CM 3230 Thermodynamics, Fall 2016

Lecture 29

1. Vapor-Liquid Equilibrium Applications

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

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

Special case 1: Raoult's Law

$$y_1 P = x_1 P_1^{sat}$$
$$\vdots$$
$$y_N P = x_N P_N^{sat}$$

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

$$P = \sum_i x_i P_i^{sat}$$

While using Antoine equation for $P_i^{sat}(T)$

$$\ln(P_i^{sat}) = A_i - \frac{B_i}{T + C_i} \quad \rightarrow \quad P_i^{sat} = \exp\left(A_i - \frac{B_i}{T + C_i}\right)$$

$$P = \sum_i x_i P_i^{sat}(T) = \sum_i x_i \exp\left(A_i - \frac{B_i}{T + C_i}\right)$$

$$\text{then} \quad y_j = \frac{x_j P_j^{sat}(T)}{P}$$

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

$$\sum_i \frac{y_i}{P_i^{sat}(T)} = \sum_i \frac{y_i}{\exp\left(A_i - \frac{B_i}{T + C_i}\right)} = \frac{1}{P}$$

$$\text{then} \quad x_j = \frac{y_j P}{P_j^{sat}(T)}$$

General Case:

$$y_1\hat{\phi}_1 P = x_1\gamma_1 f_1^{liq}$$
$$\vdots$$
$$y_N\hat{\phi}_N P = x_N\gamma_N f_N^{liq}$$

Note that:

$$\hat{\phi}_i = \hat{\phi}_i(y_1, \dots, y_N, T, P)$$
$$\gamma_i = \gamma_i(x_1, \dots, x_N, T, P)$$
$$f_i^{liq} = f_i^{liq}(T, P) = \phi_i^{sat}(T)P_i^{sat}(T)\mathcal{P}_{corr}(T, P)$$

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