$$s_{ki} = \sum_m G_{mi}\tau_{mk}, \tag{12.64}$$

$$\eta_k = \sum_i s_{ki}x_i, \tag{12.65}$$

$$\tau_{mk} = \exp\left[-\frac{a_{mk}}{T}\right]. \tag{12.66}$$

The various terms are explained below:

i	identifies component i of the solution
j	summation index running through all components
k	identifies a subgroup
m	summation index running through all subgroups present in the solution
$\nu_k^{(i)}$	number of subgroups k in component i
R_k	*relative volume* of subgroup k, tabulated
Q_k	*relative surface area* of subgroup k, tabulated
a_{mk}	interaction energy between subgroups m and k, in units of kelvin, tabulated

The above equations may be used with any number of components.[8] The procedure is tedious for hand calculations but easily automated for computer calculations. Tables listing several subgroups and the corresponding R_k and Q_k values are given in Table D-1 in the appendix. The table should be consulted before preparing the input for the UNIFAC calculation since some molecules (e.g., water, methanol, acetonitrile) constitute a single subgroup by themselves. The calculation is illustrated in the example below.

Example 12.11: A Detailed Calculation using UNIFAC

Calculate the *Pxy* graph of ethanol/acetonitrile at 40 °C and compare with the data for this system given in Table 12-1.

Solution The steps of the calculation will be demonstrated for $x_1 = 0.1$. The structural subgroups for this system were determined in Example 12.10:

Subgroup	k	$R^{(k)}$	$Q^{(k)}$	$\nu_1^{(k)}$	$\nu_2^{(k)}$
CH_3	1	0.9011	0.848	1	0
CH_2	2	0.6744	0.540	1	0
OH	14	1.0000	1.200	1	0
CH_3CN	40	1.8701	1.724	0	1

8. The extension of UNIFAC to multicomponent solutions is based on the assumption that interaction between multiple components may be obtained from pair interactions between all possible pairs. This means that no additional tabulations are needed for the calculation of multicomponent solutions.