Example 8.1

Consider the reaction: \( \text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g}) \). If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the degree of conversion, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: \( C_p^i = a + bT + cT^2 + dT^3 + eT^{-2} \) (J/mol); T(K).

<table>
<thead>
<tr>
<th>Species</th>
<th>a</th>
<th>bx10^4</th>
<th>cx10^6</th>
<th>dx10^9</th>
<th>ex10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)H(_4)</td>
<td>20.691</td>
<td>205.346</td>
<td>-99.793</td>
<td>18.825</td>
<td>-</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>4.196</td>
<td>154.565</td>
<td>-81.076</td>
<td>16.813</td>
<td>-</td>
</tr>
<tr>
<td>C(_2)H(_5)OH</td>
<td>28.850</td>
<td>12.055</td>
<td>-</td>
<td>-</td>
<td>1.006</td>
</tr>
</tbody>
</table>

From standard tables \( \Delta H_{298}^0 \approx -52.7 \text{ KJ} \); \( \Delta G_{298}^0 = 14.5 \text{ KJ} \)

Now \( \Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^T \Delta C_p^o dT \) \hspace{1cm} (A)

\( \Delta C_p^o = \sum \alpha_i C_{p,i} = \Delta a + \Delta b T + \Delta c T^2 + \Delta d T^3 + \Delta e / T^2 \) \hspace{1cm} (B)

Where:

\( \Delta a = \sum \alpha_i a_i \), \( \Delta b = \sum \alpha_i b_i \), etc

For example \( \Delta a = 20.691 - 4.196 - 28.850 = -12.355 \)

\( \Delta b = (205.346 - 154.565 - 12.055) \times 10^{-3} = 3.8726 \times 10^{-2} \)

Similarly \( \Delta c = -1.8717 \times 10^{-5} \); \( \Delta d = 2.012 \times 10^{-9} \); \( \Delta e = -1.006 \times 10^{-5} \)

Putting B in A and integrating A we get:

\( \Delta H_T^0 = -50.944(\text{KJ}) - 12.3557 T + \frac{3.8726 \times 10^{-2}}{2} T^2 - \frac{1.8717 \times 10^{-5}}{3} T^3 + \frac{2.012 \times 10^{-9}}{4} T^4 + 1.006 \times 10^{-5}/T \)

\hspace{1cm} \text{…………..(C)}

By Vant Hoff equation:

\( \frac{d(\Delta G_T^0/RT)}{dT} = -\frac{\Delta H_T^0}{RT^2} \)

\( \Delta G_T^0/RT - \Delta G_{298}^0/RT(298) = -\int_{298}^T \frac{\Delta H_T^0}{RT^2} dT \) \hspace{1cm} \text{D}

We already know \( \Delta H_T^0 \) from (C); putting C in D and integrating we obtain:

\( \Delta G_T^0 = -50.944 + 12.3557 \ln T - \frac{3.8726 \times 10^{-2}}{2} T^2 + \frac{1.8718 \times 10^{-5}}{6} T^3 - \frac{2.012 \times 10^{-9} \times 4}{12} T^4 + \frac{1.006 \times 10^{-5} \times 2}{2T} + 56.681 T \)
Putting $T=500\,k$, $\Delta G^0_r = 11.43\,kJ$

**Example 8.2**
Consider the following reaction: $A(g) + B(g) = C(g) + 3D(g)$  \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]
Initially the following number of moles are introduced in the reactor. Obtain the mole fraction expressions in terms of reaction coordinate.

$n_{0,A} = 2\,\text{mol}, \quad n_{0,B} = 1\,\text{mol}, \quad n_{0,C} = 1\,\text{mol} \quad n_{0,D} = 4\,\text{mol}$

\[ \alpha \sum_{i=1}^{4} \alpha_i = -1 - 1 + 1 + 3 = 2 \]

\[ n_o = \sum_{i} n_{0,i} = 2 + 1 + 1 + 4 = 8 \]

\[ y_i = \frac{n_i}{n_o} = \frac{n_{0,i} + \alpha_i \xi}{n_o + \alpha \xi} \]

\[ y_A = \frac{2 - \xi}{8 + 2\xi} \quad y_B = \frac{1 - \xi}{8 + 2\xi} \quad y_C = \frac{1 + \xi}{8 + 2\xi} \quad y_{D_i} = \frac{4 + \xi}{8 + 2\xi} \]

**Example 8.3**
Consider the following simultaneous reactions. Express the reaction mixture composition as function of the reaction co-ordinates. All reactants and products are gaseous.

\[ A + B = C + 3D \quad \ldots(1) \]
\[ A + 2B = E + 4D \quad \ldots(2) \]

Initial number of moles:

$n_{0,A} = 2\,\text{mol}; \quad n_{0,B} = 3\,\text{mol}$

Let the reaction co-ordinates for each reaction be $\xi_1$ and $\xi_2$ respectively.

<table>
<thead>
<tr>
<th>$j$</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>$\alpha_j = \sum \alpha_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>-2</td>
<td>-2</td>
<td>0</td>
<td>4</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

\[ y_i = \frac{n_{io} + \sum_{j} \alpha_{ij} \xi_j}{n_o + \sum_{j} \alpha_j \xi_j} \; ; \; n_o = 2 + 3 = 5 \]

\[ y_A = \frac{2 - \xi_1 - \xi_2}{5 + 2\xi_1 + 2\xi_2} \quad y_B = \frac{3 - \xi_1 - 2\xi_2}{5 + 2\xi_1 + 2\xi_2} \quad y_C = \frac{\xi_1}{5 + 2\xi_1 + 2\xi_2} \]
\[ y_D = \frac{3\xi_1 + 4\xi_2}{5 + 2\xi_1 + 2\xi_2}; \quad y_E = \frac{\xi_2}{5 + 2\xi_1 + 2\xi_2} \]

**Example 8.4**

Consider the reaction: \( \text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g}) \). If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the equilibrium constant, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: \( C_p^{i\beta} = a + bT + cT^2 + dT^3 + eT^{-2} \) (J/mol); T(K).

<table>
<thead>
<tr>
<th>Species</th>
<th>a</th>
<th>bx10^3</th>
<th>cx10^6</th>
<th>dx10^9</th>
<th>ex10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_2H_4</td>
<td>20.691</td>
<td>205.346</td>
<td>-99.793</td>
<td>18.825</td>
<td>-</td>
</tr>
<tr>
<td>H_2O</td>
<td>4.196</td>
<td>154.565</td>
<td>-81.076</td>
<td>16.813</td>
<td>-</td>
</tr>
<tr>
<td>C_2H_5OH</td>
<td>28.850</td>
<td>12.055</td>
<td>-</td>
<td>-</td>
<td>1.006</td>
</tr>
</tbody>
</table>

From standard tables \( \Delta H^0_{R,298} \approx -52.7 \text{ KJ}; \Delta G^0_{R,298} = 14.5 \text{ KJ} \)

Now \( \Delta H^0_T = \Delta H^0_{R,298} + \int_{298}^{T} \Delta C_p \text{d}T \)  ------------------------- (A)

\[ \Delta C_p = \sum \alpha_i C_{p,i}^0 = \Delta a + \Delta bT + \Delta CT^2 + \Delta dT^3 + \Delta e / T^2 \]  ---------------- (B)

Where:
\[ \Delta a = \sum \alpha_i a_i; \Delta b = \sum \alpha_i b_i; \text{etc} \]

For example \( \Delta a = 20.691 - 4.196 - 28.850 = -12.355 \)

\( \Delta b = (205.346 - 154.565 - 12.055) \times 10^{-3} = 3.8726 \times 10^{-2} \)

Similarly \( \Delta c = -1.8717 \times 10^{-5} ; \Delta d = 2.012 \times 10^{-9} ; \Delta e = -1.006 \times 10^5 \)

Putting B in A and integrating A we get:

\[ \Delta H^0_T = -50.944(\text{KJ}) - 12.355T + \frac{3.8726 \times 10^{-2}}{2} T^2 - \frac{1.8717 \times 10^{-5}}{3} T^3 + \frac{2.012 \times 10^{-9}}{4} T^4 + 1.006 \times 10^5 / T \]  

\[ \Delta H^0_T = \frac{d(\Delta G^0_T / RT)}{dT} = -\Delta H^0_T / RT^2 \]

\[ \Delta G^0_T / RT = \Delta G^0_{298} / R(298) = -\int_{298}^{T} \Delta H^0_T / RT^2 dT \quad \text{-----------------------------} \text{ D} \]

We already know \( \Delta H^0_T \) from (C); putting C in D and integrating we obtain:
\[ \Delta G_f^0 = -50.944 + 12.355T \ln T - \frac{3.8726 \times 10^{-2}}{2} T^2 + \frac{1.8718 \times 10^{-5}}{6} T^3 - \frac{2.012 \times 10^{-9}}{12} T^4 + \frac{1.006 \times 10^3}{2T} + 56.681T \]

Putting \( T=500k \), \( \Delta G_f^0 = 11.43kJ \)

Hence \( K_{500} = \exp \left[ \frac{-1143}{8.314 \times 1000} \right] = 0.064 \)

**Example 8.5**

Consider the reaction: \( \text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g}) \). If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the degree of conversion, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: \( C_p^i = a + bT + cT^2 + dT^3 + eT^{-2} \) (J/mol); T(K).

<table>
<thead>
<tr>
<th>Species</th>
<th>( a )</th>
<th>( b \times 10^3 )</th>
<th>( c \times 10^6 )</th>
<th>( d \times 10^9 )</th>
<th>( e \times 10^{-5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>20.691</td>
<td>205.346</td>
<td>-99.793</td>
<td>18.825</td>
<td>-</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>4.196</td>
<td>154.565</td>
<td>-81.076</td>
<td>16.813</td>
<td>-</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{OH} )</td>
<td>28.850</td>
<td>12.055</td>
<td>-</td>
<td>-</td>
<td>1.006</td>
</tr>
</tbody>
</table>

From standard tables \( \Delta H^0_{R,298} \approx -52.7 \text{ KJ} ; \Delta G^0_{R,298} = 14.5 \text{ KJ} \)

Now \( \Delta H_f^0 = \Delta H_{298}^0 + \int_{298}^T \Delta C_p^0 dT \)  

\[ \Delta C_p^0 = \sum \alpha_i \Delta C_p^{0i} = \Delta a + \Delta b T + \Delta c T^2 + \Delta d T^3 + \Delta e / T^2 \]  

Where:

\( \Delta a = \sum \alpha_i a_i \), \( \Delta b = \sum \alpha_i b_i \), etc

For example \( \Delta a = 20.691 - 4.196 - 28.850 = -12.355 \)

\( \Delta b = (205.346 - 154.565 - 12.055) \times 10^{-3} = 3.8726 \times 10^{-2} \)

Similarly \( \Delta c = -1.8717 \times 10^{-5} \); \( \Delta d = 2.012 \times 10^{-9} \); \( \Delta e = -1.006 \times 10^5 \)

Putting B in A and integrating A we get:

\[ \Delta H_f^0 = -50.944(\text{KJ}) - 12.355T + \frac{3.8726 \times 10^{-2}}{2} T^2 - \frac{1.8717 \times 10^{-5}}{3} T^3 + \frac{2.012 \times 10^{-9}}{4} T^4 + 1.006 \times 10^5 / T \]  

..........(C)

By Vant Hoff equation:

\[ \frac{d(\Delta G_f^0 / RT)}{dT} = -\frac{\Delta H_f^0}{RT^2} \]
\[
\frac{\Delta G^0}{RT} - \frac{\Delta G_{m}^{0}}{R(298)} = -\int_{298}^{T} \frac{\Delta H^0}{RT^2} dT
\]

We already know \( \Delta H^0 \) from (C); putting C in D and integrating we obtain:

\[
\Delta G^0 = -50.944 + 12.355T \ln T - \frac{3.8726 \times 10^{-2}}{2} T^2 + \frac{1.8718 \times 10^{-2}}{6} T^3 - \frac{2.012 \times 10^{-9}}{12} T^4 + \frac{1.006 \times 10^5}{2T} + 56.681T
\]

Putting \( T = 500 \text{k} \), \( \Delta G^0 = 11.43 \text{kJ} \)

Hence \( K_{500} = \exp \left[ -1143 / 8.314 \times 1000 \right] = 0.064 \)

\( \alpha = \sum \alpha_i = 1 - 1 - 1 = -1 \)

\[
\therefore K = K_{\varphi} K_y P^\alpha ; K_{\varphi} = 1 \text{(since ideal gas assumption is made)}
\]

\( P = 40 \text{bar} \)

<table>
<thead>
<tr>
<th>Component</th>
<th>( n_i )</th>
<th>( n_{\text{exit}} )</th>
<th>( \chi_{i}(\text{exit}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2H4</td>
<td>1</td>
<td>1 - ( \varepsilon )</td>
<td>((1-\varepsilon)/(2-\varepsilon))</td>
</tr>
<tr>
<td>H2O</td>
<td>1</td>
<td>1 - ( \varepsilon )</td>
<td>((1-\varepsilon)/(2-\varepsilon))</td>
</tr>
<tr>
<td>C2H5OH</td>
<td>0</td>
<td>( \varepsilon )</td>
<td>((\varepsilon)/(2-\varepsilon))</td>
</tr>
</tbody>
</table>

\( n_i \) (at exit) = 2 - \( \varepsilon \)

\[
\therefore K = K_y = \frac{y_{C_2H_5OH}}{y_{C_2H_4}} = \frac{\xi/(2-\xi)}{(1-\xi)/(2-\xi)} = \frac{\xi(2-\xi)}{(1-\xi)^2}
\]

Now \( K = K_{\varphi} K_y P^\alpha = (1) K_y P^{-1} \)

\[
\therefore K_y = 40 K ; K_y = \xi(2-\xi)/(1-\xi)^2
\]

\[
\therefore K_y = \frac{\xi(2-\xi)}{(1-\xi)^2} = 40 \times K_{500} = 40 \times 0.064 = 2.56
\]

On solving \( \xi = 0.47 \)

Thus \( y_{C_2H_4} = (1-\xi)/(2-\xi) = 0.3464 = y_{H_2O} \)

\( y_{C_2H_5OH} = \xi/(2-\xi) = 0.3072 \)

**Example 8.6**

The following two independent reactions occur in the steam cracking of methane at 1000 K and 1 bar: \( \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g) \); and \( \text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g) \).

Assuming ideal gas behaviour determine the equilibrium composition of the gas leaving the
reactor if an equimolar mixture of CH\(_4\) and H\(_2\)O is fed to the reactor, and that at 1000K, the equilibrium constants for the two reactions are 30 and 1.5 respectively.

Let \(\xi_1\) and \(\xi_2\) be the reaction co-ordinate for the two reactions, we have

<table>
<thead>
<tr>
<th>Comp</th>
<th>(n_{i0})</th>
<th>(n_{exit})</th>
<th>(y_{exit})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>1</td>
<td>1 - (\xi_1)</td>
<td>((1 - \xi_1) / 2(1 + \xi_1))</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>1</td>
<td>1 - (\xi_1) - (\xi_2)</td>
<td>((1 - \xi_1 - \xi_2) / 2(1 + \xi_1))</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>(\xi_1 - \xi_2)</td>
<td>((\xi_1 - \xi_2) / 2(1 + \xi_1))</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0</td>
<td>(\xi_2)</td>
<td>(\xi_2 / 2(1 + \xi_1))</td>
</tr>
<tr>
<td>H(_2)</td>
<td>0</td>
<td>3 (\xi_1 + \xi_2)</td>
<td>((3 \xi_1 + \xi_2) / 2(1 + \xi_1))</td>
</tr>
</tbody>
</table>

Total moles at equilibrium: \(2(1 + \xi_1)\)

K = \(K_\varphi K_y P^\alpha\) (for each reaction); \(K_\varphi = 1.0\) (ideal gas assumption); \(P = 1\) bar

Thus

\[
K_1 = \frac{(\xi_1 - \xi_2)^2}{2(1 + \xi_1)} \left(\frac{(3\xi_1 + \xi_2)^2}{2(1 + \xi_1)}\right) = 30 \quad \text{A}
\]

\[
K_2 = \frac{(3\xi_1 + \xi_2)^2}{(\xi_1 - \xi_2)^2(1 - \xi_1)(1 - \xi_1 - \xi_2)} = 1.5 \quad \text{B}
\]

A and B needs to be solved simultaneously; a simple way to do this is to

(i) Assume \(\xi_2\), calculate \(\xi_1\) using B

(ii) Use \(\xi_1\) and \(\xi_2\) in A to check if \(K_1 = 30\)

(iii) If \(K_1 \neq 30\), assume new \(\xi_1\) and go to step 1

Using the above algorithm, one finally obtains: \(\xi_1 = 0.7980\), \(\xi_2 = 0.0626\).

Thus: \(y_{CO_2} = 0.0174, y_{CH_4} = 0.0562, y_{H_2O} = 0.0388, y_{CO} = 0.2045, y_{H_2} = 0.6831\)

**Example 8.7**

The gas n-pentane (1) is known to isomerise into neo-pentane (2) and iso-pentane (3) according to the following reaction scheme: \(P_1 \rightleftharpoons P_2; P_2 \rightleftharpoons P_3; P_3 \rightleftharpoons P_1\). 3 moles of
pure n-pentane is fed into a reactor at 400\(^0\)K and 0.5 atm. Compute the number of moles of each species present at equilibrium.

<table>
<thead>
<tr>
<th>Species</th>
<th>(\Delta G^\circ) at 400(^0)K (Cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_1)</td>
<td>9600</td>
</tr>
<tr>
<td>(P_2)</td>
<td>8900</td>
</tr>
<tr>
<td>(P_3)</td>
<td>8200</td>
</tr>
</tbody>
</table>

We use here the method of undetermined Lagrangian Multipliers.

The set of equation to be solved are:

\[
A_c = 15, A_H = 36
\]

For \(P_1\):

\[
\frac{9600}{RT} + \ln\left(\frac{n_1}{\sum n_i}\right) + \frac{5\lambda_c}{RT} + \frac{12\lambda_H}{RT} = 0
\]

For \(P_2\):

\[
\frac{8900}{RT} + \ln\left(\frac{n_2}{\sum n_i}\right) + \frac{5\lambda_c}{RT} + \frac{12\lambda_H}{RT} = 0
\]

For \(P_3\):

\[
\frac{8200}{RT} + \ln\left(\frac{n_3}{\sum n_i}\right) + \frac{5\lambda_c}{RT} + \frac{12\lambda_H}{RT} = 0
\]

Atomic mass balance for C: \(5(n_1 + n_2 + n_3) = 15\)

For H: \(12(n_1 + n_2 + n_3) = 36\)

\(n_1 + n_2 + n_3 = 10\)

Alternately:

\[
\frac{9600}{RT} + \ln y_1 + \frac{5\lambda_c}{RT} + \frac{12\lambda_H}{RT} = 0 \quad \text{............... (A)}
\]

\[
\frac{8900}{RT} + \ln y_2 + \frac{5\lambda_c}{RT} + \frac{12\lambda_H}{RT} = 0 \quad \text{............... (B)}
\]

\(T = 400K\)

\[
\frac{8200}{RT} + \ln y_3 + \frac{5\lambda_c}{RT} + \frac{12\lambda_H}{RT} = 0 \quad \text{............... (C)}
\]

and \(y_1 + y_2 + y_3 = 1 \quad \text{............... (D)}\)

It follows from (A) – (C), \(y_2 / y_1 = 2.41; y_3 / y_2 = 2.41\)

Using eqn. (D) \(y_1 = 0.108, y_2 = 0.29, y_3 = 0.63\)

**Example 8.8**
Consider the liquid phase reaction: \( A(l) + B(l) \rightarrow C(l) + D(l) \). At 50\(^\circ\)C, the equilibrium constant is 0.09. Initial number of moles, \( n_{A,0} = 1 \) mole; \( n_{B,0} = 1 \) mol. Find the equilibrium conversion. Assume ideal solution behaviour.

\[
\therefore K = \left( x_i \gamma_i \right)^\eta \exp \left( \frac{(P-1) \sum \gamma_i V_i}{RT} \right)
\]

Also, \( \gamma_i = 1 \) (ideal solution)

Hence \( K = \pi \left( x_i \right)^\gamma \)

\( x_A = x_B = (1-\xi)/2 \); \( x_C = x_D = \xi / 2 \)

\[
\therefore K = x_C x_D / x_A x_B = [\xi/(1-\xi)]^2
\]

\( \Rightarrow 0.09 = [\xi/(1-\xi)]^2 \)

Thus, \( \xi_e = 0.23 \)

**Example 8.9**

Consider the following reaction: \( A(s) + B(g) \rightarrow C(s) + D(g) \). Determine the equilibrium fraction of B which reacts at 500\(^\circ\)C if equal number of moles of A and B are introduced into the reactor initially. The equilibrium constant for the reaction at 500\(^\circ\)C is 2.0.

The reaction is:

\( A(s) + B(g) \rightarrow C(s) + D(g) \); basis 1 mole of A & B each initially

\[
K = \hat{a}_C \hat{a}_D / \hat{a}_A \hat{a}_B
\]

For solids: \( \hat{a} = 1 \)

Thus:

\[
K = \hat{a}_D / \hat{a}_B = K_y K_y P^\alpha ; \alpha = 0, \text{ and } K_y = 1
\]

\( \therefore K = K_y \)

If one assumes equimolar feed of reactants:

\( y_B = (1-\xi) \); \( y_D = \xi \)

\( \therefore K = K_y = 2.0 = \frac{\xi}{1-\xi} \Rightarrow \xi = 0.67 \)

Thus 67\% of B reacts.