General Thermodynamics
for Process Simulation

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Four Criteria for Equilibria

<table>
<thead>
<tr>
<th>Situation</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^\alpha = T^\beta$</td>
<td>Thermal Equilibrium</td>
</tr>
<tr>
<td>$P^\alpha = P^\beta$</td>
<td>Mechanical Equilibrium</td>
</tr>
<tr>
<td>$\mu_i^y = \mu_i^l$, $\mu_i^{l1} = \mu_i^{l2}$</td>
<td>Phase Equilibria (VLE, LLE)</td>
</tr>
</tbody>
</table>
| \[
\left( \frac{\partial G}{\partial \xi} \right)_{T,P} = 0
\] | Chemical Equilibrium |

Fugacity (or chemical potential) is defined as an escaping tendency of a component ‘$i$’ in a certain phase into another phase.
Basic Phase Equilibria Relations

Vapor-liquid equilibrium calculations

The basic relationship for every component in vapor-liquid equilibrium is:

$$\hat{f}_i^v(T, P, y_i) = \hat{f}_i^l(T, P, x_i)$$  \hspace{1cm} (1)

where

$\hat{f}_i^v$: the fugacity of component $i$ in the vapor phase

$\hat{f}_i^l$: the fugacity of component $i$ in the liquid phase
There are two methods for representing liquid fugacities.

- Equation of state method
- Liquid activity coefficient method
The equation of state method defines fugacities as:

\[
\hat{f}_i^v = \hat{\phi}_i^v y_i P \tag{2}
\]
\[
\hat{f}_i^l = \hat{\phi}_i^l x_i P \tag{3}
\]

where:
- \( \hat{\phi}_i^v \) is the vapor phase fugacity coefficient
- \( \hat{\phi}_i^l \) is the liquid phase fugacity coefficient
- \( y_i \) is the mole fraction of \( i \) in the vapor
- \( x_i \) is the mole fraction of \( i \) in the liquid
- \( P \) is the system pressure
Equation of State Method

- We can then rewrite equation 1 as:

\[ \hat{\phi}_i^v y_i = \hat{\phi}_i^l x_i \]  

(4)

- This is the standard equation used to represent vapor-liquid equilibrium using the equation-of-state method.

- \( \phi_i^v \) and \( \phi_i^l \) are both calculated by the equation-of-state.

- Note that K-values are defined as:

\[ K_i = \frac{y_i}{x_i} \]  

(5)
**Liquid Activity Coefficient Method (VLE)**

The activity coefficient method defines liquid fugacities as:

\[ \hat{f}_{i}^{l} = \gamma_{i} x_{i} f_{i}^{0} \]  

(6)

The vapor fugacity is the same as the EOS approach:

\[ \hat{f}_{i}^{v} = \phi_{i}^{v} y_{i} P \]  

(7)

where:

- \( \gamma_{i} \) is the liquid activity coefficient of component \( i \)
- \( f_{i}^{0} \) is the standard liquid fugacity of component \( i \)
- \( \phi_{i}^{v} \) is calculated from an equation-of-state model

We can then rewrite equation 1 as:

\[ \phi_{i}^{v} y_{i} P = x_{i} \gamma_{i} f_{i}^{0} \]  

(8)
Liquid Activity Coefficient Method (LLE)

- For Liquid-Liquid Equilibrium (LLE) the relationship is:

\[ \hat{f}_i^{l1} = \hat{f}_i^{l2} \]  \hspace{1cm} (9)

where the designators 1 and 2 represent the two separate liquid phases.

- Using the activity coefficient definition of fugacity, this can be rewritten and simplified as:

\[ x_i^{l1} \gamma_i^{l1} = x_i^{l2} \gamma_i^{l2} \]  \hspace{1cm} (10)
The k-values can be calculated from:

\[ K_i = \frac{y_i}{x_i} = \frac{\gamma^l_i \phi_i^{sat} P_{i^{sat}} \exp\left[\frac{V_i^l}{RT} (P - P_{i^{sat}})\right]}{\hat{\phi}_i^v P} \]  \hspace{1cm} (11)

Or

\[ K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^l}{\hat{\phi}_i^v} \]  \hspace{1cm} (12)
Example 2: Ideal Raoult’s Law

The preceding equation reduces to the following ideal Raoult’s law:

\[ y_i P = x_i P_{i}^{\text{vap}} \]

Example: Pxy plot at constant T(75°C). (P in kPa, T in °C)

\[
\ln P_1^{\text{vap}} = 14.2724 - \frac{2945.47}{t + 224}, \quad \ln P_2^{\text{vap}} = 14.2043 - \frac{2972.64}{t + 209}
\]

Solution

At 75°C, \( P_1^{\text{vap}} = 83.21 \text{kPa} \) and \( P_1^{\text{vap}} = 41.98 \text{kPa} \)

The total pressure \( P = x_1 P_1^{\text{vap}} + x_2 P_2^{\text{vap}} \), \( P = P_2^{\text{vap}} + \left( P_1^{\text{vap}} - P_2^{\text{vap}} \right) x_1 \)

Vapor phase composition, \( y_1 = \frac{x_1 P_1^{\text{vap}}}{P_2^{\text{vap}} + \left( P_1^{\text{vap}} - P_2^{\text{vap}} \right) x_1} = \frac{x_1 P_1^{\text{vap}}}{P} \)
Pxy Diagram at Constant Temperature

Thermodynamic Models built in Simulator
Example 3: Slightly Non-ideal System

For systems which the liquid phase behaves nonideally:

\[ y_i P = \gamma_i x_i P_{i \text{vap}} \]

Relation between activity coefficient and excess Gibbs energy is as:

\[ \ln \gamma_i = \frac{\partial(nG_{\text{ex}}/RT)}{\partial n_i}_{T,P,n_{i,j}} \]

As an example, excess Gibbs energy expression is as:

\[ \frac{G_{\text{ex}}}{RT} = A x_1 x_2 \]

Therefore, \( \gamma_1 \) and \( \gamma_2 \) becomes.

\[ \gamma_1 = \exp(A x_2^2) \quad \gamma_2 = \exp(A x_1^2) \]

So, \( P = \exp[A(1-x_1)^2] x_1 P_{1 \text{vap}} + \exp[A x_1^2] x_2 P_{2 \text{vap}} \)

\[ y_1 = \frac{\exp[A(1-x_1)^2] x_1 P_{1 \text{vap}}}{P} \]
Prediction with Margules Equations

Unstable

A = 0.0
A = 0.5
A = 1.0
A = 2.0
A = 3.0
In general, you can expect non-ideality of unlike molecules. Either the size and shape or the intermolecular interactions between components may be dissimilar. For short, these are called size and energy asymmetry. Energy asymmetry occurs between polar and non-polar molecules and also between different polar molecules.

In the majority of mixtures, activity coefficients is greater than unity. The result is a higher fugacity than ideal. The fugacity can be interpreted as the tendency to vaporize. If compounds vaporize mere than in an ideal solution, then they increase their average distance. So activity coefficients is greater than unity indicate repulsion between unlike molecules. If the repulsion is strong, liquid-liquid separation occurs. This is another mechanism that decreases close contact between unlike molecules.

If the activity coefficient is larger than unity, the system is said to show positive deviations from Raoult’s law. Negative deviations from Raoult’s law occur when the activity coefficient is smaller than unity.
Deviations from Raoult’s Law (2 of 2)

![Graph showing deviations from Raoult’s Law with sub-cooled liquid and super-heated vapor phases.](image)

- **Sub-cooled Liquid**
- **Super-heated Vapor**

Legend:
- Blue dashed line: positive
- Red dashed line: negative
- Black line: ideal

**Pressure (kPa)**

**x₁, y₁**
Isothermal Flash Calculations

Thermodynamic Models built in Simulator
Equilibrium Flash Vaporization

The equilibrium flash separator is the simplest equilibrium-stage process with which the designer must deal. Despite the fact that only one stage is involved, the calculation of the compositions and the relative amount of the vapor and liquid phases at any given pressure and temperature usually involves a tedious trial-and-error solution.

Buford D. Smith, 1963
Flash Calculation (1 of 4)

- MESH Equation
- Material Balance
- Equilibrium Relations
- Summation of Compositions
- Enthalpy ($H$) Balance
Flash Calculation (2 of 4)

- **Overall Material Balance**
  \[ F = V + L \]  
  (1)

- **Component Material Balance**
  \[ Fz_i = Vy_i + Lx_i \]  
  (2)

- **Equilibrium Relations**
  \[ y_i = K_i x_i \]  
  (3)
Summation of Compositions

\[ \sum_{i} x_i = 1 \quad (4a) \quad \sum_{i} y_i = 1 \quad (4b) \]

Defining

\[ \phi = \frac{V}{F} \quad (5) \]

Combining (1) through (5), we obtain:

\[ F(\phi) = \sum_{i} \frac{z_i(1-K_i)}{1+\phi(K_i-1)} = 0 \quad (6) \]
From ideal Raoult’s law

\[ y_i P = x_i P_{i}^{\text{vap}} \]  \hspace{1cm} (7)

K-value can be rewritten as:

\[ K_i = \frac{y_i}{x_i} = \frac{P_{i}^{\text{vap}}}{P} \]  \hspace{1cm} (8)

From Antoine equation

\[ \log P_{i}^{\text{vap}} (kPa) = A - \frac{B}{t^{(\degree C)}+C} \]  \hspace{1cm} (9)
Antoine Coefficients

\[ \log P_{i}^{vap}(kPa) = A - \frac{B}{t(°C)} + C \]

<table>
<thead>
<tr>
<th></th>
<th>Benzene</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.01788</td>
<td>6.08436</td>
</tr>
<tr>
<td>B</td>
<td>1203.677</td>
<td>1347.620</td>
</tr>
<tr>
<td>C</td>
<td>219.904</td>
<td>219.787</td>
</tr>
</tbody>
</table>
Rachford-Rice Function

\[ \phi = 0.707 \]

\[ F(\phi) = \sum_i \frac{z_i (1 - K_i)}{1 + \phi (K_i - 1)} = 0 \]
Flash Calculation Results (1 of 3)

- **Vapor Flowrate (K-mole/hr)**

\[ V = F \phi = (100) \times (0.707) = 70.7 \]  \hspace{1cm} (1)

- **Liquid Flowrate (K-mole/hr)**

\[ L = F - V = 100 - 70.7 = 29.3 \]  \hspace{1cm} (2)
Flash Calculation Results (2 of 3)

Mole Fraction at the liquid phase

\[ x_i = \frac{z_i}{1 + \phi(K_i - 1)} \]  \hspace{1cm} (3)

\[ x_B = 0.4479 \quad x_T = 0.5521 \]  \hspace{1cm} (4)

Mole Fraction at the vapor phase

\[ y_i = K_i x_i = \frac{K_i z_i}{1 + \phi(K_i - 1)} \]  \hspace{1cm} (5)

\[ y_B = 0.6631 \quad y_T = 0.3369 \]  \hspace{1cm} (6)
Flash Calculation Results (3 of 3)

\[ x_B = 0.4329 \]
\[ y_B = 0.6429 \]
PRO/II Keyword Input for Flash Calculation

**TITLE**  PROBLEM=PRBLEM-1A, PROJECT=CLASS, USER=JHCHO

**DIMENSION**  METRIC, PRES=ATM

PRINT  INPUT=ALL, PERC=M, FRAC=M

**COMPONENT**  DATA

LIBID 1, BENZENE/2, TOLUENE

**THERMODYNAMIC**  DATA

METHOD  SYSTEM=IDEAL

**STREAM**  DATA

PROP  STREAM=1, TEMP=25, PRES=1, RATE=100, COMP=1, 60/2, 40

**UNIT OPERATION**  DATA

FLASH  UID=F01

FEED 1

PROD  V=1V, L=1L

ISO  TEMP=100, PRES=1.2

END
# PRO/II Output Summary for Flash Calculation

<table>
<thead>
<tr>
<th>STREAM ID</th>
<th>1</th>
<th>1L</th>
<th>1V</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAME</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PHASE</td>
<td>LIQUID</td>
<td>LIQUID</td>
<td>VAPOR</td>
</tr>
</tbody>
</table>

## Fluid Molar Fractions

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>1L</th>
<th>1V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 BENZENE</td>
<td>0.6000</td>
<td>0.4476</td>
<td>0.6629</td>
</tr>
<tr>
<td>2 TOLUENE</td>
<td>0.4000</td>
<td>0.5524</td>
<td>0.3371</td>
</tr>
</tbody>
</table>

## Total Rate, Kg-Mol/hr

|       | 100.0000 | 75.6710 | 24.3290 |

## Temperature, C

|       | 25.0000 | 100.0000 | 100.0000 |

## Pressure, ATM

|       | 1.0000 | 1.2000 | 1.2000 |

## Enthalpy, M*KCAL/HR

|       | 0.0865 | 0.2800 | 0.2681 |

## Molecular Weight

|       | 85.1285 | 85.8632 | 82.8433 |

## Mole Frac Vapor

|       | 0.0000 | 0.0000 | 1.0000 |

## Mole Frac Liquid

|       | 1.0000 | 1.0000 | 0.0000 |
PRO/II BVLE Analysis
Dew & Bubble Point Calculation

**Dew Point** is the very state at which condensation is about to occur.
- Dew Point Temperature Calculation at a Given Pressure
- Dew Point Pressure Calculation at a Given Temperature
- Vapor Fraction is ‘1’ at Dew Point

**Bubble Point** is the very state at which vaporization is about to occur.
- Bubble Point Temperature Calculation at a Given Pressure
- Bubble Point Pressure Calculation at a Given Temperature
- Vapor Fraction is ‘0’ at Bubble Point
Ex-1: Bubble Point Failure Case

Calculate the bubble point pressure at 85°C of the following stream. Did you get a converged solution? If not, why?

Use SRK for your simulation.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>65</td>
</tr>
<tr>
<td>C2</td>
<td>15</td>
</tr>
<tr>
<td>C3</td>
<td>15</td>
</tr>
<tr>
<td>IC4</td>
<td>5</td>
</tr>
</tbody>
</table>

Save as Filename: EX-1.inp
Difference between Gas and Vapor

- For gas, $T > T_c$
- For vapor, $T < T_c$
- $T$: System temperature, $T_c$: Critical temperature

- “Methane Gas” but not “Methane Vapor”
- “Water Vapor” but not “Water Gas”
Ex-2: C7 Plus Heavy Cut Characterization

Calculate the bubble pressure at 45\(^\circ\)C and dew temperature at 1.5bar of the following stream. Regard C6+ as NC6(1), NC7(2) and NC8(3) and compare the results. Use SRK for your simulation.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>5</td>
</tr>
<tr>
<td>C2</td>
<td>10</td>
</tr>
<tr>
<td>C3</td>
<td>15</td>
</tr>
<tr>
<td>IC4</td>
<td>10</td>
</tr>
<tr>
<td>NC4</td>
<td>20</td>
</tr>
<tr>
<td>IC5</td>
<td>15</td>
</tr>
<tr>
<td>NC5</td>
<td>20</td>
</tr>
<tr>
<td>C6+</td>
<td>5</td>
</tr>
</tbody>
</table>

Save as Filename:
EX-2A.inp for NC6,
EX-2B.inp for NC7,
EX-2C.inp for NC8
Results for EX-2

- Characterization of heavycut is very important in the calculation of dew point temperature.
- EX-2A.inp, EX-2B.inp, EX-2C.inp

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubble P at 45°C</td>
<td>Dew T at 1.5bar</td>
<td>C6 Plus</td>
</tr>
<tr>
<td>18.505</td>
<td>30.519</td>
<td>NC6</td>
</tr>
<tr>
<td>18.561</td>
<td>42.783</td>
<td>NC7</td>
</tr>
<tr>
<td>18.669</td>
<td>59.585</td>
<td>NC8</td>
</tr>
</tbody>
</table>
Results for EX-2A (C6+ $\rightarrow$ NC6)
Results for EX-2B (C6+ → NC7)
Results for EX-2C (C6+ → NC8)
The End of General Thermodynamics

The End....