Problems: predicting VLE for binary mixtures

You will need to use the JavaScript program "predicting vapour-liquid equilibrium of binary mixtures using cubic equations of state" at www.cheng.cam.ac.uk/~pjb10/thermo to do these problems.

1. Consider an equimolar liquid mixture of benzene and toluene at 350 K.

(*a*) Assume initially that the liquid behaves as an ideal mixture. In this case, the bubble point pressure is predicted to be:

$$P_{\text{bubble}} = x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}}$$

and the vapour phase composition at the bubble point is predicted to be:

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

Use these equations to predict the bubble point pressure of the mixture, and the composition of the vapour phase at the bubble point. (Note P_i^{sat} can be estimated by assuming an equation of state and setting $x_i = 1$).

(*b*) Now use the program to predict the actual bubble point pressure and vapour composition assuming the Soave-Redlich-Kwong equation applies and the binary interaction parameter k_{12} is zero. Why do you think the predictions in part (*a*) are reasonable for this system?

2. Consider modelling a mixture of methanol (1) and benzene (2) at 1.013 bar using the Peng-Robinson equation. [Methanol has T_c = 512.6 K, P_c = 80.96 bar, ω = 0.566]

(*a*) Assume initially that the binary interaction parameter k_{12} is zero.

(*i*) Calculate the bubble point temperature at values of x_1 = 0, 0.1, 0.2, …, 1.0. Then calculate the dew point temperature at values of y_1 = 0, 0.1, 0.2, …, 1. Plot a graph of these predictions.

(*ii*) At an azeotrope, the composition of liquid and vapour phases are the same at equilibrium. Use trial and error to determine the temperature and composition that is predicted for the azeotrope between methanol and benzene at this pressure if k_{12} is zero.

(*b*) The actual azeotrope of this system at 1.013 bar is at 331.1 K with $x_1 = y_1 = 0.614$.

(*i*) Find the value of k_{12} that predicts a bubble point pressure of 1.013 bar at T = 331.1 K and x_1=0.614.

(*ii*) Using this value of k_{12}, obtain bubble point and dew point temperatures as composition is varied and include these data on your graph from part (*a*). What are the temperature and composition predicted for the azeotrope at 1.013 bar with this value of k_{12}?

(*c*) Experimental VLE data for this system is given below (from Table 13-1 of the 7th edition of Perry's Chemical Engineers' Handbook). Plot these data on your graph and comment on the results.

T/K	353.25	343.82	339.59	336.02	333.35	331.79	331.17	331.25	331.62	333.05	335.86	337.85
x_1	0	0.026	0.050	0.088	0.164	0.333	0.549	0.699	0.782	0.898	0.973	1
y_1	0	0.267	0.371	0.457	0.526	0.559	0.595	0.633	0.665	0.760	0.907	1

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3. In a petroleum refinery, an equimolar stream of propane and *n*-butane is fed to a flash separator operating at 40°C. Determine the pressure at which the separator should be operated so that an equal number of moles of liquid and vapour are produced.

4. The following VLE data has been obtained at 50°C on the ethylene (1) – acetone (2) system. (Acetone has T_c = 508.2 K, P_c = 47.01 bar, ω=0.306).

P/bar	13.5	15.3	23.7	28.3	33.5	44.5	53.0	67.3	72.6	75.9
x_1	0.0958	0.1127	0.1904	0.2255	0.2715	0.3670	0.4863	0.6489	0.7440	0.8132
y_1	0.9202	0.9257	0.9456	0.9487	0.9529	0.9553	0.9584	0.9559	0.9360	0.9182

(data from C. Yokoyama et al., *J. Chem. Eng. Data*, **30**, 177, 1985)

(*a*) Plot these data points on a suitable phase diagram.

(*b*) Use the bubble point pressure calculation method to obtain bubble and dew point curves for this system assuming the system can be modelled by the modification to the Peng-Robinson equation proposed by Gasem and co-workers with k_{12} = 0, and plot these on your diagram.

(*c*) Repeat part (*b*) but assuming that the binary interaction parameter k_{12} = 0.06.

5. For the same system as question 4, use the modification to the Peng-Robinson equation proposed by Gasem and co-workers assuming k_{12} = 0.06 to plot bubble and dew point curves on a *P-T* phase diagram for an ethylene-acetone mixture with a mole fraction of ethylene of 0.40.
[Hint: get the bubble point curve from bubble point pressure calculations, but get the dew point curve from dew point temperature calculations. Calculations near the critical point can become slow and tedious. In order to save time you can assume that the equation of state predicts for a mixture of this composition that T_c = 464 K and P_c = 84.7 bar.]

What unusual phenomenon occurs near the critical point for this mixture?