# 14.9 NUMERICAL PROCEDURES FOR BINARY, TERNARY LLE

## Excel Procedure

For a binary system, the LLE iteration procedure has been outlined in Section 14.4. This section provides the detailed steps to apply that method using a spreadsheet to determine the mutual solubilities predicted by an activity coefficient expression. Two activity coefficient tables are required, one for phase $\alpha$ and one for phase $\beta$. The procedure outlined in the earlier example was based on successively updating the $K_i$ values. This will be done by using cells to hold the old and new values and copying and pasting values for updating. Two variations have been provided on the spreadsheets, UNIQUAC and UNIFAC(LLE). In both cases, an iteration table has been provided. For UNIFAC(LLE) the activity coefficient calculations are complex enough to require two spreadsheets, but cells can be referenced on the second spreadsheet by including the worksheet name in the formula.

**Step 1.** Select the activity method and open the spreadsheet, and locate the iteration table with rows for $K_{i,old}$, $K_{i,new}$, $x^{\alpha}_{i,old}$, $x^{\alpha}_{i,new}$, $x^{\beta}_{i,old}$, and $x^{\beta}_{i,new}$. The $x^{\alpha}_{i,old}$ and $x^{\beta}_{i,old}$ rows in the iteration tables will duplicate values in the activity coefficient tables, and they are for convenience to see how the values are changing since the screen is pretty crowded, and therefore during iteration only the iteration table will need to be monitored. Program the *iteration table* $x^{\alpha}_{i,old}$ and $x^{\beta}_{i,old}$ rows to duplicate the values used in the *activity coefficient table* for the specified phase by entering the cell name with the desired value. (e.g. "=A1" to duplicate cell A1). (If you are using UNIFAC with two separate spreadsheets, you can still reference values from the sheets that are not on top, just use the mouse to click on the correct cell on the correct sheet when entering the formula.)

**Step 2.** Initialize the compositions using the following steps. Before you proceed, decide which components will be rich in the $\alpha$ and $\beta$ phases, or follow the problem statement. It is usually easiest if component numbers are chosen so that component three is completely miscible in the other components. Follow the steps carefully, saving the spreadsheet often, and if the initialization goes awry, repeat the procedure.

(a) For a binary system, enter the compositions in the *activity coefficient tables* for each phase assuming infinite dilution for component 1 in one phase and infinite dilution for component 2 in the other phase. Enter these compositions for each phase before proceeding to assure proper initialization.

(b) For a ternary system, the procedure that we develop here will only work for component 3 appearing at a fixed mole fraction. The iterations are best started from a previously converged binary result, with the third component at infinite dilution in each phase, or from a previously converged ternary result. Enter these compositions for each phase before proceeding to assure proper initialization. (You may use a small number like 1E-11 for infinite dilution.)

**Step 3.** Initialize the *K*-ratios and perform the first iteration with the following steps. Enter formulae in the *iteration table* to calculate the $K_{i,new} = \gamma_i^{\alpha}/\gamma_i^{\beta}$ (Eqn. 14.4) for each component. This creates a first guess for all $K_i$. Copy the *values* from $K_{i,new}$ to $K_{i,old}$ (To do this, right-click before pasting, and choose **Paste Special...** then choose **Values** from the dialog box. Below, this procedure will be referred to as an instruction to paste *values*). For the iteration table row for $x^{\alpha}_{i,new}$ values, enter in the following order (using cell references in the formulas): Binary calculation—enter $x^{\alpha}_{1,new} = (1 - K_{2,old})/(K_{1,old} - K_{2,old})$ and $x^{\alpha}_{2,new} = 1 - x^{\alpha}_{1,new}$, and for the $x^{\beta}_{i,new}$ row, enter the formulas to calculate $x^{\beta}_{i,new} = K_{i,old} x^{\alpha}_{i,new}$ for *both* components; Ternary calculation—first enter the desired value at which $x^{\alpha}_{3,new}$ is to be constrained (use a small number like 1E-11 for zero), then enter $x^{\alpha}_{1,new} = (1 - x^{\alpha}_{3,old}(K_{3,old} - K_{2,old}) - K_{2,old})/(K_{1,old} - K_{2,old})$ (which is derived in a homework problem), and $x^{\alpha}_{2,new} = 1 - x^{\alpha}_{1,new} - x^{\alpha}_{3,new}$, and then for the $x^{\beta}_{i,new}$ row, enter the formulas to calculate

$x^{\beta}_{i,\,new} = K_{i,\,old} x^{\alpha}_{i,\,new}$ for *all three* components. Note that the ternary formula reduces to the binary formula when $x_3{}^{\alpha} = 0$, so a binary calculation can be performed from the ternary spreadsheet.

**Step 4.** Iterate. The strategy will be to update *values* for $x_i^{\alpha}$ and $x_i^{\beta}$ in the activity calculation tables and $K_i$ in the iteration table. Because some of the values are immediately recalculated, the order of the substitutions is important:

(a) Update the $K_{i,old}$ values by copying and pasting the $K_{i,new}$ *values* into the $K_{i,old}$ row. This step assures that in subsequent use, the $K_{i,old}$ will be updated to the new composition before iterations start.

(b) Update the $x_i^{\alpha}$ values in the activity coefficient table for $\alpha$ by copying and pasting *values* from the $x^{\alpha}_{i,new}$ row of the iteration table.

(c) Update the $x_i^{\beta}$ values in the activity coefficient table for $\beta$ by copying and pasting *values* from the $x^{\beta}_{i,new}$ row of the iteration table. The calculations should converge by repeating these steps over and over. The convergence of LLE can be slow. Compositions may creep a couple mole percent after they are changing on the tenths of mole percents. You may wish to write a macro to perform the iterations of step 4.

> ***Note:*** *For ternary systems, the value of $x^{\alpha}_3$ can be systematically changed to generate tie lines. Each time the value is changed the calculations need to be converged. The ternary method that is presented here is not completely general since the composition is constrained in one of the phases. A general technique can be written, but it involves a generalized flash routine which is an extension of the VLE flash routine involving nested iterations.*

## Rachford-Rice Flash

The text also includes a Rachford-Rice flash routine programmed in Matlab. The routine requires the user to specify two key immscible components. These key components (indeed all components) are specified in the code. The code is configured for UNIFAC-LLE or UNNIQUAC when distributed, but can easily be modified to use other activity coefficient methods as documented in the code.