CH365 Chemical Engineering Thermodynamics

Lesson 39
Simple and Modified VLE Models and Flash Calculations

Block 6 – Solution Thermodynamics

Today's Topic – Modified Raoult's Law

Raoult's Law

- valid from triple point to critical point
- not good for non-ideal solutions

P = total pressure

vapor pressure of i

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

y_i = mole fraction of i in vapor

x_i = mole fraction of i in liquid

$i = 1, 2, 3, \ldots, N$

(eq. 10.1)

- vapor phase is ideal gas
- liquid phase is ideal solution

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

(Ch. 10)

Equilibrium Ratio

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

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

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

Modified Equilibrium Ratio

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

activity coefficient of i in liquid

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

(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

$$\bar{G}_i = \Gamma_i(T) + RT\ \hat{f}_i$$

(Eq. 10-46, page 372)

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

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

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

Excess Gibbs energy:

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

(Definition, Lesson 37)

for ideal gases:

$$f_i^{ig} = P$$

(Eq. 10.32)

for ideal solution:

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

(Eq. 10.83)

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i}$$

(Eq. 13.2)

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

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

(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)

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

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

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

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

$$\log\gamma_1 = \frac{A_{12}}{\left[1 + (x_1A_{12})/(x_2A_{21})\right]^2}$$

$$\log\gamma_2 = \frac{A_{21}}{\left[1 + (x_2A_{21})/(x_1A_{12})\right]^2}$$

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)

$$\log\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{\left(x_2 + x_1G_{12}\right)^2}\right]$$

$$\log\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{G_{21}\tau_{21}}{\left(x_1 + x_2G_{21}\right)^2}\right]$$

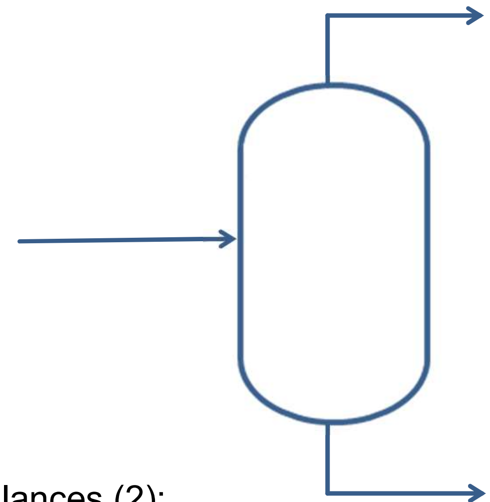
$$\tau_{12} = b_{12}/RT$$

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

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

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

Application - Rachford-Rice Equations



Species Mole Balances (2):

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

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

Equilibrium Expressions (2):

$$y_i = K_i \cdot x_i$$

$$K_i = \frac{P_i^{sat}}{P} \Leftrightarrow K_i = \frac{\gamma_i \cdot P_i^{sat}}{P}$$

$$P_i^{sat} = e^{a_i - \frac{b_i}{T + c_i}}$$

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

Summation of Mole Fractions (2):

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

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.

Independent variables needed (Duhem): IVN=2.

IVNs can be T,P or T,ψ, or P,ψ.

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

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

Questions?