OUTLINE OF CHAPTER 10

VAPOR LIQUID EQUILIBRIA

Starting Point (where is this coming from?)

\[
\bar{f}_i^L(T, P, \bar{x}) = \bar{f}_i^V(T, P, \bar{y})
\]

Equation of state method (both fluids are represented by and EOS) (What assumptions are made here?)

\[
\bar{f}_i^L(T, P, \bar{x}) = x_i P \bar{\phi}_i^L(T, P, \bar{x}) = \bar{f}_i^V(T, P, \bar{y}) = y_i P \bar{\phi}_i^V(T, P, \bar{y})
\]

where

\[
\bar{\phi}_i^L(T, P, \bar{x}) = \frac{\bar{f}_i^L(T, P, \bar{x})}{x_i P} \quad \text{and} \quad \bar{\phi}_i^V(T, P, \bar{y}) = \frac{\bar{f}_i^V(T, P, \bar{y})}{y_i P}
\]

How do we calculate the fugacity coefficient?

Activity coefficient method for liquid-EOS for vapor

\[
\bar{f}_i^L(T, P, \bar{x}) = x_i y_i(T, P, \bar{x}) P_{i, \text{sat}}(T) \bar{\phi}_i^{L, \text{sat}}(T, P) = \bar{f}_i^V(T, P, \bar{y}) = y_i P \bar{\phi}_i^V(T, P, \bar{y})
\]
VLE for IDEAL MIXTURES

Start using Lewis and Randall

\[ x_i \gamma_i(T, P, \xi) P_i^{\text{vap}}(T) \left( \frac{f}{P} \right)_{\text{sat},i} = y_i P \left( \frac{f}{P} \right)_i \]

At low pressure

\[ x_i P_i^{\text{vap}}(T) = y_i P = P_i \]

Activity coefficient = 1, gives Raoult Law

Example- Hexane-Thriethylamine system
VLE for NON-IDEAL MIXTURES

Low P. When

\[ P > \sum x_i P_i^{\text{vap}} \]

Then some activity coefficient is >1 and vice versa. These are positive and negative deviations from Raoult’s law.

To locate the extremum we set \( (\partial P/\partial x_1)_T = 0 \),

\[ \gamma_1 P_1^{\text{vap}} \left( 1 + x_1 \frac{\partial \ln \gamma_1}{\partial x_1} \right) - \gamma_2 P_2^{\text{vap}} \left( 1 + x_2 \frac{\partial \ln \gamma_2}{\partial x_2} \right) = 0 \]

Recall (what equations is this?)

\[ x_1 \left( \frac{\partial \ln \gamma_1}{\partial x_1} \right)_T + x_2 \left( \frac{\partial \ln \gamma_2}{\partial x_1} \right)_T = 0 \]

Now, it can be proven that \( (1 + x_1 \partial \ln \gamma_1 / \partial x_1)_T \neq 0 \) (Exercise 9.18)

Substituting, we get:

\[ \gamma_1 P_1^{\text{vap}} - \gamma_2 P_2^{\text{vap}} = 0 \]
Which leads to

\[ \frac{y_1}{x_1} = \frac{\gamma_1 P_1^{\text{vap}}}{P} = \frac{\gamma_2 P_2^{\text{vap}}}{P} = \frac{y_2}{x_2} \]

And together with \( x_1 + x_2 = 1 \) and \( y_1 + y_2 = 1 \), we get

\[ x_1 = y_1 \]
\[ x_2 = y_2 \]

AZEOTROPE!!!!

and

\[ \gamma_i(x^{\text{AZ}}) = \frac{P}{P_i^{\text{vap}}} \]

Ignore the rest of the chapter