(P17.1) 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° data at 550°C are given.

\[ ΔG_T = \Sigma ΔG_f (\text{product}) - \Sigma ΔG_f (\text{reactant}) = -8.84 \text{ kJ/mol} \]

\[ Ka (550°C) = \exp\left(\frac{8840}{8.314*(550+273.15)}\right) = 3.369 \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>In</th>
<th>Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.333</td>
<td>0.333−ξ</td>
</tr>
<tr>
<td>CO</td>
<td>0.333</td>
<td>0.333−ξ</td>
</tr>
<tr>
<td>H₂</td>
<td>0.333</td>
<td>0.333+ξ</td>
</tr>
<tr>
<td>CO₂</td>
<td>0</td>
<td>ξ</td>
</tr>
<tr>
<td>Total</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ Ka = \frac{(ξ)(0.333+ξ)*P^2}{(0.333−ξ)*(0.333−ξ)*P^2} = 3.369 \]

ξ = 0.176; Ans. \( y_1 = 0.157, y_2 = 0.157, y_3 = 0.509, y_4 = 0.176 \)

(P17.2) 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° = 30.08 kJ/mole.

\[ N₂ + C₂H₂ = 2HCN \]

Solution: Two mole basis. Assume ideal gas.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>In</th>
<th>Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>1</td>
<td>1−ξ</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>1</td>
<td>1−ξ</td>
</tr>
<tr>
<td>HCN</td>
<td>0</td>
<td>2ξ</td>
</tr>
<tr>
<td>Total</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

\[ Ka = \exp\left(-\frac{30080}{8.314*(300+273.15)}\right) = 0.0018 \]

\[ Ka = \frac{(2*ξ)^2*P^2}{(1−ξ)^2*P^2} = 0.0018, \quad ξ = 0.0208 \]

(Ans. \( y_1 = 0.4896, y_2 = 0.4896, y_3 = 0.0416 \)
(P.14.3) Butadiene can be prepared by the gas-phase catalytic dehydrogenation of 1-Butene: C4H8 = C4H6 + H2. 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?

\[
\begin{array}{c|c|c|c|c|c|c|c}
\hline
\Delta G^\circ & 600K & 700K & 800K & 900K \\
\hline
C4H6 & 195.73 & 211.71 & 227.94 & 244.35 \\
C4H8 & 150.92 & 178.78 & 206.89 & 235.35 \\
\hline
\end{array}
\]

Solution:

<table>
<thead>
<tr>
<th>Compound</th>
<th>In</th>
<th>Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4H8</td>
<td>1</td>
<td>1-\xi</td>
</tr>
<tr>
<td>C4H6</td>
<td>0</td>
<td>\xi</td>
</tr>
<tr>
<td>H2</td>
<td>0</td>
<td>\xi</td>
</tr>
<tr>
<td>H2O</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Total</td>
<td>13</td>
<td>13+\xi</td>
</tr>
</tbody>
</table>

\[ P = 2 \text{ bar} \]

\[
K_a = \left( \frac{\xi}{13 + \xi} \right)^2 \cdot \frac{P^2}{\left( \frac{1 - \xi}{13 + \xi} \right)P} = \frac{\xi^2 \cdot P}{(13 + \xi) \cdot (1 - \xi)P} 
\]

\[ K_a = 0.01933 \]

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

\[ y = -13996x + 14.34 \]

\[ x = 0.001306 = 1/T, \]

\[ T = 765.22 \text{ K} = 492^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>In</th>
<th>Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4H8</td>
<td>1</td>
<td>1-\xi</td>
</tr>
<tr>
<td>C4H6</td>
<td>0</td>
<td>\xi</td>
</tr>
<tr>
<td>H2</td>
<td>0</td>
<td>\xi</td>
</tr>
<tr>
<td>H2O</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td>2</td>
<td>2+\xi</td>
</tr>
</tbody>
</table>

\[ K_a = \frac{\xi^2 \cdot P}{(2 + \xi) \cdot (1 - \xi)} = 0.1118 \]

Similarly, \( T = 846.65K = 573.6^\circ C \)

\[ \Rightarrow \] We need higher \( T \).
Chapter 17 Practice Problem Solutions

(P17.4) The standard Gibbs energy change for ethylene oxide at 298K for the reaction is –79.79 kJ/mole. This large negative value of \( \Delta G^\circ \) indicates that equilibrium is far to the right at 298K but what about 550K? Heat capacity expressions are given as \( \Delta H^\circ = a + b T \).

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

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

\[
-105100 = J - 22.155 \times 298 + 0.040975 \times 298^2/2
\]

\[ J = -100317 \text{ J/mol} \]

\[
-79790/(8.314 \times 298) = -100317/(8.314 \times 298) - 79790
\]

\[
100317/22.155 = 0.040975/6.168.314*298
\]

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

(P17.6) 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 17.13 and GibbsMin from the Rxns.xls workbook, we obtain the following.

To accompany introductory chemical engineering thermodynamics
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Chapter 17 Practice Problem Solutions

(P17.7) 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 equilibrium composition at 600K, 1300K and 1, 100 bars.

\[
\begin{align*}
CH_4 + H_2O & = CO + 3H_2 \quad \text{rxn(1)} \\
H_2O + CO & = H_2 + CO_2 \quad \text{rxn(2)}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>In</th>
<th>Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>1</td>
<td>1−ξ1</td>
</tr>
<tr>
<td>H2O</td>
<td>1</td>
<td>1−ξ1−ξ2</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>ξ1−ξ2</td>
</tr>
<tr>
<td>H2</td>
<td>0</td>
<td>3ξ1+ξ2</td>
</tr>
<tr>
<td>CO2</td>
<td>0</td>
<td>ξ2</td>
</tr>
<tr>
<td>Total</td>
<td>2</td>
<td>2+2ξ1</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\Delta G_{600K} & = -164.68 + 214.01 + 22.97 = 72.3 kJ / \text{mole} \quad \text{rxn(1)} \\
\Delta G_{600K} & = -395.14 + 214.01 + 164.68 = -16.45 kJ / \text{mole} \quad \text{rxn(2)}
\end{align*}
\]

\[
\begin{align*}
K_{a_{600K,1}} & = \exp \left( \frac{-72300 J / \text{mole}}{8.314 * 600} \right) = 5.08E-7 \\
K_{a_{600K,2}} & = \exp \left( \frac{16450}{8.314 * 600} \right) = 27.05
\end{align*}
\]

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.

\[
\begin{align*}
\Delta G_{1300K} & = -226.94 + 175.81 - 53.30 = -104.73 \\
\Rightarrow K_{a_1} & = 16113 \\
\Delta G_{1300K} & = -396.14 + 226.94 + 175.81 = 6.614 \\
\Rightarrow K_{a_2} & = 0.54
\end{align*}
\]

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

\[
\begin{align*}
P(\text{bars}) & = 100 \\
T(\text{K}) & = 1300 \\
K_{a_1} & = 16113 \\
K_{a_2} & = 0.5400 \\
\xi_1 & = 0.4513 \\
\xi_2 & = 0.1491 \\
y_1 & = 0.1891 \\
y_2 & = 0.1377 \\
y_3 & = 0.1041 \\
y_4 & = 0.5178 \\
y_5 & = 0.0514 \\
\text{nTot} & = 2.9025
\end{align*}
\]

Objective Functions
\[
\begin{align*}
\text{err1} & = 0.0000 \\
\text{err2} & = 0.0000
\end{align*}
\]

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(P17.8) Is there any danger that solid carbon will form at 550°C and 1 bar by the reaction:

\[ 2CO = C_s + CO_2 \]

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H_{298K} \text{kJ/mole} )</th>
<th>( \Delta G_{298K} \text{kJ/mole} )</th>
<th>IN</th>
<th>Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>-110.53</td>
<td>-137.16</td>
<td>2</td>
<td>2-( \xi )</td>
</tr>
<tr>
<td>( C_s )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0 (gas)</td>
</tr>
<tr>
<td>CO2</td>
<td>-393.51</td>
<td>-394.38</td>
<td>0</td>
<td>( \xi )</td>
</tr>
<tr>
<td>Tot</td>
<td>2-( \xi )</td>
<td>0</td>
<td>2</td>
<td>2-( \xi )</td>
</tr>
</tbody>
</table>

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

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

Increasing \( T \), adverse affect on equilibrium

\[ Ka_{298K} = \exp \left( \frac{-\Delta G_{298K}}{RT} \right) = \exp \left( \frac{120060}{8.314 \times 298.15} \right) = 1.08E21 \]

Using Shortcut Van’t Hoff Eq. 14.31

\[ \Rightarrow \ln \left( \frac{Ka}{Ka_{298}} \right) = -\Delta H_{298K} \left( \frac{1}{T} - \frac{1}{T_{298}} \right) = \ln \left( \frac{Ka}{1.08E21} \right) = \frac{172450}{8.314} \left( \frac{1}{823.15} - \frac{1}{298.15} \right) \]

\[ \Rightarrow \ln Ka = \ln (1.08E21) - 44.4 = 4.06 \Rightarrow Ka = \exp(4.06) = 57.99 \]

\[ \Rightarrow Ka = \frac{y_{CO2} \times P}{(y_{CO} \times P)^{\xi}} = \frac{\xi^{(2-\xi)}}{(2-\xi)^{\xi}} = 57.99 = \frac{\xi (2-\xi)}{(2-\xi)^{\xi}} \]

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

Note: this exemplifies a very important and undesirable side reaction in many catalytic reactions known 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.

(P17.9) 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.

<table>
<thead>
<tr>
<th></th>
<th>In</th>
<th>Out(z_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtO</td>
<td>3</td>
<td>3-( \xi )</td>
</tr>
<tr>
<td>Water</td>
<td>1</td>
<td>(1-( \xi ))</td>
</tr>
<tr>
<td>Glycol</td>
<td>0</td>
<td>( \xi )</td>
</tr>
<tr>
<td>Tot</td>
<td>4</td>
<td>4-( \xi )</td>
</tr>
</tbody>
</table>

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

\[ Ka = \frac{y_{Gly} \times P}{y_{EtO} \times y_w \times P^2} = \exp \left( \frac{7824}{298.15 \times 8.314} \right) = 23.52 \text{ and } \Sigma y_i = 1 \text{ are constraints, } \xi \text{ and } L/F \text{ are unknown. Guess, } \xi = 0.99, \text{ } L/F = 1/3 \text{ (all glycol in liquid, all EtO in vapor).} \]
(P17.9) 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

<table>
<thead>
<tr>
<th></th>
<th>P(bar)</th>
<th>T(K)</th>
<th>Ka1</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtO</td>
<td>1.7600</td>
<td>1.7600</td>
<td>0.66676</td>
</tr>
<tr>
<td>Water</td>
<td>0.04250</td>
<td>0.04250</td>
<td>1.579E-05</td>
</tr>
<tr>
<td>Glycol</td>
<td>0.00086</td>
<td>0.00086</td>
<td>0.33295</td>
</tr>
</tbody>
</table>

\[ 1 - \xi = 8.7055E-04 \]
\[ \xi = 0.99913 \]
\[ \text{sum}(y_i-x_i) = 0.00000 \]
\[ L/F = 0.77111 \]
\[ \text{Err}K_a = 5.583E-07 \]

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.

(P17.10) Acetic acid vapor dimerizes according to \( 2A_1 = A_2 \). Assume that no higher-order associations occur. Supposing that a value for \( K_a \) 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 \( K_a \). 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:
\[ n_0 \]
\[ n_T \]
\[ y_{A_1} \]
\[ y_{A_2} \]
\[ P \]

Ideal gas \( \Rightarrow PV/n_TRT = 1 \Rightarrow PV/n_0RT = n_T/n_0 \Rightarrow \frac{1}{2-\gamma_{A_1}} \)

Note: as \( K_a \rightarrow \infty \), \( PV/n_0RT \rightarrow \frac{1}{2} \) 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 \( K_a \) 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 7.4), 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 19. Most of the physical insight contained in Chapter 19 is contained in this simple practice problem.