1. Vapor-Liquid Equilibrium Applications

a. Bubble point:
   - Starting from only liquid phase, with compositions $x_1, \ldots, x_N$
   - Want to find the conditions under which the first bubble occurs

b. Dew point:
   - Starting from only vapor phase, with compositions $y_1, \ldots, y_N$
   - Want to find the conditions under which the first dew occurs

Special case 1: Raoult’s Law

\[
\begin{align*}
  y_1 P &= x_1 P_{1 \text{sat}} \\
  \vdots \quad & \quad \vdots \\
  y_N P &= x_N P_{N \text{sat}}
\end{align*}
\]

a) Bubble point calculation (given $x_1, \ldots, x_N$)

\[
P = \sum_i x_i P_{i \text{sat}}
\]

While using Antoine equation for $P_{i \text{sat}}(T)$

\[
\ln(P_{i \text{sat}}) = A_i - \frac{B_i}{T + C_i} \quad \rightarrow \quad P_{i \text{sat}} = \exp\left(A_i - \frac{B_i}{T + C_i}\right)
\]

\[
P = \sum_i x_i P_{i \text{sat}}(T) = \sum_i x_i \exp\left(A_i - \frac{B_i}{T + C_i}\right)
\]

then

\[
y_j = \frac{x_j P_{j \text{sat}}(T)}{P}
\]

b) Dew point calculation (given $y_1, \ldots, y_N$)

\[
\sum_i \frac{y_i}{P_{i \text{sat}}(T)} = \sum_i \frac{y_i}{\exp\left(A_i - \frac{B_i}{T + C_i}\right)} = \frac{1}{P}
\]

then

\[
x_j = \frac{y_j P}{P_{j \text{sat}}(T)}
\]
General Case:

\[ y_1 \hat{\phi}_1 P = x_1 y_1 f_{1}^{\text{liq}} \]
\[ \vdots \]
\[ y_N \hat{\phi}_N P = x_N y_N f_{N}^{\text{liq}} \]

Note that:

\[ \hat{\phi}_i = \hat{\phi}_i (y_1, \ldots, y_N, T, P) \]
\[ \gamma_i = \gamma_i (x_1, \ldots, x_N, T, P) \]
\[ f_{i}^{\text{liq}} = f_{i}^{\text{liq}} (T, P) = \phi_{i}^{\text{sat}} (T) P_{i}^{\text{sat}} (T) P_{\text{corr}} (T, P) \]

Thus, we will need numerical methods to solve nonlinear equations (see project 1 as example).