LAB NUMBER - 8

Vapor – Liquid Equilibria from ideal vapor and non-ideal liquid phase

Theory: In the previous lab, you have found Vapor-Liquid phase behavior of Non-Ideal Binary mixture where we assumed non-ideal vapor and ideal liquid phase using Eqn. 1 and plotted the T-x-y and P-x-y curves for the binary mixture.

$$x_i P_i^{VP} = \phi_i y_i P \quad \text{(Non-Ideal Vapor and Ideal liquid)} \qquad (1)$$

In this lab, we will assume the vapor to behave ideally and liquid to be treated non-ideal for the binary system.

As we already know the general relationship for any liquid can be written as in Eqn. 2

$$\Upsilon_i \, x_i f_i (\text{pure liquid } i) = \phi_i y_i P \qquad (2)$$

where y denotes mole fractions in the vapor phase and x to denote mole fraction in the vapor phase can be considered ideal (so that $\phi_i = 1$) and P is the total Pressure. In addition, pure-component vapor pressures are often sufficiently low so that the fugacity of a pure liquid numerically equals to the component vapor pressure. These two conditions hold true if the vapor pressures of the pure components do not exceeded a few atmospheres. With these assumptions, Eqn. 2 becomes:

$$\Upsilon_i \, x_i P_i^{VP} = y_i P \qquad (3)$$

The significance of liquid phase activity coefficients, denoted as γ_i, is evident in their impact on the gamma/phi formulation of vapor-liquid equilibria (VLE). These coefficients have a direct correlation with the excess Gibbs energy. Typically, the excess Gibbs energy, represented as G^E/RT, is influenced by temperature (T), pressure (P), and composition; however, at low to moderate pressures for liquid systems, its sensitivity to pressure is negligible. Consequently, it is common practice to disregard its pressure dependence, and when applying it at a constant T, the excess Gibbs energy is treated as a function solely dependent on composition.

$$\frac{G^E}{RT} = g(x_1, x_2, \ldots, x_n) \qquad (4)$$

Based on above formulation for a binary system the excess Gibb's free energy can be written as

$$Y = \frac{G^E}{x_1 x_2 RT} = a + bx_1 + cx_1^2 + \ldots \qquad (5)$$

As we know $x_2 = 1 - x_1$. An equivalent power series can be represented as:

$$Y = \frac{G^E}{x_1 x_2 RT} = A_o + \sum_{n=1}^{a} A_n z^n \qquad (6)$$

where, by definition, $z = 2x_1 - 1$, a is the order of power series, and parameters A_n are functions of temperature.

Using Gibbs Duhem equation, Y_i can be written as:

$$\ln Y_i = (1 - x_i)^2 \left(Y + x_i \frac{dY}{dx_i}\right) \tag{7}$$

There are many models proposed like Margules, Van Laar, Wilson from which expression of activity coefficient Y_i can be found by choosing appropriate z and A_n values and Y_i can be found by using Eqn 7.

Wilson Model being one of the model is versatile and has been adopted to describe the VLE behaviour of many binary mixtures. The Wilson equation contains two parameters (Λ_{ij} and Λ_{ji}) for the binary system. It is written as:

$$\frac{G^E}{RT} = -x_i \ln\left(x_i + \Lambda_{ij} x_j\right) - x_j \ln\left(x_j + \Lambda_{ji} x_i\right) \tag{8}$$

$$\ln Y_i = -\ln\left(x_i + \Lambda_{ij} x_j\right) + x_j \left[\frac{\Lambda_{ij}}{x_i + \Lambda_{ij} x_j} + \frac{\Lambda_{ji}}{x_j + \Lambda_{ji} x_i}\right] \tag{9}$$

$$\ln Y_j = -\ln\left(x_j + \Lambda_{ji} x_i\right) - x_i \left[\frac{\Lambda_{ij}}{x_i + \Lambda_{ij} x_j} - \frac{\Lambda_{ji}}{x_j + \Lambda_{ji} x_i}\right] \tag{10}$$

where Wilson parameters Λ_{ij} and Λ_{ji} can be found using

$$\Lambda_{ij} = \frac{V_j}{V_i} exp\left[-\frac{(\lambda_{ij} - \lambda_{ii})}{RT}\right] \tag{11}$$

$$\Lambda_{ji} = \frac{V_i}{V_j} exp\left[-\frac{(\lambda_{ji} - \lambda_{jj})}{RT}\right] \tag{12}$$

where V_i and V_j is the molar volume, $\lambda_{ij} - \lambda_{ii}$ and $\lambda_{ji} - \lambda_{jj}$ are binary interaction parameters available from literature for a binary pair.

There is this overall constraint that the sum of the mole fractions in the liquid and vapor phases must be equal to one:

$$\sum_{i=1}^{n} x_i = \sum_{i=1}^{n} y_i = 1 \tag{13}$$

Vapor Pressure as a function of temperature of any component can be obtained from Antoine Equation.

$$\log_{10} P_i^{VP} = A - \frac{B}{C + T} \tag{14}$$

where A, B and C are Antoine parameter, T is the temperature in °C and P_i^{VP} is the vapor pressure of pure component in mm of Hg. (Note that 1 atm = 760 mm of Hg)

You have been given a binary mixture of tetrahydrofuran (THF) and water with their respective boiling points, Wilson parameters and Antoine parameters A, B and C have been given. Considering the

system as non-ideal and using the condition of Ideal Vapor and non-ideal liquid (Eqn. 3) solve the below problem statement.

Problem Statement:

1. Construct a T-x-y diagram for a binary system of THF and water at a total pressure of 1 atm using wilson model for a given T vs x data of water (water_data.txt file has been given) Consider the liquid to be non-ideal and vapor to behave ideally.

    The Wilson equation contains two parameters for the binary equation.

    $$\ln Y_i = -\ln(x_i + \Lambda_{ij}x_j) + x_j[\frac{\Lambda_{ij}}{x_i+\Lambda_{ij}x_j} + \frac{\Lambda_{ji}}{x_j+\Lambda_{ji}x_i}]$$

    $$\ln Y_j = -\ln(x_j + \Lambda_{ji}x_i) - x_i[\frac{\Lambda_{ij}}{x_i+\Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{x_j+\Lambda_{ji}x_i}]$$

    where wilson parameters Λ_{ij} and Λ_{ji} can be found using

    $$\Lambda_{ij} = \frac{V_j}{V_i}exp\left[-\frac{(\lambda_{ij}-\lambda_{ii})}{RT}\right]$$

    $$\Lambda_{ji} = \frac{V_i}{V_j}exp\left[-\frac{(\lambda_{ji}-\lambda_{jj})}{RT}\right]$$

    where V_i and V_j is the molar volume, $\lambda_{ij} - \lambda_{ii}$ and $\lambda_{ji} - \lambda_{jj}$ are binary interaction parameters available from literature for a binary pair.

Wilson Parameters	Values from literature
$\lambda_{ij} - \lambda_{ii}$	1475.26 (cal/mol)
$\lambda_{ji} - \lambda_{jj}$	1844.79 (cal/mol)
V_i	81.55 (cm³/mol)
V_j	18.07 (cm³/mol)

Considering "i" to THF and "j" to be water here.

Antoine equation is given by:

$$\log_{10} P_i^{VP} = A - \frac{B}{C+T}$$

where A, B and C are Antoine parameters, T is the temperature in °C and P_i^{VP} is the vapor pressure of pure component in mm of Hg.

Note that 1 atm = 760 mm of Hg

Component	A	B	C
THF	7.1057	1256.68	232.621
Water	8.07131	1730.63	233.426

Boiling Point of THF and water are **65 °C and 100 °C** respectively. This is the range of temperature for which T in T-x-y curve will vary whereas x, y will vary from 0 to 1.
(T-x-y diagram is to be plotted for both water and THF)

2. Construct the x vs y graph for THF (your simulated data) with the literature value x vs y (given in THF_literature.txt file) on the same plot at a total pressure of 1 atm.
3. Construct a P-x-y and x-y diagram for THF at a temperature of 50 °C.

Note that: MATLAB should be used to code the solution:

Tentative Plot: