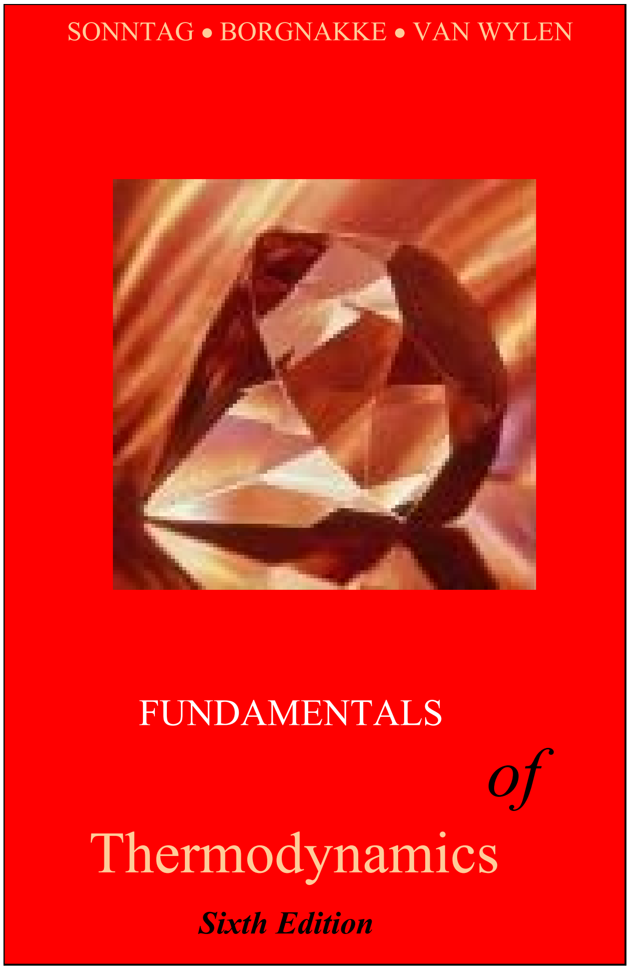
SOLUTION MANUAL
SI UNIT PROBLEMS
CHAPTER 15



SONNTAG • BORGNAKKE • VAN WYLEN

FUNDAMENTALS

of

Thermodynamics

Sixth Edition

CONTENT

Correspondence List

CHAPTER 15 6th edition Sonntag/Borgnakke/Wylen

The correspondence between the new problem set and the previous 5th edition chapter 15 problem set.

New	Old	New	Old	New	Old
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23	new	46		69	44
24	3	47	22a,c	70	45
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The English unit problems are:

New	5th	SI	New	5th	SI	New	5th	SI
89	53	21	95	62	45	101	67	71
90	new	25	96	63	54	102	68	72
91	58	31	97	64	58	103	69	73
92	59	36	98	new	59	104	70	88
93	60	37	99	new	63	105	71	80
94	61	39	100	65	68	106	72	87

Concept-Study Guide Problems

15.1

Is the concept of equilibrium limited to thermodynamics?

Equilibrium is a condition in which the driving forces present are balanced, with no tendency for a change to occur spontaneously. This concept applies to many diverse fields of study – one no doubt familiar to the student being that of mechanical equilibrium in statics, or engineering mechanics.

15.2

How does Gibbs function vary with quality as you move from liquid to vapor?

There is no change in Gibbs function between liquid and vapor. For equilibrium we have $g_g = g_f$.

15.3

How is a chemical equilibrium process different from a combustion process?

Chemical equilibrium occurs at a given state, T and P, following a chemical reaction process, possibly a combustion followed by one or more dissociation reactions within the combustion products. Whereas the combustion is a one-way process (irreversible) the chemical equilibrium is a reversible process that can proceed in both directions.

15.4

Must P and T be held fixed to obtain chemical equilibrium?

No, but we commonly evaluate the condition of chemical equilibrium at a state corresponding to a given temperature and pressure.

15.5

The change in Gibbs function for a reaction is a function of which property?

The change in Gibbs function for a reaction is a function of T and P. The change in standard-state Gibbs function is a function only of T.

15.6

In a steady flow burner T is not controlled, which properties are?

The pressure tends to be constant, only minor pressure changes due to acceleration of the products as density decreases velocity must increase to have the same mass flow rate.

15.7

In a closed rigid combustion bomb which properties are held fixed?

The volume is constant. The number of atoms of each element is conserved, although the amounts of various chemical species change. As the products have more internal energy but cannot expand the pressure increases significantly.

15.8

Is the dissociation of water pressure sensitive?

Yes, since the total number of moles on the left and right sides of the reaction equation(s) is not the same.

15.9

At 298 K, $K = \exp(-184)$ for the water dissociation, what does that imply?

This is an extremely small number, meaning that the reaction tends to go strongly from right to left – in other words, does not tend to go from left to right (dissociation of water) at all.

15.10

For a mixture of O_2 and O the pressure is increased at constant T; what happens to the composition?

An increase in pressure causes the reaction to go toward the side of smaller total number of moles, in this case toward the O_2 .

15.11

For a mixture of O_2 and O the temperature is increased at constant P; what happens to the composition?

A temperature increase causes more O_2 to dissociate to O.

15.12

For a mixture of O_2 and O I add some argon keeping constant T, P; what happens to the moles of O?

Diluting the mixture with a non-reacting gas has the same effect as decreasing the pressure, causing the reaction to shift toward the side of larger total number of moles, in this case the O .

15.13

In a combustion process is the adiabatic flame temperature affected by reactions?

The adiabatic flame temperature is decreased by dissociation reactions of the products.

15.14

When dissociations occur after combustion, does T go up or down?

Dissociation reactions of combustion products lower the temperature.

15.15

In equilibrium Gibbs function of the reactants and the products is the same; how about the energy?

The chemical equilibrium mixture at a given T, P has a certain total internal energy. There is no restriction on its division among the constituents.

15.16

Does a dissociation process require energy or does it give out energy?

Dissociation reactions require energy and is thus endothermic.

15.17

If I consider the non-frozen (composition can vary) heat capacity, but still assume all components are ideal gases, does that C become a function of temperature? of pressure?

The non-frozen mixture heat capacity will be a function of both T and P, because the mixture composition depends on T and P, while the individual component heat capacities depend only on T.

15.18

What is K for the water gas reaction in Example 15.4 at 1200 K?

Using the result of Example 15.4 and Table A.11

$\ln K = 0.5\ [\ -35.736 - (-36.363)] = +\ 0.3135\ ,\quad K = 1.3682$

15.19

Which atom in air ionizes first as T increases? What is the explanation?

Using Fig. 15.11, we note that as temperature increases, atomic N ionizes to N^+, becoming significant at about 6-8000 K. N has a lower ionization potential compared to O or Ar.

15.20

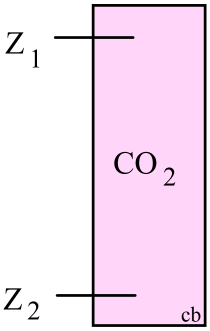
At what temperature range does air become a plasma?

From Fig. 15.11, we note that air becomes predominantly ions and electrons, a plasma, at about 10-12 000 K.

Equilibrium and Phase Equilibrium

15.21

Carbon dioxide at 15 MPa is injected into the top of a 5-km deep well in connection with an enhanced oil-recovery process. The fluid column standing in the well is at a uniform temperature of 40°C. What is the pressure at the bottom of the well assuming ideal gas behavior?



$(Z_1\text{-}Z_2) = 5000$ m, $P_1 = 15$ MPa

$T = 40\ ^oC$ = constant

Equilibrium at constant T

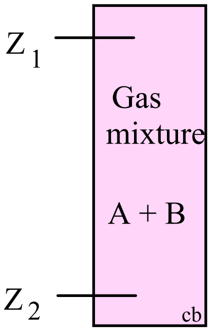
$-w_{REV} = 0 = \Delta g + \Delta PE = RT \ln (P_2/P_1) + g(Z_2\text{-}Z_1) = 0$

$$\ln (P_2/P_1) = \frac{9.807 \times 5000}{1000 \times 0.188\,92 \times 313.2} = 0.8287$$

$$P_2 = 15 \exp(0.8287) = \mathbf{34.36\ MPa}$$

15.22

Consider a 2-km-deep gas well containing a gas mixture of methane and ethane at a uniform temperature of 30°C. The pressure at the top of the well is 14 MPa, and the composition on a mole basis is 90% methane, 10% ethane. Each component is in equilibrium (top to bottom) with dG + g dZ = 0 and assume ideal gas, so for each component Eq.15.10 applies. Determine the pressure and composition at the bottom of the well.



$(Z_1\text{-}Z_2) = 2000$ m, Let $A = CH_4$, $B = C_2H_6$

$P_1 = 14$ MPa, $y_{A1} = 0.90$, $y_{B1} = 0.10$

T = 30 °C = constant

From section 15.1, for A to be at equilibrium between

1 and 2: $W_{REV} = 0 = n_A(\bar{G}_{A1}-\bar{G}_{A2}) + n_A M_A g(Z_1-Z_2)$

Similarly, for B: $W_{REV} = 0 = n_B(\bar{G}_{B1}-\bar{G}_{B2}) + n_B M_B g(Z_1-Z_2)$

Using eq. 15.10 for A: $\bar{R}T \ln (P_{A2}/P_{A1}) = M_A g(Z_1-Z_2)$

with a similar expression for B. Now, ideal gas mixture, $P_{A1} = y_{A1}P$, etc.

Substituting: $\ln\frac{y_{A2}P_2}{y_{A1}P_1} = \frac{M_A g(Z_1-Z_2)}{\bar{R}T}$ and $\ln\frac{y_{B2}P_2}{y_{B1}P_1} = \frac{M_B g(Z_1-Z_2)}{\bar{R}T}$

$$\ln (y_{A2}P_2) = \ln(0.9\times14) + \frac{16.04\times9.807(2000)}{1000\times8.3145\times303.2} = 2.6585$$

$$\Rightarrow \quad y_{A2}P_2 = 14.2748$$

$$\ln (y_{B2}P_2) = \ln(0.1\times14) + \frac{30.07\times9.807(2000)}{1000\times8.3145\times303.2} = 0.570\,43$$

$$\Rightarrow \quad y_{B2}P_2 = (1-y_{A2})P_2 = 1.76903$$

Solving: $P_2 =$ **16.044 MPa** & $y_{A2} =$ **0.8897**

15.23

A container has liquid water at 20°C , 100 kPa in equilibrium with a mixture of water vapor and dry air also at 20°C, 100 kPa. How much is the water vapor pressure and what is the saturated water vapor pressure?

From the steam tables we have for saturated liquid:

$$P_g = \mathbf{2.339\ kPa}, \quad v_f = 0.001002\ \mathrm{m^3/kg}$$

The liquid is at 100 kPa so it is compressed liquid still at 20°C so from Eq.13.15

$$g_{liq} - g_f = \int v\, dP = v_f\,(P - P_g)$$

The vapor in the moist air is at the partial pressure P_v also at 20°C so we assume ideal gas for the vapor

$$g_{vap} - g_g = \int v\, dP = RT \ln \frac{P_v}{P_g}$$

We have the two saturated phases so $g_f = g_g$ ($q = h_{fg} = Ts_{fg}$) and now for equilibrium the two Gibbs function must be the same as

$$g_{vap} = g_{liq} = RT \ln \frac{P_v}{P_g} + g_g = v_f\,(P - P_g) + g_f$$

leaving us with

$$\ln \frac{P_v}{P_g} = v_f\,(P - P_g)/\,RT = \frac{0.001002\ (100 - 2.339)}{0.4615 \times 293.15} = 0.000723$$

$$P_v = P_g \exp(0.000723) = \mathbf{2.3407\ kPa}.$$

This is only a minute amount above the saturation pressure. For the moist air applications in Chapter 12 we neglected such differences and assumed the partial water vapor pressure at equilibrium (100% relative humidity) is P_g. The pressure has to be much higher for this to be a significant difference.

15.24

Using the same assumptions as those in developing Eq. d in Example 15.1, develop an expression for pressure at the bottom of a deep column of liquid in terms of the isothermal compressibility, β_T. For liquid water at 20°C, $\beta_T = 0.0005$ [1/MPa]. Use the result of the first question to estimate the pressure in the Pacific ocean at the depth of 3 km.

$$d\,g_T = v°\,(1-\beta_T P)\,dP_T \qquad\qquad d\,g_T + g\,dz = 0$$

$$v°\,(1-\beta_T P)\,dP_T + g\,dz = 0 \quad \text{and integrate} \quad \int v°(1-\beta_T P)\,dP_T = -\,g\int dz$$

$$\int_{P_0}^{P} (1-\beta_T P)\,dP_T = +\frac{g}{v°}\int_0^{+H} dz \quad => \quad P - P_0 - \beta_T \frac{1}{2}\,[P^2 - P_0^{\,2}] = \frac{g}{v°}\,H$$

$$P\,(1 - \frac{1}{2}\,\beta_T\,P) = P_0 - \frac{1}{2}\beta_T\,P_0^{\,2} + \frac{g}{v°}\,H$$

$v° = v_{f\,20°C} = 0.001002$; $H = 3000$ m , $g = 9.80665$ m/s^2; $\beta_T = 0.0005$ 1/MPa

$$P\,(1 - \frac{1}{2} \times 0.0005P) = 0.101 - \frac{1}{2} \times 0.0005 \times 0.101^2$$

$$+ [9.80665 \times 3000/0.001002] \times 10^{-6}$$

$$= 29.462 \text{ MPa}, \quad \text{which is close to } P$$

Solve by iteration or solve the quadratic equation

P = **29.682 MPa**

Chemical Equilibrium, Equilibrium Constant

15.25

Calculate the equilibrium constant for the reaction $O_2 \Leftrightarrow 2O$ at temperatures of 298 K and 6000 K. Verify the result with Table A.11.

Reaction $O_2 \quad \Leftrightarrow \quad 2O$

At 25 °C (298.15 K):

$\Delta H^0 = 2\bar{h}^0_{f\,O} - 1\bar{h}^0_{f\,O2} = 2(249\ 170) - 1(0) = 498\ 340$ kJ/kmol

$\Delta S^0 = 2\bar{s}^0_O - 1\bar{s}^0_{O2} = 2(161.059) - 1(205.148) = 116.97$ kJ/kmol K

$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 498\ 340 - 298.15\times116.97 = 463\ 465$ kJ/kmol

$$\ln K = -\frac{\Delta G^0}{\bar{R}T} = -\frac{463\ 465}{8.3145\times298.15} = \mathbf{-186.961}$$

At 6000 K:

$\Delta H^0 = 2(249\ 170 + 121\ 264) - (0 + 224\ 210) = 516\ 658$ kJ/kmol

$\Delta S^0 = 2(224.597) -1(313.457) = 135.737$ kJ/kmol K

$\Delta G^0 = 516\ 658 - 6000\times135.737 = -297\ 764$ kJ/kmol

$$\ln K = \frac{+297\ 764}{8.3145\times6000} = \mathbf{+5.969}$$

15.26

For the dissociation of oxygen, $O_2 \Leftrightarrow 2O$, around 2000 K we want a mathematical expression for the equilibrium constant K(T). Assume constant heat capacity, at 2000 K, for O_2 and O from Table A.9 and develop the expression from Eqs. 15.12 and 15.15.

From Eq.15.15 the equilibrium constant is

$$K = \exp\left(-\frac{\Delta G^0}{\bar{R}T}\right) ; \qquad \Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

and the shift is

$$\Delta G^0 = 2\,\bar{h}_O - \bar{h}_{O2} - T(2\bar{s}^o_O - \bar{s}^o_{O_2})$$

Substitute the first order approximation to the functions $\bar{h}$ and $\bar{s}^o$ as

$$\bar{h} = \bar{h}_{2000\ K} + \bar{C}_p\,(T - 2000) \; ; \quad \bar{s}^o = \bar{s}^o_{2000\ K} + \bar{C}_p \ln\frac{T}{2000}$$

The properties are from Table A.9 and $\bar{R}$ = 8.3145 kJ/kmol K

Oxygen O_2: $\bar{h}_{2000\ K}$ = 59 176 kJ/kmol, $\bar{s}^o_{2000\ K}$ = 268.748 kJ/kmol K

$$\bar{C}_p = \frac{\bar{h}_{2200\ K} - \bar{h}_{2200\ K}}{2200 - 1800} = \frac{66\,770 - 51\,674}{400} = 37.74 \text{ kJ/kmol K}$$

Oxygen O: $\bar{h}_{2000\ K}$ = 35 713 + 249 170 = 284 883 kJ/kmol,

$\bar{s}^o_{2000\ K}$ = 201.247 kJ/kmol K

$$\bar{C}_p = \frac{\bar{h}_{2200\ K} - \bar{h}_{2200\ K}}{2200 - 1800} = \frac{39\,878 - 31\,547}{400} = 20.8275 \text{ kJ/kmol K}$$

Substitute and collect terms

$$\frac{\Delta G^0}{\bar{R}T} = \frac{\Delta H^0}{\bar{R}T} - \frac{\Delta S^0}{\bar{R}} = \frac{\Delta H^0_{2000}}{\bar{R}T} + \frac{\Delta \bar{C}_{p\,2000}}{\bar{R}}\left[\frac{T - 2000}{T} - \ln\frac{T}{2000}\right] - \frac{\Delta S^0_{2000}}{\bar{R}}$$

Now we have

$$\Delta H^0_{2000}/\bar{R} = (2 \times 284\,883 - 59\,176)/8.3145 = 61\,409.6 \text{ K}$$

$$\Delta \bar{C}_{p\,2000}/\bar{R} = (2 \times 20.8275 - 37.74)/8.3145 = 0.470864$$

$$\Delta S^0_{2000}/\bar{R} = (2 \times 201.247 - 268.748)/8.3145 = 16.08587$$

so we get

$$\frac{\Delta G^0}{\bar{R}T} = \frac{61\,409.6}{T} + 0.470864 \left[\frac{T - 2000}{T} - \ln \frac{T}{2000} \right] - 16.08587$$

$$= \frac{60\,467.9}{T} - 15.615 - 0.470864 \ln \frac{T}{2000}$$

Now the equilibrium constant K(T) is approximated as

$$K(T) = \exp \left[15.615 - \frac{60\,467.9}{T} + 0.470864 \ln \frac{T}{2000} \right]$$

Remark: We could have chosen to expand the function $\Delta G^0/\bar{R}T$ as a linear expression instead or even expand the whole $\exp(-\Delta G^0/\bar{R}T)$ in a linear function.

15.27

Calculate the equilibrium constant for the reaction $H_2 \Leftrightarrow 2H$ at a temperature of 2000 K, using properties from Table A.9. Compare the result with the value listed in Table A.11.

From Table A.9 at 2000 K we find:

$\Delta\bar{h}_{H_2}$ = 52 942 kJ/kmol; $\bar{s}_{H_2}$ = 188.419 kJ/kmol K; $\bar{h}^o_f = 0$

$\Delta\bar{h}_{H}$ = 35 375 kJ/kmol; $\bar{s}_{H}$ = 154.279 kJ/kmol K; $\bar{h}^o_f$ = 217 999 kJ/kmol

$$\Delta G^0 = \Delta H - T\Delta S = H_{RHS} - H_{LHS} - T\,(S^0{}_{RHS} - S^0{}_{LHS})$$

$$= 2 \times (35\,375 + 217\,999) - 52943 - 2000(2\times 154.279 - 182.419)$$

$$= 213\,528 \text{ kJ/kmol}$$

$\ln K = -\Delta G^0/\bar{R}T = -213\,528 / (8.3145 \times 2000) = -12.8407$

Table A.11 $\ln K = -12.841$ OK

15.28

Plot to scale the values of ln *K* versus 1/*T* for the reaction $2\ CO_2 \Leftrightarrow 2\ CO + O_2$. Write an equation for ln *K* as a function of temperature.

$$2\ CO_2 \Leftrightarrow 2\ CO + 1\ O_2$$

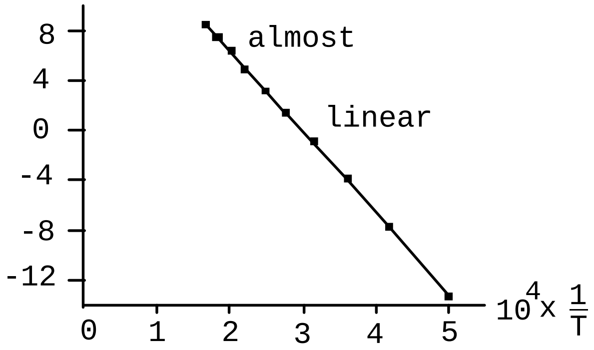
T(K)	$10^4 \times \frac{1}{T}$	ln K	T(K)	$10^4 \times \frac{1}{T}$	ln K
2000	5.000	-13.266	4000	2.500	3.204
2400	4.167	-7.715	4500	2.222	4.985
2800	3.571	-3.781	5000	2.000	6.397
3200	3.125	-0.853	5500	1.818	7.542
3600	2.778	1.408	6000	1.667	8.488

For the range below ~ 5000 K,

$\ln K \approx A + B/T$

Using values at 2000 K & 5000 K

A = 19.5056
B = -65 543 K



15.29

Calculate the equilibrium constant for the reaction:$2CO_2 \Leftrightarrow 2CO + O_2$ at 3000 K using values from Table A.9 and compare the result to Table A.11.

From Table A.9 we get:

kJ/kmol	kJ/kmol	kJ/kmol K
$\Delta\bar{h}_{CO} = 93\ 504$	$\bar{h}^o_{f\ CO} = -110\ 527$	$\bar{s}_{CO} = 273.607$
$\Delta\bar{h}_{CO_2} = 152\ 853$	$\bar{h}^o_{f\ CO_2} = -393\ 522$	$\bar{s}_{CO_2} = 334.17$
$\Delta\bar{h}_{O_2} = 98\ 013$	$\bar{h}^o_{f\ O_2} = 0$	$\bar{s}_{O_2} = 284.466$

$$\Delta G^0 = \Delta H - T\Delta S = 2\ H_{CO} + H_{O_2} - 2\ H_{CO_2} - T\ (2\bar{s}_{CO} + \bar{s}_{O_2} - 2\bar{s}_{CO_2})$$

$$= 2\ (93\ 504 - 110\ 527) + 98\ 013 + 0 - 2(152\ 853 - 393\ 522)$$

$$-3000(2\times273.607 + 284.466 - 2\times334.17) = 55\ 285 \text{ kJ/kmol}$$

$$\ln K = -\Delta G^0/\bar{R}T = -55\ 285/\ (8.31451\times3000) = -2.2164$$

Table A.11 $\ln K = -2.217$ OK

15.30

Consider the dissociation of oxygen, $O_2 \Leftrightarrow 2\ O$, starting with 1 kmol oxygen at 298 K and heating it at constant pressure 100 kPa. At which temperature will we reach a concentration of monatomic oxygen of 10%?

Look at initially 1 mol Oxygen and shift reaction with x

$$O_2 \Leftrightarrow 2\ O$$

	O_2	O	
Initial	1	0	
Change	-x	2x	
Equil.	1-x	2x	$n_{tot} = 1 - x + 2x = 1 + x$

$$y_O = \frac{2x}{1 + x} = 0.1 \quad \Rightarrow \quad x = 0.1/(2 - 0.1) = 0.0526, \quad y_{O2} = 0.9$$

$$K = \frac{y_O^2}{y_{O_2}} \left(\frac{P}{P_o}\right)^{2-1} = \frac{0.1^2}{0.9}\ 1 = 0.01111 \qquad \Rightarrow \qquad \ln K = -4.4998$$

Now look in Table A.11: T = **2980 K**

15.31

Pure oxygen is heated from 25°C to 3200 K in an steady flow process at a constant pressure of 200 kPa. Find the exit composition and the heat transfer.

The only reaction will be the dissociation of the oxygen

$O_2 \Leftrightarrow 2O$; From A.11: $K(3200) = \exp(-3.069) = 0.046467$

Look at initially 1 mol Oxygen and shift reaction with x

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

$$K = \frac{y_O^2}{y_{0_2}} \left(\frac{P}{P_o}\right)^{2-1} = \frac{4x^2}{(1 + x)^2} \frac{1 + x}{1 - x} 2 = \frac{8x^2}{1 - x^2}$$

$$x^2 = \frac{K/8}{1 + K/8} \quad \Rightarrow \quad x = 0.07599; \quad y_{0_2} = 0.859; \quad y_0 = 0.141$$

$$\bar{q} = n_{0_2ex}\bar{h}_{0_2ex} + n_{0ex}\bar{h}_{Oex} - \bar{h}_{0_2in} = (1 + x)(y_{0_2}\bar{h}_{0_2} + y_0\bar{h}_O) - 0$$

$$\bar{h}_{0_2} = 106\ 022 \text{ kJ/kmol}; \quad \bar{h}_O = 249\ 170 + 60\ 767 = 309\ 937 \text{ kJ/kmol}$$

$$\Rightarrow \quad \bar{q} = 145\ 015 \text{ kJ/kmol } O_2$$

$$q = \bar{q}/32 = 4532 \text{ kJ/kg} \ \ (= 3316.5 \text{ if no reaction})$$

15.32

Nitrogen gas, N_2, is heated to 4000 K, 10 kPa. What fraction of the N_2 is dissociated to N at this state?

$N_2 \Leftarrow\Rightarrow 2\,N$ @ T = 4000 K, lnK = -12.671

	N_2	N	
Initial	1	0	$K = 3.14\text{x}10^{-6}$
Change	-x	2x	
Equil.	1-x	2x	$n_{tot} = 1 - x + 2x = 1 + x$

$$y_{N2} = \frac{1 - x}{1 + x}, \qquad y_N = \frac{2x}{1 + x}$$

$$K = \frac{y_N^2}{y_{N2}}\left(\frac{P}{P_o}\right)^{2-1}; \quad \Rightarrow \quad 3.14\text{x}10^{-6} = \frac{4x^2}{1 - x^2}\left(\frac{10}{100}\right) \quad \Rightarrow \quad x = 0.0028$$

$$y_{N2} = \frac{1 - x}{1 + x} = \mathbf{0.9944}, \qquad y_N = \frac{2x}{1 + x} = \mathbf{0.0056}$$

15.33

Hydrogen gas is heated from room temperature to 4000 K, 500 kPa, at which state the diatomic species has partially dissociated to the monatomic form. Determine the equilibrium composition at this state.

$H_2 \Leftrightarrow 2\,H$ Equil. $n_{H2} = 1 - x$

$-x \quad +2x$ $n_H = 0 + 2x$

$n = 1 + x$

$$K = \frac{(2x)^2}{(1-x)(1+x)} \left(\frac{P}{P^0}\right)^{2-1}$$ at 4000 K: ln K = 0.934 => K = 2.545

$$\frac{2.545}{4\times(500/100)} = 0.127\,25 = \frac{x^2}{1-x^2}$$ Solving, $x = 0.3360$

$n_{H2} = 0.664$, $n_H = 0.672$, $n_{tot} = 1.336$

$y_{H2} = 0.497$, $y_H = 0.503$

15.34

One kilomole Ar and one kilomole O_2 are heated up at a constant pressure of 100 kPa to 3200 K, where it comes to equilibrium. Find the final mole fractions for Ar, O_2, and O.

The only equilibrium reaction listed in the book is dissociation of O_2.

So assuming that we find in Table A.10: $\ln(K) = -3.072$

$$Ar + O_2 \Rightarrow Ar + (1 - x)\,O_2 + 2x\,O$$

The atom balance already shown in above equation can also be done as

Species	Ar	O_2	O
Start 1	1	0	
Change	0	-x	2x
Total	1	1-x	2x

The total number of moles is $n_{tot} = 1 + 1\text{-}x + 2x = 2 + x$ so

$$y_{Ar} = 1/(2 + x);\quad y_{O_2} = 1 - x/(2 + x);\quad y_O = 2x/(2 + x)$$

and the definition of the equilibrium constant ($P_{tot} = P_o$) becomes

$$K = e^{-3.072} = 0.04633 = \frac{y_O^2}{y_{0_2}} = \frac{4x^2}{(2 + x)(1 - x)}$$

The equation to solve becomes from the last expression

$$(K + 4)x^2 + Kx - 2K = 0$$

If that is solved we get

$x = -0.0057 \pm 0.1514 = 0.1457;$ x must be positive

$y_O = 0.1358;\quad y_{0_2} = 0.3981;\quad y_{Ar} = 0.4661$

15.35

Consider the reaction $2\ CO_2 \Leftrightarrow 2\ CO + O_2$ obtained after heating 1 kmol CO_2 to 3000 K. Find the equilibrium constant from the shift in Gibbs function and verify its value with the entry in Table A.11. What is the mole fraction of CO at 3000 K, 100 kPa?

From Table A.9 we get:

$\Delta\bar{h}_{CO} = 93\ 504$ $\bar{h}^0_{f\ CO} = -110\ 527$ $\bar{s}_{CO} = 273.607$

$\Delta\bar{h}_{CO_2} = 152\ 853$ $\bar{h}^0_{f\ CO_2} = -393\ 522$ $\bar{s}_{CO_2} = 334.17$

$\Delta\bar{h}_{O_2} = 98\ 013$ $\bar{s}_{O_2} = 284.466$

$$\Delta G^0 = \Delta H - T\Delta S = 2\ H_{CO} + H_{O_2} - 2\ H_{CO_2} - T\ (2\bar{s}_{CO} + \bar{s}_{O_2} - 2\bar{s}_{CO_2})$$

$$= 2\ (93\ 504 - 110\ 527) + 98\ 013 + 0 - 2(152\ 853 - 393\ 522)$$

$$-3000(2\times 273.607 + 284.466 - 2\times 334.17) = 55\ 285$$

$\ln K = -\Delta G^0/\bar{R}T = -55\ 285/\ (8.31451\times 3000) = -2.2164$

Table A.11 $\ln K = -2.217$ OK

At 3000 K,

$\ln K = -2.217$

$K = 0.108935$

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

We have $P = P^o = 0.1$ MPa, and $n_{tot} = 1 + z$, so from Eq.15.29

$$K = \frac{y^2_{CO}y_{O_2}}{y^2_{CO_2}}\left(\frac{P}{P^0}\right) = \left(\frac{2z}{1 - 2z}\right)^2\left(\frac{z}{1 + z}\right)(1) = 0.108935\ ;$$

$$4\ z^3 = 0.108935\ (1 - 2z)^2(1 + z) \quad => \quad z = 0.22$$

$y_{CO} = 2z\ /\ (1 + z) =$ **0.36**

15.36

Air (assumed to be 79% nitrogen and 21% oxygen) is heated in a steady state process at a constant pressure of 100 kPa, and some NO is formed. At what temperature will the mole fraction of N.O be 0.001?

$0.79\ N_2 + 0.21\ O_2$ heated at 100 kPa, forms NO

$N_2 + O_2 \Leftrightarrow 2\,NO$

$-x \quad -x \quad +2x$

$n_{N2} = 0.79 - x$

$n_{O2} = 0.21 - x$

$n_{NO} = 0 \quad + 2x$

$n_{tot} = 1.0$

At exit, $y_{NO} = 0.001 = \frac{2x}{1.0} \quad \Rightarrow \quad x = 0.0005$

$\Rightarrow n_{N2} = 0.7895,\ n_{O2} = 0.2095$

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

From Table A.10, T = **1444 K**

15.37

The combustion products from burning pentane, C_5H_{12}, with pure oxygen in a stoichiometric ratio exists at 2400 K, 100 kPa. 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 2400K,

$\ln K = -7.715$

$K = 4.461 \times 10^{-4}$

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

Assuming $P = P^o = 0.1$ MPa, and $n_{tot} = 5 + z + 6 = 11 + z$

$$K = \frac{y_{CO}^2 y_{O_2}}{y_{CO_2}^2}\left(\frac{P}{P^0}\right) = \left(\frac{2z}{5 - 2z}\right)^2 \left(\frac{z}{11 + z}\right)(1) = 4.461 \times 10^{-4}\ ;$$

Trial & Error (compute LHS for various values of z): $z = 0.291$

$n_{CO_2} = 4.418$; $n_{CO} = 0.582$; $n_{O_2} = 0.291$ => $y_{CO} = \mathbf{0.0515}$

15.38

Find the equilibrium constant for the reaction $2NO + O_2 \Leftrightarrow 2NO_2$ from the elementary reactions in Table A.11 to answer which of the nitrogen oxides, NO or NO_2, is the more stable at ambient conditions? What about at 2000 K?

$$2\,NO + O_2 \Leftrightarrow 2\,NO_2 \quad (1)$$

$$\text{But } N_2 + O_2 \Leftrightarrow 2\,NO \quad (2)$$

$$N_2 + 2\,O_2 \Leftrightarrow 2\,NO_2 \quad (3)$$

Reaction 1 = Reaction 3 - Reaction 2

$$\Rightarrow \quad \Delta G_1^0 = \Delta G_3^0 - \Delta G_2^0 \quad => \quad \ln K_1 = \ln K_3 - \ln K_2$$

At 25 °C, from Table A.10: $\ln K_1 = -41.355 - (-69.868) = +28.513$

or $K_1 = 2.416 \times 10^{12}$

an extremely large number, which means reaction 1 tends to go very strongly from left to right.

At 2000 K: $\ln K_1 = -19.136 - (-7.825) = -11.311$ or $K_1 = 1.224 \times 10^{-5}$

meaning that reaction 1 tends to go quite strongly from right to left.

15.39

Pure oxygen is heated from 25°C, 100 kPa to 3200 K in a constant volume container. Find the final pressure, composition, and the heat transfer.

As oxygen is heated it dissociates

$$O_2 \Leftrightarrow 2O \qquad \ln K_{eq} = -3.069 \quad \text{from table A.11}$$

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

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

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

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

$y_{O_2 2} = (1 - x)/(1 + x)\ ; \quad y_{O2} = 2x/(1 + x)$

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

Substitute the molefractions and the pressure into the equilibrium equation

$$K_{eq} = e^{-3.069} = \frac{y_O^2}{y_{O_2}}\left(\frac{P_2}{P_o}\right) = \left(\frac{2x}{1 + x}\right)^2 \left(\frac{1 + x}{1 - x}\right)\left(\frac{1 + x}{1}\right)\left(\frac{T_2}{T_1}\right)$$

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

The final pressure is then

$$P_2 = P_o(1 + x)\frac{T_2}{T_1} = 100\ (1 + 0.0324) \times \frac{3200}{298.2} = \mathbf{1108\ kPa}$$

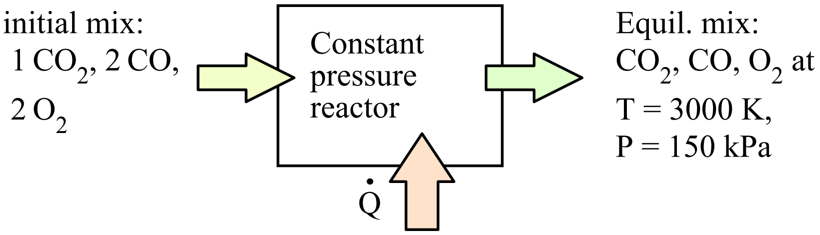
$(n_{O_2})_2 = 0.9676, \quad (n_O)_2 = 0.0648, \quad n_2 = 1.0324$

$${}_1\bar{q}_2 = 0.9676 \times 106022 + 0.0648\ (249170 + 60767) - 0$$
$$+ 8.3145\ (298.15 - 1.0324 \times 3200) = \mathbf{97681\ kJ/kmolO_2}$$

$$y_{O_2 2} = \frac{0.9676}{1.0324} = \mathbf{0.937}; \qquad y_{O2} = \frac{0.0648}{1.0324} = \mathbf{0.0628}$$

15.40

A mixture of 1 kmol carbon dioxide, 2 kmol carbon monoxide, and 2 kmol oxygen, at 25°C, 150 kPa, is heated in a constant pressure steady state process to 3000 K. Assuming that only these same substances are present in the exiting chemical equilibrium mixture, determine the composition of that mixture.



Reaction	$2\ CO_2$	⇔	$2\ CO$	+	O_2
initial	1		2		2
change	-2x		+2x		+x
equil.	(1-2x)		(2+2x)		(2+x)

From A.10 at 3000 K: K = exp(-2.217) = 0.108935

For each $n > 0 \quad \Rightarrow \quad -1 < x < +\frac{1}{2}$

$$K = \frac{y_{CO}^2 y_{O2}}{y_{CO2}^2}\left(\frac{P}{P^0}\right)^1 = 4\left(\frac{1+x}{1-2x}\right)^2\left(\frac{2+x}{5+x}\right)\left(\frac{150}{100}\right)$$

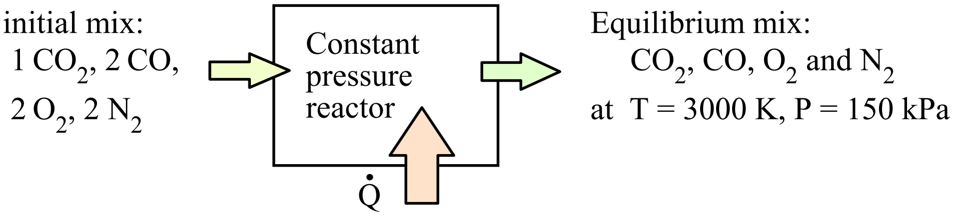
or $\left(\frac{1+x}{1-2x}\right)^2\left(\frac{2+x}{5+x}\right) = 0.018\ 156$, Trial & error: x = -0.521

$$\left.\begin{matrix} n_{CO2} = 2.042 & n_{O2} = 1.479 \\ n_{CO} = 0.958 & n_{TOT} = 4.479 \end{matrix}\right\} \left\{\begin{matrix} y_{CO2} = 0.4559 \\ y_{CO} = 0.2139 \\ y_{O2} = 0.3302 \end{matrix}\right.$$

15.41

Repeat the previous problem for an initial mixture that also includes 2 kmol of nitrogen, which does not dissociate during the process.

This problem has a dilution of the reantant with nitrogen.



Reaction	$2\ CO_2$	$\Leftrightarrow$	$2\ CO$	$+$	O_2
initial	1		2		2
change	-2x		+2x		+x
equil.	(1-2x)		(2+2x)		(2+x)

From A.10 at 3000 K: $K = \exp(-2.217) = 0.108935$

For each $n > 0 \quad \Rightarrow \quad -1 < x < +\frac{1}{2}$

Equilibrium: $n_{CO2} = (1 - 2x)$, $n_{CO} = (2 + 2x)$, $n_{O2} = (2 + x)$,

$n_{N2} = 2$ so then $n_{tot} = 7 + x$

$$K = \frac{y_{CO}^2 y_{O2}}{y_{CO2}^2} \left(\frac{P}{P^0}\right)^1 = 4 \left(\frac{1+x}{1-2x}\right)^2 \left(\frac{2+x}{7+x}\right) \left(\frac{150}{100}\right)$$

or $\left(\frac{1+x}{1-2x}\right)^2 \left(\frac{2+x}{7+x}\right) = 0.018167$ Trial & error: $x = -0.464$

$$\begin{array}{ll} n_{CO2} = 1.928 & n_{O2} = 1.536 \\ n_{CO} = 1.072 & n_{N2} = 2.0 \\ & n_{TOT} = 6.536 \end{array} \Bigg\} \left\{ \begin{array}{ll} y_{CO2} = 0.295 & y_{O2} = 0.235 \\ y_{CO} = 0.164 & y_{N2} = 0.306 \end{array} \right.$$

15.42

One approach to using hydrocarbon fuels in a fuel cell is to "reform" the hydrocarbon to obtain hydrogen, which is then fed to the fuel cell. As a part of the analysis of such a procedure, consider the reforming section and determine the equilibrium constant for this reaction at a temperature of 800 K.

For CH_4, use C_{P0} at ave. temp., 550 K. Table A.6, $\bar{C}_{P0} = 49.316$ kJ/kmol K

a) $\bar{h}^0_{800\ K} = \bar{h}^0_f + \bar{C}_{P0}\Delta T = -74\ 873 + 49.316(800-298.2) = -50\ 126$ kJ/kmol

$$\bar{s}^0_{800\ K} = 186.251 + 49.316 \ln\frac{800}{298.2} = 234.918 \text{ kJ/kmol K}$$

For $\qquad CH_4 + H_2O \Leftrightarrow 3H_2 + CO$

$$\Delta H^0_{800\ K} = 3(0+14\ 681) + 1(-110\ 527+15\ 174) - 1(-50\ 126) - 1(-241\ 826+18\ 002) = +222\ 640 \text{ kJ/kmol}$$

$$\Delta S^0_{800\ K} = 3(159.554) + 1(227.277) - 1(234.918) - 1(223.826) = +247.195 \text{ kJ/kmol K}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 222\ 640 - 800(247.195) = +24\ 884 \text{ kJ/kmol}$$

$$\ln K = -\frac{\Delta G^0}{\bar{R}T} = \frac{-24\ 884}{8.3145\times 800} = -3.7411 \quad => \quad K = \mathbf{0.0237}$$

15.43

Consider combustion of methane with pure oxygen forming carbon dioxide and water as the products. Find the equilibrium constant for the reaction at 1000 K. Use an average heat capacity of Cp = 52 kJ/kmol K for the fuel and Table A.9 for the other components.

For the reaction equation,

$$CH_4 + 2\,O_2 \Leftrightarrow CO_2 + 2\,H_2O$$

At 1000 K

$$\Delta H^0_{1000\text{ K}} = 1(-393\,522 + 33\,397) + 2(-241\,826 + 26\,000)$$
$$- 1[-74\,873 + 52(1000 - 298.2)] - 2(0 + 22\,703)$$
$$= -798\,804 \text{ kJ/kmol}$$

$$\Delta S^0_{1000\text{ K}} = 1\times269.299 + 2\times232.739 - 1(186.251 + \ln\frac{1000}{298.2}) - 2\times243.579$$
$$= 487.158 \text{ kJ/kmol K}$$

$$\Delta G^0_{1000\text{ K}} = \Delta H^0_{1000\text{ K}} - T\ \Delta S^0_{1000\text{ K}}$$
$$= -798\,804 - 1000 \times 487.158 = -1\,285\,962 \text{ kJ/kmol}$$

$$\ln K = -\frac{\Delta G^0}{\bar{R}T} = \frac{+1\,285\,962}{8.3145\times1000} = +154.665 \quad , \quad \mathbf{K = 1.4796\ E\ 67}$$

This means the reaction is shifted totally to the right.

15.44

Find the equilibrium constant for the reaction: $2NO + O_2 \Leftrightarrow 2NO_2$ from the elementary reaction in Table A.11 to answer these two questions. Which of the nitrogen oxides NO or NO_2 is the more stable at 25°C, 100 kPa? At what T do we have an equal amount of each?

The elementary reactions are the last two ones in Table A.11:

a) $N_2 + O_2 \Leftrightarrow 2\,NO$ b) $N_2 + 2O_2 \Leftrightarrow 2\,NO_2$

Actual reaction is : $c = b - a \quad \Rightarrow \quad \ln(K_c) = \ln(K_b) - \ln(K_a)$

At 25^oC (approx. 300 K) Table A.11: $\ln(K_a) = -69.868$; $\ln(K_b) = -41.355$

so now:

$$\ln(K_c) = -41.355 + 69.868 = 28.5 \quad \Rightarrow \quad K_c = 2.4 \times 10^{12}$$

meaning reaction is pushed completely to the right and **NO_2 is the stable** compound. Assume we start at room T with 1 kmol NO_2: then

	NO	O_2	NO_2	TOT
start	0	0	1	
change	2x	x	-2x	
Final	2x	x	1-2x	1+x

Equal amount of each

$$y(NO) = \frac{2x}{1+x} = y(NO_2) = \frac{1-2x}{1+x} \quad \Rightarrow \quad x = 0.25$$

$$K(T) = \frac{(1-2x)^2}{4x^3} = \frac{0.5^2}{4 \times 0.25^3} = 4 \quad \Rightarrow \quad \ln(K) = 1.386$$

We quickly see

$\ln(K)$ at 500 K $= -30.725 + 40.449 = 9.724$

$\ln(K)$ at 1000 K $= -23.039 + 18.709 = -4.33$

Linear interpolation $T = 500 + 0.406 \times 500 =$ **703 K**

15.45

The equilibrium reaction as: $CH_4 \Leftrightarrow C + 2H_2$. has ln *K* = -0.3362 at 800 K and ln*K* = -4.607 at 600 K. By noting the relation of *K* to temperature show how you would interpolate ln *K* in (1/*T*) to find K at 700 K and compare that to a linear interpolation.

A.11: ln K = - 0.3362 at 800K ln K = -4.607 at 600K

$$\ln K_{700} = \ln K_{800} + \frac{\frac{1}{700} - \frac{1}{800}}{\frac{1}{600} - \frac{1}{800}} \times (-4.607 + 0.3362)$$

$$= -0.3362 + \frac{\frac{800}{700} - 1}{\frac{800}{600} - 1} \times (-4.2708) \quad = -2.1665$$

Linear interpolation:

$$\ln K_{700} = \ln K_{600} + \frac{700 - 600}{800 - 600} (\ln K_{800} - \ln K_{600})$$

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

15.46

Water from the combustion of hydrogen and pure oxygen is at 3800 K and 50 kPa. Assume we only have H_2O, O_2 and H_2 as gases find the equilibrium composition.

With only the given components we have the reaction

$$2\,H_2O \quad \Leftrightarrow \quad 2H_2 + O_2$$

which at 3800 K has an equilibrium constant from A.11 as ln K = -1.906

Assume we start with 2 kmol water and let it dissociate x to the left then

Species	H_2O	H_2	O_2	
Initial	2	0	0	
Change	-2x	2x	x	
Final	2 – 2x	2x	x	Tot: 2 + x

Then we have

$$K = \exp(-1.906) \;= \frac{y_{H_2}^2\, y_{O_2}}{y_{H_2O}^2} \left(\frac{P}{P^0}\right)^{2+1-2} = \frac{\left(\frac{2x}{2+x}\right)^2 \frac{x}{2+x}}{\left(\frac{2-2x}{2+x}\right)^2} \frac{50}{100}$$

which reduces to

$$0.148674 = \frac{1}{(1-x)^2} \frac{4x^3}{2+x} \frac{1}{4} \frac{1}{2} \quad \text{or} \quad x^3 = 0.297348\;(1-x)^2\,(2+x)$$

Trial and error to solve for x = 0.54 then the concentrations are

$$y_{H2O} = \frac{2-2x}{2+x} = 0.362; \quad y_{O2} = \frac{x}{2+x} = 0.213; \quad y_{H2} = \frac{2x}{2+x} = 0.425$$

15.47

Complete combustion of hydrogen and pure oxygen in a stoichiometric ratio at P_o T_o to form water would result in a computed adiabatic flame temperature of 4990 K for a steady state setup.

a. How should the adiabatic flame temperature be found if the equilibrium reaction $2H_2 + O_2 \Leftrightarrow 2\,H_2O$ is considered? Disregard all other possible reactions (dissociations) and show the final equation(s) to be solved.

b. Which other reactions should be considered and which components will be present in the final mixture?

a) $2H_2 + O_2 \Leftrightarrow 2H_2O$

$H_P = H_R = H_P^o + \Delta H_P = H_R^o = 0$

Species	H_2	O_2	H_2O
Initial	2	1	0
Shift	-2x	-x	2x
Final	2-2x	1-x	2x

$$Keq = \frac{y_{H_2O}^2}{y_{H_2}^2 y_{O_2}} \left(\frac{P}{P^0}\right)^{-1}, \qquad n_{tot} = 2\text{-}2x + 1\text{-}x + 2x = 3\text{-}x$$

$$H_p = (2\text{-}2x)\Delta\bar{h}_{H_2} + (1\text{-}x)\Delta\bar{h}_{O_2} + 2x(\bar{h}^o_{fH2O} + \Delta\bar{h}_{H2O}) = 0 \qquad (1)$$

$$Keq = \frac{4x^2}{(3\text{-}x)^2}\,\frac{(3\text{-}x)^2}{(2\text{-}2x)^2}\,\frac{3\text{-}x}{1\text{-}x} = \frac{x^2(3\text{-}x)}{(1\text{-}x)^3} = Keq(T) \qquad (2)$$

$\bar{h}^o_{fH2O} = -241826;\quad \Delta\bar{h}_{H_2}(T),\quad \Delta\bar{h}_{O_2}(T),\quad \Delta\bar{h}_{H_2O}(T)$

Trial and Error (solve for x,T) using Eqs. (1) and (2).

$y_{O_2} = 0.15;\quad y_{H_2} = 0.29;\quad y_{H_2O} = 0.56]$

b) At 3800 K $\quad Keq = e^{1.906}$ (Reaction is times -1 of table)

$x^2(3\text{-}x)(1\text{-}x)^{-3} = e^{1.906} = 6.726 \;\Rightarrow\; x \cong 0.5306$

$$y_{H_2O} = \frac{2x}{3\text{-}x} = 0.43;\quad y_{O_2} = \frac{1\text{-}x}{3\text{-}x} = 0.19;\quad y_{H_2} = \frac{2\text{-}2x}{3\text{-}x} = 0.38$$

c) Other possible reactions from table A.10

$H_2 \leftrightarrow 2\,H \qquad O_2 \leftrightarrow 2\,O \qquad 2\,H_2O \leftrightarrow H_2 + 2\,OH$

15.48

The van't Hoff equation

$$d \ln K = \frac{\Delta H^o}{\bar{R}T^2}\ dT_{P^o}$$

relates the chemical equilibrium constant K to the enthalpy of reaction ΔH^o. From the value of K in Table A.11 for the dissociation of hydrogen at 2000 K and the value of ΔH^o calculated from Table A.9 at 2000 K use van't Hoff equation to predict the constant at 2400 K.

$$H_2 \Leftrightarrow 2H$$

$\Delta H° = 2 \times (35\,375+217\,999) – 52\,942 = 453\,806$ kJ/kmol

$\ln K_{2000} = -12.841;$

Assume ΔH° is constant and integrate the Van't Hoff equation

$$\ln K_{2400} - \ln K_{2000} = \int_{2400}^{2000} (\Delta H°/\bar{R}T^2)dT = -\frac{\Delta H°}{\bar{R}} \left(\frac{1}{T_{2400}} - \frac{1}{T_{2000}}\right)$$

$$\ln K_{2400} = \ln K_{2000} + \Delta H° \left(\frac{1}{T_{2400}} - \frac{1}{T_{2000}}\right) / \bar{R}$$

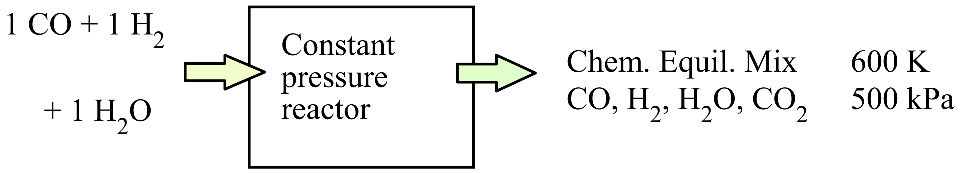
$$= -12.841 + 453\,806 \left(\frac{6-5}{12000}\right) / 8.31451 = -12.841 + 4.548$$

$$= -8.293$$

Table A.11 lists –8.280 (ΔH° not exactly constant)

15.49

Gasification of char (primarily carbon) with steam following coal pyrolysis yields a gas mixture of 1 kmol CO and 1 kmol H_2. We wish to upgrade the hydrogen content of this syngas fuel mixture, so it is fed to an appropriate catalytic reactor along with 1 kmol of H_2O. Exiting the reactor is a chemical equilibrium gas mixture of CO, H_2, H_2O, and CO_2 at 600 K, 500 kPa. Determine the equilibrium composition. Note: see Example 15.4.



$$(1)\ 1\,CO + 1\,H_2O \Leftrightarrow 1\,CO_2 + 1\,H_2$$

$$\quad -x \quad -x \quad +x \quad +x$$

$$(2)\ 2\,H_2O \Leftrightarrow 2\,H_2 + 1\,O_2 \qquad\qquad (3)\ 2\,CO_2 \Leftrightarrow 2\,CO + 1\,O_2$$

$$(1) = \frac{1}{2}(2) - \frac{1}{2}(3)$$

$$\ln K_1 = \frac{1}{2}\big[-85.79-(-92.49)\big] = +3.35, \qquad K_1 = 28.503$$

Equilibrium:

$$n_{CO} = 1-x, \quad n_{H2O} = 1-x, \quad n_{CO2} = 0 + x, \quad n_{H2} = 1 + x$$

$$\sum n = 3, \quad K = \frac{y_{CO2}\,y_{H2}}{y_{CO}\,y_{H2O}}\Big(\frac{P}{P^0}\Big)^0 = \frac{y_{CO2}\,y_{H2}}{y_{CO}\,y_{H2O}}$$

$$28.503 = \frac{x(1+x)}{(1-x)^2} \rightarrow x = 0.7794$$

	n	y	%
CO	0.2206	0.0735	7.35
H_2O	0.2206	0.0735	7.35
CO_2	0.7794	0.2598	26.0
H_2	1.7794	0.5932	59.3

15.50

Consider the water gas reaction in Example 15.4. Find the equilibrium constant at 500, 1000, 1200 and 1400 K. What can you infer from the result?

As in Example 15.4, III $H_2 + CO_2 \Leftrightarrow H_2O + CO$

I $2\,CO_2 \Leftrightarrow 2\,CO + O_2$

II $2\,H_2O \Leftrightarrow 2\,H_2 + O_2$

Then, $\ln K_{III} = 0.5\,(\ln K_I - \ln K_{II})$

At 500 K, $\ln K_{III} = 0.5\,(-115.234 - (-105.385)) = -4.9245$,
$K = 0.007\,266$

At 1000 K, $\ln K_{III} = 0.5\,(-47.052 - (-46.321)) = -0.3655$,
$K = 0.693\,85$

At 1200 K, $\ln K_{III} = 0.5\,(-35.736 - (-36.363)) = +0.3135$,
$K = 1.3682$

At 1400 K, $\ln K_{III} = 0.5\,(-27.679 - (-29.222)) = +0.7715$,
$K = 2.163$

It is seen that at lower temperature, reaction III tends to go strongly from right to left, but as the temperature increases, the reaction tends to go more strongly from left to right. If the goal of the reaction is to produce more hydrogen, then it is desirable to operate at lower temperature.

15.51

Catalytic gas generators are frequently used to decompose a liquid, providing a desired gas mixture (spacecraft control systems, fuel cell gas supply, and so forth). Consider feeding pure liquid hydrazine, N_2H_4, to a gas generator, from which exits a gas mixture of N_2, H_2, and NH_3 in chemical equilibrium at 100°C, 350 kPa. Calculate the mole fractions of the species in the equilibrium mixture.

Initially, $2\,N_2H_4 \rightarrow 1\,N_2 + 1\,H_2 + 2\,NH_3$

then,	N_2 $+$	$3\,H_2$ $\Leftrightarrow$	$2\,NH_3$	
initial	1	1	2	
change	-x	-3x	+2x	
equil.	(1-x)	(1-3x)	(2+2x)	$n_{TOTAL} = (4-2x)$

$$K = \frac{y_{NH3}^2}{y_{N2}\,y_{H2}^3}\left(\frac{P}{P^0}\right)^{-2} = \frac{(2+2x)^2(4-2x)^2}{(1-x)(1-3x)^3}\left(\frac{350}{100}\right)^{-2}$$

At 100 °C = 373.2 K, for NH_3 use A.5 $\quad \bar{C}_{P0} = 17.03\times2.130 = 36.276$

$$\bar{h}^0_{NH3} = -45\,720 + 36.276(373.2-298.2) = -42\,999 \text{ kJ/kmol}$$

$$\bar{s}^0_{NH3} = 192.572 + 36.276\ln\frac{373.2}{298.2} = 200.71 \text{ kJ/kmol K}$$

Using A.8,

$$\Delta H^0_{100\,C} = 2(-42\,999) - 1(0+2188) - 3(0+2179) = -94\,723 \text{ kJ}$$

$$\Delta S^0_{100\,C} = 2(200.711) - 1(198.155) - 3(137.196) = -208.321 \text{ kJ/K}$$

$$\Delta G^0_{100\,C} = \Delta H^0 - T\Delta S^0 = -94\,723 - 373.2(-208.321) = -16\,978 \text{ kJ}$$

$$\ln K = -\frac{\Delta G^0}{\bar{R}T} = \frac{+16\,978}{8.3145\times373.2} = 5.4716 \quad => \quad K = 237.84$$

Therefore,

$$\left[\frac{(1+x)(2-x)}{(1-3x)}\right]^2\frac{1}{(1-x)(1-3x)} = \frac{237.84\times3.5^2}{16} = 182.096$$

By trial and error, x = 0.226

$$\left.\begin{matrix} n_{N2} = 0.774 & n_{NH3} = 2.452 \\ n_{H2} = 0.322 & n_{TOT} = 3.518 \end{matrix}\right\} \left\{\begin{matrix} y_{N2} = 0.2181 \\ y_{H2} = 0.0908 \\ y_{NH3} = 0.6911 \end{matrix}\right.$$

15.52

A piston/cylinder contains 0.1 kmol hydrogen and 0.1 kmol Ar gas at 25°C, 200 kPa. It is heated up in a constant pressure process so the mole fraction of atomic hydrogen is 10%. Find the final temperature and the heat transfer needed.

When gas is heated up H_2 splits partly into H as

$H_2 \Leftrightarrow 2H$ and the gas is diluted with Ar

Component	H_2	Ar	H	
Initial	0.1	0.1	0	
Shift	-x	0	2x	
Final	0.1-x	0.1	2x	Total = 0.2 + x

$y_H = 0.1 = 2x/(0.2+x) \Rightarrow 2x = 0.02+0.1x \quad \Rightarrow \quad x = 0.010526$

$\Rightarrow n_{tot} = 0.21053$

$y_{H2} = 0.425 = [(0.1\text{-}x)/(0.2+x)]; \quad y_{Ar} = 1 - \text{rest} = 0.475$

Do the equilibrium constant:

$$K(T) = \frac{y_H^2}{y_{H2}} \left(\frac{P}{P^0}\right)^{2-1} = \left(\frac{0.01}{0.425}\right) \times \left(\frac{200}{100}\right) = 0.047059$$

ln (K) = -3.056 so from Table A.10 interpolate to get T = 3110 K

To do the energy eq., we look up the enthalpies in Table A.8 at 3110K

$h_{H2} = 92\,829.1$; $h_H = 217\,999 + 58\,447.4 = 276\,445.4$ $(= h_f + \Delta h)$

$h_{Ar} = C_P(3110–298.15) = 20.7863 \times (3110\text{-}298.13) = 58\,447.9$

(same as Δh for H)

Now get the total number of moles to get

$n_H = 0.021053; \quad n_{H2} = n_{tot} \times \frac{1\text{-}x}{2+x} = 0.08947; \quad n_{Ar} = 0.1$

Since pressure is constant W = PΔV and Q becomes differences in h

$$Q = n\Delta h = 0.08947 \times 92\,829.1 - 0 + 0.021053 \times 276\,446.4$$
$$- 0 + 0.1 \times 58\,447.9$$

= **19 970 kJ**

15.53

A tank contains 0.1 kmol hydrogen and 0.1 kmol of argon gas at 25°C, 200 kPa and the tank keeps constant volume. To what T should it be heated to have a mole fraction of atomic hydrogen, H, of 10%?

For the reaction $H_2 \Leftrightarrow 2H$, $K = \frac{y_H^2}{y_{H_2}} \left(\frac{P}{P^o}\right)^{2-1}$

Assume the dissociation shifts right with an amount x then we get

reaction	H_2	⇔	2 H	also,	Ar	
initial	0.1		0		0.1	
change	-x		2x		0	
equil.	0.1 - x		2x		0.1	Tot: 0.2 + x

$$y_H = \frac{2x}{0.2 + x} = 0.10 \quad \Rightarrow \quad x = 0.010526$$

We need to find T so K will take on the proper value, since K depends on P we need to evaluate P first.

$$P_1V = n_1\bar{R}T_1; \quad P_2V = n_2\bar{R}T_2 \quad \Rightarrow \quad P_2 = P_1 \frac{n_2T_2}{n_1T_1}$$

where we have $n_1 = 0.2$ and $n_2 = 0.2 + x = 0.210526$

$$K = \frac{y_H^2}{y_{H_2}} \left(\frac{P}{P^o}\right)^{2-1} = \frac{(2x)^2}{(0.1 - x)\, n_2} \frac{200}{100} \frac{n_2T_2}{0.2 \times 298.15} = 0.0001661\ T_2$$

Now it is trial and error to get T_2 so the above equation is satisfied with K from A.11 at T_2.

3600 K: ln K = -0.611, K = 0.5428, RHS = 0.59796, error = 0.05516

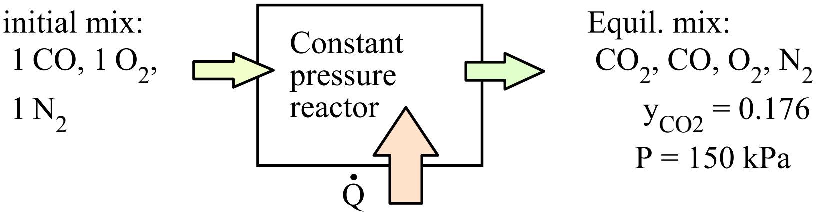
3800 K: ln K = 0.201, K = 1.22262, RHS = 0.63118, error = -0.59144

Linear interpolation between the two to make zero error

$$T = 3600 + 200 \times \frac{0.05516}{0.05516 + 0.59144} = \mathbf{3617\ K}$$

15.54

A gas mixture of 1 kmol carbon monoxide, 1 kmol nitrogen, and 1 kmol oxygen at 25°C, 150 kPa, is heated in a constant pressure 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	$2\ CO_2$	$\Leftrightarrow$	$2\ CO$	+	O_2	also,	N_2
initial	0		1		1		1
change	+2x		-2x		-x		0
equil.	2x		(1-2x)		(1-x)		1

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

$$\left.\begin{matrix} n_{CO2} = 0.4853 & n_{O2} = 0.7574 \\ n_{CO} = 0.5147 & n_{N2} = 1 \end{matrix}\right\} \left\{\begin{matrix} y_{CO2} = 0.176 \\ y_{CO} = 0.1867 \end{matrix}\right. y_{O2} = 0.2747$$

$$K = \frac{y_{CO}^2 y_{O2}}{y_{CO2}^2}\left(\frac{P}{P^0}\right)^1 = \frac{0.1867^2 \times 0.2747}{0.176^2}\left(\frac{150}{100}\right) = 0.4635$$

From A.10, $T_{PROD} = 3213$ K

From A.9, $H_R = -110\ 527$ kJ

$$H_P = 0.4853(-393\ 522 + 166\ 134) + 0.5147(-110\ 527 + 101\ 447)$$
$$+ 0.7574(0 + 106\ 545) + 1(0 + 100\ 617)$$
$$= +66\ 284 \text{ kJ}$$

$Q_{CV} = H_P - H_R = 66\ 284 - (-110\ 527) =$ **+176 811 kJ**

15.55

A rigid container initially contains 2 kmol of carbon monoxide and 2 kmol of oxygen at 25°C, 100 kPa. The content is then heated to 3000 K at which point an equilibrium mixture of CO_2, CO, and O_2 exists. Disregard other possible species and determine the final pressure, the equilibrium composition and the heat transfer for the process.

$2\,CO + 2\,O_2 \Leftrightarrow 2\,CO_2 + O_2$ Species: CO O_2 CO_2

Initial 2 2 0

Shift -2x -2x+x 2x

Final 2-2x 2-x 2x : $n_{tot} = 2\text{-}2x + 2\text{-}x + 2x = 4\text{-}x$

$$y_{CO} = \frac{2-2x}{4-x};\quad y_{O_2} = \frac{2-x}{4-x};\quad y_{CO_2} = \frac{2x}{4-x}$$

$$U_2 - U_1 = {}_1Q_2 = H_2 - H_1 - P_2v + P_1v$$

$$= (2 - 2x)\bar{h}_{CO\,2} + (2 - x)\bar{h}_{O_2 2} + 2x\bar{h}_{CO_2} - 2\bar{h}^o_{fCO_2} - 2\bar{h}^o_{fO_2}$$

$$- \bar{R}(4 - x)T_2 + 4\bar{R}T_1$$

$$K_{eq} = e^{2.217} = \frac{y^2_{CO_2}}{y_{0_2}y^2_{CO}}\left(\frac{P_2}{P_o}\right)^{-1} = \frac{4x^2}{4(1-x)^2}\,\frac{4-x}{2-x}\,\frac{4T_1}{(4-x)T_2}$$

$$\Rightarrow\ \left(\frac{x}{1-x}\right)^2\frac{1}{2-x} = \frac{1}{4}\frac{T_2}{T_1}\,e^{2.217} = 23.092$$

$x = 0.8382$; $y_{CO} = \mathbf{0.102}$; $y_{O_2} = \mathbf{0.368}$; $y_{CO_2} = \mathbf{0.53}$

$P_2 = P_1(4\text{-}x)T_2/4T_1 = 100(3.1618)(3000/4)(298.15)$ = **795.4 kPa**

$${}_1Q_2 = 0.3236(-110527 + 93504) + 1.1618(98013) + 1.6764(-393522$$

$$+ 152853) - 2(-110527) - 2(0) + 8.3145(4(298.15) - 3000(3.1618))$$

$$= \mathbf{-142991\ kJ}$$

15.56

A coal gasifier produces a mixture of 1 CO and $2H_2$ that is fed to a catalytic converter to produce methane. The reaction is $CO + 3H_2 \Leftrightarrow CH_4 + H_2O$. The equilibrium constant at 600 K is $K = 1.83 \times 10^6$. What is the composition of the exit flow assuming a pressure of 600 kPa?

The reaction equation is:

	CO	+	3 H_2	$\Leftrightarrow$	CH_4	+	H_2O	
initial	1		2		0		0	
change	–x		–3x		+x		+x	
equil.	1 – x		2 – 3x		x		x	$n_{TOTAL} = 3 - 2x$

$$K = \frac{y_{CH_4}\, y_{H_2O}}{y_{H_2}^3\, y_{CO}} \left(\frac{P}{P^o}\right)^{1+1-1-3} = \frac{x^2\,(3 - 2x)^2}{(1-x)(2 - 3x)^3} \left(\frac{P}{P^o}\right)^{-2}$$

$$1.83 \times 10^6 \times \left(\frac{600}{100}\right)^2 = 6.588 \times 10^7 = \frac{x^2\,(3 - 2x)^2}{(1-x)(2 - 3x)^3}$$

Trial and error to solve for x.

$x = 0.6654$ LHS $= 6.719 \times 10^7$

$x = 0.66538$ LHS $= 6.41 \times 10^7$

$x = 0.66539$ LHS $= 6.562 \times 10^7$ close enough

$n_{CH4} = 0.66539$, $n_{H2O} = 0.66539$, $n_{CO} = 0.66539$, $n_{H2} = 0.00383$

so we used up nearly all the hydrogen gas.

15.57

One approach to using hydrocarbon fuels in a fuel cell is to “reform” the hydrocarbon to obtain hydrogen, which is then fed to the fuel cell. As a part of the analysis of such a procedure, consider the reaction $CH_4 + H_2O \Leftrightarrow CO + 3H_2$. One kilomole each of methane and water are fed to a catalytic reformer. A mixture of CH_4, H_2O, H_2, and CO exits in chemical equilibrium at 800 K, 100 kPa; determine the equilibrium composition of this mixture using an equilibrium constant of K = 0.0237.

The reaction equation is:

	CH_4	+	H_2O	$\Leftrightarrow$	$3\,H_2$	+	CO
initial	1		1		0		0
change	-x		-x		+3x		+x
equil.	(1-x)		(1-x)		3x		x

$n_{TOTAL} = 2 + 2x$

$$K = \frac{y_{H2}^3 y_{CO}}{y_{CH4} y_{H2O}} \left(\frac{P}{P^0}\right)^2 = \frac{(3x)^3 x}{(1-x)(1-x)(2+2x)^2} \left(\frac{100}{100}\right)^2$$

$$\text{or} \quad \left(\frac{x}{1-x}\right)^2 \left(\frac{x}{1+x}\right)^2 = \frac{4 \times 0.0237}{27 \times 1} = 0.003\,51$$

$$\text{or} \quad \frac{x^2}{1-x^2} = \sqrt{0.003\,51} = 0.059\,25 \qquad \text{Solving,} \quad x = 0.2365$$

$$\left.\begin{array}{l} n_{CH4} = 0.7635 \\ n_{H2O} = 0.7635 \\ n_{H2} = 0.7095 \\ n_{CO} = 0.2365 \\ n_{TOT} = 2.473 \end{array}\right\} \left\{\begin{array}{l} y_{CH4} = 0.3087 \\ y_{H2O} = 0.3087 \\ y_{H2} = 0.2870 \\ y_{CO} = 0.0956 \end{array}\right.$$

15.58

Use the information in Problem 15.45 to estimate the enthalpy of reaction, ΔH^o, at 700 K using Van't Hoff equation (see problem 15.48) with finite differences for the derivatives.

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

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

$$= 8.31451 \times 700^2 \times \frac{-0.3362 + 4.607}{800 - 600} = 86\ 998 \text{ kJ/kmol}$$

[Remark: compare this to A.9 values + A.5, A.10,

$$\Delta H° = H_C + 2H_{H_2} - H_{CH_4} = 0.61 \times 12 \times (700\text{-}298) + 2 \times 11730$$

$$- 2.254 \times 16.04 \times (700\text{-}298) - (-74873) = 86\ 739 \text{ kJ/kmol}]$$

15.59

Acetylene gas at 25°C is burned with 140% theoretical air, which enters the burner at 25°C, 100 kPa, 80% relative humidity. The combustion products form a mixture of CO_2, H_2O, N_2, O_2, and NO in chemical equilibrium at 2200 K, 100 kPa. This mixture is then cooled to 1000 K 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: $P_V = 0.8 \times 3.169 = 2.535$ kPa

$n_V = n_A P_V/P_A = (3.5+13.16)\, 2.535/97.465 = 0.433$

So, total H_2O in products is 1.433.

a) reaction: $N_2 + O_2 \ \ \text{<->} \ \ 2\ NO$

change : $-x \quad -x \qquad +2x$

at 2200 K, from A.10: $K = 0.001\ 074$

Equil. products: $n_{CO2} = 2$, $n_{H2O} = 1.433$, $n_{O2} = 1-x$,

$n_{N2} = 13.16-x$, $n_{NO} = 0+2x$, $n_{TOT} = 17.593$

$$K = \frac{(2x)^2}{(1-x)(13.16-x)} = 0.001\ 074 \quad => \quad x = 0.0576$$

$$y_{NO} = \frac{2 \times 0.0576}{17.593} = \mathbf{0.006\ 55}$$

b) Final products (same composition) at 1000 K

$H_R = 1(226\ 731) + 0.433(-241\ 826) = 122\ 020$ kJ

$H_P = 2(-393\ 522 + 33\ 397) + 1.433(-241\ 826+26\ 000)$

$+ 0.9424(0+22\ 703) + 13.1024(0+21\ 463) + 0.1152(90\ 291+22\ 229)$

$= -713\ 954$ kJ

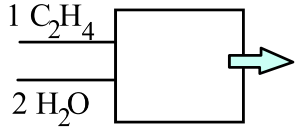
$Q_{CV} = H_P - H_R = \mathbf{-835\ 974\ kJ}$

15.60

A step in the production of a synthetic liquid fuel from organic waste matter is the following conversion process: 1 kmol of ethylene gas (converted from the waste) at 25°C, 5 MPa, and 2 kmol of steam at 300°C, 5 MPa, enter a catalytic reactor. An ideal gas mixture of ethanol, ethylene, and water in chemical equilibrium leaves the reactor at 700 K, 5 MPa. Determine the composition of the mixture and the heat transfer for the reactor.

25 °C, 5 MPa

300 °C, 5 MPa



IG chem. equil. mixture
C_2H_5OH, C_2H_4, H_2O
700 K, 5 MPa

$$1\,C_2H_4 + 1\,H_2O \Leftrightarrow 1\,C_2H_5OH$$

A.6 at ~ 500 K: $\bar{C}_{P0\ C2H4} = 62.3$

init	1	2	0
ch.	-x	-x	+x
equil.	(1-x)	(2-x)	x

a) $\Delta H^0_{700\ K} = 1(-235\ 000 + 115(700\text{-}298.2)) - 1(+52\ 467 + 62.3(700\text{-}298.2))$

$- 1(-241\ 826 + 14\ 190) = -38\ 656$ kJ

$$\Delta S^0_{700\ K} = 1(282.444 + 115 \ln\frac{700}{298.2}) - 1(219.330 + 62.3 \ln\frac{700}{298.2}) - 1(218.739)$$

$= -110.655$ kJ/K

$\Delta G^0_{700\ K} = \Delta H^0 - T\Delta S^0 = +38\ 803$ kJ

$$\ln K = \frac{-\Delta G^0}{\bar{R}T} = -6.667 \quad => \quad K = 0.001\ 272 = \frac{y_{C2H5OH}}{y_{C2H4}y_{H2O}}\left(\frac{P}{P^0}\right)^{-1}$$

$$\Rightarrow \left(\frac{x}{1\text{-}x}\right)\left(\frac{3\text{-}x}{2\text{-}x}\right) = 0.001272 \times \frac{5.0}{0.1} = 0.0636$$

By trial and error: x = 0.0404 => C_2H_5OH: n = 0.0404, y = 0.01371

C_2H_4: n = 0.9596, y = 0.3242, H_2O: n = 1.9596 , y = 0.6621

b) Reactants: C_2H_4: $T_r = 298.2/282.4 = 1.056$, $P_r = 5/5.04 = 0.992$

A.15: $(\bar{h}^*\text{-}\bar{h}) = 1.30 \times 8.3145 \times 282.4 = 3062$ kJ

$\Rightarrow H_{C2H4} = 1(+52\ 467 - 3062) = +49\ 405$ kJ

H_2O, LIQ Ref. + St. Table:

$H_{H2O} = 2(-285830 + 18.015(2924.5\text{-}104.9)) = -470\ 070$ kJ

$H_{PROD} = 0.0404(-235\ 000 + 115(700\text{-}298.2)) + 0.9596(+52\ 467$

$+ 62.3(700\text{-}298.2)) + 1.9596(-241\ 826 + 14\ 190) = -379\ 335$ kJ

$Q_{CV} = H_P - H_R =$ **+41 330 kJ**

15.61

Methane at 25°C, 100 kPa, is burned with 200% theoretical oxygen at 400 K, 100 kPa, in an adiabatic steady state process, and the products of combustion exit at 100 kPa. Assume that the only significant dissociation reaction in the products is that of carbon dioxide going to carbon monoxide and oxygen. Determine the equilibrium composition of the products and also their temperature at the combustor exit.

Combustion: $CH_4 + 4O_2 \rightarrow CO_2 + 2H_2O + 2O_2$

Dissociation:

	$2\,CO_2$	$\Leftrightarrow$	$2\,CO$	$+$	O_2	$,H_2O$	inert
initial	1		0		2	2	
change	-2x		+2x		+x	0	
equil.	1-2x		2x		2+x	2	$n_{TOT} = 5+x$

$$\text{Equil. Eq'n: } K = \frac{y_{CO}^2 y_{O2}}{y_{CO2}^2}\left(\frac{P}{P^0}\right) = \left(\frac{x}{0.5-x}\right)^2\left(\frac{2+x}{5+x}\right)\left(\frac{P}{P^0}\right)$$

$$\text{or} \quad \left(\frac{x}{0.5-x}\right)^2\left(\frac{2+x}{5+x}\right) = \frac{K}{(P/P^0)}$$

1st law: $H_P - H_R = 0$

$$(1-2x)(-393\,522 + \Delta\bar{h}_{CO2}) + 2x(-110\,527 + \Delta\bar{h}_{CO})$$
$$+ 2(-241\,826 + \Delta\bar{h}_{H2O}) + (2+x)\Delta\bar{h}_{O2} - 1(-74\,873) - 4(3027) = 0$$

$$\text{or} \quad (1-2x)\Delta\bar{h}_{CO2} + 2x\Delta\bar{h}_{CO} + 2\Delta\bar{h}_{H2O} + (2+x)\Delta\bar{h}_{O2} + 565\,990x - 814\,409 = 0$$

Assume $T_P = 3256$ K. From A.10: $K = 0.6053$

Solving (1) by trial & error, $x = 0.2712$

Substituting x and the $\Delta\bar{h}$ values from A.8 (at 3256 K) into (2)

$$0.4576\times168\,821 + 0.5424\times103\,054 + 2\times140\,914$$
$$+ 2.2712\times108\,278 + 565\,990\times0.2712 - 814\,409 \approx 0 \text{ OK}$$

$T_P = 3256$ K & $x = 0.2712$

$n_{CO2} = 0.4576$, $n_{CO} = 0.5424$, $n_{H2O} = 2.0$, $n_{O2} = 2.2712$

15.62

Calculate the irreversibility for the adiabatic combustion process described in the previous problem.

From solution of Prob. 15.61, it is found that the product mixture consists of 0.4576 CO_2, 0.5424 CO, 2.0 H_2O & 2.2712 O_2 at 3256 K, 100 kPa. The reactants include

1 CH_4 at 25 °C, 100 kPa and 4 O_2 at 400 K, 100 kPa.

Reactants:

$S_R = 1(186.251) + 4(213.873) = 1041.74$ kJ/K

Products:

	n_i	y_i	$\bar{s}_i^0$	$-\bar{R}\ln\frac{y_iP}{P_0}$	$\bar{S}_i^*$
CO_2	0.4576	0.0868	339.278	+20.322	359.600
CO	0.5424	0.1029	276.660	+18.907	295.567
H_2O	2.0	0.3794	291.099	+8.058	299.157
O_2	2.2712	0.4309	287.749	+7.000	294.749

$S_P = 0.4576(359.600) + 0.5424(295.567) + 2.0(299.157)$

$+ 2.2712(294.749) = 1592.62$ kJ/K

$I = T_0(S_P - S_R) - Q_{CV} = 298.15(1592.62 - 1041.74) - 0 =$ **164 245 kJ**

15.63

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 150°C.

b. For an initial composition of 25% nitrogen, 75% hydrogen, on a mole basis, calculate the equilibrium composition at 150°C, 5 MPa.

$$1N_2 + 3H_2 \Leftrightarrow 2NH_3 \quad \text{at } 150\ ^oC$$

$$\bar{h}^o_{NH3\ 150\ C} = -45\ 720 + 2.13\times17.031(150-25) = -41\ 186$$

$$\bar{s}^o_{NH3\ 150\ C} = 192.572 + 2.13\times17.031 \ln\frac{423.2}{298.2} = 205.272$$

$$\Delta H^o_{150\ C} = 2(-41\ 186) - 1(0+3649) - 3(0+3636) = -96\ 929 \text{ kJ}$$

$$\Delta S^0_{150\ C} = 2(205.272) - 1(201.829) - 3(140.860) = -213.865 \text{ kJ/K}$$

$$\Delta G^0_{150\ C} = -96\ 929 - 423.2(-213.865) = -6421 \text{ kJ/kmol}$$

$$\ln K = \frac{+6421}{8.3144\times423.2} = 1.8248, \quad \mathbf{K = 6.202}$$

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

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

$$\text{or} \quad \left(\frac{x}{1-x}\right)^2\left(\frac{2-x}{1-x}\right)^2 = \frac{27}{16}\times 6.202 \times \left(\frac{5}{0.1}\right)^2 = 26165$$

$$\text{or} \quad \left(\frac{x}{1-x}\right)\left(\frac{2-x}{1-x}\right) = 161.755$$

→ Trial & Error:

x = 0.9215

	n	y
NH_3	1.843	0.8544
N_2	0.0785	0.0364
H_2	0.2355	0.1092

15.64

One kilomole of carbon dioxide, CO_2, and 1 kmol of hydrogen, H_2 at room temperature, 200 kPa is heated to 1200 K at 200 kPa. Use the water gas reaction to determine the mole fraction of CO. Neglect dissociations of H_2 and O_2.

$$1\,CO_2 + 1\,H_2 \Leftrightarrow 1\,CO + 1\,H_2O$$

Initial	1	1	0	0	
Shift	-x	-x	+x	+x	
Total	1-x	1-x	x	x;	$n_{tot} = 2$

$y_{H2O} = y_{CO} = x/2, \quad y_{H2} = y_{CO2} = (1-x)/2$

From solution to problem 15.36, K = 1.3682

$$\frac{(x/2)(x/2)}{(\frac{1-x}{2})(\frac{1-x}{2})} = K = \frac{x^2}{(1-x)^2} \quad => \quad \frac{x}{1-x} = 1.1697$$

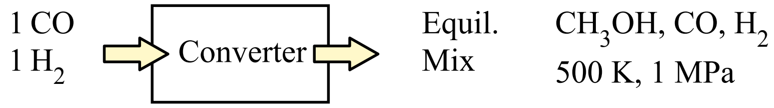
$x = 1.1697 / 2.1697 = 0.5391$

$y_{H2O} = y_{CO} = x/2 = \mathbf{0.27}, \quad y_{H2} = y_{CO2} = (1-x)/2 = \mathbf{0.23}$

15.65

Consider the production of a synthetic fuel (methanol) from coal. A gas mixture of 50% CO and 50% H_2 leaves a coal gasifier at 500 K, 1 MPa, and enters a catalytic converter. A gas mixture of methanol, CO and H_2 in chemical equilibrium with the reaction: $CO + 2H_2 \Leftrightarrow CH_3OH$ leaves the converter at the same temperature and pressure, where it is known that ln K = -5.119.

a. Calculate the equilibrium composition of the mixture leaving the converter.
b. Would it be more desirable to operate the converter at ambient pressure?



Reaction:	CO +	$2\,H_2$ $\Leftrightarrow$	CH_3OH
initial	1	1	0
change	-x	-2x	+x
equil.	(1-x)	(1-2x)	x

a) $$K = \frac{y_{CH3OH}}{y_{CO}y_{H2}^2}\left(\frac{P}{P^0}\right)^{-2} = \left(\frac{x}{1-x}\right)\left(\frac{2-2x}{1-2x}\right)^2\left(\frac{P}{P^0}\right)^{-2} \quad => \quad \frac{x(1-x)}{(1-2x)^2} = \frac{K}{4}\left(\frac{P}{P^0}\right)^2$$

$\ln K = -5.119, \qquad K = 0.005\,98$

$$\frac{x(1-x)}{(1-2x)^2} = \frac{0.005\,98}{4}\left(\frac{1}{0.1}\right)^2 = 0.1495 \quad => \quad x = 0.1045$$

$n_{CH3OH} = x = 0.1045, \quad n_{CO} = 1\text{-}x = 0.8955, \quad n_{H2} = 1 - 2x = 0.791$

$y_{CH3OH} = 0.0583, \quad y_{CO} = 0.5000, \quad y_{H2} = \mathbf{0.4417}$

b) For P = 0.1 MPa

$$\frac{x(1-x)}{(1-2x)^2} = \frac{0.005\,98}{4}\left(\frac{0.1}{0.1}\right)^2 = 0.001\,495$$

x is much smaller (~ 0.0015) **not good**

15.66

Hydrides are rare earth metals, M, that have the ability to react with hydrogen to form a different substance MH_x with a release of energy. The hydrogen can then be released, the reaction reversed, by heat addition to the MH_x. In this reaction only the hydrogen is a gas so the formula developed for the chemical equilibrium is inappropriate. Show that the proper expression to be used instead of Eq. 15.14 is

$$\ln (P_{H2}/P^o) = \Delta G^o/RT$$

when the reaction is scaled to 1 kmol of H_2.

$$M + \frac{1}{2} x\ H_2 \quad \Leftrightarrow \quad MH_x$$

At equilibrium $G_P = G_R$, assume g of the solid is a function of T only.

$$\bar{g}_{MHx} = \bar{h}^0_{MHx} - T\bar{s}^0_{MHx} = \bar{g}^0_{MHx} , \quad \bar{g}_M = \bar{h}^0_M - T\bar{s}^0_M = \bar{g}^0_M$$

$$\bar{g}_{H2} = \bar{h}^0_{H2} - T\bar{s}^0_{H2} + \bar{R}T \ln(P_{H2}/P_o) = \bar{g}^0_{H2} + \bar{R}T \ln(P_{H2}/P_o)$$

$$G_P = G_R: \quad \bar{g}_{MHx} = \bar{g}_M + \frac{1}{2} x\ \bar{g}_{H2} = \bar{g}^0_M + \frac{1}{2} x[\bar{g}^0_{H2} + \bar{R}T \ln(P_{H2}/P_o)]$$

$$\Delta\bar{G}^0 = \bar{g}^0_{MHx} - \bar{g}^0_M - x\ \bar{g}^0_{H2}/2 = \bar{g}^0_{MHx} - \bar{g}^0_M$$

Scale to 1 mole of hydrogen

$$\Delta\bar{G}^0 = (\bar{g}^0_{MHx} - \bar{g}^0_M)/(x/2) = \bar{R}T \ln(P_{H2}/P^o)$$

which is the desired result.

Simultaneous Reactions

15.67

Water from the combustion of hydrogen and pure oxygen is at 3800 K and 50 kPa. Assume we only have H_2O, O_2, OH and H_2 as gases with the two simple water dissociation reactions active find the equilibrium composition.

This problem is very similar to Example 15.7 in the text. The only difference is that we have T = 3800 K and P = 50 kPa. From table A.11 we have

$\ln K_1 = -1.906$; $K_1 = 0.14867$; $\ln K_2 = -0.984$; $K_2 = 0.3738$

$$K_1 = \left(\frac{2a + b}{1 - 2a - 2b}\right)^2 \frac{a}{1 + a + b}\left(\frac{P}{P^0}\right); \qquad K_2 = \frac{2a + b}{1 + a + b}\left(\frac{2b}{1 - 2a - 2b}\right)^2\left(\frac{P}{P^0}\right)$$

So we have two equations as

$$\left(\frac{2a + b}{1 - 2a - 2b}\right)^2 \frac{a}{1 + a + b} = K_1 / \left(\frac{P}{P^0}\right) = 0.29734 \qquad (1)$$

$$\frac{2a + b}{1 + a + b}\left(\frac{2b}{1 - 2a - 2b}\right)^2 = K_2 / \left(\frac{P}{P^0}\right) = 0.7476 \qquad (2)$$

Divide the second equation by the first to give

$$\frac{4b^2}{(2a + b)\, a} = \frac{0.7476}{0.29734} = 2.5143$$

or

$$2a^2 + ba - 1.5909\, b^2 = 0$$

$$a = -(b/4) \pm (1/4)\sqrt{b^2 - 4 \times 2 \times (-1.5909\, b^2)} = 0.676256\, b$$

Now we can do trial and error on equation 1 for only one variable, say b:

$a = 0.14228$, $b = 0.2104$

$n_{H2O} = 1 - 2a - 2b = 0.29464$, $n_{H2} = 2a + b = 0.49496$,

$n_{O2} = a = 0.14228$, $n_{OH} = 2b = 0.4208$

15.68

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 1800 K, 1 MPa. Determine the mole fraction of NO in the products. Is it reasonable to ignore CO in the products?

Combustion:

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

Products at 1800 K, 1 MPa

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

$$K = 1.192\times10^{-4} = \frac{y_{NO}^2}{y_{N2}y_{O2}}\left(\frac{P}{P^0}\right)^0 = \frac{4x^2}{(19.74-x)(1.75-x)}$$

Solving, x = 0.031 75

$$y_{NO} = \frac{2\times0.031\ 75}{26.49} = \mathbf{0.0024}$$

b)

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

$$K = 4.194\times10^{-8} = \frac{y_{CO}^2 y_{O2}}{y_{CO2}^2}\left(\frac{P}{P^0}\right)^1 = \left(\frac{2a}{2-2a}\right)^2\left(\frac{1.75-x+a}{26.49+a}\right)\times\frac{1}{0.1}$$

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 = 0.031 75 in the equation above, and solve for a.

$$\left(\frac{a}{1-a}\right)^2\left(\frac{1.75-0.031\ 75+a}{26.49+a}\right) = \left(\frac{0.1}{1.0}\right)\times4.194\times10^{-8}$$

Solving, a = 0.000 254 or $y_{CO} = 1.92\times10^{-5}$ negligible for most applications.

15.69

Butane is burned with 200% theoretical air, and the products of combustion, an equilibrium mixture containing only CO_2, H_2O, O_2, N_2, NO, and NO_2, exit from the combustion chamber at 1400 K, 2 MPa. Determine the equilibrium composition at this state.

Combustion:

$$C_4H_{10} + 13\, O_2 + 48.9\, N_2 \;\rightarrow\; 4\, CO_2 + 5\, H_2O + 6.5\, O_2 + 48.9\, N_2$$

Dissociation:

$$1)\quad N_2 + O_2 \Leftrightarrow 2\,NO \qquad\qquad 2)\quad N_2 + 2O_2 \Leftrightarrow 2\,NO_2$$

$$\text{change}\quad -a \quad -a \quad +2a \qquad\quad \text{change}\quad -b \quad -2b \quad +2b$$

At equilibrium:

$n_{H2O} = 5$ $\quad n_{N2} = 48.9\text{-a-b}$ $\quad n_{NO} = 2a$

$n_{CO2} = 4$ $\quad n_{O2} = 6.5\text{-a-2b}$ $\quad n_{NO2} = 2b$

$n_{TOT} = 64.4\text{-b}$

At 1400 K, from A.10: $\quad K_1 = 3.761\times10^{-6}$, $\; K_2 = 9.026\times10^{-10}$

$$K_1 = \frac{(2a)^2}{(48.9\text{-a-b})(6.5\text{-a-2b})}\;; \qquad\qquad K_2 = \frac{(2b)^2(64.4\text{-b})}{(6.5\text{-a-2b})^2(48.9\text{-a-b})}\left(\frac{P}{P^0}\right)^{-1}$$

As K_1 and K_2 are both very small, with $K_2 << K_1$, the unknowns a & b will both be very small, with b << a. From the equilibrium eq.s, for a first trial

$$a \sim \frac{1}{2}\sqrt{K_1\times48.9\times6.5} \sim 0.0173\;; \qquad b \sim \frac{1}{2}\times6.5\sqrt{K_2\times\frac{2}{0.1}\times\frac{48.9}{64.4}} \sim 0.000\,38$$

Then by trial & error,

$$\frac{a^2}{(48.9\text{-a-b})(6.5\text{-a-2b})} = \frac{3.761\times10^{-6}}{4} = 0.940\,25\times10^{-6}$$

$$\frac{b^2(64.4\text{-b})}{(6.5\text{-a-2b})^2(48.9\text{-a-b})} = \frac{9.026\times10^{-10}\times(\frac{2}{0.1})}{4} = 45.13\times10^{-10}$$

Solving, $\quad a = 0.017\,27$, $\quad b = 0.000\,379$

$n_{CO2} = 4$, $\quad n_{H2O} = 5$, $\quad n_{N2} = 48.882$, $\quad n_{O2} = 6.482$,

$y_{CO2} = 0.062\,11$, $\quad y_{H2O} = 0.077\,64$, $\quad y_{N2} = 0.759\,04$, $\quad y_{O2} = 0.100\,65$

$n_{NO} = 0.034\,54$, $\quad n_{NO2} = 0.000\,76$

$y_{NO} = 0.000\,55$, $\quad y_{NO2} = 0.000\,01$

15.70

A mixture of 1 kmol water and 1 kmol oxygen at 400 K is heated to 3000 K, 200 kPa, in a steady flow process. Determine the equilibrium composition at the outlet of the heat exchanger, assuming that the mixture consists of H_2O, H_2, O_2, and OH.

Reactions and equilibrium eq'ns the same as in example 15.7 (but different initial composition).

At equil.: $n_{H2O} = 1 - 2a - 2b$, $n_{H2} = 2a + b$, $n_{O2} = 1 + a$

$n_{OH} = 2b$, $n_{TOT} = 2 + a + b$

Since T = 3000 K is the same, the two equilibrium constants are the same:

From Table A.11: $K_1 = 0.002\,062$, $K_2 = 0.002\,893$

The two equilibrium equations are

$$K_1 = \left(\frac{2a + b}{1 - 2a - 2b}\right)^2 \frac{1 + a}{2 + a + b}\left(\frac{P}{P^0}\right); \quad K_2 = \frac{2a + b}{2 + a + b}\left(\frac{2b}{1 - 2a - 2b}\right)^2\left(\frac{P}{P^0}\right)$$

which must be solved simultaneously for a & b. If solving manually, it simplifies the solution to divide the first by the second, which leaves a quadratic equation in a & b - can solve for one in terms of the other using the quadratic formula (with the root that gives all positive moles). This reduces the problem to solving one equation in one unknown, by trial & error.

Solving => $b = 0.116$, $a = -0.038$ =>

$n_{H2O} = 0.844$, $n_{H2} = 0.0398$, $n_{O2} = 0.962$, $n_{OH} = 0.232$, $n_{TOT} = 2.0778$

$y_{H2O} = 0.4062$, $y_{H2} = 0.0191$, $y_{O2} = 0.4630$, $y_{OH} = 0.1117$

15.71

One kilomole of air (assumed to be 78% nitrogen, 21% oxygen, and 1% argon) at room temperature is heated to 4000 K, 200 kPa. Find the equilibrium composition at this state, assuming that only N_2, O_2, NO, O, and Ar are present.

1 kmol air (0.78 N_2, 0.21 O_2, 0.01 Ar) heated to

4000 K, 200 kPa.

Equil.:

1) $N_2 + O_2 \Leftrightarrow 2\,NO$ $\qquad n_{N2} = 0.78\text{-}a$

change -a -a +2a $\qquad n_{O2} = 0.21\text{-}a\text{-}b$

$n_{Ar} = 0.01$

2) $O_2 \Leftrightarrow 2\,O$ $\qquad n_O = 2b$

change -b +2b $\qquad n_{NO} = 2a$

$n_{tot} = 1\text{+}b$

$$K_1 = 0.0895 = \frac{4a^2}{(0.78\text{-}a)(0.21\text{-}a\text{-}b)}\left(\frac{200}{100}\right)^0$$

$$K_2 = 2.221 = \frac{4b^2}{(1\text{+}b)(0.21\text{-}a\text{-}b)}\left(\frac{200}{100}\right)$$

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

$$X = \frac{K_1}{K_2}\left(\frac{P}{P^0}\right) = 0.0806$$

Get

$$a = \frac{Xb^2}{2(1\text{+}b)}\left[-1+\sqrt{1+\frac{4\times 0.78(1\text{+}b)}{Xb^2}}\right] \qquad (1)$$

Also

$$\frac{b^2}{(1\text{+}b)(0.21\text{-}a\text{-}b)} = \frac{K_2}{4(P/P^0)} = 0.277\,63 \qquad (2)$$

Assume b = 0.1280 $\qquad$ From (1), get a = 0.0296

Then, check a & b in (2) ⇒ OK

Therefore,

$n_{N2} = 0.7504$ $\quad n_O = 0.2560$ $\quad y_{N2} = 0.6652$ $\quad y_O = 0.2269$

$n_{O2} = 0.0524$ $\quad n_{NO} = 0.0592$ $\quad y_{O2} = 0.0465$ $\quad y_{NO} = 0.0525$

$n_{Ar} = 0.01$ $\qquad y_{Ar} = 0.0089$

15.72

One kilomole of water vapor at 100 kPa, 400 K, is heated to 3000 K 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) $2\,H_2O \Leftrightarrow 2\,H_2 + O_2$ 2) $2\,H_2O \Leftrightarrow H_2 + 2\,OH$

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

3) $H_2 \Leftrightarrow 2\,H$

change -c +2c

At equilibrium (3000 K, 100 kPa)

n_{H2O} =	1-2a-2b	n_{O2} =	a	n_H =	2c
n_{H2} =	2a+b-c	n_{OH} =	2b	n_{TOT} =	1+a+b+c

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

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

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

These three equations must be solved simultaneously for a, b & c:

a = 0.0622, b = 0.0570, c = 0.0327

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

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

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

$n_{OH} = 0.1140$ $y_{OH} = 0.0990$

$n_H = 0.0654$ $y_H = 0.0568$

15.73

Acetylene gas and *x* times theoretical air (*x* > 1) at room temperature and 500 kPa are burned at constant pressure in an adiabatic steady flow process. The flame temperature is 2600 K, 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 2600 K, 500 kPa: N_2, O_2, CO_2, H_2O, CO & NO

2 Reactions:

$$1)\quad 2\,CO_2 \Leftrightarrow 2\,CO + O_2 \qquad\qquad 2)\quad N_2 + O_2 \Leftrightarrow 2\,NO$$

$$\text{change}\;\; -2a \quad +2a \quad +a \qquad\qquad \text{change}\;\; -b \quad -b \quad +2b$$

Equil. Comp.: $n_{N2} = 9.4x-b$, $n_{H2O} = 1$, $n_{CO} = 2a$, $n_{NO} = 2b$

$n_{O2} = 2.5x - 2.5 + a - b$, $n_{CO2} = 2 - 2a$, $n_{TOT} = 11.9x + 0.5 + a$

At 2600 K, from A.11: $K_1 = 3.721 \times 10^{-3}$, $K_2 = 4.913 \times 10^{-3}$

$$\text{EQ1:}\qquad \frac{K_1}{(P/P^o)} = \frac{3.721\times10^{-3}}{5} = \left(\frac{a}{1-a}\right)^2 \left(\frac{2.5x - 2.5 + a - b}{11.9x + 0.5 + a}\right)$$

$$\text{EQ2:}\qquad K_2 = 4.913\times10^{-3} = \frac{(2b)^2}{(9.4 - b)(2.5x - 2.5 + a - b)}$$

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

$H_R = 1(+226\,731) + 0 + 0 = +226\,731$ kJ

$H_P = (9.4x - b)(0 + 77\,963) + (2.5x - 2.5 + a - b)(0 + 82\,225)$

$+ (2 - 2a)(-393\,522 + 128\,074) + 1(-241\,826 + 104\,520)$

$+ 2a(-110\,527 + 78\,679) + 2b(90\,291 + 80\,034)$

Substituting,

EQ3: $988\,415x + 549\,425a + 180\,462b - 1\,100\,496 = 0$

which results in a set of 3 equations in the 3 unknowns x, a, b. Assume x = 1.07 Then

$$\text{EQ1:}\quad 7.442 \times 10^{-2} = \left(\frac{a}{1-a}\right)^2\left(\frac{0.175 + a - b}{13.233 + a}\right)$$

$$\text{EQ2:}\quad 1.2283 \times 10^{-3} = \frac{b^2}{(10.058 - b)(0.175 + a + b)}$$

Solving, $a = 0.1595$, $b = 0.0585$ Then checking in EQ3,

$$988\,415\times1.07 + 549\,425\times0.1595 + 180\,462\times0.0585 - 1\,100\,496 \approx 0$$

Therefore, x = **1.07**

Ionization

15.74

At 10 000 K the ionization reaction for Ar is: $\mathrm{Ar} \Leftrightarrow \mathrm{Ar}^+ + e^-$ with equilibrium constant of $K = 4.2 \times 10^{-4}$. What should the pressure be for a mole concentration of argon ions (Ar^+) of 10%?

From the reaction (ionization) we recognize that the concentration of electrons must equal that of argon ions so

$$y_{Ar^+} = y_{e^-} = 0.1 \qquad \text{and} \qquad y_{Ar} = 1 - y_{Ar^+} - y_{e^-} = 0.8$$

Now

$$K = 4.2 \times 10^{-4} = \frac{y_{Ar^+}\, y_{e^-}}{y_{Ar}} \left(\frac{P}{P^o}\right)^{1+1-1} = \frac{0.1 \times 0.1}{0.8} \frac{P}{100}$$

$$P = 0.00042 \times \frac{0.8}{0.1 \times 0.1} \times 100 = \mathbf{3.36\ kPa}$$

15.75

Operation of an MHD converter requires an electrically conducting gas. It is proposed to use helium gas “seeded” with 1.0 mole percent cesium, as shown in Fig. P15.75. The cesium is partly ionized ($Cs \Leftrightarrow Cs^+ + e^-$) by heating the mixture to 1800 K, 1 MPa, in a nuclear reactor to provide free electrons. No helium is ionized in this process, so that the mixture entering the converter consists of He, Cs, Cs^+, and e^-. Determine the mole fraction of electrons in the mixture at 1800 K, where ln K = 1.402 for the cesium ionization reaction described.

Reaction:	Cs ⇔	Cs^+ +	e^-,	Also He	ln K = 1.402
initial	0.01	0	0	0.99	=> K = 4.0633
change	-x	+x	+x	0	
Equil	(0.01-x)	x	x	0.99 ;	total: 1 + x

$$K = \frac{y_{e-}\, y_{Cs+}}{y_{Cs}} \left(\frac{P}{P^0}\right) = \left(\frac{x}{0.01 - x}\right) \left(\frac{x}{1 + x}\right) \left(\frac{P}{P^0}\right)$$

$$\text{or} \quad \left(\frac{x}{0.01 - x}\right) \left(\frac{x}{1 + x}\right) = 4.0633 / (1/0.1) = 0.40633$$

Quadratic equation: $x = 0.009767$

$$\Rightarrow \quad y_{e-} = \frac{x}{1 + x} = \mathbf{0.00967}$$

15.76

One kilomole of argon gas at room temperature is heated to 20000 K, 100 kPa. Assume that the plasma in this condition consists of an equilibrium mixture of Ar, $\mathrm{Ar}^{`}$, $\mathrm{Ar}^{``}$, and e^{-} according to the simultaneous reactions

(1) $\mathrm{Ar} \Leftrightarrow \mathrm{Ar}^{+} + \mathrm{e}^{-}$ (2) $\mathrm{Ar}^{+} \Leftrightarrow \mathrm{Ar}^{++} + \mathrm{e}^{-}$

The ionization equilibrium constants for these reactions at 20000 K have been calculated from spectroscopic data as $\ln K_1 = 3.11$ and $\ln K_2 = -4.92$. Determine the equilibrium composition of the plasma.

1) $\mathrm{Ar} \Leftrightarrow \mathrm{Ar}^{+} + \mathrm{e}^{-}$ 2) $\mathrm{Ar}^{+} \Leftrightarrow \mathrm{Ar}^{++} + \mathrm{e}^{-}$

ch. -a +a +a ch. -b +b +b

Equil. Comp.: $n_{Ar} = 1\text{-}a$, $n_{Ar+} = a\text{-}b$, $n_{Ar++} = b$, $n_{e-} = a+b$, $n_{TOT} = 1+a+b$

$$K_1 = \frac{y_{Ar+}y_{e-}}{y_{Ar}}\left(\frac{P}{P^0}\right) = \frac{(a - b)(a + b)}{(1 - a)(1 + a + b)}(1) = 22.421$$

$$K_2 = \frac{y_{Ar++}y_{e-}}{y_{Ar+}}\left(\frac{P}{P^0}\right) = \frac{b(a + b)}{(a - b)(1 + a + b)}(1) = 0.0073$$

By trial & error: $a = 0.978\,57$, $b = 0.014\,13$

$n_{Ar} = 0.02143$, $n_{Ar+} = 0.96444$, $n_{Ar++} = 0.01413$, $n_{e-} = 0.9927$

$y_{Ar} = 0.0107$, $y_{Ar+} = 0.484$, $y_{Ar++} = 0.0071$, $y_{e-} = 0.4982$

15.77

At 10 000 K the two ionization reactions for N and Ar as

1: $\quad Ar \Leftrightarrow Ar^+ + e^-$ $\qquad$ 2: $\quad N \Leftrightarrow N^+ + e^-$

have equilibrium constants of $K_1 = 4.2 \times 10^{-4}$ and $K_2 = 6.3 \times 10^{-4}$, respectively. If we start out with 1 kmol Ar and 0.5 kmol N_2, what is the equilibrium composition at a pressure of 10 kPa?

At 10 000 K we assume all the nitrogen is dissociated to N.

Assume we shift the argon ionization with a and the nitrogen ionization with b we get

	Ar	Ar^+	e^-	N	N^+	
Initial	1	0	0	1	0	
Change	-a	a	a + b	-b	b	
Final	1-a	a	a + b	1-b	b	Tot: 2 + a + b

$$K_1 = 4.2 \times 10^{-4} = \frac{y_{Ar+}y_{e-}}{y_{Ar}}\left(\frac{P}{P^0}\right) = \frac{a\,(a + b)}{(1 - a)(2 + a + b)}\left(\frac{10}{100}\right) \qquad (1)$$

$$K_2 = 6.3 \times 10^{-4} = \frac{y_{N+}y_{e-}}{y_{N}}\left(\frac{P}{P^0}\right) = \frac{b\,(a + b)}{(1 - b)(2 + a + b)}\left(\frac{10}{100}\right) \qquad (2)$$

Divide the second equation with the first to get

$$\frac{b}{(1 - b)}\frac{(1 - a)}{a} = \frac{K_2}{K_1} = 1.5 \quad \Rightarrow \quad \frac{b - ab}{a - ab} = 1.5$$

$$b - ab = 1.5\ a - 1.5\ ab \quad \Rightarrow \quad b = 1.5\ a - 0.5\ ab = a(1.5 - 0.5\ b)$$

$a = \dfrac{b}{1.5 - 0.5\ b}$ trial and error on equation (1)

$a = 0.059$ and $b = 0.086$

$n_{Ar} = 0.941$, $n_{Ar+} = 0.059$, $n_N = 0.914$, $n_{N+} = 0.086$, $n_{e-} = 0.145$

$y_{Ar} = 0.439$, $y_{Ar+} = 0.027$, $y_N = 0.426$, $y_{N+} = 0.04$, $y_{e-} = 0.068$

15.78

Plot to scale the equilibrium composition of nitrogen at 10 kPa over the temperature range 5000 K to 15000 K, assuming that N_2, N, N^+, and e^- are present. For the ionization reaction N ⇔ $N^+ + e^-$, the ionization equilibrium constant *K* has been calculated from spectroscopic data as

T [K]	10000	12 000	14 000	16 000
100*K*	0.0626	1.51	15.1	92

$$1)\ N_2 \Leftrightarrow 2N \qquad 2)\ N \Leftrightarrow N^+ + e^-$$

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

Equil. Comp.: $n_{N2} = 1\text{-}a$, $n_N = 2a\text{-}b$, $n_{N+} = b$, $n_{e-} = b$

EQ1: $$K_1 = \frac{y_N^2}{y_{N2}}\left(\frac{P}{P^0}\right) = \frac{(2a - b)^2}{(1 - a)(1 + a + b)}\left(\frac{P}{P^0}\right)$$

EQ2: $$K_2 = \frac{y_{N+}y_{e-}}{y_N}\left(\frac{P}{P^0}\right) = \frac{b^2}{(2a - b)(1 + a + b)}\left(\frac{P}{P^0}\right)$$

For T < 10 000 K: b ~ 0 so neglect EQ2: $\Rightarrow\ K_1 = \frac{4a^2}{(1\text{-}a^2)}\left(\frac{10}{100}\right)$

To extrapolate K_1 above 6000 K: $\ln K_1 \approx 16.845 - \frac{118\ 260}{T}$

(from values at 5000 K & 6000 K)

T(K)	K_1	a	y_N	y_{N2}
5000	0.0011	0.0524	0.0996	0.9004
6000	0.0570	0.3532	0.5220	0.4780
7000	0.9519	0.8391	0.9125	0.0875
8000	7.866	0.9755	0.9876	0.0124
10000	151.26	0.9987	0.9993	0.0007

For T > 10 000 K: a ≈ 1.0 => $K_2 = \frac{b^2}{(2\text{-}b)(2\text{+}b)}\left(\frac{10}{100}\right) = \frac{b^2}{(4\text{-}b^2)}\ 0.1$

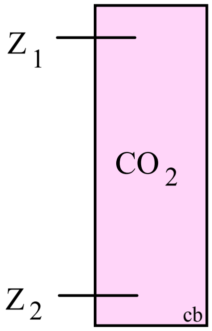
T(K)	K_2	b	y_N	y_{N+}
10 000	6.26×10^{-4}	0.1577	0.8538	0.0731
12 000	1.51×10^{-2}	0.7244	0.4862	0.2659
14 000	0.151	1.5512	0.1264	0.4368
16 000	0.92	1.8994	0.0258	0.4871

Note that b ≈ 0 is not a very good approximation in the vicinity of 10 000 K. In this region, it would be better to solve the original set simultaneously for a & b. The answer would be approximately the same.

Review Problems

15.79

Repeat Problem 15.21 using the generalized charts, instead of ideal gas behavior.



$(Z_1\text{-}Z_2) = 5000$ m, $P_1 = 15$ MPa

$T = 40\ ^oC = \text{const}$

$$T_r = \frac{313.2}{304.1} = 1.03, \quad P_{r1} = \frac{15}{7.38} = 2.033$$

Equilibrium: $-w_{REV} = 0 = \Delta g + \Delta PE$

$$g_2 - g_1 = h_2 - h_1 - T(s_2 - s_1) = g(Z_1 - Z_2) = \frac{9.807 \times 5000}{1000} = 49.04 \text{ kJ/kg}$$

From Figures D.2 and D.3,

$h^*_1 - h_1 = RT_c \times 3.54 = 203.4$ kJ/kg ; $s^*_1 - s_1 = R \times 2.61 = 0.4931$ kJ/kg K

$h^*_2 - h^*_1 = 0$; $s^*_2 - s^*_1 = 0 - R \ln(P_2 /P_1) = 0.18892 \ln(P_2 /15)$

Trial and error. Assume $P_2 = 55$ MPa ($P_{r2} = 55/7.38 = 7.45$)

$h^*_2 - h_2 = RT_c \times 3.60 = 206.8$ kJ/kg ; $s^*_2 - s_2 = R \times 2.14 = 0.4043$ kJ/kg K

$\Delta g = -206.8 + 0 + 203.4 - 313.2[-0.4043 - 0.18892 \ln(55/15) + 0.4931] = 45.7$

Too low so assume $P_2 = 60$ MPa ($P_{r2} = 60/7.38 = 8.13$)

$h^*_2 - h_2 = RT_c \times 3.57 = 205.1$ kJ/kg ; $s^*_2 - s_2 = R \times 2.11 = 0.3986$ kJ/kg K

$\Delta g = -205.1 + 0 + 203.4 - 313.2[-0.3986 - 0.18892 \ln(60/15) + 0.4931] = 50.7$

Make linear interpolation $\Rightarrow$ $P_2 =$ **58 MPa**

15.80

In a test of a gas-turbine combustor, saturated-liquid methane at 115 K is to be burned with excess air to hold the adiabatic flame temperature to 1600 K. 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.

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

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

Then	N_2 +	O_2 ⇔	2 NO	Also	CO_2	H_2O
initial	7.52x	2x-2	0		1	2
change	-a	-a	+2a		0	0
final	(7.52x-a)	(2x-2-a)	2a		1	2

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

1600 K: $\ln K = -10.55$, $K = 2.628\times10^{-5}$

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

From A.9 and B.7,

$$H_R = 1\big[-74\,873 + 16.043(-274.7-624.1)\big] + 0 + 0 = -89\,292\text{ kJ}$$

(Air assumed 25 °C)

$$H_P = 1(-393\,522 + 67\,569) + 2(-241\,826 + 52\,907)$$

$$+ (7.52x-a)(41\,904) + (2x-2-a)(44\,267) + 2a(90\,291 + 43\,319)$$

$$= -792\,325 + 403\,652\,x + 181\,049\,a$$

Assume a ~ 0, then from $H_P - H_R = 0 \rightarrow x = 1.7417$ and substitute

$$\frac{a^2}{(13.098-a)(1.483-a)} = \frac{2.628\times10^{-5}}{4}, \qquad \text{get} \quad a \approx 0.0113$$

Use this a in the energy equation

$$x = \frac{703\,042 - 181\,049\times0.0113}{403\,652} = 1.7366$$

$$\Rightarrow \frac{a^2}{(13.059-a)(1.4732-a)} = \frac{2.628\times10^{-5}}{4},\ a = 0.0112 \qquad \Rightarrow \qquad x = 1.7366$$

% excess air = **73.7 %**

$$\%\ NO = \frac{2\times0.0112\times100}{1+9.52\times1.7366} = \mathbf{0.128\ \%}$$

15.81

A space heating unit in Alaska uses propane combustion is the heat supply. Liquid propane comes from an outside tank at -44°C and the air supply is also taken in from the outside at -44°C. The airflow regulator is misadjusted, such that only 90% of the theoretical air enters the combustion chamber resulting in incomplete combustion. The products exit at 1000 K as a chemical equilibrium gas mixture including only CO_2, CO, H_2O, H_2, and N_2. Find the composition of the products. Hint: use the water gas reaction in Example 15.4.

Propane: Liquid, $T_1 = -44^oC = 229.2$ K

Air: $T_2 = -44^oC = 229.2$ K, 90% Theoretical Air

Products: $T_3 = 1000$ K, CO_2, CO, H_2O, H_2, N_2

Theoretical Air:

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

90% Theoretical Air:

$$C_3H_8 + 4.5O_2 + 16.92N_2 \;\Rightarrow\; aCO_2 + bCO + cH_2O + dH_2 + 16.92N_2$$

Carbon: $a + b = 3$

Oxygen: $2a + b + c = 9$ Where: $2 \le a \le 3$

Hydrogen: $c + d = 4$

Reaction:	CO	$+ \; H_2O$	$\leftrightarrow CO_2$	$+ \; H_2$
Initial:	b	c	a	d
Change:	-x	-x	x	x
Equil:	b - x	c - x	a + x	d + x

Chose an Initial guess such as: a = 2, b = 1, c = 4, d = 0

Note: A different initial choice of constants will produce a different value for x, but will result in the same number of moles for each product.

$n_{CO2} = 2 + x$, $n_{CO} = 1 - x$, $n_{H2O} = 4 - x$, $n_{H2} = x$, $n_{N2} = 16.92$

The reaction can be broken down into two known reactions to find K

(1) $2CO_2 \leftrightarrow 2CO + O_2$ @ 1000 K $\ln(K_1) = -47.052$

(2) $2H_2O \leftrightarrow 2H_2 + O_2$ @ 1000 K $\ln(K_2) = -46.321$

For the overall reaction: $\ln K = (\ln(K_2) - \ln(K_1))/2 = 0.3655$; $K = 1.4412$

$$K = \frac{y_{CO2}y_{H2}}{y_{CO}y_{H2O}}\left(\frac{P}{P_o}\right)^{1+1-1-1} = \frac{y_{CO2}y_{H2}}{y_{CO}y_{H2O}} = 1.4412 = \frac{(2+x)x}{(1-4)(4-x)}$$

$\Rightarrow \quad x = 0.6462$

$\mathbf{n_{CO2} = 2.6462}$ $\mathbf{n_{CO} = 0.3538}$ $\mathbf{n_{N2} = 16.92}$

$\mathbf{n_{H2O} = 3.3538}$ $\mathbf{n_{H2} = 0.6462}$

15.82

Consider the following coal gasifier proposed for supplying a syngas fuel to a gas turbine power plant. Fifty kilograms per second of dry coal (represented as 48 kg C plus 2 kg H) enter the gasifier, along with 4.76 kmol/s of air and 2 kmol/s of steam. The output stream from this unit is a gas mixture containing H_2, CO, N_2, CH_4, and CO_2 in chemical equilibrium at 900 K, 1 MPa.

a. Set up the reaction and equilibrium equation(s) for this system, and calculate the appropriate equilibrium constant(s).

b. Determine the composition of the gas mixture leaving the gasifier.

a) Entering the gasifier: $4\,C + 1\,H_2 + 1\,O_2 + 3.76\,N_2 + 2\,H_2O$

Since the chem. equil. outlet mixture contains no C, O_2 or H_2O, we must first consider “preliminary” reaction (or reactions) to eliminate those substances in terms of substances that are assumed to be present at equilibrium. One possibility is

$$4\,C + 1\,O_2 + 2\,H_2O \rightarrow 4\,CO + 2\,H_2$$

such that the "initial" composition for the equilibrium reaction is

$$4\,CO + 3\,H_2 + 3.76\,N_2$$

(or convert equal amounts of CO and H_2 to half of CH_4 and CO_2 - also present at equilibrium. The final answer will be the same.)

reaction	2 CO	+	$2\,H_2$	⇔	CH_4	+	CO_2	also N_2
initial	4		3		0		0	3.76
change	-2x		-2x		+x		+x	0
equil.	(4-2x)		(3-2x)		x		x	3.76

$$n_{TOT} = 10.76 - 2x$$

For CH_4 at 600 K (formula in Table A.6), $\bar{C}_{P0} = 52.22$

At 900 K

$$\bar{h}^0_{CH4} = -74\,873 + 52.22(900 - 298.2) = -43\,446 \text{ kJ/kmol}$$

$$\bar{s}^0_{CH4} = 186.251 + 52.22 \ln (900 / 298.2) = 243.936 \text{ kJ/kmol K}$$

(The integrated-equation values are -43 656 and 240.259)

$$\Delta H^0_{900\text{ K}} = 1(-43\,447) + 1(-393\,522 + 28\,030)$$
$$- 2(-110\,527 + 18\,397) - 2(0 + 17\,657) = -259\,993 \text{ kJ}$$

$$\Delta S^0_{900\text{ K}} = 1(243.935) + 1(263.646)$$
$$- 2(231.074) - 2(163.060) = -280.687 \text{ kJ/K}$$

$$\Delta G^0_{900\ K} = -259\ 993 - 900(-280.687) = -7375\ \text{kJ}$$

$$\ln K = \frac{+7375}{8.3145\times 900} = 0.9856, \qquad K = \mathbf{2.679}$$

b) $$K = \frac{y_{CH4}y_{CO2}}{y^2_{CO}y^2_{H2}}\left(\frac{P}{P^0}\right)^{-2} = \frac{x\times x\times(10.76\text{-}2x)^2}{(4\text{-}2x)^2(3\text{-}2x)^2}\left(\frac{P}{P^0}\right)^{-2}$$

or $$\frac{x(10.76\text{-}2x)}{(4\text{-}2x)(3\text{-}2x)} = \frac{P}{P^0}\sqrt{K} = \frac{1}{0.1}\sqrt{2.679} = 16.368$$

By trial & error, $x = 1.2781$

$n_{CO} = 1.444$, $n_{H2} = 0.444$, $n_{CH4} = n_{CO2} = 1.278$, $n_{N2} = 3.76$

$y_{CO} = 0.176$, $y_{H2} = 0.054$, $y_{CH4} = y_{CO2} = 0.156$, $y_{N2} = 0.458$

15.83

One kilomole of liquid oxygen, O_2, at 93 K, and *x* kmol of gaseous hydrogen, H_2, at 25°C, are fed to a combustion chamber. *x* is greater than 2, such that there is excess hydrogen for the combustion process. There is a heat loss from the chamber of 1000 kJ per kmol of reactants. Products exit the chamber at chemical equilibrium at 3800 K, 400 kPa, and are assumed to include only H_2O, H_2, and O.

a. Determine the equilibrium composition of the products and also *x*, the amount of H_2 entering the combustion chamber.

b. Should another substance(s) have been included in part (a) as being present in the products? Justify your answer.

$$x\,H_2 + 1\,O_2 \rightarrow 2\,H_2O + (x-2)\,H_2$$

$$(1)\quad 1\,H_2O \Leftrightarrow 1\,H_2 + 1\,O$$

shift	-a	+a	+a	and a > 0
Equil	2-a	x-2+a	a	a < 2 and $n_{tot} = x + a$

$$(2)\ 2\,H_2O \Leftrightarrow 2\,H_2 + 1\,O_2 \qquad \ln K_2 = -1.906$$

$$(3)\quad 1\,O_2 \Leftrightarrow 2\,O \qquad \ln K_3 = -0.017$$

$$\ln K_1 = 0.5(\ \ln K_2 + \ln K_3\ ) = -0.9615 \quad => \quad K_1 = 0.3823$$

$$\text{Equil.:}\quad \frac{K_1}{(P/P_o)^1} = \frac{(x-2+a)a}{(2-a)(x+a)} = \frac{0.3823}{4} = 0.95575$$

1st law: $Q + H_R = H_P$, $Q = (1+x)(-1000)$ kJ

Table A.8: $\Delta\bar{h}^*_{IG} = -5980$ kJ/kmol

$[\text{or} = 0.922 \times 32(93 - 298.2) = -\ 6054 \text{ kJ/kmol}\ ]$

Fig. D.2: $T_r = 93/154.6 = 0.601$, $\Delta\bar{h}_f = -5.16\times\bar{R}\times154.6 = -6633$

$$H_R = x(0 + 0) + 1(0 + \Delta\bar{h}^*_{IG} + \Delta\bar{h}_f) = 1(-5980 - 6633) = -\ 12613 \text{ kJ}$$

$$H_P = (2-a)(-241\,826 + 171\,981) + (x-2+a)(0 + 119077)$$
$$+\ a(249170 + 73424) \ = 119077\,x + 511516\,a - 377844$$
$$= Q + H_R = -1000 - 1000\,x - 12613$$

Rearrange eq. to: $x + 4.2599\,a = 3.03331$

Substitute it into the equilibrium eq.: $\dfrac{(1.03331 + 5.2599\,a)\,a}{(2-a)(3.03331-3.2599\,a)} = 0.095575$

Solve $a = 0.198$, LHS = 0.09547, $\mathbf{x = 2.1898}$

$$y_{H2O} = \frac{2-a}{x+a} = 0.755, \quad y_{H2} = \frac{x-2+a}{x+a} = 0.162, \quad y_O = \frac{a}{x+a} = 0.083$$

Other substances and reactions: $2\,H_2O <=> H_2 + 2\,OH$, $\ln K = -0.984$,

$H_2 <=> 2\,H$, : $\ln K = 0.201$, $O_2 <=> 2\,O$, : $\ln K = -0.017$

All are significant as K's are of order 1.

15.84

Saturated liquid butane (note: use generalized charts) enters an insulated constant pressure combustion chamber at 25°C, and *x* times theoretical oxygen gas enters at the same pressure and temperature. The combustion products exit at 3400 K. Assuming that the products are a chemical equilibrium gas mixture that includes CO, what is *x*?

Butane: $T_1 = 25^oC$, sat. liq., $x_1 = 0$, $T_c = 425.2$ K, $P_c = 3.8$ MPa

$T_{r1} = 0.7$, Figs. D.1and D.2, $P_{r1} = 0.10$, $P_1 = P_{r1}P_c = 380$ kPa

Fig D.2: $\left(\bar{h}^*_1 - \bar{h}_1\right)_f = 4.85\ RT_c$

Oxygen: $T_2 = 25^oC$, X * theoretical air Products: $T_3 = 3400$ K

$$C_4H_{10} + 6.5X\ O_2 \;\Rightarrow\; 4\ CO_2 + 5\ H_2O + 6.5(X-1)\ O_2$$

	$2CO_2$ <=>	$2CO$ +	O_2	
Initial	4	0	6.5(X-1)	
Change	-2a	2a	a	
Equil.	4-2a	2a	6.5(X-1) + a	$n_{tot} = 2.5 + a + 6.5X$

$n_{CO_2} = 4 - 2a$, $n_{CO} = 2a$, $n_{O_2} = 6.5(X-1) + a$, $n_{H2O} = 5$,

$$y_{CO} = \frac{2a}{2.5 + a + 6.5X},\quad y_{CO2} = \frac{4 - 2a}{2.5 + a + 6.5X},\quad y_{O2} = \frac{6.5(x - 1) + a}{2.5 + a + 6.5X}$$

The equilibrium constant is

$$K = \frac{y^2_{CO}y_{O_2}}{y^2_{CO_2}}\left(\frac{P_1}{P_o}\right)^{2+1-2} = \left(\frac{a}{2-a}\right)^2\left(\frac{6.5X - 6.5 + a}{6.5X - 2.5 + a}\right)\left(\frac{P_1}{P_o}\right)$$

@ $T_3 = 3400$ K Table A.11, $\ln(K) = 0.346$, $K = 1.4134$

$$1.4134 = \left(\frac{a}{2-a}\right)^2\left(\frac{6.5X - 6.5 + a}{6.5X - 2.5 + a}\right)(3.76) \qquad \text{Equation 1.}$$

Need a second equation:

Energy eq.: $Q_{CV} + H_R = H_P + W_{CV}$; $Q_{CV} = 0$, $W_{CV} = 0$

$$H_R = \left(\bar{h}^o_f + \Delta\bar{h}\right)_{C_4H_{10}} = (-126\ 200 - 17\ 146) = -143\ 346 \text{ kJ}$$

Products @ 3400 K:

$$H_P = n\left(\bar{h}_f^o + \Delta\bar{h}\right)_{CO2} + n\left(\bar{h}_f^o + \Delta\bar{h}\right)_{CO} + n\left(\bar{h}_f^o + \Delta\bar{h}\right)_{O2} + n\left(\bar{h}_f^o + \Delta\bar{h}\right)_{H2O}$$

$= (4 - 2a)(-393\ 522 + 177\ 836) + 2a(-110\ 527 + 108\ 440)$

$+ [6.5(X - 1) + a](0 + 114101) + 5(-241\ 826 + 149\ 073)$

$= -463\ 765$ kJ/kmol

$H_P = H_R$ => $1924820 = 541299a + 741656.5\ X$ Equation 2.

Two equations and two unknowns, solve for X and a.

$a \cong \mathbf{0.87}, \quad X \cong \mathbf{1.96}$

15.85

Derive the van't Hoff equation given in problem 15.48, using Eqs.15.12 and 15.15. Note: the d($\bar{g}$/T) at constant P for each component can be expressed using the relations in Eqs. 13.18 and 13.19.

Eq. 15.12: $\Delta G^0 = v_C\, \bar{g}_C^0 + v_D\, \bar{g}_D^0 - v_A\, \bar{g}_A^0 - v_B\, \bar{g}_B^0$

Eq. 15.15: $\ln K = \Delta G^0/RT$ Eq. 13.19: $\Delta G^0 = \Delta H^\circ - T\, \Delta S^0$

$$\frac{d\ln K}{dT} = - \frac{d}{dT}\left(\frac{\Delta G^0}{RT}\right) = -\frac{1}{RT}\frac{dG^0}{dT} + \frac{\Delta G^0}{RT^2} = \frac{1}{RT^2}\left[\Delta G^0 - T\frac{dG^0}{dT}\right]$$

$$= \frac{1}{RT^2}\left[\Delta G^0 + T\, \Delta S^0\right] \qquad \text{used Eq.13.19} \qquad \frac{d\bar{g}}{dT} = - \bar{s}$$

$$= \frac{1}{RT^2}\, \Delta H^0$$

15.86

A coal gasifier produces a mixture of 1 CO and $2H_2$ that is then fed to a catalytic converter to produce methane. A chemical-equilibrium gas mixture containing CH_4, CO, H_2, and H_2O exits the reactor at 600 K, 600 kPa. Determine the mole fraction of methane in the mixture.

$$CO \; + 3H_2 \leftrightarrow CH_4 \; + H_2O$$

Initial	1	2	0	0
Change	-x	-3x	x	x
Equil.	1-x	2-3x	x	x

$n = (1 - x) + (2 - 3x) + x + x = 3 - 2x$

$$K = \frac{y_{CH4}y_{H2O}}{y_{CO}y_{H2}^{3}}\left(\frac{P}{P_o}\right)^{(1+1-1-3) = -2} = \frac{x^2}{(1-x)(2-3x)^3}\left(\frac{P}{P_o}\right)^{-2}$$

$\ln K = - \Delta G^o/\bar{R}; \quad \Delta G^o = \Delta H^o - T\Delta S^o$

$$H_P = n_{CH4}\,[\bar{h}_f^o + \bar{C}_P(T - T_o)] + n_{H2O}\left(\bar{h}_f^o + \Delta\bar{h}\right)$$

$$= [-74873 + 2.254\times16.04(600 - 298.15)] + (-241826 + 10499) = -295290$$

$$H_R = n_{CO}\left(\bar{h}_f^o + \Delta\bar{h}\right) + n_{H2}\left(\bar{h}_f^o + \Delta\bar{h}\right) = 1(-110527 + 8942) + 3(0 + 8799)$$

$$= -75188 \text{ kJ}$$

$$\Delta H_{600}^o = H_P - H_R = -295290 - (-75188) = -220102 \text{ kJ}$$

$$(\bar{s}_T^o)_{CH4} = \bar{s}_{To}^o + \bar{C}_P\ln(T/T_o) = 186.251 + 2.254\times16.04 \ln(600/298.2) = 211.549$$

$(\bar{s}_T^o)_{H2O} = 213.051$ kJ/kmol-K; $\quad S_P = 424.6$ kJ/K

$(\bar{s}_T^o)_{CO} = 218.321$ kJ/kmol-K, $\quad (\bar{s}_T^o)_{H2} = 151.078$ kJ/kmol-K

$$\Delta S_{600}^o = S_P - S_R = (n\bar{s}_T^o)_{CH4} + (n\bar{s}_T^o)_{H2O} - (n\bar{s}_T^o)_{CO} - (n\bar{s}_T^o)_{H2}$$

$$= (211.549 + 213.051) - (218.321 + 3 \times 151.078) = -246.955 \text{ kJ/K}$$

$\Delta G^o = \Delta H^o - T\Delta S^o = -220\,102 - 600(-246.955) = -71929$ kJ,

$\ln K = -(-71915)/(8.31451\times600) = 14.418 \quad => \quad K = 1.827\times10^6$

Solve for x, $\quad x = 0.6667$, $\quad n_{tot} = 1.6667$, $\quad \mathbf{y_{CH4} = 0.4}$

15.87

Dry air is heated from 25°C to 4000 K in a 100-kPa 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 we have at 4000 K (A.10)

(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

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

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

From which the molefractions are formed and substituted into the three equilibrium equations. The result is

$$K_1 = 2.221 = y_O^2/y_{O2} = 4a^2/[(1+a+b)(0.21\text{-}a\text{-}c)]$$

$$K_2 = 3.141 \times 10^{-6} = y_N^2/y_{N2} = 4b^2/[(1+a+b)(0.79\text{-}b\text{-}c)]$$

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

which gives 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 $K_1>K_3>K_2$

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

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

$$Q = H_{ex} - H_{in} = n_{O2}\Delta\bar{h}_{O2} + n_{N2}\Delta\bar{h}_{N2} + n_O(\bar{h}_{fO} + \Delta\bar{h}_O) + n_N(\bar{h}_{fN} + \Delta\bar{h}_N) + n_{NO}(\bar{h}_{fNO} + \Delta\bar{h}_{NO}) - 0$$

$$= 0.0356 \times 138705 + 0.765 \times 130027 + 0.3(249170 + 77675) + 0.00167(472680 + 77532) + 0.049(90291 + 132671)$$

= **214 306 kJ/kmol air**

[If no reac. $Q = n_{O2}\Delta\bar{h}_{O2} + n_{N2}\Delta\bar{h}_{N2}$ = 131 849 kJ/kmol air]

15.88

Methane is burned with theoretical oxygen in a steady flow process, and the products exit the combustion chamber at 3200 K, 700 kPa. 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) $2\,H_2O \Leftrightarrow 2\,H_2 + O_2$ 2) $2\,H_2O \Leftrightarrow H_2 + 2\,OH$

change -2a +2a +a 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_{O2} = a+c n_{CO2} = 1-2c

N_{H2} = 2a+b n_{OH} = 2b n_{CO} = 2c

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

Products at 3200 K, 700 kPa

$$K_1 = 0.007\,328 = \left(\frac{2a+b}{2-2a-2b}\right)^2\left(\frac{a+c}{3+a+b+c}\right)\left(\frac{700}{100}\right)$$

$$K_2 = 0.012\,265 = \left(\frac{2b}{2-2a-2b}\right)^2\left(\frac{2a+b}{3+a+b+c}\right)\left(\frac{700}{100}\right)$$

$$K_3 = 0.426\,135 = \left(\frac{2c}{1-2c}\right)^2\left(\frac{a+c}{3+a+b+c}\right)\left(\frac{700}{100}\right)$$

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 = 0.024, b = 0.1455, c = 0.236

Substance:	H_2O	H_2	O_2	OH	CO_2	CO
n	1.661	0.1935	0.260	0.291	0.528	0.472
y	0.4877	0.0568	0.0764	0.0855	0.1550	0.1386