CHAPTER TWO: THERMODYNAMICS

SEPARATION PROCESSES:

CHAPTER 2: THERMODYNAMICS

SEPARIATIONS

EQUILIBRIUM
(THERMODYNAMICS)

- EQUATIONS OF STATE
- IDEAL/NON-IDEAL
- NO DRIVING FORCE
- ACTIVITY COEFFICIENTS
  e.g., DISTILLATION

RATES-BASED
(MASS TRANSFER)

- DIFFUSIVITIES
- SOLUBILITIES
- MASS TRANSFER
  COEFFICIENTS
  e.g., ABSORPTION

EQUILIBRIUM
OPERATION

\[ \text{VAPOR, } y_i \]
\[ \text{FEED, } z_i \]
\[ \Rightarrow T^v = T^l = T \]
\[ p^v = p^l = p \]
\[ \text{LIQUID, } x_i \]
For vapor-liquid equilibrium (VLE)

\[ z = \text{feed mole fraction} \]
\[ y = \text{vapor mole fraction} \]
\[ x = \text{liquid mole fraction} \]

How do we relate \( y \) and \( x \)?

\[ y_i = K_i \cdot x_i \quad \text{at equilibrium} \]

Thermodynamics is in here.

VLE:

1. Ideal gas / Ideal liquid

\[ y_i \cdot P = x_i \cdot P_i^{\text{sat}} \quad \text{Raoult's law} \]

\[ K_i = \frac{P_i^{\text{sat}}}{P} \]

Example: System of alkanes
(2) IDEAL GAS / NON-IDEAL LIQUID

\[ y_i P = x_i \delta_i P_i^{\text{sat}} \]

**MODIFIED RAOULT'S LAW**

\[ K_i = \frac{y_i P_i^{\text{sat}}}{P} \]

**EXAMPLE:** ETHANOL/WATER @ atmospheric pressure

(3) NON-IDEAL GAS / NON-IDEAL LIQUID

\[ y_i \Phi_i P = x_i \delta_i P_i^{\text{sat}} \]

\[ K_i = \frac{\delta_i P_i^{\text{sat}}}{\Phi_i P} \]

**EXAMPLE:** HIGHER PRESSURE VLE

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**LLE:**

\[ X_i^\alpha y_i^\alpha (f_i^o)^\alpha = x_i^\beta y_i^\beta (f_i^o)^\beta \]

\[ \uparrow \quad \uparrow \]

pure component liquid pure component liquid

\[ \Rightarrow (f_i^o)^\alpha = (f_i^o)^\beta \]
\[ \Rightarrow x_i^{\alpha} \delta_i^{\beta} = x_i^{\beta} \delta_i^{\alpha} \]

\[ k_i = \]

If ideal, do you get a separation?

WHERE DO THESE EXPRESSIONS COME FROM?

PHASE EQUILIBRIUM

\[ \Rightarrow \text{Defined by} \]

\[ \mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\delta} = \ldots \]

Chemical Potential

WHAT IS A CHEMICAL POTENTIAL?

\[ \Rightarrow \text{ABSTRACT (CAN'T REALLY MEASURE)} \]

\[ \Rightarrow \text{THINK OF AS AN ESCAPING TENDENCY} \]

\[ \Rightarrow \text{HIGHER } \mu \Rightarrow \text{BETTER CHANCE TO ESCAPE (OR CHANGE PHASE)} \]
\[ \mu_i = \left[ \frac{\partial (nG)}{\partial n_i} \right]_{p, T, n_j} \]

**NOTICE:**

\[ G = f(p, T, n_i) \]

\[ \Rightarrow \mu = f(p, T, n_i) \]

*All things we can modify and measure*

\[ p + T \text{ give energy to system} \]

*Use ways to add*

\[ n_i \text{ lets us change concentration} \]

We'd like to start from here and get to a usable expression (e.g., Raoult's law)
RAOUlt'S LAW: DERIVATION

$\Rightarrow$ IDEAL GAS, IDEAL LIQUID

\[ \Rightarrow \mu_i^V = \mu_i^L \]

\[ \mu_i^V = G_i^g + RT \ln y_i \]

\[ \mu_i^L = G_i^l + RT \ln x_i \]

Note strong dependence on composition

\[ G_i^g + RT \ln y_i = G_i^l + RT \ln x_i \]

↑

Pure Species

↑

Pure Species

\[ \Rightarrow G = f(T, P) \text{ only} \]
\[ RT \ln y_i - RT \ln x_i = G_i^l (T, P) - G_i^g (T, P) \]

**Aside:** \( G_i^l (T, P) \)

**Know liquid properties not strong function of pressure**

**Why?**

\[ \Rightarrow G_i^l (T, P) = G_i^l (T, P_{sat}) \]

**Aside:** \( G_i^g (T, P) \)

\( G_i^g (T, P) = V_i^g dP - S_i^g dT \)

**Why not cancel out \( dP \) term?**

Integrate from \( P \) to \( P_{sat} \) @ constant \( T \)

\[ G_i^{ig} (T, P_{sat}) - G_i^{ig} (T, P) = \int_{P}^{P_{sat}} \frac{RT}{P} dP \]

ideal gas law
\[ G_i^G(T, P) = RT \ln \frac{P_i^{sat}}{P} \]

\[ \Rightarrow G_i^G(T, P) = G_i^{iG}(T, P^{sat}) - RT \ln \frac{P_i^{sat}}{P} \]

**Back to derivation** ...

\[ RT \ln \left( \frac{\gamma_i}{X_i} \right) = G_i^G(T, P^{sat}) - \left\{ G_i^{iG}(T, P^{sat}) - RT \ln \frac{P_i^{sat}}{P} \right\} \]

But, for pure component at equilibrium, \( G_i^A = G_i^B \)

\[ \Rightarrow G_i^G(T, P^{sat}) = G_i^{iG}(T, P^{sat}) \]

\[ \Rightarrow RT \ln \frac{\gamma_i}{X_i} = RT \ln \frac{P_i^{sat}}{P} \]

\[ \ln \frac{\gamma_i}{X_i} = \ln \frac{P_i^{sat}}{P} \]

\[ \Rightarrow \frac{\gamma_i}{X_i} = \frac{P_i^{sat}}{P} \quad \text{or} \quad y_i P = x_i P_i^{sat} \]
**Notes:**

- $x_i$ and $y_i$ are mole fractions
- $P$ is total system pressure
- $P_i^{sat}$ is saturation pressure of pure component "i" @ mixture $T$

$\Rightarrow P_i^{sat} = f(T)$ only. Get from Antoine Equation

$$\ln P_i^{sat} = A - \frac{B}{T+C}$$

Coefficients $A$, $B$, and $C$ from literature

*Raoults Law for Ideal Gas/Ideal Liquid*

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**What if Non-Ideal?**

**IG/NIIL:** Modified Raoults Law

$$y_i P = x_i \delta_i P_i^{sat}$$

$\delta_i$ from Activity Coefficient Models

$P_i^{sat}$ from Antoine Equation
NIG/NIL:

\[ y_i \frac{\sigma_i}{P_i} = \chi_i \gamma_i \rho_i^{\text{sat}} \]

- \(\sigma_i\): from equation of state
- \(\gamma_i\): from activity coefficient models
- \(\rho_i^{\text{sat}}\): from Antoine Equation

NIL/NIL: (for LLE)

\[ x_i^\alpha \delta_i^\alpha = x_i^\beta \delta_i^\beta \]

- \(x_i^\alpha, \delta_i^\alpha\): from activity coefficient model

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**PHASE DIAGRAMS:**

1. **IDEAL GAS / IDEAL LIQUID** (BINARY SYSTEM)

    **NEED:** RAOULT'S LAW EXPRESSIONS

    **SUMMATIONS** (MOLE FRACTIONS)
PXY Phase Diagram for n-Hexane (1) and n-Heptane (2)

(Temperature Constant)

LIQUID

VAPOR
TXY Phase Diagram for n-Hexane (1) and n-Heptane (2)

(PRESSURE CONSTANT)
### Point Description

<table>
<thead>
<tr>
<th>Point</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Subcooled liquid, one phase</td>
</tr>
<tr>
<td>b</td>
<td>Bubble point, $x_1 = z_1$</td>
</tr>
<tr>
<td>b'</td>
<td>Bubble point vapor composition (but no vapor yet)</td>
</tr>
<tr>
<td>c</td>
<td>Two-phase region</td>
</tr>
<tr>
<td>c'</td>
<td>$x_1$ for pressure @ c</td>
</tr>
<tr>
<td>c''</td>
<td>$y_1$ for pressure @ c</td>
</tr>
<tr>
<td>d</td>
<td>Dew point, $y_1 = z_1$</td>
</tr>
</tbody>
</table>
Dew point liquid composition (but no liquid phase)

Super-heated vapor, one phase

Note: At points A & E, no separation. Why? Only one phase

How to generate PXY diagrams (IG/IL):

T is constant

$p_i^{Sat} = f(T)$ only, so can calculate $p_i^{Sat}$ immediately.

Binary system:

$y_1 p = x_1 p_i^{Sat}$  \hspace{1cm} (1)

$y_2 p = x_2 p_2^{Sat}$  \hspace{1cm} (2)

$x_1 + x_2 = 1$  \hspace{1cm} (3)

$y_1 + y_2 = 1$  \hspace{1cm} (4)
Combine (1) + (2)

\[ p \left( \frac{y_1 + y_2}{y_1} \right) = x_1 p_1 \text{sat} + x_2 p_2 \text{sat} \]

\[ p = x_1 p_1 \text{sat} + (1-x_1) p_2 \text{sat} \]

\[ p = p_2 \text{sat} + (p_1 \text{sat} - p_2 \text{sat}) x_1 \]

≤ Saturated Liquid Line

\[ y_1, p = x_1 p_1 \text{sat} \]

\[ y_1 = \frac{x_1 p_1 \text{sat}}{p} \]

Plot \((y_1, p)\) for Saturated Vapor Line

Notes:

- Both lines terminate at pure components \((x_1=1, y_1=1)\) so endpoints are \(p_2 \text{sat} + p_1 \text{sat}\)

- Saturated liquid line is straight for \(\pm G/\pm L\)
PX Y (IDEAL GAS/IDEAL LIQUID)

- Raoult's Law Applies
- Antoine Eqn. for $P_i^\text{sat}$
- Constant $T$

1. **Calculate** $P_i^\text{sat} + P_2^\text{sat}$
2. **Pick** $X_1$
3. **Calculate** $P = P_2^\text{sat} + (P_1^\text{sat} - P_2^\text{sat})X_1$
4. **Calculate** $y_1 = \frac{X_1 P_i^\text{sat}}{P}$
5. **Across** $X_1$ Range?
   - **No**
   - **Yes**
     - **Plot PX Y Diagram**
     - **Plot XY Diagram**
How to Generate TXY Diagrams (±G/±L)

P is constant

At endpoints, $P = P_i^{sat}$, so calculate $T_i^{sat}$ at endpoints. Then, for any $T$, calculate $P_i^{sat}$, then

$$P = P_2^{sat} + (P_1^{sat} - P_2^{sat}) X_1$$

$$\Rightarrow X_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}}$$

$$y_1 = \frac{x_1 P_1^{sat}}{P}$$

Notes:

- Plot $(x_1, T)$ for saturated liquid line
- Plot $(y_1, T)$ for saturated vapor line
- Recall that most industrial separations are set pressures, so TXY data most commonly used for design.
TXY (Ideal Gas/Ideal Liquid)

- Raoult's Law Applies
- Antoine Equation for $p_i^{sat}$
- Constant $p$

From $P$, Calculate $T_1^{sat} + T_2^{sat}$

Pick $T$

Calculate $P_1^{sat} + P_2^{sat}$

Calculate $X_1$:
$$X_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}}$$

Calculate $Y_1$:
$$Y_1 = \frac{X_1 P_1^{sat}}{P}$$

Across $T$ range?

- NO
- YES

Plot TXY Diagram

Plot XY Diagram
ACTIVITY COEFFICIENT MODELS:

TYPES:
1) POLYNOMIAL EXPANSIONS WITH MULTIPLE, EMPIRICALLY FITTED, ADJUSTABLE PARAMETERS

2) FLORY-HUGGINS: EXTENDS LATTICE THEORY TO DIFFERENT SHAPED MOLECULES

3) LOCAL COMPOSITION EFFECTS TO ACCOUNT FOR NON-RANDOM MOLECULAR LEVEL DISTRIBUTION

4) QUASI-CHEMICAL THAT ACCOUNT FOR MOLECULAR SIZE (AREA + VOLUME)

DEVIATIONS CAN BE POSITIVE OR NEGATIVE
Positive Deviations:

\[ i \leftrightarrow i \]

\[ j \leftrightarrow j \]

E.g., methyl ethyl ketone/toluene

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C} \\
\text{CH}_2\text{CH}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \\
\end{array}
\]

Negative Deviations:

\[ i \leftrightarrow j \]

E.g., chloroform/dioxane

\[
\begin{array}{c}
\text{CHCl}_3 \\
\end{array}
\]

Very Large Deviations $\Rightarrow$ Azeotrope Formation

Very Large Deviations $\Rightarrow$ Azeotrope Formation

General:

\[
y_i \Phi_i p = x_i \delta_i p_i^{sat}
\]

Low pressure, $\Phi_i = 1$

Most cases (industrial important), $\delta_i \neq 1$

$\Rightarrow$ Modified Raoult's Law

\[
y_i p = x_i \delta_i p_i^{sat}
\]

How to Get $\delta_i$
MARGULES, VAN LAAR

- OLDER MODELS
- BASED ON POLYNOMIAL EXPANSION + CURVE FITTING
- GOOD FOR SIMPLE MIXTURES
- GOOD FOR COMPONENTS THAT ARE SIMILAR IN NATURE + SIZE

1) MARGULES -2 SUFFIX

\[ RT \ln \gamma_1 = A X_2^2 \]
\[ RT \ln \gamma_2 = A X_1^2 \]

one parameter: A

2) VAN LAAR -

\[ RT \ln \gamma_1 = A \left( 1 + \frac{A X_1}{B X_2} \right)^{-2} \]
\[ RT \ln \gamma_2 = B \left( 1 + \frac{B X_2}{A X_1} \right)^{-2} \]
3) Margules - 3 Suffix

\[ RT \ln \gamma_1 = (A + 3B)X_2^2 - 4B \, X_2^3 \]
\[ RT \ln \delta_2 = (A - 3B)X_1^2 + 4B \, X_1^3 \]

4) Wilson Equation:

\[ \text{Good for strongly non-ideal} \]
e.g. alcohols & hydrocarbons

- 2 parameter
- local composition effects
- good for VLE, but \underline{not} LLE

\[ \ln y_1 = -\ln (x_1 + \Lambda_{12} x_2) + x_2 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \]

\[ \ln y_2 = -\ln (x_2 + \Lambda_{21} x_1) - x_1 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \]

\underline{NRTL: (Non-Random Two Liquid)}

- 3 parameter
- strongly non-ideal
- local compositions
- good for VLE + LLE

\underline{UNIQUAC: (Universal Quasi-Chemical)}

- group contribution
- VLE, LLE
- 2 parameter
- small T dependence
- good for polymers
Pxy Diagrams (Fixed T)  
(binary ideal gas / nonideal liquid)

1. Pick $x_1$  
   Calculate $x_2 = 1 - x_1$

2. Calculate $\gamma_i + \gamma_2$

3. Calculate $p_i^{\text{sat}}$

4. Calculate $p_i = \gamma_i \cdot x_i \cdot p_i^{\text{sat}}$

5. Calculate $P = \sum p_i$

6. Calculate $y_i = \frac{p_i}{P}$

7. X range satisfied?

   - **NO**

   - **YES**
     - **STOP**
     - PLOT Pxy Diagram

   *Appropriate Activity Coefficient Model*

   *Antoine Equation, etc.*

   *Modified Raoult's Law*

   *Not straight line because $\gamma_i = f(x)$*
Txy Diagrams (Fixed P) (binary ideal gas/non ideal liquid)

1. Pick $X_1$
   - Calculate $X_2 = 1 - X_1$

2. Assume $T$ in feasible range

3. Calculate $\gamma_1$, $\gamma_2$

4. Calculate $p_i^{sat}$

5. Calculate $p_i = \gamma_i X_i p_i^{sat}$ at assumed $T$

6. No $P_T = P_1 + P_2$?
   - Yes
     - $y_i = \frac{\gamma_i X_i p_i^{sat}}{P}$

7. No $x$ range satisfied?
   - Yes
     - STOP, PLOT Txy Diagram