The activity coefficient depends on temperature, pressure and composition but the most critical variable is composition. The main challenge is how to obtain the activity coefficient for a given system, if experimental data at the desired conditions are not available. Models such as the Margules, van Laar, and the like, provide a correlation between activity coefficients and composition via an equation with a small number of adjustable parameters. These parameters are fitted using experimental data and ~~generally~~ the agreement between the resulting correlation and the original data is generally very good. UNIFAC contains no adjustable parameters but uses values that have been obtained by regressing a large number of experimental data for several different mixtures. As a result, the accuracy of its predictions varies from system to system. For example, the system n-pentane/1-butanol is predicted fairly accurately, even though it is quite strongly no-ideal (notice the magnitude of the activity coefficients at infinite dilution). By contrast, the system ethanol/acetonitrile is predicted less accurately. The predictive advantage of UNIFAC comes at the expense of accuracy, which is not guaranteed. In the literature we find recommendations that provide decision trees for selecting the appropriate model based on the chemical character of the components. Unfortunately, there is no foolproof method by which to determine which model is best for a given system. The best approach is try various models and validate them against available data before a final choice is made.

12.8 Problems

Problem 12.1: A binary solution is described by the one-parameter equation

$$\frac{G^{\mathrm{E}}}{RT} = A(x_1 - x_2^2),$$

where A is constant. At 50 °C and $x_1 = 0.30$ the partial pressures of the two components in the vapor are $P_1 = 105.3$ mm Hg, $P_2 = 288$ mm Hg respectively. The saturation pressure of pure components at 50 °C: $P_1 = 228$ mm Hg, $P_2 = 380$ mm Hg. Calculate the Pxy graph of this system at 50 °C.

Problem 12.2: The table below gives the enthalpy of benzene(1)-heptane(2) solutions at 20 °C 1 bar as a function of the mol fraction of benzene.
a) Calculate and plot the excess enthalpy at 20 °C, 1 bar.
b) Calculate the partial molar excess enthalpy at $x_1 = 0.2$, 20 °C, 1 bar.
c) Calculate the heat that is released or absorbed when 10 mol of benzene is mixed with 40 mol of heptane isothermally at 20 °C, 1 bar.

d) Calculate the temperature change when 10 mol of benzene is mixed with 40 mol of heptane adiabatically, 1 bar., if the initial temperature of the pure components is 20 °C. The heat capacity of the pure liquids are $C_{P1} = 134$ J/mol, $C_{P2} = 222$ J/mol K.

x_1	H (J/mol)	x_1	H (J/mol)
0	635.00	0.50	1229.51
0.14	956.91	0.58	1185.85
0.20	1035.06	0.65	1110.76
0.22	1066.37	0.71	1005.74
0.30	1174.31	0.83	688.42
0.33	1184.04	0.88	537.71
0.37	1203.61	1	−50.00
0.44	1237.33		

Problem 12.3: The table below gives the excess enthalpy for the system acetone(1)-water(2) at 25 °C, 1 bar.
a) Calculate the partial molar enthalpy of each component at $x_1 = 0.5$, 25 °C, 1 bar. The reference state for each component is the pure liquid at 25 °C, 1 bar.
b) Repeat the previous part with the reference state for water changed to the pure liquid at 2 bar,
c) A solution that contains 50% by mole acetone is mixed with ~~an equal volume~~ equal moles of a solution that contains 80% by mole acetone. The mixing takes place in a heat bath at 25 °C. Determine whether any amount of heat is exchanged between the system and the surroundings. If so, calculate that heat and report whether the mixing is endo- or exothermic.

x_{acetone}	H^{E} (J/mol)	x_{acetone}	H^{E} (J/mol)
0.0000	0.00	0.5000	−167.57
0.0424	−388.11	0.6271	70.27
0.1186	−630.27	0.7246	200.00
0.1314	−638.92	0.7542	234.60
0.2458	−612.97	0.8771	277.84
0.2542	−591.35	0.9534	234.60
0.3729	−414.05	1.0000	0.00

Problem 12.4: a) Based on Figure 12-5, is the mixing of hydrazine and water an endothermic or exothermic process?
b) Calculate the excess enthalpy ~~of mixing~~ for a solution that contains 60% by mol hydrazine at 20 °C.

remove "a)"

Problem 12.5: ~~a)~~ Determine the phase of a mixture of hydrazine and water at 1 bar, 110 °C if the overall mol fraction of hydrazine is 20%. If the state is a mixture of vapor and liquid, report the amounts and compositions in each phase.
(Use Figure 12-5 to answer these questions.)

Problem 12.6: Pure hydrazine is mixed with pure water to form a solution that contains 40% hydrazine (by mol). Both components are initially at 20 °C.
a) Determine the temperature of the final solution if mixing is adiabatic.
b) Determine the amount of heat exchanged with the surroundings if mixing is isothermal.
(Use Figure 12-5 to answer these questions.)

Problem 12.7: The activity coefficients of the system benzene(1)/acetonitrile(2) are given by

$$\ln \gamma_1 = A x_2^2, \quad \ln \gamma_2 = A x_1^2.$$

At 45 °C, $A = 1$.
a) Obtain the activity coefficients of the two components at infinite dilution.
b) Does this system form an azeotrope at 45 °C? If so, report the pressure and the azeotropic composition.
c) Calculate the bubble and dew pressure of a system containing 30% benzene by mole at 45 °C.
Additional data. The saturation pressures of components 1 and 2 at 45 are 223.7 ~~°C~~ and 208.4 Torr, respectively.

45 °C (add degree C)

remove "°C"

Problem 12.8: At 50 °C the system acetone(1) and chloroform(2) forms an azeotrope with composition $x_1 = 0.416$.
a) What is the pressure at the azeotropic composition at 50 °C?
b) 1 mole of acetone is mixed with one mole of chloroform at 50 °C, 0.5 bar. What is the phase of the pure components before mixing? What is the phase of the system after mixing?
remove part (d) ~~c) Do you expect the two liquids to be fully miscible at 50 °C or not?~~
Additional information: The activity coefficients are given by the following equations:

$$\ln \gamma_i = A x_i^2.$$

replace xi with (1-xi)

where A is an unknown constant. The saturation pressures of the pure components at 50 °C are: $P_{\text{acetone}} = 0.81$ bar, $P_{\text{chloroform}} = 0.41$ bar.

Problem 12.9: Use the data below for the system benzene(1)/acetonitrile(2) at 45 °C to answer the following questions: