

Chapter 14 Practice Problem Solutions

(P14.1) An equimolar mixture of H₂ and CO can be obtained by the reaction of steam with coal. Compute the equilibrium compositions at 550 C based on an equimolar feed of H₂, CO, and H₂O. The reaction is H₂O + CO = H₂ + CO₂. ΔG_f^o data at 550 C are given.

$$\Delta G_r = \Sigma \Delta G_f (\text{product}) - \Sigma \Delta G_f (\text{reactant}) = -8.84 \text{ kJ/mol}$$

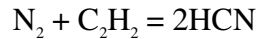
$$K_a (550^\circ\text{C}) = \exp(8840/(8.314*(550+273.15))) = 3.369$$

Compound	In	Out
H ₂ O	0.333	0.333-ξ
CO	0.333	0.333-ξ
H ₂	0.333	0.333+ξ
CO ₂	0	ξ
Total	1	1

$$K_a = \frac{(\xi)(0.333 + \xi) * P^2}{(0.333 - \xi) * (0.333 - \xi) * P^2} = 3.369$$

$$\xi = 0.176; \text{ Ans. } y_1 = 0.157, y_2 = 0.157, y_3 = 0.509, y_4 = 0.176$$

(P14.2) One method for the production of hydrogen cyanide is by the gas-phase nitrogenation of acetylene according to the reaction below. For a stoichiometric feed at 300°C, calculate the product composition at 1 and 200 bar given ΔG_r^o = 30.08 kJ/mole.



Solution: Two mole basis. Assume ideal gas.

of moles (N₂) = # of moles (C₂H₂) = 1.0

Compound	In	Out
N ₂	1	1-ξ
C ₂ H ₂	1	1-ξ
HCN	0	2ξ
Total	2	2

$$K_a = \exp(-30080/(8.314*(300+273.15))) = 0.0018$$

$$K_a = \frac{(2 * \xi)^2 * P^2}{(1 - \xi)^2 * P^2} = 0.0018, \quad \xi = 0.0208$$

$$(\text{Ans. } y_1 = 0.4896, y_2 = 0.4896, y_3 = 0.0416)$$

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(P.14.3) Butadiene can be prepared by the gas-phase catalytic dehydrogenation of 1-Butene: $C_4H_8 = C_4H_6 + H_2$. In order to suppress side reactions, the butene is diluted with steam before it passes into the reactor.

- (a) Estimate the temperature at which the reactor must be operated in order to convert 30% of the 1-butene to 1,3-butadiene at a reactor pressure of 2 bar from a feed consisting of 12 mol of steam per mole of 1-butene.
- (b) If the initial mixture consists of 50 mol% steam and 50mol% 1-butene, how will the required temperature be affected?

ΔG_f°	600K	700K	800K	900K
C4H6	195.73	211.71	227.94	244.35
C4H8	150.92	178.78	206.89	235.35

Solution:

Compound	In	Out
C4H8	1	1- ξ
C4H6	0	ξ
H2	0	ξ
H2O	12	12
Total	13	13+ ξ

$P = 2$ bar

$$K_a = \frac{\left(\frac{\xi}{13+\xi}\right)^2 * P^2}{\left(\frac{1-\xi}{13+\xi}\right) P} = \frac{\xi^2 * P}{(13+\xi)*(1-\xi)}$$

$$K_a = 0.01933$$

Noting that $\ln K_a = -\Delta G_{tot}/RT$, we can identify the temperature by fitting a trendline to the given data.

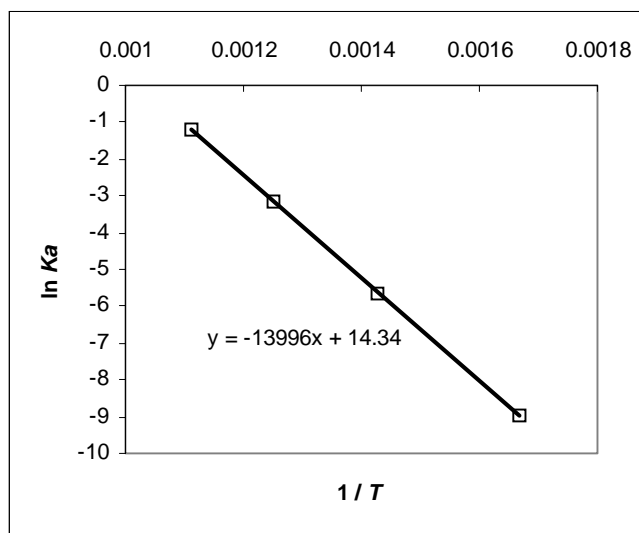
$$\Rightarrow \ln 0.01933 = -3.95,$$

substitute in the equation of straight line,

$$\Rightarrow x = -(-14.34 - 3.95)/13996.$$

$$\Rightarrow x = 0.001306 = 1/T,$$

$$\Rightarrow T = 765.22 \text{ K} = 492^\circ\text{C}$$



Compound	In	Out
C4H8	1	1- ξ
C4H6	0	ξ
H2	0	ξ
H2O	1	1
Total	2	2+ ξ

$$K_a = \frac{\xi^2 * P}{(2+\xi)*(1-\xi)} = 0.1118$$

$$\text{Similarly, } T = 846.65 \text{ K} = 573.6^\circ\text{C}$$

\Rightarrow We need higher T .

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(P14.4) The standard Gibbs energy change for ethylene oxide at 298K for the reaction is -79.79 kJ/mole. This large negative value of ΔG_T° indicates that equilibrium is far to the right at 298K but what about 550K? Heat capacity expressions are given as $C_p = a + b T$.

Solution: The heat of reaction must be looked up. Referring to Apx E.6 for ethylene and the DIPPR handbook for ethylene oxide, $\Delta H_{298}^\circ = -52.6 - 52.51 = -105.1$ kJ/mol. Following Eqs. 14.28 and 14.30,

$$-105100 = J + (6.57 - 15.4 - 26.65/2) 298 + (0.1389 - 0.0937 - 0.00845/2) 298^2/2$$

$$-105100 = J - 22.155 * 298 + 0.040975 * 298^2/2 \Rightarrow J = -100317 \text{ J/mol}$$

$$-79790/(8.314 * 298) = -100317/(8.314 * 298) -$$

$$\frac{-79790}{8.314 * 298} = \frac{-100317}{8.314 * 298} - \frac{-22.155}{8.314} \ln 298 - \frac{0.040975}{2 * 8.314} 298 + I \Rightarrow I = -6.16$$

$$\frac{\Delta G^\circ}{8.314 * 550} = \frac{-100317}{8.314 * 550} - \frac{-22.155}{8.314} \ln 550 - \frac{0.040975}{2 * 8.314} 550 + 6.16 = 12.6$$

$\Rightarrow \Delta G^\circ = -57.7$ kJ/mol. If $T = 550$ K, increasing T will give an adverse effect on equilibrium, but the reaction is still very strongly favored and the impact will be indistinguishable.

(P14.5) The “water gas” shift is to be carried out at a specified temperature and pressure employing a feed containing only CO and H₂O. Show that the maximum equilibrium mole fraction of H₂ in the product results when the feed contains CO and H₂O in their stoichiometric proportions. Assume ideal gas behavior.

Solution: $CO + H_2O = CO_2 + H_2$

Compound	In	Out	$Ka = \frac{\xi^2}{(z - \xi)(1 - \xi)}$ $\Rightarrow \xi^2 - Ka(z - \xi)(1 - \xi) = 0$ $0 = \xi^2 - Ka[z - (1 + z)\xi + \xi^2]$
CO	z	$z - \xi$	
H ₂ O	1	$1 - \xi$	
CO ₂	0	ξ	
H ₂	0	ξ	
Total	$1 + z$	$1 + z$	

$$\xi^2(1 - Ka) + Ka(1 + z)\xi - Ka z = 0 \Rightarrow \xi = \{-Ka(1 + z) + [Ka^2(1 + z)^2 + 4z(1 - Ka)Ka]^{1/2}\} / [2(1 - Ka)]$$

$$y_{H_2} = \xi / (1 + z) = \{-Ka(1 + z) + [Ka^2(1 + z)^2 + 4z(1 - Ka)Ka]^{1/2}\} / [2(1 + z)(1 - Ka)]$$

$$y_{H_2} = \xi / (1 + z) = \{-Ka + [Ka^2 + 4z(1 - Ka)Ka / (1 + z)^2]^{1/2}\} / [2(1 - Ka)]$$

To find maximum, take derivative and set equal to zero.

$$dy/dz = 0.5[Ka^2 + 4z(1 - Ka)Ka / (1 + z)^2]^{-1/2} [4(1 - Ka)Ka / (1 + z)^2 - 8z(1 - Ka)Ka / (1 + z)^3] = 0$$

$$1 = 2z / (1 + z) \Rightarrow z = 1. \text{ QED.}$$

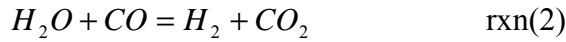
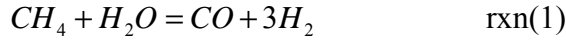
(P14.6) Assuming ideal gas behavior, estimate the equilibrium composition at 400K and 1 bar of a reactive mixture containing the three isomers of pentane. Formation data are given at 400K.

Solution: This is best solved by the Gibbs minimization method, adapting Example 14.10 and GibbsMin from the Rxns.xls workbook, we obtain the following.

	Gf(J/mole)	Gf400/RT	feed	n_i	$\log(n_i)$	y_i	$n_i(G_i/RT + \ln y_i)$
nPentane	40170	12.08	0	0.111	-0.95	0.111	1.100
iPentane	34310	10.32	1	0.648	-0.19	0.648	6.408
neoPentane	37610	11.31	0	0.240	-0.62	0.240	2.376
Tot			1	1.000			9.884
		Out	In				
C-bal		5	5				
Hbal		12	12				

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(P14.7) One method for the manufacture of synthesis gas depends on the vapor-phase catalytic reaction of methane with steam according to the equation below. The water-gas shift reaction also is important. Bases on stoichiometric feed of methane and steam, compute the eq composition at 600K, 1300K and 1, 100 bars.



Compound	In	Out
CH4	1	1-ξ ₁
H2O	1	1-ξ ₁ -ξ ₂
CO	0	ξ ₁ -ξ ₂
H2	0	3ξ ₁ +ξ ₂
CO2	0	ξ ₂
Total	2	2+2ξ ₁

$$\Delta G_{600K} = -164.68 + 214.01 + 22.97 = 72.3kJ / mole \dots \dots \dots \text{rxn(1)}$$

$$\Delta G_{600K} = -395.14 + 214.01 + 164.68 = -16.45kJ / mole \dots \dots \dots \text{rxn(2)}$$

$$K_{a_{600K,1}} = \exp\left(\frac{-72300J / mole}{8.314 * 600}\right) = 5.08E - 7$$

$$K_{a_{600K,2}} = \exp\left(\frac{16450}{8.314 * 600}\right) = 27.05$$

$K_{a1} = \frac{(\xi_1 - \xi_2)(3\xi_1 + \xi_2)^3 * P^4}{(1 - \xi_1)(1 - \xi_1 - \xi_2) * P^2} \bigg/ \frac{(2 + 2\xi_1)^4}{(2 + 2\xi_1)^2}$ $= \frac{(\xi_1 - \xi_2)(3\xi_1 + \xi_2)^3 * P^2}{(1 - \xi_1)(1 - \xi_1 - \xi_2)(2 + 2\xi_1)^2}$ $K_{a2} = \frac{\xi_2(\xi_1 + \xi_2) * P^2}{(1 - \xi_1)(\xi_1 - \xi_2) * P^2} \bigg/ \frac{4}{4} = \frac{\xi_2(\xi_1 + \xi_2)}{(1 - \xi_1)(\xi_1 - \xi_2)}$	<p>PP 14.7</p> <p>Two simultaneous reactions:</p> <p>CH4 + H2O = CO + 3H2</p> <p>H2+CO2 = CO + H2O</p> <p>(Details of equations described in text)</p> <table border="1"> <tbody> <tr> <td>P(bars)</td> <td>100</td> </tr> <tr> <td>T(K)</td> <td>1300</td> </tr> <tr> <td>K_{a1}</td> <td>16113</td> </tr> <tr> <td>K_{a2}</td> <td>0.5400</td> </tr> <tr> <td>ξ₁</td> <td>0.4513</td> </tr> <tr> <td>ξ₂</td> <td>0.1491</td> </tr> <tr> <td>y₁</td> <td>0.1891</td> </tr> <tr> <td>y₂</td> <td>0.1377</td> </tr> <tr> <td>y₃</td> <td>0.1041</td> </tr> <tr> <td>y₄</td> <td>0.5178</td> </tr> <tr> <td>y₅</td> <td>0.0514</td> </tr> <tr> <td>nTot</td> <td>2.9025</td> </tr> </tbody> </table> <p>Objective Functions</p> <table border="1"> <tbody> <tr> <td>err1</td> <td>0.0000</td> </tr> <tr> <td>err2</td> <td>0.0000</td> </tr> </tbody> </table>	P(bars)	100	T(K)	1300	K_{a1}	16113	K_{a2}	0.5400	ξ₁	0.4513	ξ₂	0.1491	y₁	0.1891	y₂	0.1377	y₃	0.1041	y₄	0.5178	y₅	0.0514	nTot	2.9025	err1	0.0000	err2	0.0000
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Note: high pressure tends to disfavor rxn (1). Rxn 1 is negligible at 600K, and rxn (2) requires CO to run or ξ₁-ξ₂ will be less than zero. So both reactions are zero. At 1300 K, the situation is quite different.

$$\Delta G_{1300K} = -226.94 + 175.81 - 53.30 = -104.73$$

$$\Rightarrow K_{a1} = 16113$$

$$\Delta G_{1300K} = -396.14 + 226.94 + 175.81 = 6.614$$

$$\Rightarrow K_{a2} = 0.54$$

Solving by method of Example 14.9, ξ₁ = 0.972 and ξ₂ = 0.015 at 1 bar. At 100 bar, ξ₁ = 0.451 and ξ₂ = 0.149 at 100 bar

(P14.8) Is there any danger that solid carbon will form at 550°C and 1 bar by the reaction:
 $2CO = C_s + CO_2$

	$\Delta H_{298K} \text{ kJ / mole}$	$\Delta G_{298K} \text{ kJ / mole}$	IN	Out
CO	-110.53	-137.16	2	2-2ξ
C _s	0	0	0	0 (gas)
CO ₂	-393.51	-394.38	0	ξ
Tot				2-ξ

$$\Delta G_{298K,T} = -394.38 + 2 * 137.16 = -120.06 \text{ kJ / mole}$$

$$\Delta H_{298K,T} = -393.51 + 2 * 110.53 = -172.45 \text{ kJ / mole}$$

Increasing T , adverse affect on equilibrium

$$K_{a_{298K}} = \exp\left[\frac{-\Delta G_{298K}}{RT}\right] = \exp\left(\frac{120060}{8.314 * 298.15}\right) = 1.08E21$$

Using Shortcut Van't Hoff Eq. 14.31

$$\Rightarrow \ln\left(\frac{K_a}{K_{a_{298}}}\right) = \frac{-\Delta H_{298}}{R} \left(\frac{1}{T} - \frac{1}{T_{298}}\right) = \ln\left(\frac{K_a}{1.08E21}\right) = \frac{172450}{8.314} \left(\frac{1}{823.15} - \frac{1}{298.15}\right)$$

$$\Rightarrow \ln K_a = \ln(1.08E21) - 44.4 = 4.06 \Rightarrow K_a = \exp(4.06) = 57.99$$

$$\Rightarrow K_a = \frac{y_{CO_2} * P}{(y_{CO} * P)^2} = \frac{\left(\frac{\xi}{(2-\xi)}\right)}{\left(\frac{(2-2\xi)}{(2-\xi)}\right)^2} = 57.99 = \frac{\xi * (2-\xi)}{(2-2\xi)^2}$$

$$\xi = 0.9345 \Rightarrow \text{ratio of carbon solid to feed is } \frac{0.9345}{2} = 0.46725. \Rightarrow \text{There is danger.}$$

Note: this exemplifies a very important and undesirable side reaction in many catalytic reactions know as “coking.” The carbon tends to clog the catalyst pores and substantially reduce its effectiveness. Because of this problem, fluidized catalytic crackers were developed (aka. Cat crackers). The solid catalyst particles are fluidized by the upflow of gaseous reactants. As they ultimately settle at the bottom, they are removed and recirculated through an oxidation zone that burns off the coke then recycles the catalyst to the top of the bed. This is a good example of how thermodynamics impacts reactor design.

(P14.9) Calculate the equilibrium percent conversion of ethylene oxide to ethylene glycol at 298K and 1 bar if the initial molar ratio of ethylene oxide to water is 3.

	In	Out(z _i)
EtO	3	3-ξ
Water	1	(1-ξ)
Glycol	0	ξ
Tot		4-ξ

$$K_w = P^{sat}/P = 0.0425; K_{EtO} = 1.76; K_{Gly} = 8.6E-4; y_i = z_i K_i / [K_i + L/F * (1 - K_i)]$$

$$K_a = \frac{y_{Gly} P}{y_{EtO} * y_w * P^2} = \exp\left(\frac{7824}{298.15 * 8.314}\right) = 23.52 \quad \text{and } \sum y_i = 1 \text{ are constraints, } \xi \text{ and } L/F \text{ are unknown. Guess, } \xi = 0.99, L/F = 1/3 \text{ (all glycol in liquid, all EtO in vapor).}$$

To accompany *Introductory Chemical Engineering Thermodynamics*

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(P14.9) Sample solution of one reaction with vle:

(Details of input equations described in text by Elliott and Lira)

P(bar)	T(K)	Ka1			
1.000	298	23.52			
	pSat(bar)	K-ratios	zFeed	yi	xi
EtO	1.76000	1.76000	0.66676	0.99961	0.56796
Water	0.04250	0.04250	0.00029	1.579E-05	0.00037
Glycol	0.00086	0.00086	0.33295	0.00037	0.43167
			1.0000	1.0000	1.0000
1-ξ	8.7055E-04				
ξ	0.99913		sum(yi-xi)	0.00000	
L/F	0.77111		ErrKa	5.583E-07	

As it turns out, the ethylene oxide is not so volatile after all and dissolves a fair amount in the liquid. The guess about the extent of conversion being high was good though. A more clever engineering approach would be to assume complete conversion and solve the simple flash. Then back out the exact conversion assuming L/F does not change.

(P14.10) Acetic acid vapor dimerizes according to $2A_1 = A_2$. Assume that no higher-order associations occur. Supposing that a value for Ka is available, and that the monomers and dimers behave as an ideal gas, derive an expression for y_{A_1} in terms of P and Ka . Then develop an expression for PV/n_0RT in terms of y_{A_1} , where n_0 is the superficial number of moles neglecting dimerization. Hint: write n_0/n_T in terms of y_{A_1} where $n_T = n_1 + n_2$.

Solution:

$$\frac{n_0}{n_T} = \frac{n_1 + 2n_2}{n_T} = y_{A_1} + 2(1 - y_{A_1}) = 2 - y_{A_1}$$

$$\frac{y_{A_2}}{y_{A_1}^2 P} = Ka \Rightarrow 1 - y_{A_1} = y_{A_1}^2 PKa \Rightarrow y_{A_1} = \frac{-1 + \sqrt{1 + 4PKa}}{2PKa}$$

$$\text{Ideal gas} \Rightarrow \frac{PV}{n_T RT} = 1 \Rightarrow \frac{PV}{n_0 RT} = \frac{n_T}{n_0} = \frac{1}{2 - y_{A_1}}$$

Note: as $Ka \rightarrow \infty$, $PV/n_0RT \rightarrow 1/2$ because the monomer is converted to dimer. Note also that PV/n_0RT is what we normally refer to as the compressibility factor, Z . This is an interesting result with regard to equations of state and phase equilibria. Since Ka is simply a function of temperature [ie. $\exp(-\Delta G/RT)$], it says that we can compute Z given a pressure and temperature. This is analogous to the pressure explicit virial equation (Section 6.4), but the form of the pressure dependence is more complex. Exploring this perspective, generalizing to density-dependent equations, and adapting to multimer-forming species and mixtures is the subject of Chapter 15. Most of the physical insight contained in Chapter 15 is contained in this simple practice problem.