CH365 Chemical Engineering Thermodynamics

Lesson 39
Simple and Modified VLE Models and Flash Calculations

Block 6 – Solution Thermodynamics

Homework, continued

Problem 13.1

Assuming the validity of Raoult's Law, perform the following calculations for the benzene(1)/toluene(2) system:

(a) Given x_1=0.33 and T =100 deg C, find y_1 and P.
(b) Given y_1=0.33 and T =100 deg C, find x_1 and P.

Today's Topic – Modified Raoult's Law

Raoult's Law

P = total pressure

vapor pressure of i

- valid from triple point to critical point

- not good for non-ideal solutions

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

$$i = 1, 2, 3, ..., N$$

(eq. 10.1)

y_i = mole fraction of i in vapor

x_i = mole fraction of i in liquid

- vapor phase is ideal gas

- liquid phase is ideal solution

$$\overline{V}_i^{id} = V_i$$

(Ch. 10)

Equilibrium Ratio

"i" in liquid $\rightleftharpoons$ "i" in vapor

$$K_i = \frac{y_i}{x_i}$$

$$\therefore K_i = \frac{P_i^{sat}}{P}$$

$$\therefore K_i = \frac{\gamma P_i^{sat}}{P}$$

Modified Equilibrium Ratio

$$K = \frac{y_i}{\gamma_i x_i}$$

activity coefficient of i in liquid

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

(eq. 13.19)

Activity Coefficient

The circumflex ^ designates that this property is in solution. This is not a partial molar property, which is why we do not use an overbar.

f_i has units of pressure

"escaping tendency"

tendency of a substance to pass from one phase to another

for ideal gases:

$$f_i^{ig} = P$$

(Eq. 10.32)

for ideal solution:

$$\hat{f}_i^{id} = x_i f_i$$

(Eq. 10.83)

$$\overline{G}_i = \Gamma_i(T) + RT\,\hat{f}_i \qquad \text{(Eq. 10-46, page 372)}$$

$$\overline{G}_i^{id} = \Gamma_i(T) + RT \ln x_i f_i$$

$$\overline{G}_i - \overline{G}_i^{id} = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

$$\overline{G}_i^E = \overline{G}_i - \overline{G}_i^{id} = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i} \qquad \text{(Eq. 13.2)}$$

Excess Gibbs energy:

$$\overline{G}_i^E = \overline{G}_i - \overline{G}_i^{id}$$

(Definition, Lesson 37)

$$\hat{f}_i^{liq} = x_i \gamma_i^{liq} f_i^{liq}$$

$$\boxed{\overline{G}_i^E = RT \ln \gamma_i}$$

(Eq. 13.3)

Activity Coefficient Models

All models have corresponding G^E functions (not shown here).

Margules
(2-constant)
(eq. 13.40-13.41, p. 477)

$$\log\gamma_1 = x_2^2\left[A_{12} + 2x_1\left(A_{21} - A_{12}\right)\right]$$

$$\log\gamma_2 = x_1^2\left[A_{21} + 2x_2\left(A_{12} - A_{21}\right)\right]$$

Margules
(1-constant)
(eq. 13.37-13.38, p. 476)

$$\log\gamma_1 = A\,x_2^2$$

$$\log\gamma_2 = A\,x_1^2$$

$$A_{21} = A_{12} = A$$

van Laar
(2-constant)
(eq. 13.43-13.44, p. 479)

$$\log\gamma_1 = \frac{A_{12}}{\left[1 + \left(x_1 A_{12}\right)/\left(x_2 A_{21}\right)\right]^2}$$

$$\log\gamma_2 = \frac{A_{21}}{\left[1 + \left(x_2 A_{21}\right)/\left(x_1 A_{12}\right)\right]^2}$$

Wilson
(2-constant)
(eq. 13.46-13.47, p. 480)

$$\log\gamma_1 = -\ln\left(x_1 + \Lambda_{12}x_2\right) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$$

$$\log\gamma_2 = -\ln\left(x_2 + \Lambda_{21}x_1\right) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$$

NRTL
(3-constant)
(eq. 13.49-13.50, p. 480
and G_{ij} and τ_{ij}, p. 481)

(a_{ij}, b_{ij}, and b_{ji} are in CC)

$$\log\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{\left(x_2 + x_1 G_{12}\right)^2}\right]$$

$$\log\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{G_{21}\tau_{21}}{\left(x_1 + x_2 G_{21}\right)^2}\right]$$
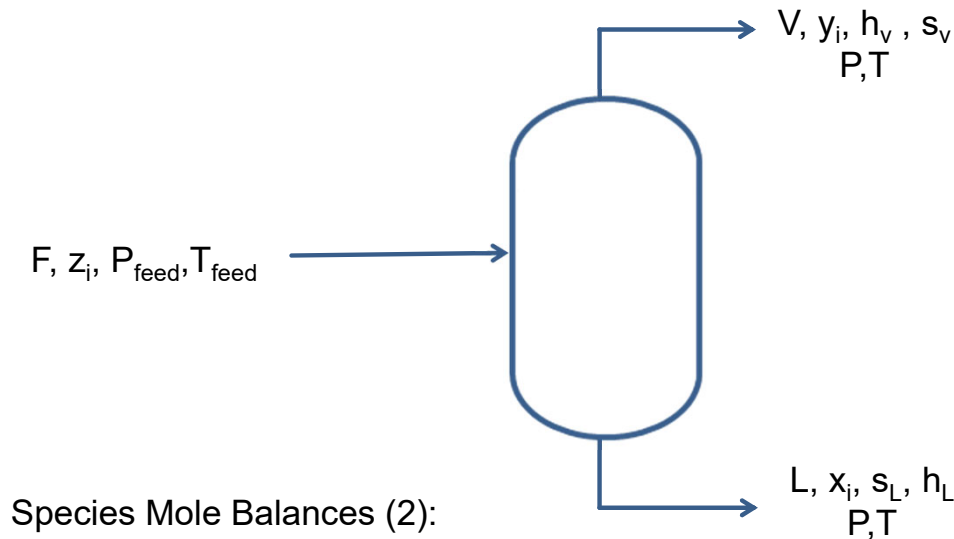
$$\tau_{12} = b_{12}/RT$$

$$\tau_{21} = b_{21}/RT$$

$$G_{12} = \exp\left(-\alpha\tau_{12}\right)$$

$$G_{21} = \exp\left(-\alpha\tau_{21}\right)$$

Application - Rachford-Rice Equations

V, y_i, h_v , s_v
P,T

F, z_i, P_{feed}, T_{feed}

L, x_i, s_L, h_L
P,T

Raoult's Law reflects ideal solution behavior:

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

Raoult's Law is modified with activity for real solution.

Species Mole Balances (2):

$$z_i = \psi\, y_i + (1 - \psi) x_i$$

$$\psi = \frac{V}{F} \quad \text{and} \quad 1\text{-}\psi = \frac{L}{F}$$

Independent variables needed (Duhem): IVN=2.

Equilibrium Expressions (2):

$$y_i = K_i \cdot x_i$$

$$K_i = \frac{P_i^{sat}}{P} \Leftrightarrow K_i = \frac{\gamma_i \cdot P_i^{sat}}{P} \qquad P_i^{sat} = e^{\,a_i - \frac{b_i}{T + c_i}}$$

IVNs can be T,P or T,ψ, or P,ψ.

Antoine equation - importance of the *Clapeyron equation* from lesson 31.

Summation of Mole Fractions (2):

$$0 = \sum_i x_i - \sum_i y_i$$

Example Problem 1

Chapter Problem 13.17

For the system ethyl acetate (1) / n-heptane (2) at 345.15 K,

$$\ln \gamma_1 = 0.95\, x_2^2 \qquad P_1^{sat} = 79.80 \text{ kPa}$$

$$\ln \gamma_2 = 0.95\, x_1^2 \qquad P_2^{sat} = 40.50 \text{ kPa}$$

Assume the validity of Eq. 13-19, $\quad y_i P = \gamma_i x_i P_i^{sat} \quad$ (p. 465)

(a) Make a bubble point calculation for T = 343.15 K, x_1 = 0.05, and
(b) Make a dew point calculation for T = 343.15 K, y_1 = 0.05, and

Example Problem 2

A liquid stream containing 0.35 mole fraction acetone and 0.65 mole fraction methanol is flashed at 2 bar (200 kPa) so that 50% of the liquid is evaporated.

a) Calculate the flash temperature and the compositions of the resulting liquid and vapor, assuming the system follows the ideal solution form of Raoult's Law.

b) Calculate the flash temperature and the compositions of the resulting liquid and vapor, using eq. 13.19 and assuming activity coefficients for the liquid phase can be obtained from the 1-parameter Margules equations

$$\ln \gamma_1 = 0.64 x_2^2 \quad \text{and} \quad \ln \gamma_2 = 0.64 x_1^2$$

Questions?