% hydrogen, on a mole basis, calculate the equilibrium composition at 300 F, 750 lbf/in.$^2$.

$$1N_2 + 3H_2 \Leftarrow\Rightarrow 2NH_3 \text{ at } 300 \text{ F}$$

a) $\bar{h}^o_{NH3\ 300\ F} = -19\ 656 + 0.509\times17.031(300\text{-}77) = -17723$

$\bar{s}^o_{NH3\ 300\ F} = 45.969 + 0.509\times17.031 \ln\frac{760}{537} = 48.980$

$\Delta H^o_{300\ F} = 2(-17723) - 1(0 + 1557) - 3(0 + 1552) = -41\ 659$ Btu

$\Delta S^0_{300\ F} = 2(48.98) - 1(48.164) - 3(33.60) = -51.0$ Btu/R

$\Delta G^0_{300\ F} = -41\ 659 - 760(-51.0) = -2899$ Btu

$\ln K = \frac{+2899}{1.98589\times760} = 1.9208, \qquad K = \mathbf{6.826}$

b) $n_{NH3} = 2x, \quad n_{N2} = 1\text{-}x, \quad n_{H2} = 3\text{-}3x$

$$K = \frac{y^2_{NH3}}{y_{N2}y^3_{H2}}\left(\frac{P}{P^0}\right)^{-2} = \frac{(2x)^2 2^2 (2\text{-}x)^2}{3^3(1\text{-}x)^4}\left(\frac{P}{P^0}\right)^{-2}$$

$$\text{or } \left(\frac{x}{1\text{-}x}\right)^2\left(\frac{2\text{-}x}{1\text{-}x}\right)^2 = \frac{27}{16}\times6.826\times\left(\frac{750}{14.7}\right)^2 = 29985$$

$$\text{or } \left(\frac{x}{1\text{-}x}\right)\left(\frac{2\text{-}x}{1\text{-}x}\right) = 173.16$$

→ Trial & Error:

x = 0.9242

| | n | y |
|---|---|---|
| $NH_3$ | 1.848 | 0.8591 |
| $N_2$ | 0.0758 | 0.0352 |
| $H_2$ | 0.2273 | 0.1057 |

## Simultaneous Reactions

**15.100E**

Ethane is burned with 150% theoretical air in a gas turbine combustor. The products exiting consist of a mixture of $CO_2$, $H_2O$, $O_2$, $N_2$, and NO in chemical equilibrium at 2800 F, 150 lbf/in.$^2$. Determine the mole fraction of NO in the products. Is it reasonable to ignore CO in the products?

Combustion:

$$C_2H_6 + 5.25\,O_2 + 19.74\,N_2 \rightarrow 2\,CO_2 + 3\,H_2O + 1.75\,O_2 + 19.74\,N_2$$

a) Products at 2800 F, 150 lbf/in$^2$. Equilibrium mixture: $CO_2$, $H_2O$, $O_2$, $N_2$, NO

| | $N_2$ | + | $O_2$ | ⇔ | 2 NO |
|---|---|---|---|---|---|
| initial | 19.74 | | 1.75 | | 0 |
| change | -x | | -x | | +2x |
| equil. | 19.74-x | | 1.75-x | | 2x |

Equil. comp. $n_{CO2} = 2$, $n_{H2O} = 3$, $n_{O2} = 1.75\text{-}x$, $n_{N2} = 19.74\text{-}x$, $n_{NO} = 2x$

$$K = 1.283\times10^{-4} = \frac{y_{NO}^2}{y_{N2}y_{O2}}\left(\frac{P}{P^0}\right)^0 = \frac{4x^2}{(19.74-x)(1.75-x)}$$

Solving, x = 0.032 95

$$y_{NO} = \frac{2\times0.032\,95}{26.49} = \mathbf{0.002\,49}$$

b)

| | 2 $CO_2$ | ⇔ | 2 CO | + | $O_2$ |
|---|---|---|---|---|---|
| initial | 2 | | 0 | | 0 |
| change | -2a | | +2a | | +2x |
| equil. | 2-2a | | 2a | | 2x |

$$K = 5.259\times10^{-8} = \frac{y_{CO}^2 y_{O2}}{y_{CO2}^2}\left(\frac{P}{P^0}\right)^1 = \left(\frac{2a}{2-2a}\right)^2\left(\frac{1.75-x+a}{26.49+a}\right)\left(\frac{150}{14.504}\right)$$

Since Table A.11 corresponds to a pressure $P_o$ of 100 kPa, which is 14.504 lbf/in$^2$. This equation should be solved simultaneously with the equation solved in part a) (modified to include the unknown a). Since x was found to be small and also a will be very small, the two are practically independent. Therefore, use the value x = 0.032 95 in the equation above, and solve for a.

$$\left(\frac{a}{1-a}\right)^2\left(\frac{1.75-0.032\,95+a}{26.49+a}\right) = \left(\frac{14.504}{150}\right)\times5.259\times10^{-8}$$

Solving, a = 0.000 28 or $y_{CO} = 2.1\times10^{-5}$ negligible for most applications.

**15.101E**

One pound mole of air (assumed to be 78% nitrogen, 21% oxygen, and 1% argon) at room temperature is heated to 7200 R, 30 lbf/in.$^2$. Find the equilibrium composition at this state, assuming that only $N_2$, $O_2$, NO, O, and Ar are present.

1 lbmol air (0.78 $N_2$, 0.21 $O_2$, 0.01 Ar) heated to 7200 R, 30 lbf/in$^2$.

$$1)\quad N_2 + O_2 \Leftrightarrow 2\,NO \qquad\qquad 2)\quad O_2 \Leftrightarrow 2\,O$$

change -a -a +2a change -b +2b

Equil.:

$n_{N2} =$ 0.78-a $n_{Ar} =$ 0.01 $n_{NO} =$ 2a

$n_{O2} =$ 0.21-a-b $n_O =$ 2b $n =$ 1+b

$$K_1 = 0.0895 = \frac{4a^2}{(0.78-a)(0.21-a-b)}\left(\frac{30}{14.504}\right)^0$$

$$K_2 = 2.221 = \frac{4b^2}{(1+b)(0.21-a-b)}\left(\frac{30}{14.504}\right)$$

Divide 1st eq'n by 2nd and solve for a as function(b), using

$$X = \frac{K_1}{K_2}\left(\frac{P}{P^0}\right) = 0.083\,35$$

Get

$$a = \frac{Xb^2}{2(1+b)}\left[-1 + \sqrt{1 + \frac{4\times0.78(1+b)}{Xb^2}}\right] \tag{1}$$

Also

$$\frac{b^2}{(1+b)(0.21-a-b)} = \frac{K_2}{4(P/P^0)} = 0.268\,44 \tag{2}$$

Assume b = 0.1269 From (1), get a = 0.0299

Then, check a & b in (2) $\Rightarrow$ OK

Therefore,

| Subst. | N2 | O2 | Ar | O | NO |
|---|---|---|---|---|---|
| n | 0.7501 | 0.0532 | 0.01 | 0.2538 | 0.0598 |
| y | 0.6656 | 0.0472 | 0.0089 | 0.2252 | 0.0531 |

**15.102E**

One pound mole of water vapor at 14.7 lbf/in.$^2$, 720 R, is heated to 5400 R in a constant pressure steady flow process. Determine the final composition, assuming that $H_2O$, $H_2$, H, $O_2$, and OH are present at equilibrium.

Reactions:

1) $2\,H_2O \Leftrightarrow 2\,H_2 + O_2$ change $-2a$ $+2a$ $+a$

2) $2\,H_2O \Leftrightarrow H_2 + 2\,OH$ change $-2b$ $+b$ $+2b$

3) $H_2 \Leftrightarrow 2\,H$ change $-c$ $+2c$

At equilibrium (5400 R, 14.7 lbf/in$^2$)

$n_{H2O} = 1-2a-2b$ $\quad n_{OH} = 2b$

$n_{H2} = 2a+b-c$ $\quad n_H = 2c$

$n_{O2} = a$ $\quad n_{TOT} = 1+a+b+c$

$$\frac{K_1}{(P/P^0)} = \frac{2.062\times10^{-3}}{1.03} = \left(\frac{2a+b-c}{1-2a-2b}\right)^2\left(\frac{a}{1+a+b+c}\right)$$

$$\frac{K_2}{(P/P^0)} = \frac{2.893\times10^{-3}}{1.03} = \left(\frac{2a+b-c}{1+a+b+c}\right)\left(\frac{2b}{1-2a-2b}\right)^2$$

$$\frac{K_3}{(P/P^0)} = \frac{2.496\times10^{-2}}{1.03} = \frac{(2a)^2}{(2a+b-c)(1+a+b+c)}$$

These three equations must be solved simultaneously for a, b & c: $a = 0.0622$, $b = 0.0570$, $c = 0.0327$

and $n_{H2O} = 0.7616$ $\quad y_{H2O} = 0.6611$

$n_{H2} = 0.1487$ $\quad y_{H2} = 0.1291$

$n_{O2} = 0.0622$ $\quad y_{O2} = 0.0540$

**15.103E**

Acetylene gas and *x* times theoretical air ($x > 1$) at room temperature and 75 lbf/in.$^2$ are burned at constant pressure in an adiabatic steady flow process. The flame temperature is 4600 R, and the combustion products are assumed to consist of $N_2$, $O_2$, $CO_2$, $H_2O$, CO, and NO. Determine the value of *x*.

Combustion:

$$C_2H_2 + 2.5x\,O_2 + 9.4x\,N_2 \rightarrow 2\,CO_2 + H_2O + 2.5(x-1)O_2 + 9.4x\,N_2$$

Eq. products 4600 R, 75 lbf/in$^2$: $N_2$, $O_2$, $CO_2$, $H_2O$, CO, NO

2 Reactions:

$$\begin{array}{llll} 1) & 2\,CO_2 \Leftrightarrow 2\,CO + O_2 & 2) & N_2 + O_2 \Leftrightarrow 2\,NO \\ \text{change} & -2a \quad +2a \quad +a & \text{change} & -b \quad -b \quad +2b \end{array}$$

Equil. Comp.:

$$\begin{array}{llll} n_{N2} = & 9.4x-b & n_{CO2} = & 2-2a \\ n_{O2} = & 2.5x-2.5+a-b & n_{H2O} = & 1 \\ n_{CO} = & 2a & n_{NO} = & 2b \\ \hline n_{TOT} = & 11.9x+0.5+a & & \end{array}$$

At 4600 R, from A.17: $K_1 = 2.359\times10^{-3}$, $K_2 = 4.249\times10^{-3}$

$$\frac{K_1}{(P/P^0)} = \frac{2.359\times10^{-3}}{5.103} = 4.622\times10^{-4} = \left(\frac{a}{1-a}\right)^2\left(\frac{2.5x-2.5+a-b}{11.9x+0.5+a}\right)$$

$$K_2 = 4.249\times10^{-3} = \frac{(2b)^2}{(9.4-b)(2.5x-2.5+a-b)}$$

Also, from the 1st law: $H_P - H_R = 0$ where

$$H_R = 1(+97\,477) + 0 + 0 = +97\,497 \text{ Btu}$$

$$H_P = (9.4x-b)(0+32\,817) + (2.5x-2.5+a-b)(0+34\,605)$$
$$+ (2-2a)(-169\,184+53\,885) + 1(-103\,966+43\,899)$$
$$+ 2a(-47\,518+33\,122) + 2b(38\,818+31\,161)$$

Substituting,

$$394\,992 \times x + 236\,411 \times a + 72\,536 \times b - 377\,178 = 97477$$

which results in a set of 3 equations in the 3 unknowns x,a,b. Trial and error solution from the last eq. and the ones for $K_1$ and $K_2$. The result is

**x = 1.12** , $a = 0.1182$, $b = 0.05963$

## Review problems

**15.104E**

Methane is burned with theoretical oxygen in a steady flow process, and the products exit the combustion chamber at 5300 F, 100 lbf/in.$^2$. Calculate the equilibrium composition at this state, assuming that only $CO_2$, CO, $H_2O$, $H_2$, $O_2$, and OH are present.

Combustion: $CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$

Dissociation reactions:

1) $2\,H_2O \Leftrightarrow 2\,H_2 + O_2$

change $-2a$ $+2a$ $+a$

2) $2\,H_2O \Leftrightarrow H_2 + 2\,OH$

change $-2b$ $+b$ $+2b$

3) $2\,CO_2 \Leftrightarrow 2\,CO + O_2$

change $-2c$ $+2c$ $+c$

At equilibrium:

$n_{H2O} = 2-2a-2b$

$n_{H2} = 2a+b$

$n_{O2} = a+c$

$n_{OH} = 2b$

$n_{CO2} = 1-2c$

$n_{CO} = 2c$

$n_{TOT} = 3+a+b+c$

Products at 5300F, 100 lbf/in$^2$

$$K_1 = 0.007\,328 = \left(\frac{2a+b}{2-2a-2b}\right)^2\left(\frac{a+c}{3+a+b+c}\right)\left(\frac{100}{14.504}\right)$$

$$K_2 = 0.012\,265 = \left(\frac{2b}{2-2a-2b}\right)^2\left(\frac{2a+b}{3+a+b+c}\right)\left(\frac{100}{14.504}\right)$$

$$K_3 = 0.426\,135 = \left(\frac{2c}{1-2c}\right)^2\left(\frac{a+c}{3+a+b+c}\right)\left(\frac{100}{14.504}\right)$$

These 3 equations must be solved simultaneously for a, b, & c. If solving by hand divide the first equation by the second, and solve for c = fn(a,b). This reduces the solution to 2 equations in 2 unknowns. Solving,

a = 0.0245, b = 0.1460, c = 0.2365

| Substance: | H2O | H2 | O2 | OH | CO2 | CO |
|---|---|---|---|---|---|---|
| n | 1.659 | 0.195 | 0.260 | 0.292 | 0.527 | 0.473 |
| y | 0.4871 | 0.0573 | 0.0763 | 0.0857 | 0.1547 | 0.1389 |

**15.105E**

In a test of a gas-turbine combustor, saturated-liquid methane at 210 R is to be burned with excess air to hold the adiabatic flame temperature to 2880 R. It is assumed that the products consist of a mixture of $CO_2$, $H_2O$, $N_2$, $O_2$, and NO in chemical equilibrium. Determine the percent excess air used in the combustion, and the percentage of NO in the products.

$$CH_4 + 2x\,O_2 + 7.52x\,N_2$$

$$\rightarrow 1\,CO_2 + 2\,H_2O + (2x\text{-}2)\,O_2 + 7.52x\,N_2$$

| Then | $N_2$ | + $O_2$ | $\Leftrightarrow$ 2 NO | Also | $CO_2$ | $H_2O$ |
|---|---|---|---|---|---|---|
| init | 7.52x | 2x-2 | 0 | | 1 | 2 |
| ch. | -a | -a | +2a | | 0 | 0 |
| equil. | (7.52x-a) | (2x-2-a) | 2a | | 1 | 2 |

$$n_{TOT} = 1 + 9.52x$$

2880 R: $\quad \ln K = -10.55, \quad K = 2.628\times10^{-5}$

$$2.628\times10^{-5}\ K = \frac{y_{NO}^2}{y_{N2}y_{O2}}\left(\frac{P}{P^0}\right)^0 = \frac{y_{NO}^2}{y_{N2}y_{O2}} = \frac{4a^2}{(7.52x\text{-}a)(2x\text{-}2\text{-}a)}$$

$$H_R = 1\big[-32\,190 + (-1854-4300)\big] + 0 + 0 \text{ (assume 77 F)} = -38\,344 \text{ Btu}$$

$$H_P = 1(-169\,184 + 29\,049) + 2(-103\,966 + 22\,746)$$

$$+ (7.52x\text{-}a)(18\,015) + (2x\text{-}2\text{-}a)(19\,031) + 2a(38\,818 + 18\,624)$$

$$= -340\,639 + 173\,535\,x + 77\,838\,a$$

Assume $\quad a \sim 0$, then from $\quad H_P - H_R = 0 \quad \rightarrow\ x = 1.742$

Subst.

$$\frac{a^2}{(13.1\text{-}a)(1.484\text{-}a)} = \frac{2.628\times10^{-5}}{4}, \qquad \text{get} \qquad a \approx 0.01125$$

Use this a in 1st law

$$x = \frac{302\,295 - 77\,838\times0.01125}{173\,535} = 1.737$$

$$\Rightarrow \qquad \frac{a^2}{(13.062\text{-}a)(1.474\text{-}a)} = \frac{2.628\times10^{-5}}{4},\ a = 0.0112$$

$\Rightarrow \qquad x = 1.737 \qquad\qquad$ % excess air = **73.7 %**

$$\%\ NO = \frac{2\times0.0112\times100}{1+9.52\times1.737} = \mathbf{0.128\ \%}$$

**15.106E**

Dry air is heated from 77 F to 7200 R in a 14.7 lbf/in.$^2$ constant-pressure process. List the possible reactions that may take place and determine the equilibrium composition. Find the required heat transfer.

Air assumed to be 21% oxygen and 79% nitrogen by volume.

From the elementary reactions at 4000 K = 7200 R (A.11):

(1) $O_2 \Leftrightarrow 2\,O$ $\quad K_1 = 2.221 = y_O^2/y_{O2}$

(2) $N_2 \Leftrightarrow 2\,N$ $\quad K_2 = 3.141 \times 10^{-6} = y_N^2/y_{N2}$

(3) $N_2 + O_2 \Leftrightarrow 2\,NO$ $\quad K_3 = 0.08955 = y_{NO}^2/y_{N2}\,y_{O2}$

Call the shifts a,b,c respectively so we get

$n_{O2} = 0.21\text{-}a\text{-}c,\quad n_O = 2a,\quad n_{N2} = 0.79\text{-}b\text{-}c,\quad n_N = 2b,$

$n_{NO} = 2c,\quad n_{tot} = 1+a+b$

From which the molefractions are formed and substituted into the three equilibrium equations. The result is corrected for 1 atm = 14.7 lbf/in$^2$ = 101.325 kPa versus the tables 100 kPa

$$K_1 = 2.1511 = y_O^2/y_{O2} = 4a^2/[(1+a+b)(0.21\text{-}a\text{-}c)]$$

$$K_2 = 3.042\times10^{-6} = y_N^2/y_{N2} = 4b^2/[(1+a+b)(0.79\text{-}b\text{-}c)]$$

$$K_3 = 0.08955 = y_{NO}^2/y_{N2}\,y_{O2} = 4c^2/[(0.79\text{-}b\text{-}c)(0.21\text{-}a\text{-}c)]$$

which give 3 eqs. for the unknowns (a,b,c). Trial and error assume b = c = 0 solve for a from $K_1$ then for c from $K_3$ and finally given the (a,c) solve for b from $K_2$. The order chosen according to expected magnitude $K_1 > K_3 > K_2$

$a = 0.15,\ \ b = 0.000832,\ \ c = 0.0244\ \ \Rightarrow$

$n_{O2} = 0.0356,\ \ n_O = 0.3,\ \ n_{N2} = 0.765,\ \ n_N = 0.00167,\ \ n_{NO} = 0.049$

$$Q = H_{ex} - H_{in} = n_{O2}\Delta\bar{h}_{O2} + n_{N2}\Delta\bar{h}_{N2} + n_O(\bar{h}_{fO} + \Delta\bar{h}_O)$$

$$+ n_N(\bar{h}_{fN} + \Delta\bar{h}_N) + n_{NO}(\bar{h}_{fNO} + \Delta\bar{h}_{NO}) - 0$$

$$= 0.0356 \times 59\,632 + 0.765 \times 55\,902 + 0.3(107\,124 + 33\,394)$$

$$+ 0.00167(203\,216 + 33\,333) + 0.049(38\,818 + 57\,038)$$

= **92 135 Btu/lbmol air**

[If no reaction: $Q = n_{O2}\Delta\bar{h}_{O2} + n_{N2}\Delta\bar{h}_{N2}$ = 56 685 Btu/lbmol air]