13.7 The flash point of liquid mixtures is discussed in Section 10.5. For the following mixtures, estimate the flash point temperature of the following components and their equimolar mixtures using UNIFAC:

(a) methanol (LFL = 7.3%) + 2-butanone (LFL = 1.8%)
(b) ethanol (LFL = 4.3%) + 2-butanone (LFL = 1.8%).

13.8 Use the UNIFAC model to predict the VLE behavior of the n-pentane(1) + acetone(2) system at 1 bar and compare to the experimental data in problem 11.11.

13.9 According to Gmehling et al. (1994),[23] the system acetone + water shows azeotropes at: (1) 2793 mmHg, 95.1 mol% acetone, and 100°C; and (2) 5155 mmHg, 88.4 mol% acetone and 124°C. What azeotropic pressures and compositions does UNIFAC indicate at 100°C and 124°C? Othmer et al. (1946) (*cf.* Gmehling[24]) have studied this system at 2570 mmHg. Prepare *T-x-y* or *P-x-y* plots comparing the UNIFAC predictions to the experimental data.

13.10 Consider the experimental data of Brown and Smith (1954) cited in problem 10.2. Prepare a *P-x-y* plot and a plot of experimental activity coefficients vs. composition. Then use UNIFAC to predict the activity coefficients across the composition range and add the calculations to the plots.

13.11 Flash separations are fundamental to any process separation train. A full steady-state process simulation consists largely of many consecutive flash calculations. Use UNIFAC to determine the temperature at which 20 mol% will be vaporized at 760 mmHg of an equimolar mixture liquid feed of n-pentane and acetone.

13.12 A preliminary evaluation of a new process concept has produced a waste stream of the composition given below. It is desired to reduce the waste stream to 10% of its original mass while recovering essentially pure water from the other stream. Since the solution is very dilute, we can use a simple equation known as Henry's law to represent the system. According to Henry's law, $f_i^L = h_i x_i = x_i \gamma_i^\infty P_i^{sat}$. Use UNIFAC to estimate the Henry's law constants when UNIFAC parameters are available. Use the Scatchard-Hildebrand theory when UNIFAC parameters are not available. Estimate the relative volatilities (relative to water) of each component. Relative volatilities are defined in problem 11.2.

Compositions in mg/liter are:

Methanol	H2S	Methyl Mercaptan	Dimethyl Sulfoxide	Dimethyl Disulfide
5100	30	50	50	100

13.13 Derive the form of the excess enthalpy predicted by Wilson's equation assuming that A_{ij}'s and ratios of molar volumes are temperature-independent.

13.14 Orbey and Sandler (1995. *Ind. Eng. Chem. Res.* 34:4351.) have proposed a correction term to be added to the excess Gibbs energy of mixing given by UNIQUAC. To a reasonable degree of accuracy the new term can be written

23. Gmehling, et al., 1994. *Azeotropic Data,* NY: VCH.
24. Gmehling, J., Onken, V., Arlt, W. 1977. *Vapor-Liquid Equilibrium Data Collection*, Frankfurt, Germany: DECHEMA.

$$\frac{G_{HB}^E}{RT} = \sum_i x_i \left[-2\ln(1 + a_i F) + \frac{a_i F}{1 + a_i F} - C_i^{pure} \right]$$

where

$$F \equiv \sum_i \frac{x_j a_j}{1 + a_j F}$$

Derive an expression for the correction to the activity coefficient. [Hint: Do you remember how to differentiate implicitly?]

13.15 The energy equation for mixtures can be written for polymers in the form:

$$\frac{U - U^{ig}}{RT} = \frac{\rho}{2} \sum_i \sum_j x_i x_j N_{d,i} N_{d,j} \int \frac{N_A u_{ij}}{RT} g_{ij} 4\pi r^2 dr$$

By analogy to the development of the Scatchard-Hildebrand theory, this can be rearranged to:

$$\frac{U - U^{ig}}{RT} = \frac{-\rho}{2RT} \sum_i \sum_j x_i x_j N_{d,i} N_{d,j} N_A \varepsilon_{ij} \sigma_{ij}^3 a_{ij}^*$$

where

$N_{d,i}$ = degree of polymerization for the ith component

ρ = molar density

x_i = mole fraction of the ith component

N_A = Avogadro's number

U = molar internal energy.

$a_{ii}^* = 3 + 2/Nd_i$

$a_{ij}^* = (a_{ii}^* a_{jj}^*)^{1/2}$

$\sigma_{ij}^3 = (\sigma_i^3 + \sigma_i^3)/2$

$\varepsilon_{ij} = (\varepsilon_{ii} \varepsilon_{jj})^{1/2}$

Derive an expression for $\ln \gamma_1$ for the activity coefficient model presented above.

13.16 Use the UNIFAC model to predict P-x-y data at 90°C and x_1, = {0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0} for propanoic acid + water. Fit the UNIQUAC model to the predicted P-x-y data and report your UNIQUAC a_{12} and a_{21} parameters in kJ/mole.

13.17 (a) Rearrange Eqn. 13.22 to obtain Eqn. 13.23.

(b) Use Eqns. 13.16 and 13.18 in Eqn. 13.17 and perform the integration to obtain Eqn. 13.19.

(c) Use Eqns. 13.16 and 13.31 in Eqn. 13.17 and perform the integration to obtain Eqn. 13.40.

13.18 Fit the data from problem 11.11 to the following model by regression over all points, and compare with the experimental data on the same plot, using the

(a) Wilson equation
(b) NRTL equation
(c) UNIQUAC equation

13.19 Work problem 11.25 using the

(a) Wilson equation
(b) NRTL equation
(c) UNIQUAC equation

13.20 Work problem 11.26 using the

(a) Wilson equation
(b) NRTL equation
(c) UNIQUAC equation

13.21 Using the data from problem 11.27, fit the specified model equation and then plot the *P-x-y* diagram at 80°C using the

(a) Wilson equation
(b) NRTL equation
(c) UNIQUAC equation