Contents

Chapter 1

Multireaction Equilibria and Calculations

1.1 Calculation of Equilibrium Constant At Other Than The Standard State

The basic formula to calculate the equilibrium constant is given as

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) \tag{1.1}$$

remember that the Gibbs free energy change is related to the enthalpy and entropy changes by

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \tag{1.2}$$

We can divide the dependence of the equilibrium constant on temperature into three contributions written as

$$K = K_0 K_1 K_2 \tag{1.3}$$

- The first factor K_0 represents the equilibrium constant at the reference temperature T_0 which is usually set to 298.15 K

$$K_0 = \exp\left(-\frac{\Delta_r G^\circ}{RT_0}\right) \tag{1.4}$$

- The second factor K_1 is a multiplier that supplies the major effect of temperature, such that the product $K_0 K_1$ is the equilibrium constant at temperature T when the heat of reaction is assumed independent of temperature:

$$K_1 = \exp\left[\frac{\Delta_r H^\circ}{RT_0}\left(1 - \frac{T_0}{T}\right)\right] \tag{1.5}$$

- The third factor K_2 accounts for the much smaller temperature influence resulting from the change of $\Delta_r H^\circ$ with temperature

$$K_2 = \exp\left[-\frac{1}{T}\int_{T_0}^{T}\frac{\Delta C_P^\circ}{R}dT + \int_{T_0}^{T}\frac{\Delta C_P^\circ}{R}\frac{1}{T}dT\right] \tag{1.6}$$

The heat capacities are usually expressed as polynomials or combination of polynomials and reciprocals in temperature e.g.,

$$\frac{C_P^\circ}{R} = A + BT + CT^2 + DT^{-2} \tag{1.7}$$

or

$$\frac{C_P^\circ}{R} = A + BT + CT^2 + DT^3 \tag{1.8}$$

where

$$\Delta C_P^\circ = \sum_j \nu_j C_{P,j}^\circ \tag{1.9}$$

Integration for equation 1.7 yields the following expression for K_2:

$$K_2 = \exp\left\{\Delta A\left[\ln\tau - \left(\frac{\tau-1}{\tau}\right)\right] + \frac{1}{2}\Delta B T_0\frac{(\tau-1)^2}{\tau} + \frac{1}{6}\Delta C T_0^2\frac{(\tau-1)^2(\tau+2)}{\tau} + \frac{1}{2}\frac{\Delta D}{T_0^2}\frac{(\tau-1)^2}{\tau^2}\right\} \tag{1.10}$$

where $\tau = T/T_0$.

Remember that the proper units to use in reaction calculation is moles. Hence, convert all heat capacity to per mole if they are given in other system of units such as gram or kilogram. Make sure to use consistent units with the universal gas constant you are using.

Example 1.1 Calculate the equilibrium constant for the vapor phase hydration of ethylene at 145 and 320°C.

$$C_2H_{4(g)} + H_2O_{(g)} \rightleftharpoons C_2H_5OH_{(g)} \tag{1.11}$$

Construct the reaction matrix with the heat capacity coefficients filled in from available data

	1 C_2H_4	2 H_2O	3 C_2H_5OH
ν_j	−1	−1	1
A	1.424	3.470	3.518
$B \times 10^3$	14.394	1.450	20.001
$C \times 10^6$	−4.392	0.000	−6.002
$D \times 10^{-5}$	0.000	0.121	−0.000
$\Delta_f G^\circ$	68,460	−228,572	−168,490
$\Delta_f H^\circ$	52,510	−241,818	−235,100

Calculate the standard heat of reaction and Gibbs free energy difference as

$$\begin{aligned}
\Delta &= (C_2H_5OH) - (C_2H_4) - (H_2O) \\
\Delta_{\text{rxn}} G^\circ &= -168490 - 68460 - (-228572) = -8378 \text{ J.mol}^{-1} \\
\Delta_{\text{rxn}} H^\circ &= -235100 - 52510 - (-241818) = -45\,792 \text{ J.mol}^{-1} \\
\Delta A &= 3.518 - 1.424 - 3.470 = -1.376 \text{ J.mol}^{-1}.\text{K}^{-1} \\
\Delta B &= (20.001 - 14.394 - 1.450) \times 10^{-3} = 4.157 \times 10^{-3} \\
\Delta C &= (-6.002 - -4.392 - 0.000) \times 10^{-6} = -1.61 \times 10^{-6} \\
\Delta D &= (-0.000 - 0.000 - 0.121) \times 10^{5} = -0.121 \times 10^{5}
\end{aligned}$$

Subsequently, calculate the various contributions to the equilibrium constant

$$\begin{aligned}
K_{0,418.15\text{K}} &= \exp\left(\frac{8378}{(8.314)(298.15)}\right) = 29.366 \\
K_{1,418.15\text{K}} &= \exp\left(\frac{-45792}{(8.314)(298.15)}\left(1 - \frac{298.15}{418.15}\right)\right) = 4.9844 \times 10^{-3} \\
K_{2,418.15\text{K}} &= 0.9860 \\
K_{418.15\text{K}} &= (29.366)(4.9844 \times 10^{-3})(0.9860) = 0.14432
\end{aligned}$$

Similar calculations at the other temperature will yield the following table

T(K)	τ	K_0	K_1	K_2	K
298.15	1	29.366	1	1	29.366
418.15	1.4025	29.366	4.985×10^{-3}	0.9860	1.443×10^{-1}
593.15	1.9894	29.366	1.023×10^{-4}	0.9794	2.942×10^{-3}

The following Matlab script calculates the results of this example and can be extended to any system with proper input modified.

```
%input parameters and defined constants
R = 8.314;
T0 = 298.15;
T = 145 + 273.15;
tau = T/T0

%stoichiometric numbers
nuj = [-1 -1 1];
% Gibbs free energy and enthalpy of formation at standard state
DG0 = [68460 -228572 -168490];
DH0=[52510 -241818 -235100];
%Heat capacity for each component with the form
% CP/R =A + BT + CT^2 + D/T^2
CP0 = [1.424 3.470 3.518
```

```
       14.394 1.450 20.001
       -4.392 0.000 -6.002
       0.000 0.121 -0.000];
CP0(2,:) = CP0(2,:)*1e-3;
CP0(3,:) = CP0(3,:)*1e-6;
CP0(4,:) = CP0(4,:)*1e5;
%Calculate the rxn changes at standard conditions
DG0Rxn = sum(nuj .* DG0)
DH0Rxn = sum(nuj .* DH0)
%Calculate the first two contributions K0 and K1
K0 = exp(-DG0Rxn/R/T0)
K1 = exp(DH0Rxn/R/T0*(1- 1/tau))
%Calcualte changes due to specific heat that leads to K2
DA = sum(nuj .* CP0(1,:))
DB = sum(nuj .* CP0(2,:))
DC = sum(nuj .* CP0(3,:))
DD = sum(nuj .* CP0(4,:))
t1 = DA*(log(tau) - (tau-1)/tau);
t2 = 0.5 * DB * T0 *(tau-1)^2/tau;
t3 = DC/6*T0^2*(tau-1)^2*(tau+2)/tau;
t4 = DD/2/T0^2*(tau-1)^2/tau^2;
K2 =exp(t1+t2+t3+t4)
K = K0 * K1 * K2

===========
Output
===========
tau =    1.4025
DG0Rxn =       -8378
DH0Rxn =      -45792
K0 =   29.3659
K1 =    0.0050
DA =   -1.3760
DB =    0.0042
DC = -1.6100e-006
DD =      -12100
K2 =    0.9862
K =    0.1443
```

1.2 Calculation of Composition From Knowledge Of The Equilibrium Constant

Example 1.2 A feed stock of pure n-butane is cracked at 750 K and 1.2 bar to produce olefins. Only two reactions have favorable equilibrium conversions at these conditions

$$C_4H_{10(g)} \rightleftharpoons C_2H_{4(g)} + C_2H_{6(g)} \tag{1.12}$$

$$C_4H_{10(g)} \rightleftharpoons C_3H_{6(g)} + CH_{4(g)} \tag{1.13}$$

If these reactions reach equilibrium, what is the product composition?(Example 13.12, page 503 in Smith, van Ness and Abbot, 6th edition)

Construct the reaction matrix to obtain the mole fractions as a function of the extent of reaction for each reaction. The reported equilibrium constants are: $K_1 = 3.856$ and $K_2 = 268.4$, respectively.

	j					
	1	2	3	4	5	
i	C_4H_{10}	C_2H_4	C_2H_6	C_3H_6	CH_4	ν_i
1	-1	1	1	0	0	1
2	-1	0	0	1	1	1

Next, obtain the mole fractions as a function of the extent of reactions from

$$y_j = \frac{n_{j,0} + \sum_{i=1}^{2} \nu_{ij}\xi_i}{n_0 + \sum_{i=1}^{2} \nu_i\xi_i} \tag{1.14}$$

where

$$n_0 = \sum_{j=1}^{5} n_{j,0} \tag{1.15}$$

$$
\begin{aligned}
n_0 &= 1+0+0+0+0 = 1 \text{ mole.}\\
y_1 = y_{C_4H_{10}} &= \frac{1-\xi_1-\xi_2}{1+\xi_1+\xi_2}\\
y_2 = y_{C_2H_4} &= \frac{\xi_1}{1+\xi_1+\xi_2}\\
y_3 = y_{C_2H_6} &= \frac{\xi_1}{1+\xi_1+\xi_2}\\
y_4 = y_{C_3H_6} &= \frac{\xi_2}{1+\xi_1+\xi_2}\\
y_5 = y_{CH_4} &= \frac{\xi_2}{1+\xi_1+\xi_2}
\end{aligned}
$$

The equilibrium constant is fundamentally defined in term of activities as

$$K = \prod_j a_j^{\nu_j} \tag{1.16}$$

Therefore, for the two reactions concerned, we have

$$
\begin{aligned}
K_1 &= a_{C_4H_{10}}^{-1} a_{C_2H_4} a_{C_2H_6} = \left(\frac{f}{f^\circ}\right)_{C_4H_{10}}^{-1} \left(\frac{f}{f^\circ}\right)_{C_2H_4} \left(\frac{f}{f^\circ}\right)_{C_2H_6}\\
K_2 &= a_{C_4H_{10}}^{-1} a_{C_3H_6} a_{CH_4} = \left(\frac{f}{f^\circ}\right)_{C_4H_{10}}^{-1} \left(\frac{f}{f^\circ}\right)_{C_3H_6} \left(\frac{f}{f^\circ}\right)_{CH_4}
\end{aligned}
$$

Subsequently, we cam use any simplifying assumptions that can be justified. The temperature is high enough and the total pressure (P_T) is low enough to justify the assumption of ideal gases at these conditions. The activity then can be defined in terms of partial pressures. The partial pressures are related to the total pressure by Dalton's law.

$$
\begin{aligned}
K_1 &= \left(\frac{P}{P^\circ}\right)_{C_4H_{10}}^{-1} \left(\frac{P}{P^\circ}\right)_{C_2H_4} \left(\frac{P}{P^\circ}\right)_{C_2H_6} = \left(\frac{yP_T}{P^\circ}\right)_{C_4H_{10}}^{-1} \left(\frac{yP_T}{P^\circ}\right)_{C_2H_4} \left(\frac{yP_T}{P^\circ}\right)_{C_2H_6}\\
K_2 &= \left(\frac{P}{P^\circ}\right)_{C_4H_{10}}^{-1} \left(\frac{P}{P^\circ}\right)_{C_3H_6} \left(\frac{P}{P^\circ}\right)_{CH_4} = \left(\frac{yP_T}{P^\circ}\right)_{C_4H_{10}}^{-1} \left(\frac{yP_T}{P^\circ}\right)_{C_3H_6} \left(\frac{yP_T}{P^\circ}\right)_{CH_4}
\end{aligned}
$$

Dropping out the reference pressures as their values are unity to obtain

$$
\begin{aligned}
\frac{K_1}{P_T} &= \frac{y_{C_2H_4} y_{C_2H_6}}{y_{C_4H_{10}}}\\
\frac{K_2}{P_T} &= \frac{y_{C_3H_6} y_{CH_4}}{y_{C_4H_{10}}}
\end{aligned}
$$

What we have managed to is to relate the known quantities: equilibrium constant and total pressure to the unknown quantities; the mole fractions. A further reduction is possible by substituting the mole fractions in terms of the extents of reaction to arrive finally at a system of two nonlinear equations in two unknowns.

$$\frac{K_1}{P_T} = \frac{\frac{\xi_1}{1+\xi_1+\xi_2}\frac{\xi_1}{1+\xi_1+\xi_2}}{\frac{1-\xi_1-\xi_2}{1+\xi_1+\xi_2}} = \frac{\xi_1^2}{(1+\xi_1+\xi_2)(1-\xi_1-\xi_2)}$$
$$\frac{K_2}{P_T} = \frac{\frac{\xi_2}{1+\xi_1+\xi_2}\frac{\xi_2}{1+\xi_1+\xi_2}}{\frac{1-\xi_1-\xi_2}{1+\xi_1+\xi_2}} = \frac{\xi_2^2}{(1+\xi_1+\xi_2)(1-\xi_1-\xi_2)}$$

To solve these equations, divide to eliminate the denominator

$$\frac{K_1}{K_2} = \frac{\xi_1^2}{\xi_2^2} \rightarrow \xi_2 = \sqrt{\frac{K_2}{K_1}}\xi_1 = \kappa\xi_1$$

substitute back to obtain after some reduction

$$\xi_1 = \left[\frac{\frac{K_1}{P}}{1+\frac{K_1}{P}(\kappa+1)^2}\right]^{1/2}$$

Numerical values are now ready to be substituted

$$\kappa = \sqrt{\frac{K_2}{K_1}} = \sqrt{\frac{268.4}{3.856}} = 8.343$$
$$\xi_1 = \left[\frac{\frac{K_1}{P}}{1+\frac{K_1}{P}(\kappa+1)^2}\right] = \left[\frac{\frac{3.856}{1.2}}{1+\frac{3.856}{1.2}(8.343+1)^2}\right]^{1/2} = 0.1068$$
$$\xi_2 = \kappa\xi_1 = (8.343)(0.1068) = 0.8914.$$

For this simple reaction scheme, analytical solution is possible. More often, numerical techniques are required for solution of multireaction-equilibrium problems. Substitute in the mole fractions to obtain the mole fractions at equilibrium

$$y_{\mathrm{C_4H_{10}}} = \frac{1-\xi_1-\xi_2}{1+\xi_1+\xi_2} = \frac{1-0.1068-0.8914}{1+0.1068+0.8914} = 0.0009$$
$$y_{\mathrm{C_2H_4}} = \frac{\xi_1}{1+\xi_1+\xi_2} = \frac{0.1068}{1+0.1068+0.8914} = 0.0534$$
$$y_{\mathrm{C_2H_6}} = \frac{\xi_1}{1+\xi_1+\xi_2} = 0.0534$$
$$y_{\mathrm{C_3H_6}} = \frac{\xi_2}{1+\xi_1+\xi_2} = \frac{0.8914}{1+0.1068+0.8914} = 0.4461$$
$$y_{\mathrm{CH_4}} = \frac{\xi_2}{1+\xi_1+\xi_2} = 0.4461.$$

A simple Matlab code to solve this problem directly yields four different solutions as below and only one of them is feasible which is the same as the analytical solution.

```
sol = solve('x1^2/(1-x1-x2)/(1+x1+x2)-3.856/1.2','x2^2/(1-x1-x2)/(1+x1+x2)-268.4/1.2')
```

```
sol =
    x1: [4x1 sym]
    x2: [4x1 sym]
>> sol.x1
ans =
  .10684161203330833258894635099873
  .13579263654174696244637684433921
 -.10684161203330833258894635099873
 -.13579263654174696244637684433921
>> sol.x2
ans =
  .89138059450799891857872452149436
 -1.1329192698127333932584203277471
 -.89138059450799891857872452149436
  1.1329192698127333932584203277471
```

Also, the following Matlab script is used to numerically solve for the solution and, again, it converges at the correct solution.

```
x0 = [0.5; 0.5];           % Make a starting guess at the solution
options = optimset('Display','iter','TolFun',1e-50, 'TolX',1e-15)
% Option to display output
[x,fval] = fsolve(@ExtentRxns,x0,options)  % Call optimizer

function F = ExtentRxns(x)
 K1 = 3.856;
 K2 = 268.4;
 P = 1.2;
 F = [x(1)^2 - (1 - x(1) - x(2))*(1 + x(1) + x(2))* K1/P;
      x(2)^2 - (1 - x(1) - x(2))*(1 + x(1) + x(2)) * K2/P];

=========
Output
=========
                                          Norm of      First-order   Trust-region
 Iteration  Func-count     f(x)            step         optimality    radius
     0          3             0.125                          114               1
     1          6        0.00693553        0.342784         26.7               1
     2          9       0.000277695        0.153336         5.35               1
     3         12     3.43963e-006        0.0511542        0.595               1
     4         15     1.44476e-009       0.00732322       0.0122               1
     5         18     3.01393e-016      0.000156503     5.57e-006              1
     6         21     1.63929e-028     7.15511e-008     5.55e-012              1
```

```
Optimization terminated: relative function value changing by less
 than max(options.TolFun^2,eps) and sum-of-squares of function
 values is less than sqrt(options.TolFun).
x =
    0.1068
    0.8914
 fval =
   1.0e-013 *
     0.0347
    0.1232
```

1.3 The Gibbs Free Energy Minimization as an Alternative to Equilibrium Constants

For gas phase reactions the following equations are used to obtain the vector of mole fractions at equilibrium. This vector of mole fractions is by definition the vector that minimizes the total Gibbs free energy of the system.

$$\Delta G^{\circ}_{fi} + RT \ln \frac{y_i \phi_i P}{P^{\circ}} + \sum_k \lambda_k a_{ik} = 0, \qquad i = 1, 2, ..., N \tag{1.17}$$

$$\sum_i n_i a_{ik} - A_k = 0, \qquad k = 1, 2, ..., w \tag{1.18}$$

Example 1.3 Calculate the equilibrium compositions at 1000 K and 1 bar of a gas phase system containing the species CH_4, H_2O, CO, CO_2, and H_2. In the initial unreacted state there are present 2 mole of CH_4 and 3 mole of H_2O. Values of ΔG°_{fi} at 1000 K are (in J/mole) given below.

			Element k		
			Carbon	Oxygen	Hydrogen
			A_k : atomic masses of k in the system		
			$A_1 = A_C = 2$	$A_2 = A_O = 3$	$A_3 = A_H = 14$
i	Species	ΔG°_{fi}	a_{ik} : atoms of k per molecule i		
1	CH_4	19720	1	0	4
2	H_2O	−192420	0	1	2
3	CO	−200240	1	1	0
4	CO_2	−395790	1	2	0
5	H_2	0	0	0	2

Write down the equilibrium equations for the five species as

$$\frac{19720}{RT} + \ln \frac{n_1}{\sum_i n_i} + \frac{\lambda_1}{RT} + \frac{4\lambda_3}{RT} = 0 \tag{1.19}$$

$$\frac{-192420}{RT} + \ln \frac{n_2}{\sum_i n_i} + \frac{\lambda_2}{RT} + \frac{2\lambda_3}{RT} = 0 \tag{1.20}$$

$$\frac{-200240}{RT} + \ln \frac{n_3}{\sum_i n_i} + \frac{\lambda_1}{RT} + \frac{\lambda_2}{RT} = 0 \tag{1.21}$$

$$\frac{-395790}{RT} + \ln \frac{n_4}{\sum_i n_i} + \frac{\lambda_1}{RT} + \frac{2\lambda_2}{RT} = 0 \tag{1.22}$$

$$\ln \frac{n_5}{\sum_i n_i} + \frac{2\lambda_3}{RT} = 0 \tag{1.23}$$

Then write down the atomic balances

$$n_1 + n_3 + n_4 = 2 \tag{1.24}$$

$$4n_1 + 2n_2 + 2n_5 = 14 \tag{1.25}$$

$$n_2 + n_3 + 2n_4 = 3 \tag{1.26}$$

Use Matlab to solve the set of eight equations.

```
natoms = 3;
nspecies = 5;
neq = natoms + nspecies;
x0 = [1 1 1 1 1 0.7 25 .2]';           % Make a starting guess at the solution
[x,fval] = fsolve(@MinimizeGibbsRxn,x0);  % Call optimizer
nt = sum(x(1:nspecies));
y(1:nspecies) = x(1:nspecies)/nt;
y = y'
lambda = x(nspecies+1:neq)

function F = MinimizeGibbsRxn(x)
R = 8.314;
T = 1000;
RT = R*T;
natoms = 3;
nspecies = 5;
neq = natoms + nspecies;
n0 = [2 3 0 0 0]';
aik = [1 0 4;0 1 2; 1 1 0;1 2 0;0 0 2];
DGF = [19720 -192420 -200240 -395790 0]';
Ak=[];
for k = 1:natoms
    Ak(k)=sum(n0 .* aik(:,k));
end
Ak = Ak';
nt = sum(x(1:nspecies));
for i = 1:nspecies
    lamx = 0.0;
    for k = 1:natoms
        lamx = lamx + x(k+nspecies)*aik(i,k);
    end
    F(i) = DGF(i)/RT + log(x(i)/nt) + lamx/RT;
end
for k = 1 : natoms
    F(nspecies+k) = sum(x(1:nspecies) .* aik(:,k)) - Ak(k);
```

```
end
=========
Output
=========
 Optimization terminated: first-order optimality is less than options.TolFun.
y =
    0.0196
    0.0980
    0.1743
    0.0371
    0.6711
lambda =
  1.0e+005 *
    0.0635
    2.0842
    0.0166
```