

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

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

y_i = mole fraction of i in vapor
 x_i = mole fraction of i in liquid
 P = total pressure
 P_i^{sat} = vapor pressure of i
 $i = 1, 2, 3, \dots, N$
 $y_i P = x_i P_i^{\text{sat}}$ (eq. 10.1)

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

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

(Ch. 10)

Equilibrium Ratio

“ i ” in liquid \rightleftharpoons “ i ” in vapor
 $K_i = \frac{y_i}{x_i}$
 $\therefore K_i = \frac{P_i^{\text{sat}}}{P}$
 $\therefore K_i = \frac{\gamma_i P_i^{\text{sat}}}{P}$

Modified Equilibrium Ratio

$K = \frac{y_i}{\gamma_i x_i}$
 activity coefficient of i in liquid
 $y_i P = \gamma_i x_i P_i^{\text{sat}}$ (eq. 13.19)

Foundation of Vapor-Liquid Equilibrium Calculations

(Escaping tendencies are equal between phases)

fugacity of pure
species i

$$f_i \quad \phi_i$$

fugacity of species i in
solution in phase α

$$\hat{f}_i \quad \hat{\phi}_i$$

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.

$$f_i^{\text{vapor}} = f_i^{\text{liquid}} = f_i^{\text{sat}} \quad (\text{Eq. 10.39, page 377 and Lesson 36 Slide 6})$$

In solution, $\hat{f}_i^\alpha = \hat{f}_i^\beta = \dots = \hat{f}_i^\pi$ (Eq. 10.47, page 382)

$$\hat{f}_i^{\text{vapor}} = \hat{f}_i^{\text{liquid}} \quad (i = 1, 2, \dots, N)$$

(Eq. 10.48, page 382)

(analogous) $\phi_i \equiv \frac{f_i}{P}$ (Eq. 10.34, page 376)

$\hat{\phi}_i \equiv \frac{\hat{f}_i}{y_i P}$ (Eq. 10.52, *defined* on page 383)

$$\therefore \hat{f}_i^{\text{vapor}} = \hat{\phi}_i^{\text{vapor}} y_i P$$

(Eq. 13.1, page 460)

Activity Coefficient

f_i has units of pressure

“escaping tendency”

tendency of a
substance to pass from
one phase to another

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.

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

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

for ideal gases:

$$f_i^{\text{ig}} = P \quad (\text{Eq. 10.32})$$

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

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

Excess Gibbs energy:

$$\bar{G}_i^{\text{E}} = \bar{G}_i - \bar{G}_i^{\text{id}} \quad (\text{Definition, Lesson 37})$$

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

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

$$\bar{G}_i^{\text{E}} = RT \ln \gamma_i \quad (\text{Eq. 13.3})$$

Gibbs Energy Generating Functions

(Derived from Eq. 13-4, p. 452)

$$\frac{V^E}{RT} = \left[\frac{\partial (G^E / RT)}{\partial P} \right]_{T,x} \quad (\text{Eq. 13.5})$$

$$\frac{H^E}{RT} = -T \left[\frac{\partial (G^E / RT)}{\partial T} \right]_{P,x} \quad (\text{Eq. 13.6})$$

$$\ln \gamma_i = -T \left[\frac{\partial (nG^E / RT)}{\partial n_i} \right]_{P,T,n_j} \quad (\text{Eq. 13.7})$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P} \right)_{T,x} = \frac{\bar{V}_i^E}{RT} \quad (\text{Eq. 13.8})$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P,x} = -\frac{\bar{H}_i^E}{RT^2} \quad (\text{Eq. 13.9})$$

From Gibbs-Duhem:

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i \quad (\text{Eq. 13.10})$$

$$\sum_i x_i d \ln \gamma_i = 0 \quad (\text{Eq. 13.11})$$

Modified Raoult's Law

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

y_i = mole fraction of i in vapor

P = total pressure

vapor pressure of i

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

(eq. 10.1)

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

x_i = mole fraction of i in liquid

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

$$y_i \hat{\phi}_i^{\text{vap}} P = x_i \gamma_i f_i^{\text{liq}}$$

(eq. 13.12)

$$f_i^{\text{liq}} = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left(\frac{V_i^{\text{liq}} (P - P_i^{\text{sat}})}{RT} \right)$$

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

(eq. 13.13)

(eq. 10.44)

Poynting Factor:

$$\Phi_i = \frac{\hat{\phi}_i^{\text{vap}}}{\hat{\phi}_i^{\text{sat}}} \exp \left[- \frac{V_i^{\text{liq}} (P - P_i^{\text{sat}})}{RT} \right] \approx \frac{\hat{\phi}_i^{\text{vap}}}{\hat{\phi}_i^{\text{sat}}} \quad (\text{eq. 10.44})$$

Activity Coefficient Models

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

Margules

(2-constant)

(eq. 13.40-13.41, p. 477)

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

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

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)

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

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

Wilson

(2-constant)

(eq. 13.46-13.47, p. 480)

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

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

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)

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

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

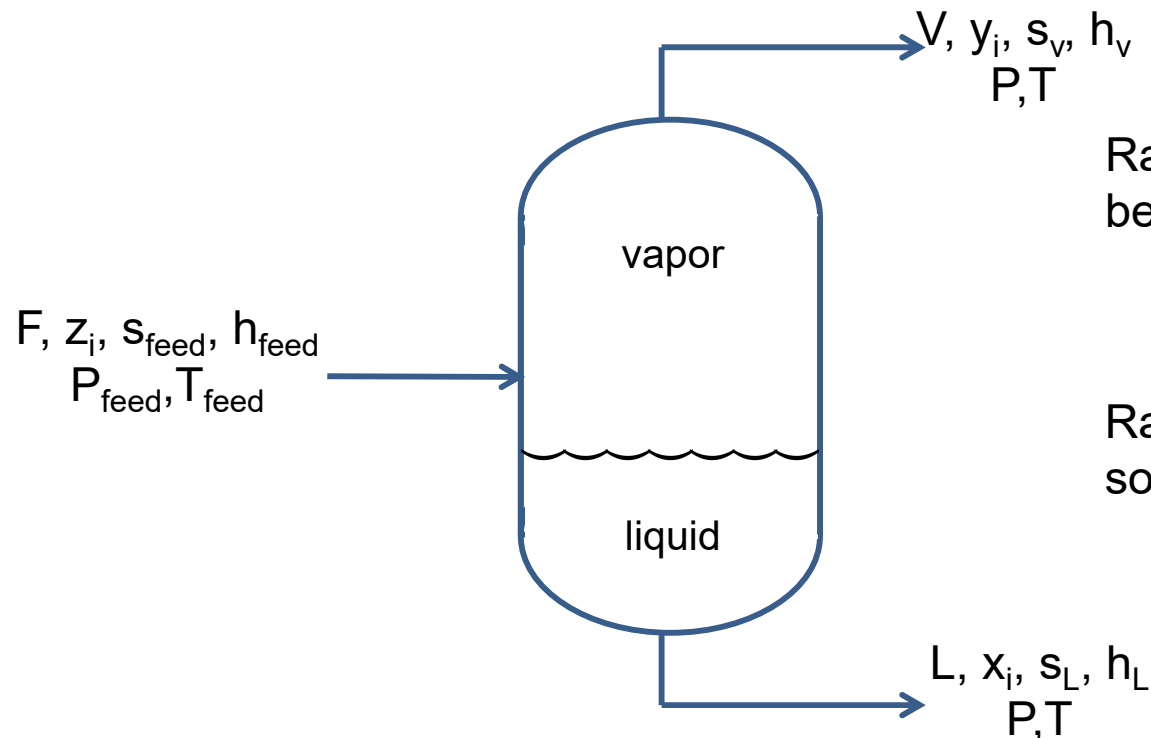
$$\tau_{12} = b_{12}/RT$$

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

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

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

Application - Rachford-Rice Equations



Raoult's Law reflects ideal solution behavior.

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

Raoult's Law is modified for real solution.

$$x_i = \frac{z_i}{1 + \psi(K_i - 1)} \quad \psi = \frac{V}{F}$$

$$y_i = K_i \cdot x_i$$

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

$$f(\psi) = \sum_i x_i - \sum_i y_i$$

Antoine equation gives P_i^{sat}

- 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,

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

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

$$P_1^{\text{sat}} = 79.80 \text{ kPa}$$

$$P_2^{\text{sat}} = 40.50 \text{ kPa}$$

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

- (a) Make a bubble point calculation for $T = 343.15 \text{ K}$, $x_1 = 0.05$, and
- (b) Make a dew point calculation for $T = 343.15 \text{ K}$, $y_1 = 0.05$, and

Example Problem 2

A liquid stream containing 0.35 mole fraction acetone and 0.65 mole fraction methanol is flashed at 2 bar 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

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