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

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)

Foundation of Vapor-Liquid Equilibrium Calculations

(Escaping tendencies are equal between phases)

fugacity of pure species i

$f_i \qquad \phi_i$

fugacity of species i in solution in phase α

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

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.

$$f_i^{vapor} = f_i^{liquid} = f_i^{sat}$$

(Eq. 10.39, page 377 and Lesson 36 Slide 6)

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

$$\hat{f}_i^{vapor} = \hat{f}_i^{liquid}$$

(i = 1, 2, …, N)

(Eq. 10.48, page 382)

$$\phi_i \equiv \frac{f_i}{P}$$

(Eq. 10.34, page 376)

(analogous)

$$\hat{\phi}_i \equiv \frac{\hat{f}_i}{y_i P}$$

(Eq. 10.52, *defined* on page 383)

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

(Eq. 13.1, page 460)

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)

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

for ideal gases:

$$f_i^{ig} = P$$

(Eq. 10.32)

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

Excess Gibbs energy:

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

(Definition, Lesson 37)

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

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

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

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

(Eq. 13.3)

Gibbs Energy Generating Functions

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

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

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

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

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

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

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

P = total pressure

vapor pressure of i

y_i = mole fraction of i in vapor

x_i = mole fraction of i in liquid

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

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

(eq. 10.1)

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

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

(eq. 13.12)

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

(eq. 10.44)

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

(eq. 13.13)

Poynting Factor: $$\Phi_i = \frac{\hat{\phi}_i^{vap}}{\hat{\phi}_i^{sat}} \exp\left[-\frac{V_i^l\left(P - P_i^{sat}\right)}{RT}\right] \approx \frac{\hat{\phi}_i^{vap}}{\hat{\phi}_i^{sat}}$$

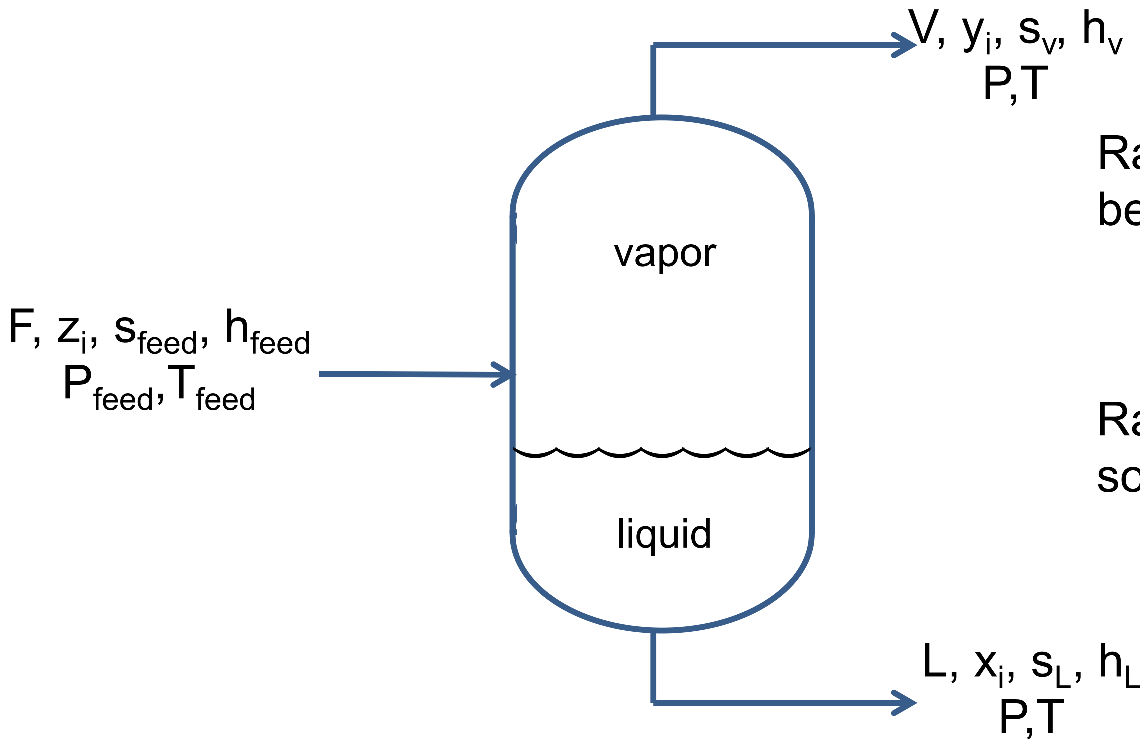
(eq. 10.44)

Activity Coefficient Models

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

Model	Equations	
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)	$\log\gamma_1 = \dfrac{A_{12}}{\left[1+\left(x_1A_{12}\right)/\left(x_2A_{21}\right)\right]^2}$	$\log\gamma_2 = \dfrac{A_{21}}{\left[1+\left(x_2A_{21}\right)/\left(x_1A_{12}\right)\right]^2}$
Wilson (2-constant) (eq. 13.46-13.47, p. 480)	$\log\gamma_1 = -\ln\left(x_1 + \Lambda_{12}x_2\right) + x_2\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}} - \dfrac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$ $\log\gamma_2 = -\ln\left(x_2 + \Lambda_{21}x_1\right) - x_1\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}} - \dfrac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$	
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)	$\log\gamma_1 = x_2^2\left[\tau_{21}\left(\dfrac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \dfrac{G_{12}\tau_{12}}{\left(x_2 + x_1G_{12}\right)^2}\right]$ $\log\gamma_2 = x_1^2\left[\tau_{12}\left(\dfrac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \dfrac{G_{21}\tau_{21}}{\left(x_1 + x_2G_{21}\right)^2}\right]$	$\tau_{12} = b_{12}/RT$ $\tau_{21} = b_{21}/RT$ $G_{12} = \exp\left(-\alpha\tau_{12}\right)$ $G_{21} = \exp\left(-\alpha\tau_{21}\right)$

Application - Rachford-Rice Equations



Raoult's Law reflects ideal solution behavior.

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

Raoult's Law is modified for real solution.

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

$$y_i = K_i \cdot x_i$$

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

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

- IVN satisfied when two independent variables specified.
- IVNs can be T,P or T,ψ, or P,ψ.
- IVN's can also be h_V, h_L, s_V, s_L, L, V

Antoine equation gives P_i^{sat}

Example Problem 1

Chapter Problem 13.17

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

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

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

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

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

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 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

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