

Laboratory and Homework Assignment 2

Reading Assignment

1. "Chapter 8: Activity Coefficient Models" from Jana, Amiya K. Chemical process modelling and computer simulation. PHI Learning Pvt. Ltd. 2011.
2. "Chapter 13: Equation of State Models" from Jana, Amiya K. Chemical process modelling and computer simulation. PHI Learning Pvt. Ltd. 2011.

Laboratory Assignment (Due after laboratory session)

1. a) [100 points] In our last homework assignment we used Raoult's law to study chloroform/ethanol binary system. In this assignment, we will use modified Raoult's law with activity coefficients given by Wilson's equation to study the same system. Compute **a)** isobaric T vs x , y diagram; and **b)** isothermal P vs x , y diagram. For both the cases also plot y vs x diagram. Compare with experimental results given in Tables 1 and 2.

You need to do this exercise first using Matlab and then using ASPEN PLUS.

The Antoine equation parameters are (Chloroform: $A = 6.9546$, $B = 1170.966$, and $C = 226.232$; $-10 < T < 60^\circ\text{C}$; Ethanol: $A = 8.11220$, $B = 1592.864$, $C = 226.184$; $20 < T < 93^\circ\text{C}$). The values are taken from DECHEMA chemical data series. The form of equation used is $\log_{10} P^{sat} = A - B/(T + C)$ with pressure in mmHg and temperature in $^\circ\text{C}$.

Wilson's equation is given by:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right), \quad (1)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1 \left(\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} \right), \quad (2)$$

where,

$$\Lambda_{12} = \frac{v_2^L}{v_1^L} \exp\left(-\frac{A_{12}}{RT}\right) \quad (3)$$

$$\Lambda_{21} = \frac{v_1^L}{v_2^L} \exp\left(-\frac{A_{21}}{RT}\right). \quad (4)$$

Chloroform is indexed as '1' and Ethanol is indexed as '2', $A_{12} = -268.7676$ cal/gmol and $A_{21} = 1270.3897$ cal/gmol. v_i^L is the molar volume of pure liquid component i th. Here take $v_1^L = 80.67$ cm³/gmol and $v_2^L = 58.68$ cm³/gmol.

Table 1: Experimental VLE data at $T = 308.15$ K. Taken from DECHEMA chemical data series.

P (kPa)	x_1	y_1
13.703	0.00000	0.00000
13.982	0.00620	0.02540
14.840	0.02410	0.09910
15.147	0.02970	0.12100
16.471	0.05420	0.21540
16.775	0.05940	0.23430
19.766	0.11090	0.38850
23.678	0.17300	0.53040
27.422	0.23610	0.62070
30.006	0.28730	0.67470
30.563	0.30140	0.68700
31.531	0.32270	0.70090
33.783	0.38450	0.73700
34.035	0.39220	0.74120
35.684	0.43840	0.76460
36.536	0.48270	0.77970
38.923	0.61850	0.81810
39.587	0.67830	0.83270
40.403	0.77460	0.85540
40.715	0.82650	0.86980
40.679	0.84230	0.87520
40.830	0.84830	0.87830
40.803	0.93150	0.91610
40.646	0.95600	0.93630
40.553	0.95860	0.93850
40.489	0.96000	0.94030
40.518	0.96160	0.94140
39.345	1.00000	1.00000

Table 2: Experimental VLE data at $P = 94$ kPa. Taken from DECHEMA chemical data series.

T (K)	x_1	y_1
349.7	0.000	0.000
349.0	0.022	0.047
348.2	0.038	0.091
345.9	0.080	0.206
343.7	0.122	0.305
341.7	0.163	0.403
340.4	0.203	0.449
338.9	0.237	0.504
337.5	0.277	0.552
336.6	0.293	0.587
334.3	0.399	0.670
332.1	0.559	0.748
331.1	0.681	0.792
330.6	0.819	0.841
330.7	0.898	0.881
332.3	1.000	1.000

Practice Homework Assignment

1. a) Derive the following expressions for gas-phase fugacity coefficient of the i^{th} component in the mixture ($\hat{\phi}_i$).

$$\ln(\hat{\phi}_i) = \frac{1}{RT} \int_0^P \left[\left(\frac{\partial(nV)}{\partial n_i} \right)_{T,P,n_j} - \frac{RT}{P} \right] dP, \quad (5)$$

and,

$$\ln(\hat{\phi}_i) = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln z, \quad (6)$$

where z is the compressibility factor of the mixture. All the other symbols are self explanatory.

- b) Using these equations to get the fugacity coefficient for a mixture of an ideal gas.
c) Now assume that the molar volume is a linear function of the mole fraction, i.e.

$$V = \sum_i n_i v_i, \quad (7)$$

where v_i is the partial molar volume of the i^{th} component. This is known as Amagat's Law. This approximation will lead you to what is known as Lewis fugacity rule. Derive the expression for fugacity coefficient under Amagat's law approximation. What is the physical meaning of this result? How is this different from assuming ideal gas law?

d) Now using the above equations, derive expressions for fugacity coefficient of the i^{th} component in the gas phase mixture using Redlich-Kwong equation of state.

2. In this exercise we will study vapor-liquid equilibria of acetone-water system. We will compute T vs x , y diagram for **a)** $P = 101.325$ kPa and **b)** $P = 3446.0633$ kPa. The experimental data for this system can be obtained from "Othmer, Donald F., Manu M. Chudgar, and Sherman L. Levy. *Binary and ternary systems of acetone, methyl ethyl ketone, and water*. Industrial & Engineering Chemistry 44.8 (1952): 1872-1881".

Use activity coefficient approach to obtain the VLE in Matlab, i.e., use the following equation:

$$y_i \hat{\phi}_i^v P = \gamma_i x_i \hat{\phi}_i^{\text{sat}} P_i^{\text{sat}} \exp \left(\frac{v_i^{0L} (P - P_i^{\text{sat}})}{RT} \right) \quad (8)$$

Take Redlich-Kwong equation of state to obtain gas-phase fugacity coefficients and pure liquid saturated fugacity coefficients; and Wilson's equation for computing activity coefficients in the liquid phase.

If acetone is indexed as '1' and water is indexed as '2', the Wilson's equation parameters are: $A_{12} = 489.3727$ cal/gmol and $A_{21} = 1422.849$ cal/gmol. Here take $v_1^L = 74.05$ cm³/gmol and $v_2^L = 18.07$ cm³/gmol.

Use Rackett equation to obtain corrections to pure component liquid molar volumes. Pure component properties can be obtained from NIST database or DECHEMA chemistry data series or Dortmund Data Bank. Clearly mention the source where you obtained the parameters.

You need to do this exercise both with Matlab and ASPEN.

Also, as a next exercise in ASPEN try out various base methods to obtain the most accurate method for this system. Pen down this method along with the relevant equations.