King Fahd University of Petroleum & Minerals
Chemical Engineering Department
CHE 560 –Numerical Methods in Chemical Engineering
2010 - 2011 (102)

HW#2

Due: Tue. 8-March-2011

For the vapor liquid equilibrium (VLE), the following information is available for a binary system containing species α and β:

$$\frac{G^E}{RT} = 3\,e^{-280/T}\,x_1 x_2$$

$$\ln\left(P_1^{sat}\right) = 16.6 - \frac{3600}{T - 33}$$

$$\ln\left(P_2^{sat}\right) = 16.3 - \frac{3800}{T - 47}$$

in the above equations, G^E is the excess Gibbs energy, P_i^{sat} is the vapor pressure of species i in kPa, T is the absolute temperature in K and x_i is the mole fraction of species i in the liquid phase. For the above system, the modified Raoult's law:

$$y_i\ P = x_i\ \gamma_i\ P_i^{sat} \qquad (i = 1, 2)$$

is adequate for the description of the VLE, where y_i, x_i are the mole fractions of species i in the vapor and liquid phase, respectively, P is the total pressure, and γ_i is the activity coefficient of species i defined as:

$$\ln\left(\gamma_1\right) = \frac{G^E}{RT} + x_2 \frac{\partial \frac{G^E}{RT}}{\partial x_1} \qquad \text{and} \qquad \ln\left(\gamma_2\right) = \frac{G^E}{RT} - x_1 \frac{\partial \frac{G^E}{RT}}{\partial x_1}$$

Note that according to Gibbs phase rule, the above binary system has two degrees of freedom. Also, $y_1 + y_2 = 1$, $x_1 + x_2 = 1$ and $\frac{\partial x_1}{\partial x_2} = -1$. A good starting guess can be obtained by solving a simpler version of the VLE model given by Raoult's law: $y_i\ P = x_i\ P_i^{sat}$, i.e., ideal liquid solution ($\gamma_1 = \gamma_2 = 1$).

Perform the following tasks:

(a) <u>(20 Points)</u> Show that the following two equations are applicable for the above system:

$$y_1\, P = x_1\, e^{\left[3\left(e^{\frac{-280}{T}}\right)(1-x_1)^2+\left(16.6-\frac{3600}{T-33}\right)\right]}$$

$$(1-y_1)\, P = (1-x_1)\, e^{\left[3\left(e^{\frac{-280}{T}}\right)x_1^2+\left(16.3-\frac{3800}{T-47}\right)\right]}$$

(b) <u>(5 Points)</u> For a known liquid composition, x_1 and pressure, P, show that the equations that allow the calculation of the bubble point temperature, T, and the mole fraction in the vapor phase, y_1, are given by:

$$P\, U(1) = x_1\, e^{\left[3(1-x_1)^2\left(e^{\frac{-280}{U(2)}}\right)+\left(16.6-\frac{3600}{U(2)-33}\right)\right]}$$

$$P\, (1-U(1)) = (1-x_1)\, e^{\left[3x_1^2\left(e^{\frac{-280}{U(2)}}\right)+\left(16.3-\frac{3800}{U(2)-47}\right)\right]}$$

where $\underline{U} = \begin{bmatrix} y_1 \\ T \end{bmatrix}$ is the vector of unknowns.

(c) <u>(10 Points)</u> Using the Newton-Raphson's method, derive the residual equations and the Jacobian matrix.

(d) <u>(10 Points)</u> Solve the equations derived in part (c) using the sample program provided for you in class for $x_1 = 0.1$, $P = 100$. Keep x_1 and P as input variables by adding the following statement in the main program:
PARAMETER (x1 = 0.1, P=100)
and making them common by adding the following statement:
COMMON /PARAM/ x1, P
to the main program, subroutine residuals and subroutine jacobian. Upload this program to WebCT (call it yourname-hw3.f).

(e) <u>(20 Points)</u> Prepare two graphs for y_1 as a function of x_1 and T as a function of x_1 for P = 100. Use values of x1 = 0.1, 0.3, …, 0.9.