Chapter 17. Reaction Equilibria

$$K_a = \prod (y_i P)^{\nu_i} \qquad \text{(ig) 17.1}$$

1. Ascertain how many phases are present and the method to be used for the equilibrium calculations. Our initial examples will use only a gas phase and determine equilibrium compositions using an equilibrium constant method. Later we will show how to use liquid and solid phases and how to use the Gibbs energy directly.

2. Use standard state properties to obtain the value of the equilibrium constant at the reaction temperature, or for the Gibbs minimization method find the Gibbs energies of the species. Usually this consists of two substeps:

a. Perform a calculation using the standard state Gibbs energies at a reference temperature and pressure.

b. Correct the temperature (and pressure for Gibbs method) to the reaction conditions.

3. Perform a material balance on the reactant and product species and relate the composition to the equilibrium constant or standard state properties from steps (1) and (2).

4. Solve for the equilibrium compositions.

17.7
17.22
Practice Problems 17.1, 17.4, 17.9
Test-yourself's OK but short

Example 17.1. Computing the reaction coordinate

CO and H_2 are fed to a reactor in a ratio of 2:1 at 500 K and 20 bar, where the equilibrium constant is $K_a = 0.00581$. (We will illustrate how to calculate K_a in Section 17.7.)

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$

Compute the equilibrium conversion of CO.

Solution

In the expression for K_a we insert each $y_i P$ with the appropriate exponent and then insert the numerical value of pressure:

$$K_a = (y_{CH_3OH}P)^1(y_{CO}P)^{-1}(y_{H_2}P)^{-2} \tag{17.2}$$

$$0.00581 = \frac{y_{CH_3OH}P}{y_{CO}P(y_{H_2}P)^2} \text{ but } P = 20 \text{ bar} \Rightarrow \frac{y_{CH_3OH}}{y_{CO}y_{H_2}^2} = 0.00581P^2 = 2.32$$

To relate the composition to the mass balance, we select a basis and use the reaction coordinate. **Basis:** 2 mole CO fed. Note the excess CO at the feed conditions. The **reaction coordinate** and method of selecting a basis have already been introduced in Section 3.6. The stoichiometry table becomes

n_{CO}	=	$2-\xi$
n_{H_2}	=	$1-2\xi$
n_{CH_3OH}	=	ξ
n_T	=	$3-2\xi$

Note that all n values must stay positive, constraining the range for a physically acceptable solution to be $0 \le \zeta \le 0.5$. The mole fractions can be written in terms of ζ using the stoichiometry table.

$$y_{CO} = \frac{2-\xi}{3-2\xi} \quad y_{H_2} = \frac{1-2\xi}{3-2\xi}\ ; \quad y_{CH_3OH} = \frac{\xi}{3-2\xi} \tag{17.3}$$

Substituting the mole fractions into the equilibrium constant expression,

$$\frac{\frac{\xi}{(3-2\xi)}}{\frac{(2-\xi)(1-2\xi)^2}{(3-2\xi)^3}} = 2.32 \Rightarrow \frac{\xi(3-2\xi)^2}{(2-\xi)(1-2\xi)^2} = 2.32 \tag{17.4}$$

$$\text{Rearranging} \Rightarrow F(\xi) \equiv 2.32 \cdot (2-\xi)(1-2\xi)^2 - \xi(3-2\xi)^2 = 0 \tag{17.5}$$

A trial-and-error solution is much more robust by using the difference of Eqn. 17.5 rather than the ratio of Eqn. 17.4. We solve by trial and error and substitute to get ζ recalling $0 \le \zeta \le 0.5$. A summary of guesses:

ξ	$F(\xi)$
0.10	2.04
0.25	–0.548
0.20	0.151
0.2099	0.0006

At reaction equilibrium for the given feed conditions, equilibrium is represented by $\zeta = 0.21$. Now Eqn. 17.3 may be used to find the y's. The conversion of CO is $0.21/2 \cdot 100\% = 10.5\%$; conversion of H_2 is $2(0.21)/1 \cdot 100\% = 42\%$. Note the conversion is species-dependent with nonstoichiometric feed. Conversion can be increased further by increasing the pressure further, or by changing T where K_a is larger, provided a catalyst is available and kinetics are adequate at that T.

This example demonstrates the method to use K_a to calculate the reaction coordinate. Readers should note that the value of K_a is fixed at a given temperature, but the equilibrium value of ζ may vary for different feed conditions and often pressure for gas phase reactions as we will show in other examples. To relate the equilibrium conditions to reaction engineering textbooks, we note that most reaction engineering textbooks use conversion rather than reaction coordinate to track reaction progress. By convention, **conversion** is tracked for the limiting species (the species used up first at the value of ζ closest to zero in the direction of the reaction). A relation is shown in the footnote of Section 3.6.

17.2. Reaction Equilibrium Constraint

$$d\underline{G} = -\underline{S}dT + \underline{V}dP + \sum_i \mu_i dn_i \quad (\text{Recall } \mu_i \equiv (\partial \underline{G}/\partial n_i)_{T,P,n_{i\neq j}}) \tag{17.6}$$

The fact that species are being created or consumed by a reaction does not alter this equation. At constant temperature and pressure, the first two terms on the right-hand side drop out:[1]

$$d\underline{G} = \sum_i \mu_i dn_i \tag{17.7}$$

Substituting the definition of reaction coordinate from Eqn. 3.39,

$$d\underline{G} = \sum_i \mu_i \nu_i d\xi \tag{17.8}$$

Because $\underline{G}$ is minimized at equilibrium at fixed T and P, the derivative with respect to reaction coordinate is zero:

$$d\underline{G}/d\xi = \sum_i \mu_i \nu_i = 0 \tag{17.9}$$

$$0 = \left(\sum_i \nu_i G_i^\circ\right)/(RT) + \sum_i \ln\left[\frac{\hat{f}_i}{f_i^\circ}\right]^{\nu_i} \quad \text{(equilibrium constraint)} \qquad 17.12$$

$$a_i \equiv \frac{\hat{f}_i}{f_i^\circ} \qquad 17.13$$

$$\sum_i \ln\left[\frac{\hat{f}_i}{f_i^\circ}\right]^{\nu_i} = \sum_i \ln(a_i)^{\nu_i} = \ln\prod_i a_i^{\nu_i} \qquad 17.14$$

$$\boxed{K_a = \prod_i a_i^{\nu_i} = \prod_i \left[\frac{\hat{f}_i}{f_i^\circ}\right]^{\nu_i}} \qquad 17.15$$

$$0 = \left(\sum_i \nu_i G_i^\circ\right)/(RT) + \ln K_a \text{ or } \exp\left(-\left(\sum_i \nu_i G_i^\circ\right)/(RT)\right) = K_a \qquad 17.16$$

The Equilibrium Constant for Ideal Gases

$$K_a = \prod_i a_i^{\nu_i} = \prod_i \left[\frac{\hat{f}_i}{f_i^\circ}\right]^{\nu_i} = \prod_i (y_i P)^{\nu_i} \qquad \text{(ig) 17.17}$$

17.4. The Standard State Gibbs Energy of Reaction

$$\Delta G_T^o \equiv \sum_i \nu_i G_i^o = \sum_{\text{products}} |\nu_i| \Delta G_{f,i}^o - \sum_{\text{reactants}} |\nu_i| \Delta G_{f,i}^o$$

$$\Delta G_T^o = \sum_i \nu_i \Delta G_{f,i}^o \qquad 17.19$$

$$\exp(-\Delta G_T^o/(RT)) = K_a \qquad 17.20$$

Example 17.2. Calculation of standard state Gibbs energy of reaction

Butadiene is prepared by the gas phase catalytic dehydrogenation of 1-butene:

$$C_4H_{8(g)} \rightleftarrows C_4H_{6(g)} + H_{2(g)}$$

Calculate the standard state Gibbs energy of reaction and the equilibrium constant at 298.15 K.

Solution

We find values tabulated for the standard state enthalpies of formation and standard state Gibbs energy of formation at 298.15 K.

Compound	$\Delta H^o_{f,\,298.15}$ (J/mole)	$\Delta G^o_{f,\,298.15}$ (J/mole)
1-butene (g)	−540	70,240
1,3-butadiene (g)	109,240	149,730
Hydrogen (g)	0	0

$$\Delta G^o_{298.15} = 149{,}730 + 0 - 70{,}240 = 79{,}490 \text{ J/mole}$$

The equilibrium constant is determined from Eqn. 17.16;

$$\exp\left(\frac{-\Delta G^o_{298.15}}{RT}\right) = \exp\left(\frac{-79,490}{8.314(298.15)}\right) = 1.18\times10^{-14} = K_{a,\,298.15}$$

This reaction is not favorable at room temperature because the equilibrium constant is small.

Composition and Pressure Independence of K_a

Le Châtelier's principle

$$\left(\prod y_i^{\nu_i}\right) P^{\Sigma \nu_i} = K_a \qquad \text{(ig) 17.21}$$

Example 17.3. Butadiene production in the presence of inerts

Consider again the butadiene reaction of Example 17.2 on page 648. Butadiene is prepared by the gas phase catalytic dehydrogenation of 1-butene, at 900 K and 1 bar.

$$C_4H_{8(g)} \rightleftarrows C_4H_{6(g)} + H_{2(g)}$$

a. In order to suppress side reactions, the butene is diluted with steam before it passes into the reactor. Estimate the conversion of 1-butene for a feed consisting of 10 moles of steam per mole of 1-butene.

b. Find the conversion if the inerts were absent and side reactions are ignored.

c. Find the total pressure that would be required to obtain the same conversion as in (a) if no inerts were present.

In the earlier example, we determined the value at 298.15 K for ΔG_f°. Now we need a value at 900 K. The next section explains how the value at 900 K may be obtained. For now, use the following data for ΔG_f° (kJ/mole) at 900 K and 1 bar:

Component	$\Delta G_{f,900}^\circ$ (kJ/mole)
1,3 Butadiene	243.474
1-Butene	232.854
Hydrogen	0

Solution

$$\Delta G_{900}^o = 243.474 - 232.854 = 10.62 \text{ kJ/mole}$$

$$K_a = \exp(-\Delta G_{900}^o / RT) = 0.242$$

a. Basis of 1 mole 1-butene feed. Set up reaction coordinate, using *I* to indicate inerts,.

$$n_{C_4H_8} \qquad 1 - \xi$$

a. Basis of 1 mole 1-butene feed. Set up reaction coordinate, using *I* to indicate inerts,.

$n_{C_4H_8}$	$1-\xi$
$n_{C_4H_6}$	ξ
n_{H_2}	ξ
n_I	10
n_T	$11+\xi$

$$0.242 = \left(\frac{\xi}{11+\xi}\right)^2 P \Big/ \left(\frac{1-\xi}{11+\xi}\right)$$

The physical range of the solution is $0 \le \xi \le 1$. $P = 1$ bar $\Rightarrow 1.242\,\xi^2 + 2.42\,\xi - 2.662 = 0 \Rightarrow \xi = 0.784$. For the basis of 1 mol 1-butene feed, the conversion is 78.4%.

b. $n_I = 0$ and the basis of feed is the same and $0 \le \xi \le 1$. The total number of moles is $n_T = 1 + \xi$; $1.242\xi^2 - 0.242 = 0$; $\xi = 0.44$, so conversion decreases to 44% without inert.

c. Rearranging the equilibrium expression for pressure, $P^{-1} = \xi^2 / [0.242 \cdot (1-\xi) \cdot (1+\xi)]$, $0 \le \xi \le 1$.

Inserting a reaction coordinate of $\xi = 0.784$ gives $P = 0.152$ bar. So the reaction would need to run at a much lower pressure without the inerts to achieve the same conversion. In other words, inerts serve to dilute the fugacities of the products and suppress the reverse reaction since there are more moles of product than reactant.

17.6. Determining the Spontaneity of Reactions

$$\sum_i \nu_i \mu_i = \sum_i \nu_i G_i^\circ + RT \sum_i \nu_i \ln\left[\frac{\hat{f}_i}{f_i^\circ}\right] \qquad 17.22$$

The term $\sum_i \nu_i \mu_i$ on the left side is called the **Gibbs energy of reaction** and is given the symbol ΔG_T. Note that this is a different term than the **standard state Gibbs energy of reaction** (the second term) that uses the superscript °. Thus, we can write,

$$\Delta G_T = \Delta G_T^\circ + RT \sum_i \nu_i \ln\left[\frac{\hat{f}_i}{f_i^\circ}\right] = \Delta G_T^\circ + RT \ln \prod_i \left[\frac{\hat{f}_i}{f_i^\circ}\right]^{\nu_i} \quad \text{(general relation)} \qquad 17.23$$

A reaction with $\Delta G_T^o < 0$ is called **exergonic** and results in $K_a > 1$, and a reaction with $\Delta G_T^o > 0$ is called **endergonic**, resulting in $K_a < 1$. This provides an indication of whether the equilibrium favors products or reactants, but does not mean that reactions with small values of K_a cannot be conducted industrially. For example, Example 17.1 involved a small K_a (thus endergonic with $\Delta G_T^o > 0$), yet the conversion of H_2 was 42%. The propensity for the reaction to go forward or backward depends instead on the Gibbs energy of reaction ΔG_T at the concentrations represented by the fugacity ratios. If the conditions provide $\Delta G_T < 0$, then the Gibbs energy is lowered when the reaction proceeds in the forward direction. If we evaluate conditions and $\Delta G_T > 0$, then the reaction goes in the reverse direction than what we have written. In either case, the concentrations adjust until the system reaches the equilibrium condition, $\Delta G_T = 0$, and then Eqn. 17.12 applies. In summary, the direction a reaction

proceeds is determined by ΔG_T, not by $^{\Delta G^\circ_T}$. Note when evaluating the fugacity term for determining

spontaneity that the actual conditions are used, not the equilibrium conditions. At the feed conditions of Example 17.1, $y_{CH_3OH} = 0$, which ensures $\Delta G_T < 0$ at the feed conditions even though $^{\Delta G^o_T > 0}$.

❗ The propensity for a reaction to go forward or backward under actual conditions is determined by ΔG_T, not $^{\Delta G^\circ_T}$.

17.7. Temperature Dependence of K_a

classical thermodynamics to the change in Gibbs energy with respect to temperature using the **Gibbs-Helmholtz relation,**

$$\frac{\partial(\Delta G/RT)}{\partial T} = \frac{1}{RT}\left(\frac{\partial \Delta G}{\partial T}\right)_P - \frac{\Delta G}{RT^2} = -\frac{\Delta S}{RT} - \left(\frac{\Delta H}{RT^2} - \frac{\Delta S}{RT}\right) = \frac{-\Delta H}{RT^2} \qquad 17.24$$

which results in the **van't Hoff equation:**

$$\boxed{\frac{\partial(\Delta G_T^\circ/RT)}{\partial T} = \frac{\partial(-\ln K_a)}{\partial T} = \frac{-\Delta H_T^\circ}{RT^2}} \qquad 17.25$$

$$\boxed{\frac{\Delta G_T^\circ}{RT} = -\int_{T_R}^{T} \frac{\Delta H_T^\circ}{RT^2} dT + \frac{\Delta G_R^\circ}{RT_R} = -\ln K_a = -\int_{T_R}^{T} \frac{\Delta H_T^\circ}{RT^2} dT - \ln K_{aR}} \qquad 17.26$$

$$\Delta H_T^o = \Delta H_R^o + \Delta a(T - T_R) + \frac{\Delta b}{2}(T^2 - T_R^2) + \frac{\Delta C}{3}(T^3 - T_R^3) + \frac{\Delta d}{4}(T^4 - T_R^4)$$

$$= J + \Delta a T + \frac{\Delta b}{2}T^2 + \frac{\Delta c}{3}T^3 + \frac{\Delta d}{4}T^4 \qquad 3.46$$

$$\boxed{\frac{\Delta G^\circ}{RT} = -\ln K_a = \frac{J}{RT} - \frac{\Delta a}{R}\ln T - \frac{\Delta b T}{2R} - \frac{\Delta c T^2}{6R} - \frac{\Delta d T^3}{12R} + I} \qquad 17.28$$

Example 17.4. Equilibrium constant as a function of temperature

The heat capacities of ethanol, ethylene, and water can be expressed as $C_P = a + bT + cT^2 + dT^3$ where values for *a, b, c,* and *d* are given below along with standard energies of formation. Calculate the equilibrium constant $[\exp(-\Delta G_T^\circ/RT)]$ for the vapor phase hydration of ethylene at 145°C and 320°C.

$$C_2H_{4(g)} + H_2O_{(g)} \rightleftarrows C_2H_5OH_{(g)}$$

	$\Delta H^o_{f,298}$ kJ/mol	$\Delta G^o_{f,298}$ kJ/mol	*a*	*b*	*c*	*d*
Ethylene	52.51	68.43	3.806	1.566E-01	−8.348E-05	1.755E-08
Water	−241.835	−228.614	32.24	1.924E-03	1.055E-05	−3.596E-09
Ethanol	−234.95	−167.73	9.014	2.141E-01	−8.390E-05	1.373E-09

Solution

	C_2H_4	$+H_2O$	$\rightleftarrows$	C_2H_5OH
ν_i	−1	−1		+1

The workbook Kcalc.xlsx or MATLAB Kcalc.m are helpful in doing these calculations.

Taking 298.15 K as the reference temperature,

$$\Delta H^\circ_R = \Delta H^\circ_{298.15} = -234.95 - [52.51 + (-241.835)] = -45{,}625 \text{ J/mole}$$
$$\Delta G^\circ_R = \Delta G^\circ_{298.15} = -167.73 - [68.43 + (-228.614)] = -7546 \text{ J/mole}$$

Solution

	C_2H_4	$+ H_2O$	$\rightleftarrows$	C_2H_5OH
ν_i	−1	−1		+1

The workbook Kcalc.xlsx or MATLAB Kcalc.m are helpful in doing these calculations.

Taking 298.15 K as the reference temperature,

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$$\Delta G_R^\circ = \Delta G_{298.15}^\circ = -167.73 - [68.43 + (-228.614)] = -7546 \text{ J/mole}$$

The variable J may be found with Eqn. 3.46 on page 113 at 298.15 K.

$$\Delta H_{298.15}{}^o = -45{,}625 = J + \Delta a T + (\Delta b/2)\cdot T^2 + (\Delta c/3)\cdot T^3 + (\Delta d/4)T^4 = J + (9.014 - 3.806 - 32.24)$$
$$T + [(0.2141 - 0.1566 - 0.0019)/2]\ T^2 + [(-8.39 + 8.348 - 1.055)(1\text{E-}5)/3]\ T^3 + [(1.373 - 17.55 + 3.596)(1\text{E-}9)/4]\ T^4$$
$$= J - 27.032\ T + 0.02779\ T^2 - (3.657\text{E-}6)T^3 - (3.145\text{E-}9)T^4$$

Plugging in $T = 298.15$ K, and solving for J, $J = -39.914$ kJ/mole. Using this result in Eqn. 17.28 at 298.15 K will yield the variable I.

$$\Delta G_T{}^o/RT = -39{,}914/(8.314\cdot T) + 27.032/8.314 \ln T - [(5.558\text{E-}2)/(2\cdot 8.314)]\ T + [(1.097\text{E-}5)/(6\cdot 8.314)]T^2 + [(1.258\text{E-}8)/(12\cdot 8.314)]T^3 + I$$

Plugging in $\Delta G_R{}^o$ at 298.15K, $\Delta G_T{}^o/RT = -7546/8.314/298.15 = 3.0442$. Plugging in for T on the right-hand side results in $I = -4.494$.

The resultant formula to calculate ΔG_T° at any temperature is

$$\Delta G_T^\circ = -39{,}914 + 27.032\ T \ln T - 0.0278\ T^2 + (1.828\text{E-}6)T^3 + (1.048\text{E-}9)T^4 - 37.363\ T$$

at 145°C $\Delta G_T^\circ = 7997$ J/mol $\Rightarrow K_a = 0.1002$;

at 320°C $\Delta G_T^\circ = 31{,}045$ J/mol $\Rightarrow K_a = 0.00185$

17.8. Shortcut Estimation of Temperature Effects

what we refer to as the **shortcut van't Hoff equation:**

$$\ln\left(\frac{K_a}{K_{aR}}\right) = \frac{\Delta G_R^\circ}{RT_R} - \frac{\Delta G_T^\circ}{RT} = \frac{-\Delta H_R^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right) \qquad 17.29$$

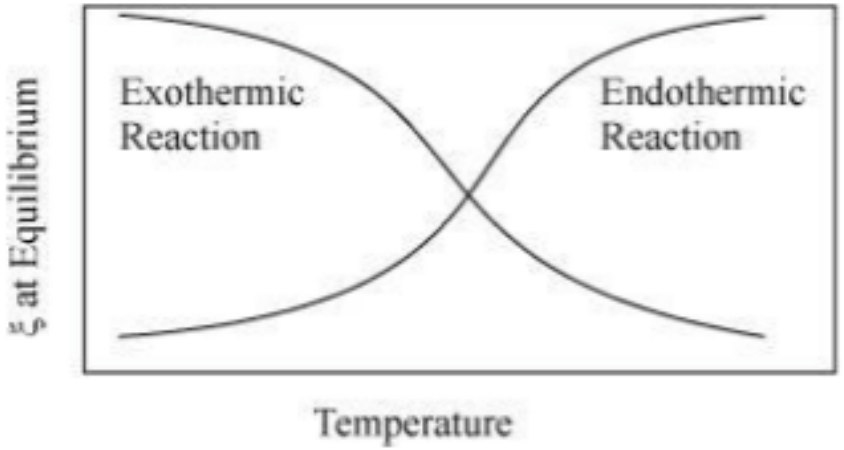


Figure 17.1. Qualitative behavior of equilibrium conversion for exothermic and endothermic reactions.

Example 17.5. Application of the shortcut van't Hoff equation

Apply the shortcut approximation to the vapor phase hydration of ethylene. This reaction has been studied in the previous example, and the Gibbs energy of reaction and heat of reaction can be obtained from that example.

Solution

$$K_{a,298.15} = \exp(7546/8.314/298) = 21.03$$

$$\ln\left(\frac{K_a}{21.03}\right) = \frac{45,625}{8.314}\left(\frac{1}{T} - \frac{1}{298.15}\right)$$

$$K_a = 0.106 \text{ at } 145°C;\ K_a = 0.0022 \text{ at } 320°C$$

The results are very similar to the answer obtained by the general van't Hoff equation in Example 17.4.

17.9. Visualizing Multiple Equilibrium Constants

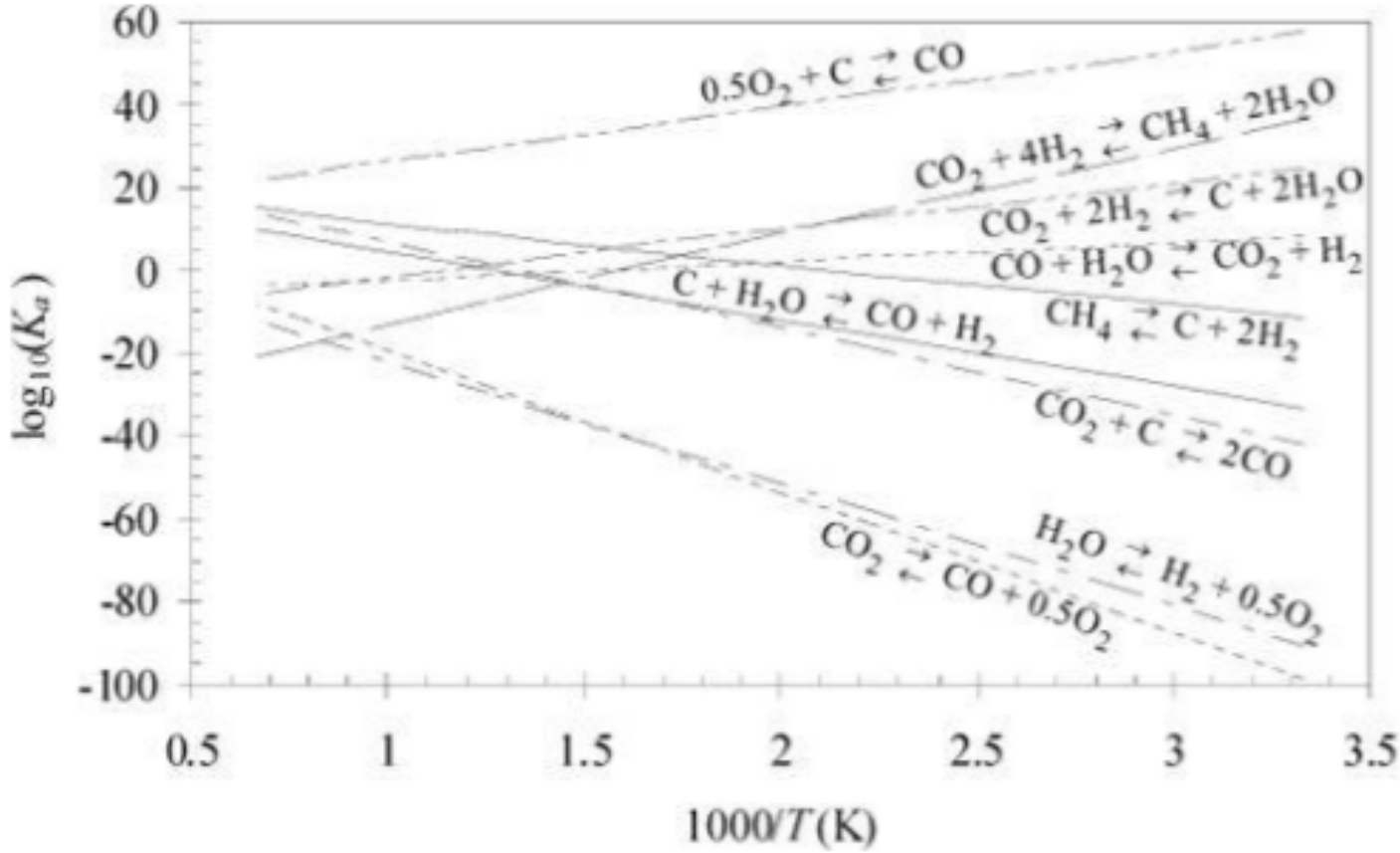


Figure 17.2. Graphical analysis of competing reactions.

nearly linear as would be approximated by the short-cut van't Hoff. Exothermic reactions have a negative slope and endothermic reactions have a positive slope. When dealing frequently with a set of

Reaction	Name	
$H_2O_{(g)} + C_{(s)} \rightleftarrows CO_{(g)} + H_{2(g)}$	Syngas	17.30
$CO_{2(g)} + 4H_{2(g)} \rightleftarrows CH_{4(g)} + 2H_2O_{(g)}$	Sabatier	17.31
$CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2(g)} + H_{2(g)}$	Water-gas shift	17.32
$CO_{2(g)} + C_{(s)} \rightleftarrows 2CO_{(g)}$	Boudouard	17.33
$0.5O_{2(g)} + C_{(s)} \rightleftarrows CO_{(g)}$	Partial oxidation	17.34
$CH_{4(g)} \rightleftarrows C_{(s)} + 2H_{2(g)}$	Methane pyrolysis	17.35
$CO_{2(g)} + 2H_{2(g)} \rightleftarrows C_{(s)} + 2H_2O_{(g)}$	Bosch	17.36
$H_2O_{(g)} \rightleftarrows H_{2(g)} + 0.5O_{2(g)}$	Water decomposition	17.37
$CO_{2(g)} \rightleftarrows CO_{(g)} + 0.5O_{2(g)}$	CO oxidation	17.38

17.10. Solving Equilibria for Multiple Reactions

Example 17.6. Simultaneous reactions that can be solved by hand

We can occasionally come across multiple reactions which can be solved without a computer. These are generally limited to textbook problems, but provide a starting point and test case for applying the general approach. Consider the two series/parallel gas phase reactions:

$$\begin{aligned} A + B &\rightleftarrows C + D & K_{a1} &= 2.667 \\ A + C &\rightleftarrows 2E & K_{a2} &= 3.200 \end{aligned}$$

The reactions are considered series reactions because *C* is a product of the first reaction, but a reactant in the second. They are parallel because *A* is a reactant in both reactions. The pressure in the reactor is 10 bar, and the feed consists of 2 moles of *A* and 1 mole of *B*. Calculate the composition of the reaction mixture if equilibrium is reached with respect to both reactions.

Solution

The material balance gives:

$$\begin{aligned} n_A &= 2 - \xi_1 - \xi_2 \\ n_B &= 1 - \xi_1 \\ n_C &= \xi_1 - \xi_2 \\ n_D &= \xi_1 \\ n_E &= 2\xi_2 \\ \hline n_T &= 3 \end{aligned}$$

$$
\begin{aligned}
n_A &= 2 - \xi_1 - \xi_2 \\
n_B &= 1 - \xi_1 \\
n_C &= \quad \xi_1 - \xi_2 \\
n_D &= \quad \xi_1 \\
n_E &= \qquad 2\xi_2 \\
\hline
n_T &= 3
\end{aligned}
$$

Note that for a physical solution, $0 \le \xi_1 \le 1$, $0 \le \xi_2 \le \xi_1$ to ensure that all mole numbers are positive. This reaction network is independent of P because $\Sigma \nu_i = 0$. The equilibrium constants are

$$\frac{y_C y_D P^2}{y_A y_B P^2} = 2.667 \text{ ; and } \frac{y_E^2 P^2}{y_A y_C P^2} = 3.200 \text{ ; or in terms of reaction coordinates,}$$

$$\frac{(\xi_1 - \xi_2)\xi_1}{(2 - \xi_1 - \xi_2)(1 - \xi_1)} = 2.667; \quad \frac{4\xi_2^2}{(2 - \xi_1 - \xi_2)(\xi_1 - \xi_2)} = 3.2$$

Solving the first equation for ξ_1 using the quadratic equation,

$$\xi_1 = 2.4 - 1.1\xi_2 - \sqrt{(2.4 - 1.1\xi_2)^2 - 1.6(2 - \xi_2)} \qquad 17.39$$

Similarly, for the second reaction,

$$\xi_2 = -4 + \sqrt{16 + 4\xi_1(2 - \xi_1)} \qquad 17.40$$

MATLAB Ex17_06.m.

We may now solve by trial and error. The procedure is: 1) guess ξ_1; 2) solve Eqn. 17.40 for ξ_2; 3) solve Eqn. 17.39 for ξ_1^{new}; 4) if $\xi_1^{new} \neq \xi_1$, go to step 1. The iterations are summarized below.

ξ_1	ξ_2	ξ_1^{new}
1.0000	0.4721	0.8355
0.8355	0.4600	0.8342
0.8342	0.4598	0.83415

Further iteration results in no further significant change.

These equations were amenable to the quadratic formula, but in general equilibrium criteria can be more complicated. Fortunately, standard programs available that are formulated to solve numerically multiple nonlinear systems of equations, so we can concentrate on applying the program to thermodynamics instead of developing the numerical analysis. Many software packages like Mathematica, Mathcad, MATLAB, and even Excel offer the capability to solve nonlinear systems of equations. Excel provides an especially convenient basis for illustrating the methods presented here.

Example 17.7. Solving multireaction equilibria with Excel

Methanol has a lower vapor pressure than gasoline. That can make it difficult to start a car fueled by pure methanol. One potential solution is to convert some of the methanol to methyl ether *in situ* during the start-up phase of the process (i.e., automobile). At a given temperature, 1 mole of MeOH is fed to a reactor at atmospheric pressure. It is assumed that only the two reactions given below take place. Compute the extents of the two simultaneous reactions over a range of temperatures from 200°C to 300°C. Also include the equilibrium mole fractions of the various species.

$$CH_3OH_{(g)} \rightleftarrows CO_{(g)} + 2H_{2(g)} \quad (1)$$

$$2CH_3OH_{(g)} \rightleftarrows CH_3OCH_{3(g)} + H_2O_{(g)} \quad (2)$$

Solution

A worksheet used for this solution is available in the workbook Rxns.xlsx.

Data for reaction (1) have been tabulated by Reactions Ltd.[a]—at 473.15 K, $\Delta H_T = 96{,}865$ J/mol and $\ln K_{a1,473} = 3.8205$. Over the temperature range of interest we can apply the shortcut van't Hoff equation assuming constant heat of reaction using the data at 200°C as a reference.

$$\ln K_{a1} = -\frac{96865}{8.314}\left(\frac{1}{T} - \frac{1}{473.15}\right) + 3.8205$$

Data for reaction (2) can be obtained from Appendix E for MeOH and water. For DME, the values are from Reid et al. (1987).[b]

Component		ΔH_f° kJ/mole	ΔG_f° kJ/mole
MeOH	−2	−200.94	−162.24
H_2O	1	−241.835	−228.614
MeOMe	1	−184.2	−113.0
		−24.155	−17.134

The shortcut van't Hoff equation for this reaction gives:

$$\text{at 298 K, } \ln K_{a2,298.15} = \frac{17134}{8.314(298)} = 6.9156$$

$$\ln K_{a2} = \frac{24,155}{8.314}\left(\frac{1}{T} - \frac{1}{298.15}\right) + 6.9156$$

Material balances:

Specie	Initial	Final
1 MeOH	1	$1-\xi_1-2\xi_2$
2 CO	0	ξ_1
3 H_2	0	$2\xi_1$
4 MeOMe	0	ξ_2
5 H_2O	0	ξ_2
Total	1	$1+2\xi_1$

Writing equations for reaction coordinates for reaction 1:

$$\frac{4\xi_1^3}{(1-\xi_1-2\xi_2)(1+2\xi_1)^2} = K_{a1} \Rightarrow \quad 4\xi_1^3 - K_{a1}\cdot(1-\xi_1-2\xi_2)\cdot(1+2\xi_1)^2 = 0 = \text{"}err1\text{"}$$

and for reaction 2:

$$\frac{\xi_2^2}{(1-\xi_1-2\xi_2)^2} = K_{a2} \Rightarrow \quad \xi_2^2 - K_{a2}\cdot(1-\xi_1-2\xi_2)^2 = 0 = \text{"}err2\text{"}$$

These two equations are solved simultaneously for ξ_1 and ξ_2. We have rearranged the objective functions to eliminate the ratios of ξ functions and use differences instead because the Excel Solver is much more robust with this mathematical form. The solution is implemented in the worksheet DUALRXN in Rxns.xlsx or Matlab Ex17_07.m. In the example here (see Fig. 17.3), the ΔC_P for both reactions is neglected. The equations derived above are entered directly into the cells, and the Solver tool is called.[c] You will need to designate one of the reaction equations as the target cell, the value of which is set to zero. The other reaction equation should be designated as a constraint (also set to zero). The cells with the reaction coordinates are the variables to be changed to obtain a solution. Under "options," you may want to specify the "conjugate" method, since that generally seems to converge more robustly for the reacting systems typically encountered. Generally, the Solver tool will require a reasonably accurate initial guess to keep it from converging on absurd results (e.g., $y_i < 0$). The initial guess can be easily developed by varying the values in the reaction-extent cells until the target cells move in the right direction. It sounds difficult, but the given worksheet will get you started, then you can experiment with initial guesses and experience how good your initial guesses need to be.

Rxns.xlsx, Worksheet DUALRXN of MATLAB Ex17_07.m.

Sample solution of two simultaneous reactions:

$$CH_3OH = CO + 2H_2$$

$$2CH_3OH = CH_3OCH_3 + H_2O$$

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

T(K)	473	493	513	533	553	573
K_{a1}	45.272	122.971	308.986	724.512	1597.281	3332.341
K_{a2}	27.4786	21.4179	17.0214	13.7627	11.3002	9.4069
ξ_1	0.9048	0.9651	0.9870	0.9951	0.9979	0.9991
ξ_2	0.0435	0.0158	0.0058	0.0022	0.0009	0.0004
y_1	0.0030	0.0012	0.0005	0.0002	0.0001	0.0000
y_2	0.3220	0.3294	0.3319	0.3328	0.3331	0.3332
y_3	0.6441	0.6587	0.6637	0.6656	0.6662	0.6665
y_4	0.0155	0.0054	0.0020	0.0007	0.0003	0.0001
y_5	0.0155	0.0054	0.0020	0.0007	0.0003	0.0001
Objective Functions						
err1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
err2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Figure 17.3. Worksheet DUALRXN from workbook Rxns.xlsx for Example 17.7 showing converged answers at several temperatures.

17.11. Driving Reactions by Chemical Coupling

Example 17.8. Chemical coupling to induce conversion

Example 17.3(a) considered use of steam as a diluent where the conversion was found to be 78% using 10 moles of steam as diluent and only 44% without the diluent. Consider the conversion by inducing higher conversion by replacing the 10 mole steam with 10 mole CO_2 which adds the water-gas shift reaction. For the water-gas shift written as $CO_{2(g)} + H_{2(g)} \rightleftarrows CO_{(g)} + H_2O_{(g)}$, $K_{a2} = 0.441$ at 900 K. What is the conversion of 1-butene at 900 K and 1 bar?

Solution

The butadiene reaction has been written in Example 17.3(a) and ξ_1 will be used for that 1-butene reaction and ξ_2 will be used for the water-gas shift reaction. The stoichiometry table is,

$n_{C_4H_8}$	$1 - \xi_1$
$n_{C_4H_6}$	ξ_1
n_{H_2}	$\xi_1 - \xi_2$
n_{CO_2}	$10 - \xi_2$
n_{CO}	ξ_2
n_{H_2O}	ξ_2
n_T	$11 + \xi_1$

$$K_{a1} = 0.242 = \left(\frac{\xi_1}{11+\xi_1}\right)\left(\frac{\xi_1 - \xi_2}{11+\xi_1}\right)P \Big/ \left(\frac{1-\xi_1}{11+\xi_1}\right) \text{ or}$$

$$0.242(1-\xi_1)(11+\xi_1) - (\xi_1)(\xi_1 - \xi_2) = 0 \qquad 17.41$$

$$K_{a2} = 0.441 = \frac{\xi_2^2}{(10-\xi_1)(\xi_1-\xi_2)} \text{ or } 0.441(10-\xi_1)(\xi_1-\xi_2) - \xi_2^2 = 0 \qquad 17.42$$

Physical limits for the reaction coordinates are $0 \le \xi_1 \le 1$ and $0 \le \xi_2 \le \xi_1$. Solving Eqns. 17.41 and 17.42 simultaneously, we find $\xi_1 = 0.949$ and $\xi_2 = 0.792$. Reviewing previous examples, the conversion at 1 bar was only 44% without an inert, increased to 78% with an inert, and increased to 95% using CO_2 to induce conversion by reaction coupling. Note that even though the water-gas shift equilibrium constant is not very large, it makes a significant difference in the conversion of 1-butene. Whether this is implemented depends on the feasibility of economically separating the products.

Chemical coupling can be classified in three ways: (1) induction, where a second reaction "pulls" a desired reaction by removing a product as in Example 17.8; (2) pumping, where the second reaction creates additional reactant for the desired reaction to "pump"; or (3) complex, where both induction and pumping are operative.[3] An example of chemical pumping starts with the reaction of methyl chloride and water to form methanol and hydrochloric acid.

$$CH_3Cl_{(g)} + H_2O_{(g)} \rightleftarrows CH_3OH_{(g)} + HCl_{(g)} \qquad K_{a,400} \sim 10^{-3} \qquad 17.43$$

By adding the methyl chloride synthesis reaction,

$$CH_{4(g)} + Cl_{2(g)} \rightleftarrows CH_3Cl_{(g)} + HCl_{(g)} \qquad K_a(400) \sim 10^{9} \qquad 17.44$$

This overall reaction becomes (adding the reactions, and take the product of the K_as):

$$CH_{4(g)} + Cl_{2(g)} + H_2O_{(g)} \rightleftarrows CH_3OH_{(g)} + 2HCl \qquad K_a(400) \sim 10^{6} \qquad 17.45$$

The large equilibrium constant of 17.44 forms $CH_3Cl_{(g)}$ readily, to pump reaction 17.43 via Le Châtelier's principle. Through chemical coupling, the prospects of developing a feasible reaction network are virtually endless.

17.12. Energy Balances for Reactions

Adiabatic Reactors

The energy balance for a steady-state adiabatic flow reactor is given in Eqn. 3.53 on page 118. The variables T^{out} and $\dot{\xi}$ from the energy balance also appear in the equilibrium constraint that will govern maximum conversion. Earlier, in Chapter 3, we considered the reaction coordinate to be specified. However, in a reaction-limited adiabatic reactor, we must solve the energy balance together with the equilibrium constraint to simultaneously determine the maximum conversion and adiabatic outlet temperature. Using the energy balance from Eqn. 3.53, do the following.

1. Write the energy balance, Eqn 3.53. Calculate the enthalpy of the inlet components at T^{in}.

2. Guess the outlet temperature, T^{out}. Calculate the enthalpy of the outlet components at T^{out}.

3. Determine $\dot{\xi}$ at T^{out} using the chemical equilibrium constant constraint.

4. Calculate $\dot{\xi}\Delta H_R^o$ for this conversion.

5. Check the energy balance for closure.

6. If the energy balance does not close, go to step 2.

As you might expect, this type of calculation lends itself to numerical solution, such as the Solver in Excel.

$$0 = \sum_{components} \dot{n}_i^{in} \int_{T_R}^{T^{in}} C_{P,i} dT - \sum_{components} \dot{n}_i^{out} \int_{T_R}^{T^{out}} C_{P,i} dT - \dot{\xi}\Delta H_R^o \qquad 3.53$$

Adiabatic Reactors

Suppose that a reactor is adiabatic $(\dot{Q} = 0)$. For the Heat of Reaction method, the energy balance becomes (for a reaction without phase transformations between T_R and the inlets or outlets),

$$0 = \sum_{components} \dot{n}_i^{in} \int_{T_R}^{T^{in}} C_{P,i} dT - \sum_{components} \dot{n}_i^{out} \int_{T_R}^{T^{out}} C_{P,i} dT - \dot{\xi} \Delta H_R^o \qquad 3.53$$

and as before, any latent heats must be added to the flow terms. An exothermic heat of reaction will raise the outlet temperature above the inlet temperature. For an endothermic heat of reaction, the outlet temperature will be below the inlet temperature. At steady state, the system finds a temperature where the heat of reaction is just absorbed by the enthalpies of the process streams. This temperature is known as the adiabatic reaction temperature, and the maximum reactor temperature change is dependent on the kinetics and reaction time, or on equilibrium. For fixed quantities and temperature of feed, Eqn. 3.53 involves two unknowns, T^{out} and $\dot{\xi}$, and, *if the reaction is not limited by equilibrium,* the kinetic model and reaction time determine these variables. If a reaction time is sufficiently large, equilibrium may be approached. Equilibrium reactors will be considered in Chapter 17.

Example 17.9. Adiabatic reaction in an ammonia reactor

Estimate the outlet temperature and equilibrium mole fraction of ammonia synthesized from a stoichiometric ratio of N_2 and H_2 fed at 400 K and reacted at 100 bar. How would these change if the pressure was 200 bar?

$$1/2\ N_{2(g)} + 3/2\ H_{2(g)} \rightleftarrows NH_{3(g)}$$

Solution

For a rough estimate we will use the shortcut approximation of temperature effects. Furthermore, we will assume $K_\phi \approx 1$. (Is this a good approximation or not?[a]) Therefore we obtain,

$$P\,K_a = y_{NH3} / [(y_{N2})\,(y_{H2})^3]^{1/2}$$

Basis: Stoichiometric ratio in feed.

$$\dot{n}_{N_2}^{out} = \frac{1}{2} - \frac{1}{2}\xi = \frac{1}{2}(1-\xi);\ \dot{n}_{H_2}^{out} = \frac{3}{2} - \frac{3}{2}\xi = \frac{3}{2}(1-\xi);\ \dot{n}_{NH_3}^{out} = \xi;\ \dot{n}_T^{out} = 2 - \xi \qquad 17.46$$

For the purposes of the example, the shortcut van't Hoff equation will be used to iterate on the adiabatic reactor temperature. However, the full van't Hoff method will be used to obtain $\Delta G^\circ_{T\text{near}}$ and $\Delta H^\circ_{T\text{near}}$ at an estimated nearby temperature T_{near} = 600K as suggested in Section 17.8. Then the shortcut van't Hoff equation will be used over a limited temperature range for less error. The energy balance will also use $\Delta H^\circ_{T\text{near}}$; we will create an energy balance path through T_{near} = 600K rather than 298.15K. We will compare the approximate answer with the full van't Hoff method at the end of the example.

For ammonia, $\Delta G^{\circ}_{f,298.15} = -16{,}401.3$ J/mol, $\Delta H^{\circ}_{f,298.15} = -45{,}940$ J/mol. Since the reactants are in the pure state, the respective reactant formation values are zero, and therefore the formation values for ammonia represent the standard state values for the reaction. Inserting the formation values along with the heat capacities into the detailed van't Hoff equation—one of the K_a calculators highlighted in the margin note to Example 17.4 on page 653 is used—at an assumed temperature of 600 K, the values obtained are $\Delta H^{\circ}_{600} = -51{,}413$ J/mol and $K_{a,600} = 0.0417659$. Then the shortcut van't Hoff in the vicinity will be

$$\ln\left(\frac{K_{a,T}}{0.0417659}\right) = \frac{51,413}{8.314}\left(\frac{1}{T} - \frac{1}{600}\right) \qquad 17.47$$

From an assumed value of T, this equation will provide the equilibrium constant. Some manipulation is necessary to obtain the material balance from $K_{a,T}$. Plugging the mole fraction expressions into Eqn. 17.17, and collecting the fractions 1/2 and 3/2,

$$PK_{a,T}\left(\frac{3^3}{2^4}\right)^{1/2} = \frac{\dot{\xi}(2-\dot{\xi})}{(1-\dot{\xi})^2} \Rightarrow 2\dot{\xi} - \dot{\xi}^2 = \frac{\sqrt{27}}{4}PK_{a,T}(1-\dot{\xi})^2$$

defining $M = \frac{\sqrt{27}}{4}PK_{a,T} \Rightarrow (M+1)\dot{\xi}^2 - 2(M+1)\dot{\xi} + M = 0 \Rightarrow \dot{\xi}^2 - 2\dot{\xi} + \left(\frac{M}{M+1}\right) = 0$

Applying the quadratic formula,

$$\dot{\xi} = \frac{2 \pm \sqrt{4 - 4M/(1+M)}}{2} = 1 - \sqrt{1 - M/(1+M)} \qquad 17.48$$

The strategy will be to guess T, and calculate $K_{a,T}$, M, and $\dot{\xi}$. $\dot{\xi}$ will be used in Eqn. 17.46 to perform the material balance. The material balance will be combined with the energy balance using the Heat of Reaction method (*cf.* Example 3.6), until the energy balance closes as represented by:

$$F(T) = \sum_{components} \dot{n}_i^{in} \int_{T_R}^{T^{in}} C_{P,i}\,dT - \sum_{components} \dot{n}_i^{out} \int_{T_R}^{T^{out}} C_{P,i}\,dT - \dot{\xi}\Delta H^{o}_{R} = 0 \qquad 17.49$$

The strategy will be to guess T, and calculate $K_{a,T}$, M, and ξ. ξ will be used in Eqn. 17.46 to perform the material balance. The material balance will be combined with the energy balance using the Heat of Reaction method (*cf.* Example 3.6), until the energy balance closes as represented by:

$$F(T) = \sum_{components} \dot{n}_i^{in} \int_{T_R}^{T^{in}} C_{P,i} dT - \sum_{components} \dot{n}_i^{out} \int_{T_R}^{T^{out}} C_{P,i} dT - \dot{\xi} \Delta H_R^o = 0 \qquad 17.49$$

Heat capacity integrals and the energy balance have been entered in the workbook Rxns.xlsx. At the initial guess of 600 K, the $F(T)$ of Eqn. 17.49 is 19.4 kJ. A converged result is found at 699 K shown in Fig. 17.4 and the $\xi = 0.33$, conversion of feed is 33%. At 200 bar, the answer is 739 K, and conversion is 38%.

Adiabatic Synthesis of Ammonia — Protected without a password

Feed Temperature (K)	400	
Outlet Temperature(K)	699.07	
P(bar)	100	
T_R(K)	600	K
Standard State Hrxn(T_R)	-51413	J/mol
Ka (T_R)	0.04177	
ln[K_a (T)]	-4.63623	
K_a at reaction T	0.00969	

	$\Delta H°_{f,298}$ (kJ/mol)	$\Delta G°_{f,298}$ (kJ/mol)	Heat Capacity Constants a	b	c	d
H2	0	0	2.71E+01	9.27E-03	-1.38E-05	7.65E-09
N2	0	0	3.12E+01	-1.36E-02	2.68E-05	-1.17E-08
NH3	-45.94	-16.4013	2.73E+01	2.38E-02	1.71E-05	-1.19E-08
Δ	-45.94	-16.4013				
M			1.259311 ξ		0.3347085	

	Inlet moles	Inlet H(J/mol)	Inlet totals	Outlet moles	Outlet H(J/mol)	Outlet totals
H2	1.5	-5854.46	-8781.7	0.99794	2915.96	2909.94
N2	0.5	-5927.19	-2963.59	0.33265	3016.21	1003.33
NH3	0	-8401.78	0	0.33471	4630.33	1549.81
Total			-11745.3			5463.08

Balance($\Sigma H^{in} n^{in} - \Sigma H^{out} n^{out} - \xi \Delta H$)=	6.665E-07 J

NOTE: The inlet moles cannot be changed without recalulating a formula for ξ

Use solver to set value of Balance to zero by adjusting Feed Temperature, Outlet Temperature, or P.

Figure 17.4. Display from Rxns.xlsx showing a converged answer.

Graphical Visualization of the Energy Balance

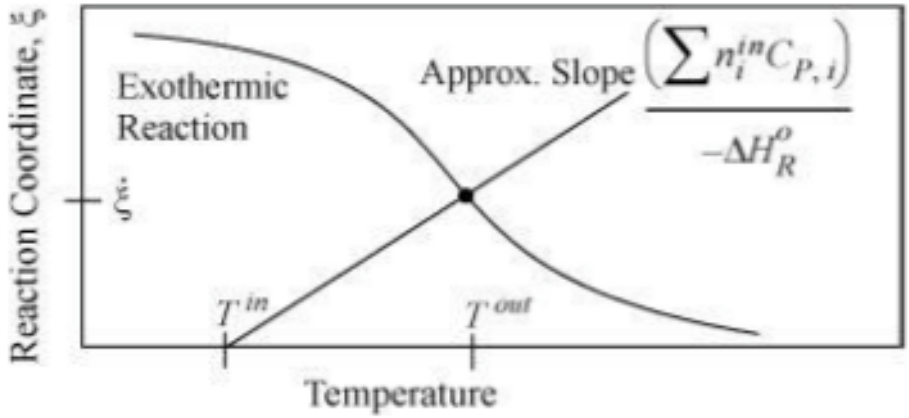


Figure 17.5. Approximate energy balance for an exothermic reaction. The dot simultaneously represents the equilibrium outlet conversion and reaction coordinate value at the adiabatic outlet temperature. The plot for an endothermic reaction will be a mirror image of this figure as explained in the text.

17.13. Liquid Components in Reactions

$$\frac{\hat{f}_i}{f_i^\circ} = a_i = \frac{x_i \gamma_i \varphi_i^{sat} P_i^{sat} \exp\left(\frac{V^L (P - P^{sat})}{RT}\right)}{\varphi_i^{sat} P_i^{sat} \exp\left(\frac{V^L (1 - P^{sat})}{RT}\right)} = x_i \gamma_i \exp\left(\frac{V^L (P - 1)}{RT}\right) \approx x_i \gamma_i \qquad 17.50$$

where P is expressed in bar, and the Poynting correction is often negligible, as shown. Another important change in working with liquid components is that in determining K_a liquid phase values are used for $\Delta G^o_{f,i}$, not the ideal gas values. Frequently these values are not available in the literature, so it is common to express equilibrium in terms of temperature-dependent correlations for K_a as described in Section 17.18.

Example 17.10. Oligomerization of lactic acid

Lactic acid is a bio-derived chemical intermediate produced in dilute solution by fermentation. Lactic acid is an α-hydroxy carboxylic acid. As an aqueous solution of lactic acid is concentrated by boiling off water, the carboxylic acid on one molecule reacts with a hydroxyl on another forming a dimer and releasing water. Denoting the "monomer" as L_1 and a dimer as L_2,

$$2L_1 \rightleftarrows L_2 + H_2O \qquad 17.51$$

The dimer has a hydroxyl and carboxylic acid that can react further to form trimer L_3,

$$L_2 + L_1 \rightleftarrows L_3 + H_2O \qquad 17.52$$

As more water is removed, the chain length grows, forming oligomers. The oligomerization can be represented by a recurring reaction for chain formation. Each liquid phase reaction that adds a lactic acid molecule can be modeled with a universal temperature-independent value of $K_a = 0.2023$ and the solutions may be considered ideal.[a] Commercial lactic acid solutions are sold based on the wt% of equivalent lactic acid monomer. So 100 g of 50 wt% solution would be composed of 50 g of lactic acid monomer and 50 g of water that react to form an equilibrium distribution of oligomers. The importance of including modeling of higher oligomers increases as the concentration of lactic acid increases.

a. Determine the mole fractions and wt% of species in a 50 wt% lactic acid solution in water where the distribution is approximated by only reaction 17.51.

b. Repeat the calculations for an 80 wt% lactic acid solution in water where both reactions are necessary to approximate the distribution.

💻 MATLAB Ex17_10.m may be helpful in calculations for this example.

Solution

a. Basis: 100 g total, 50 g of L_1 = (50 g)/(90.08 g/mol) = 0.555 mol initially, 50 g = (50 g)/(18.02 g/mol) = 2.775 mol water initially, and 3.330 mol total. The equilibrium relation is $K_a = 0.2023 = x_{L_2} x_{H_2O}/(x_{L_1})^2$. Since the total number of moles does not change with reaction, it cancels out of the ratio, and we can write $0.2023 = n_{L_2} n_{H_2O}/(n_{L_1})^2$. Introducing reaction coordinate,

$$0.2023 = \xi(2.775 + \xi)/(0.555\text{-}2\xi)^2 \qquad 17.53$$

Solving, we find, $\xi = 0.0193$, $x_{L_1} = (0.555 - 2(0.0193))/3.33 = 0.155$, $x_{L_2} = 0.0193/3.33 = 0.006$, $x_{H_2O} = (2.775 + 0.0193)/3.33 = 0.839$. Note that although the mole fraction of L_2 seems small, converting to wt%, the water content is (2.775 + 0.0193)(18.02 g/mol)/(100 g)·100% = 50.4 wt%, L_1 is (0.555 – 2(0.0193))(90.08 g/mol)/(100 g)·100% = 46.5 wt%, and L_2 is 0.0193(162.14 g/mol)/(100 g) · 100% = 3.1 wt%.

b. Basis: 100 g total, 80 g of L_1 = (80 g)/(90.08 g/mol) = 0.888 mol initially, 20 g = (20 g)/(18.02 g/mol) = 1.110 mol water initially, and 1.998 mol total. Moles are conserved in both reactions. The equilibrium relations are $K_{a1} = 0.2023 = x_{L_2} x_{H_2O}/(x_{L_1})^2$, $K_{a2} = 0.2023 = x_{L_3} x_{H_2O}/(x_{L_2} x_{L_1})$. Introducing the mole numbers and reaction coordinates,

$$0.2023 = (\xi_1 - \xi_2)(1.110 + \xi_1 + \xi_2)/(0.888 - 2(\xi_1) - \xi_2)^2 \qquad 17.54$$

$$0.2023 = \xi_2(1.110 + \xi_1 + \xi_2)/((\xi_1 - \xi_2)(0.888 - 2(\xi_1) - \xi_2)) \qquad 17.55$$

Solving simultaneously, $\xi_1 = 0.0907$, $\xi_2 = 0.009$, $x_{L_1} = (0.888 - 2(0.0907) - 0.009)/1.998 = 0.349$, $x_{L_2} = (0.0907 - 0.009)/1.998 = 0.041$, $x_{L_3} = 0.009/1.998 =$

0.0045, x_{H_2O} = (1.110 + 0.0907 + 0.009)/1.998 = 0.6055. The weight fractions are: (1.110 + 0.0907 + 0.009)(18.02 g/mol)/(100 g)·100% = 21.8 wt% water, (0.888 – 2(0.0907) – 0.009)(90.08 g/mol)/(100 g)·100% = 62.8 wt% L_1, and (0.0907 – 0.009)(162.14 g/mol)/(100 g)·100% = 13.2 wt% L_2, 0.009(234.2 g/mol)/(100 g)·100% = 2.1 wt% L_3.

17.14. Solid Components in Reactions

$$\frac{\hat{f}_i}{f_i^\circ} = a_i = \frac{x_i\gamma_i\varphi_i^{sat}P_i^{sat}\exp\left(\frac{V^S(P-P^{sat})}{RT}\right)}{\varphi_i^{sat}P_i^{sat}\exp\left(\frac{V^S(1-P^{sat})}{RT}\right)} = x_i\gamma_i\exp\left(\frac{V^L(P-1)}{RT}\right) \approx x_i\gamma_i \quad \text{solid solution} \quad 17.56$$

$$\frac{f_i}{f_i^\circ} = a_i = \frac{\varphi_i^{sat}P_i^{sat}\exp\left(\frac{V^S(P-P^{sat})}{RT}\right)}{\varphi_i^{sat}P_i^{sat}\exp\left(\frac{V^S(1-P^{sat})}{RT}\right)} = \exp\left(\frac{V^L(P-1)}{RT}\right) \approx 1 \quad \text{pure solid} \quad 17.57$$

Consider the reaction:

$$CO_{(g)} + H_{2(g)} \rightleftarrows C_{(s)} + H_2O_{(g)} \qquad 17.58$$

The carbon formed in this reaction comes out as coke, a solid which is virtually pure carbon and separate from the gas phase. What is the activity of this carbon? Since it is pure, $a_C = 1$. Would its presence in excess ever tend to push the reaction in the reverse direction? Since the activity of solid carbon is always 1 it cannot influence the extent of this reaction. How can we express these observations quantitatively? Eqn. 17.15 becomes

$$K_a = \exp\left[\frac{-\Delta G_T^\circ}{RT}\right] = \frac{\left(\hat{f}_{H2O}/f_{H2O}^\circ\right)\cdot 1.0}{\left(\hat{f}_{H2}/f_{H2}^\circ\right)\left(\hat{f}_{CO}/f_{CO}^\circ\right)} = \frac{y_{H2O}}{y_{H2}y_{CO}}\frac{1}{P} \qquad 17.59$$

To compute $\Delta G^o{}_T$ as a function of temperature, we apply the usual van't Hoff procedure. This means that $C_{P,c}$ can be treated just like C_P of the gaseous species.

Example 17.11. Thermal decomposition of methane

A 2-liter constant-volume pressure vessel is evacuated and then filled with 0.10 moles of methane, after which the temperature of the vessel and its contents is raised to 1273 K. At this temperature the equilibrium pressure is measured to be 7.02 bar. Assuming that methane dissociates according to the reaction $CH_{4(g)} \rightleftarrows C_{(s)} + 2H_{2(g)}$, compute K_a for this reaction at 1273 K from the experimental data.

Solution

$$K_a = \frac{\left(\hat{f}_{H_2}/f^{\circ}_{H_2}\right)^2 \cdot 1.0}{\left(\hat{f}_{CH_4}/f^{\circ}_{CH_4}\right)} = \frac{y^2_{H_2}}{y_{CH_4}} P$$

We can calculate the mole fractions of H_2 and CH_4 as follows. Since the temperature is high, the total number of moles finally in the vessel can be determined from the ideal gas law (assuming that the solid carbon has negligible volume): $n = PV/RT = 0.702 \cdot 2000/(8.314)(1273) = 0.1327$. Now assume that ξ moles of CH_4 reacted. Then we have the following total mass balance: $n_T = 0.10 + \xi$. Therefore, $\xi = 0.0327$ and

$$K_a = \frac{\left(\frac{2\xi}{0.1327}\right)^2 P}{\left(\frac{(0.1-\xi)}{0.1327}\right)} = \frac{0.493^2}{0.507} 7.02 = 3.37$$

Note that the equilibrium constant indicates that significant decomposition will occur (the reaction is exergonic, $K_a > 1$) and that graphite forms. Such behavior is known as "coking" and is common during industrial catalysis. Industrial application of catalysis often includes consideration of "regeneration'" of the catalyst by burning off the coke and using the heat of combustion elsewhere in the chemical plant.

17.15. Rate Perspectives in Reaction Equilibria

$$2A_{(g)} + B_{(g)} \rightleftarrows C_{(g)} + D_{(g)} \tag{17.60}$$

$$-r_{A,f} = k_f [A]^2 [B] \tag{17.61}$$

$$r_{A,r} = k_r [C][D] \tag{17.62}$$

$$r_{A,f} + r_{A,r} = -k_f [A]^2 [B] + k_r [C][D] = 0 \tag{17.63}$$

$$\frac{[C][D]}{[A]^2[B]} = \frac{k_f}{k_r} = \frac{(y_C P)(y_D P)}{(y_A P)^2 (y_B P)} (RT)^1 = K_a (RT)^{-\Sigma \nu_i} \tag{17.64}$$

17.17. Gibbs Minimization

$$\frac{G}{RT} = \sum_i n_i \left(\frac{\Delta G^o_{f,i}}{RT} \right) + \sum_i n_i \ln y_i P \qquad \text{(ig) 17.69}$$

To find equilibrium compositions, we just need to minimize Eqn. 17.69 by varying the mole numbers n_i of each component while simultaneously satisfying the atom balance. Note that the mole

Example 17.12. Butadiene by Gibbs minimization

Review Example 17.3(a) where steam is used to enhance conversion for 1-butene dehydrogenation. Gibbs energies of formation at 900 K for the hydrocarbons are summarized in that example.

The Gibbs energy of formation for water at 900 K is –198.204 kJ/mol. Vary conversion by selecting values of the reaction coordinate, calculating the Gibbs energy by Eqn. 17.69, and plotting the total Gibbs energy as a function of reaction coordinate. Demonstrate that Gibbs energy is minimized. Compare the equilibrium composition with that found in Example 17.3(a).

Solution

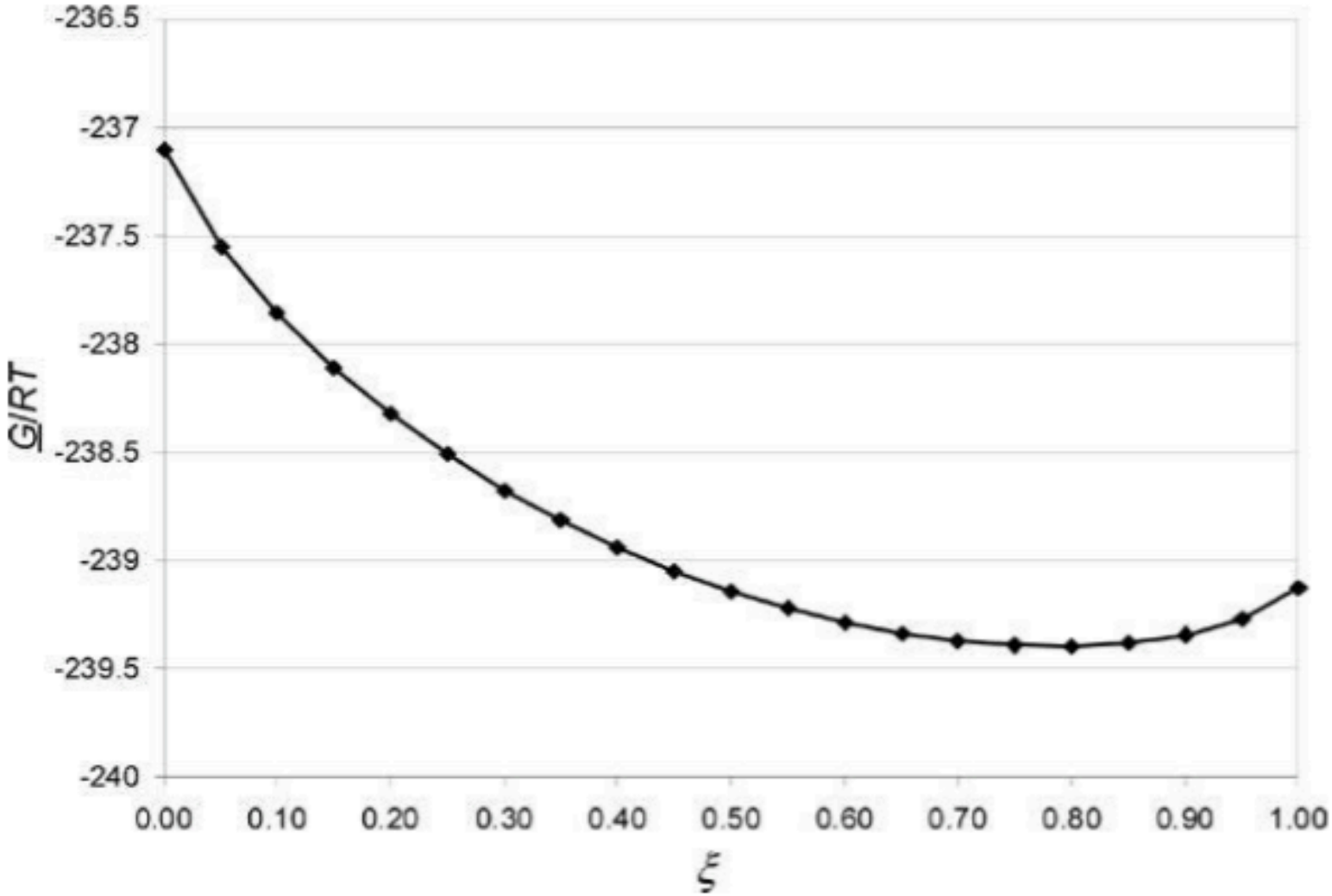
The initial moles of feed are 1 mol of 1-butene and 10 moles of steam. As an example calculation, select $\xi = 0.1$. Then the material balance provides, $n_{C_4H_8} = 0.9$, $n_{C_4H_6} = n_{H_2} = 0.1$, $n_{H_2O} = 10$. The mole fractions are $y_{C_4H_8} = 0.9/(0.9 + 2(0.1) + 10) = 0.08108$, $y_{C_4H_6} = y_{H_2} = 0.0090$, $y_{H_2O} = 0.9009$, and inserting the quantities into Eqn. 17.69, gives (inserting components in the order given above)

$$\frac{G}{RT} = \sum_i n_i\left(\frac{\Delta G^o_{f,i}}{RT}\right) + \sum_i n_i \ln y_i P$$

$$= 0.9\frac{(232854)}{8.3145(900)} + 0.1\frac{(243474)}{8.3145(900)} + 0.1(0) + 10\frac{(-198204)}{8.3145(900)} +$$

$$0.9\ln(0.08108 \cdot 1) + 0.1\ln(0.009 \cdot 1) + 0.1\ln(0.009 \cdot 1) = -237.858$$

Repeating the calculation at various extents of reaction results in the following plot:



Careful analysis would show that the minimum is at $\xi = 0.784$ as in the earlier example. Note the changes in values are a small percentage of the absolute values of the total Gibbs energy, a numerical observation that is important in setting up convergence in Excel.

Example 17.13. Direct minimization of the Gibbs energy with Excel

Apply the Gibbs minimization method to the problem of steam cracking of ethane at 1000 K and 1 bar where the ratio of steam to ethane in the feed is 4:1. Determine the distribution of C_1 and C_2 products, neglecting the possible formation of aldehydes, carboxylic acids, and higher hydrocarbons.

Solution

The solution is obtained using the worksheet GIBBSMIN contained in the workbook Rxns.xlsx (see Fig. 17.6).

Values for $\Delta G_f^\circ/RT$ are determined by using Kcalc.xls at 1000 K prior to using this spreadsheet.

	$\Delta G/RT$ 1000 K	Moles Fed	log(n_i)	n_i	y_i	$n_i(G_i/RT+\ln y_i)$
CH_4	2.456		-1.207132929	0.062067903	0.007	-0.15560
C_2H_4	14.27		-6.988574695	1.02666E-07	0.000	0.00000
C_2H_2	20.427		-9.430100874	3.71449E-10	0.000	0.00000
CO_2	-47.612		-0.258598372	0.55131731	0.062	-27.78131
CO	-24.089		0.141955136	1.386612582	0.156	-35.97632
O_2	0		-20.11203877	7.72612E-21	0.000	0.00000
H_2	0		0.729578484	5.36510819	0.604	-2.70090
H_2O	-23.178	4	0.179193408	1.510752799	0.170	-37.69136
C_2H_6	13.33	1	-6.000000002	1E-06	0.000	0.00000
Total				8.875859886		-104.30549

Balances	O-bal	4	4
	H-bal	14	14
	C-bal	2	2

Figure 17.6. Worksheet GIBBSMIN from the workbook Rxns.xlsx for Example 17.13.

Workbook, Rxns.xlsx, Worksheet GIBBSMIN, or MATLAB Gibbsmin.m.

Example 17.14. Pressure effects for Gibbs energy minimization

Apply the Gibbs energy minimization method to the methanol synthesis reaction using stoichiometric feed at 50 bar and 500 K. The reaction has been discussed in Example 17.1 on page 643, and in Section 17.5 on page 649.

Solution

It is convenient to first find $\Delta G^{o}_{f,1\ bar}$ and then find G_i/RT for each species, and then apply these values in the Gibbs minimization.

Compound	$\Delta G_{f,1\text{bar}}$(kJ/mole)	G_i/RT	
Methanol	−134.04	−134.04/8.314E-3/500 + ln(50)	= −28.332
CO	−155.38	−155.38/8.314E-3/500 + ln(50)	= −33.466
H_2	0	ln(50)	= 3.9120

For a basis of 1 mole CO: $n_{C,feed} = 1 = n_{CO} + n_{MeOH}$; $n_{H,feed} = 4 = 2n_{H_2} + 4n_{MeOH}$; $n_{O,feed} = n_{CO} + n_{MeOH}$; the C-balance is redundant with the O-balance so only one of these should be included as a constraint to improve convergence. Minimizing the Gibbs energy gives $y_{MeOH} = 0.42$ in agreement with the other method in Section 17.5 on page 649.

Note: The objective function changes weakly with mole numbers near the minimum, so tighten the convergence criteria or re-run the Solver after the first convergence. Convergence is sensitive to the initial guess. An initial guess which works is $\log(n_i) = -0.1$ for all i.

17.19. Simultaneous Reaction and VLE

Example 17.15. The solvent methanol process

In a process being considered for methanol synthesis, a heavy liquid phase is added directly to the reactor to absorb the heat of reaction. The liquid is then circulated through an external heat exchanger. Usually, the catalyst is slurried in the liquid phase. An alternative to be considered is putting the catalyst in a fixed bed and adding just enough liquid so that a fairly small amount of vapor is left at the end of the reaction. Supposing naphthalene was used as the heavy liquid phase, use the Peng-Robinson equation to obtain approximate vapor-liquid *K*-value expressions of the form

$$K_i = \frac{a_i 10^{[b_i(1-1/Tr)]}}{P}$$

for each component at a temperature of 200–250°C and pressures from 50–100 bar.[a] In the worksheet computations, you may assume the *K*-value of naphthalene to be negligible.

Solution

A worksheet used for this solution is available in the workbook Rxns.xlsx.

Computing the *K*-value would normally require calling the Peng-Robinson equation during every flash and reaction iteration. This approximate correlation enables you to use Excel to perform the calculations since it is independent of any external programming requirements. The correlation should be suitably accurate if you "guess" compositions for developing the correlation that are reasonably close to the compositions at the outlet of the reactor. We suggest a guess for feed composition of

{0.02, 0.10, 0.02, 0.035, 0.005, 0.82} for {CO, H_2, CO_2, methanol, water, and naphthalene}.

As an example of a way to develop a synthetic data base, perform flash calculations at 75 bars and temperatures of {200, 210, 220, 230, 240, 250} and the suggested feed composition. Tabulate the *K*-values for each component and plot them logarithmically with reciprocal temperature on the abscissa. Select a set of points, then select "add trendline" from the Chart menu. Select the options for a logarithmic fit, and displaying the equation on the chart. The coefficients of the equation give the *a* and *b* for the local "shortcut" correlation. (This step simplifies the implementation in Excel, but would be unnecessary if you were writing a dedicated program with access to a Peng-Robinson subroutine.)

Designating the solvent as component 6, the vapor-liquid *K*-values can be estimated as follows.

$$K_1 = (9.9/P) \cdot 10 \wedge (2.49(1-133/T))$$
$$K_2 = (970/P)$$
$$K_3 = (23/P) \cdot 10 \wedge (2.87(1-304/T))$$
$$K_4 = (61/P) \cdot 10 \wedge (3.64(1-513/T))$$
$$K_5 = (410/P) \cdot 10 \wedge (3.14(1-647/T))$$
$$K_6 \approx 0$$

Solve for the simultaneous reaction and phase equilibria at 240°C and $P = 100$ bars considering the following two reactions:

$$CO + 2H_2 \rightleftarrows CH_3OH \qquad (1)$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad (2)$$

Add moles of the heavy liquid until 9 moles of liquid is obtained for every mole of vapor *output*. The gases are fed in proportions 2:7:1 $CO:H_2:CO_2$.

Applying the shortcut van't Hoff equation (calculated at 503 K using $\ln K_a$ and $\Delta H°_R$, all reacting species gases),

$$\ln K_{a1} = 11746/T - 28.951$$

$$\ln K_{a2} = 6940/T - 24.206$$

Stoichiometry

Comp #		n_i^i	ν_{1i}	ν_{2i}	n_i^f
1	CO	2	−1	0	$2-\xi_1$
2	H_2	7	−2	−3	$7-2\xi_1-3\xi_2$
3	CO_2	1	0	−1	$1-\xi_2$
4	MeOH	0	1	1	$\xi_1+\xi_2$
5	H_2O	0	0	1	ξ_2
					$10-2\xi_1-2\xi_2$

Imagine performing a flash at each new extent of conversion:

$$n_T = n_{T0} - 2\xi_1 - 2\xi_2$$

$$z_i = (n_{0i} + \nu_{1i}\xi_1 + \nu_{2i}\xi_2)/n_T$$

$$y_i = \frac{z_i K_i}{K_i + \frac{L}{F}(1-K_i)}$$

Writing objective functions:

$$F(1) = err1 = (P^2 K_{a1} y_1 y_2^2 - y_4)$$

$$F(2) = err2 = (P^2 K_{a2} y_3 y_2^3 - y_4 y_5)$$

$$F(3) = 1 - \sum_i y_i$$

This worksheet is called SMPRXN. An example of the output from a feed of 2,7,1,0,0 mole each of CO, H_2, CO_2, CH_3OH, H_2O is shown in Fig. 17.7.

P(bar)	50					
T(K)	513	533	553	573	593	613
Ka_1	0.002347712	0.000994295	0.0004481	0.0002135	0.00010694	5.6037E-05
Ka_2	2.30525E-05	1.38758E-05	8.66454E-06	5.59125E-06	3.71625E-06	2.53674E-06
K_1	13.839	14.633	15.410	16.170	16.912	17.637
K_2	19.400	19.400	19.400	19.400	19.400	19.400
K_3	6.792	7.867	9.016	10.235	11.520	12.867
K_4	1.220	1.671	2.237	2.934	3.779	4.788
K_5	1.241	1.747	2.399	3.223	4.245	5.491
K_6	0.000	0.000	0.000	0.000	0.000	0.000
ξ_1	1.845	1.604	1.185	0.694	0.302	0.058
ξ_2	0.361	0.253	0.198	0.179	0.180	0.191
L/F	0.900	0.900	0.900	0.900	0.900	0.900
moles solv	16.368	23.680	32.671	41.780	48.658	52.826
y_1	0.043	0.082	0.129	0.168	0.192	0.206
y_2	0.692	0.691	0.691	0.693	0.693	0.692
y_3	0.125	0.116	0.101	0.087	0.080	0.076
y_4	0.120	0.097	0.069	0.043	0.025	0.014
y_5	0.020	0.014	0.010	0.009	0.010	0.012
err1	0.000	0.000	0.000	0.000	0.000	0.000
err2	0.000	0.000	0.000	0.000	0.000	0.000
$\Sigma(y_i)$	1.000	1.000	1.000	1.000	1.000	1.000
z_1	0.007	0.013	0.020	0.026	0.029	0.031
z_2	0.101	0.101	0.101	0.101	0.102	0.101
z_3	0.029	0.025	0.020	0.016	0.014	0.013
z_4	0.101	0.062	0.035	0.017	0.008	0.004
z_5	0.016	0.008	0.005	0.004	0.003	0.003

Figure 17.7. Worksheet SMPRXN from workbook Rxns.xlsx for Example 17.15 at several temperatures.

Example 17.16. NO_2 absorption[a]

The strength of concentrated acid which can be produced is limited by the back pressure of NO_2 over the acid leaving the absorbers. The overall reaction, obtained by adding reactions (*a*) and (*b*), is shown as (*c*). Here we assume that N_2O_4 is equivalent to $2NO_2$.

$$2NO_2 + H_2O \rightleftarrows HNO_3 + HNO_2 \quad (a)$$

$$3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O \quad (b)$$

$$3NO_{2(g)} + H_2O_{(l)} \rightleftarrows 2HNO_{3(l)} + NO_{(g)} \quad (c)$$

The gas entering the bottom plate of a nitric acid absorber contains 0.1 mole of NO per mole of mixture and 0.25 mole of NO_2 per mole mixture. The entering gas also contains 0.3 bar partial pressure of oxygen, in addition to inert gas. The total pressure is 1 bar. The acid made by the absorption operation contains 50% by weight of HNO_3, and the operation is isothermal at 86°F. Estimate the composition of the gas entering the second plate and the strength of the gas leaving the second plate.

Solution

(Basis: 1 mole gaseous feed)

Assume $y_w = y_{HNO_3} = 0$ and $x_{NO_2} = x_{NO} = 0$.

For liquid:

	In	Δ	Out
H_2O	W	$-\xi$	$W - \xi$
HNO_3	0	2ξ	2ξ
Total			$W + \xi$

For vapor:

	In	Δ	Out
NO_2	0.25	-3ξ	$0.25 - 3\xi$
NO	0.10	ξ	$0.10 + \xi$
O_2	0.30	0	0.30
I	0.35	0	0.35
Total			$1 - 2\xi$

$$K_a = \frac{\left(\hat{f}_{NO}/f^{\circ}_{NO}\right)\left(\hat{f}_{HNO_3}/f^{\circ}_{HNO_3}\right)^2}{\left(\hat{f}_{H_2O}/f^{\circ}_{H_2O}\right)\left(\hat{f}_{NO_2}/f^{\circ}_{NO_2}\right)^3} = \frac{y_{NO}(x_{HNO_3}\gamma_{HNO_3})^2}{y^3_{NO_2}(x_{H_2O}\gamma_{H_2O})}\frac{1}{P^2}$$

We can determine the mole fractions from the weight fractions:

$$x_{HNO_3} = (0.5/63)/[(0.5/63) + (0.5/18)] = 0.222$$

Noting from the *CRC Handbook*[b] the vapor pressure of HNO_3 is 64.6 mmHg, we can estimate the activity coefficients of HNO_3 and water from the *x-y* data in *The Chemical Engineers' Handbook*.[c]

$$\gamma_{HNO_3} = \frac{y_{HNO_3} P}{x_{HNO_3} P^{sat}_{HNO_3}} = \frac{0.39 \text{ mmHg}}{0.222 \cdot 64.6 \text{ mmHg}} = 0.027$$

$$\gamma_{H_2O} = \frac{10.7 \text{ mmHg}}{0.778 \cdot 23.8 \text{ mmHg}} = 0.5785$$

Gibbs energies of formation are available in Appendix E for all but nitrogen dioxide, and Reid et al.[d] give the standard Gibbs energy of formation as 52 kJ/mol and the standard heat of formation as 33.87 kJ/mol. Performing a shortcut calculation using Kcalc.xlsx, the equilibrium constant at 303.15 K is $K_a = 0.0054$.

At $P = 1$ bar:

$$K_a = \frac{y_{NO}(0.222 \cdot 0.027)^2}{y^3_{NO_2}(0.778 \cdot 0.5785)} = 0.0054 = \frac{y_{NO}}{y^3_{NO_2}} \cdot 0.00007983$$

Substituting for the reaction coordinate:

$$\frac{y_{NO}}{y^3_{NO_2}} = \frac{0.054}{0.00007983} = 67.65 = \left(\frac{0.1 + \xi}{1 - 2\xi}\right) \Big/ \left(\frac{0.25 - 3\xi}{1 - 2\xi}\right)^3$$

Solving the cubic equation, $\xi = 0.0431$.

$x_{HNO_3} = (2\xi/(W + \xi) = 2 \cdot 0.0431/(W + 0.0431) = 0.222$ tells us that

$W = -0.0431 + 2 \cdot 0.0431/0.222 = 0.345$ moles

So the composition of gas entering the second stage is $y_{NO} = 0.157$; $y_{NO_2} = 0.132$; $y_{O_2} = 0.328$; $y_I = 0.383$. Computations for further stages would be similar.

17.20. Summary

$$\ln\left(\frac{K_a}{K_{aR}}\right) = \frac{\Delta G_R^\circ}{RT_R} - \frac{\Delta G_T^\circ}{RT} = \frac{-\Delta H_R^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right) \qquad 17.29$$

$$K_a = \prod_i a_i^{\nu_i} = \prod_i \left[\frac{\hat{f}_i}{f_i^\circ}\right]^{\nu_i} \qquad 17.15$$

$$K_a = \prod_i (y_i P)^{\nu_i} \qquad \text{(ig) } 17.17$$