Appendix G

UNIFAC Method

The UNIQUAC equation[1] treats $g \equiv G^E/RT$ as the sum of two parts, a *combinatorial* term g^C to account for molecular size and shape differences, and a *residual* term g^R (not a residual property as defined in Sec. 6.2) to account for molecular interactions:

$$g \equiv g^C + g^R \tag{G.1}$$

Function g^C contains pure-species parameters only, whereas function g^R incorporates two *binary* parameters for each pair of molecules. For a multicomponent system,

$$g^C = \sum_i x_i \ln \frac{\Phi_i}{x_i} + 5\sum_i q_i x_i \ln \frac{\theta_i}{\Phi_i} \tag{G.2}$$

$$g^R = -\sum_i q_i x_i \ln \left(\sum_j \theta_j \tau_{ji} \right) \tag{G.3}$$

where

$$\Phi_i \equiv \frac{x_i r_i}{\sum_j x_j r_j} \tag{G.4}$$

$$\theta_i \equiv \frac{x_i q_i}{\sum_j x_j q_j} \tag{G.5}$$

Subscript i identifies species, and j is a dummy index; all summations are over all species. Note that $\tau_{ji} \neq \tau_{ij}$; however, when $i = j$, then $\tau_{ii} = \tau_{jj} = 1$. In these equations r_i (a relative molecular volume) and q_i (a relative molecular surface area) are pure-species parameters. The influence of temperature on g enters through the interaction parameters τ_{ji} of Eq. (G.3), which are temperature dependent:

$$\tau_{ji} = \exp \frac{-(u_{ji} - u_{ii})}{RT} \tag{G.6}$$

Parameters for the UNIQUAC equation are therefore values of $(u_{ji} - u_{ii})$.

[1] D. S. Abrams and J. M. Prausnitz, *AIChE J.*, vol. 21, pp. 116–128, 1975.

An expression for $\ln \gamma_i$ is found by application of Eq. (13.7) to the UNIQUAC equation for g [Eqs.(G.1) through (G.3)]. The result is given by the following equations:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{G.7}$$

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}\right) \tag{G.8}$$

$$\ln \gamma_i^R = q_i\left(1 - \ln s_i - \sum_j \theta_j \frac{\tau_{ij}}{s_j}\right) \tag{G.9}$$

where in addition to Eqs. (G.5) and (G.6),

$$J_i = \frac{r_i}{\sum_j r_j x_j} \tag{G.10}$$

$$L_i = \frac{q_i}{\sum_j q_j x_j} \tag{G.11}$$

$$S_i = \tau_{li} \sum_l \theta_l \tag{G.12}$$

Again subscript i identifies species, and j and l are dummy indices. All summations are over all species, and $\tau_{ij} = 1$ for $i = j$. Values for the parameters $(u_{ij} - u_{jj})$ are found by regression of binary VLE data and are given by Gmehling et al.[2]

The UNIFAC method for estimation of activity coefficients[3] depends on the concept that a liquid mixture may be considered a solution of the structural units from which the molecules are formed rather than a solution of the molecules themselves. These structural units are called *subgroups,* and a few of them are listed in the second column of Table G.1. A number, designated k, identifies each subgroup. The relative volume R_k and relative surface area Q_k are properties of the subgroups, and values are listed in columns 4 and 5 of Table G.1. Also shown (columns 6 and 7) are examples of molecular species and their constituent subgroups. When a molecule can be constructed from more than one set of subgroups, the set containing the least number of *different* subgroups is the correct set. The great advantage of the UNIFAC method is that a relatively small number of subgroups combine to form a very large number of molecules.

Activity coefficients depend not only on the subgroup properties R_k and Q_k, but also on interactions between subgroups. Here, similar subgroups are assigned to a main group, as shown in the first two columns of Table G.1. The designations of main groups, such as "CH_2," "ACH," etc., are descriptive only. All subgroups belonging to the same main group are

[2]J. Gmehling, U. Onken, and W. Arlt, *Vapor-Liquid Equilibrium Data Collection*, Chemistry Data Series, vol. I, parts 1–8 and supplements, DECHEMA, Frankfurt/Main, 1974–1999.

[3]Aa. Fredenslund, R. L. Jones, and J. M. Prausnitz, *AIChE J.*, vol. 21, pp. 1086–1099, 1975.

Table G.1: UNIFAC-VLE Subgroup Parameters†

Main group	Subgroup	k	R_k	Q_k	Examples of molecules and their constituent groups	
1 "CH_2"	CH_3	1	0.9011	0.848	*n*-Butane:	$2CH_3$, $2CH_2$
	CH_2	2	0.6744	0.540	Isobutane:	$3CH_3$, 1CH
	CH	3	0.4469	0.228	2,2-Dimethyl	
	C	4	0.2195	0.000	propane:	$4CH_3$, 1C
3 "ACH" (AC = aromatic carbon)	ACH	10	0.5313	0.400	Benzene:	6ACH
4 "$ACCH_2$"	$ACCH_3$	12	1.2663	0.968	Toluene:	5ACH, $1ACCH_3$
	$ACCH_2$	13	1.0396	0.660	Ethylbenzene:	$1CH_3$, 5ACH, $1ACCH_2$
5 "OH"	OH	15	1.0000	1.200	Ethanol:	$1CH_3$, $1CH_2$, 1OH
7 "H_2O"	H_2O	17	0.9200	1.400	Water:	$1H_2O$
9 "CH_2CO"	CH_3CO	19	1.6724	1.488	Acetone:	$1CH_3CO$, $1CH_3$
	CH_2CO	20	1.4457	1.180	3-Pentanone:	$2CH_3$, $1CH_2CO$, $1CH_2$
13 "CH_2O"	CH_3O	25	1.1450	1.088	Dimethyl ether:	$1CH_3$, $1CH_3O$
	CH_2O	26	0.9183	0.780	Diethyl ether:	$2CH_3$, $1CH_2$, $1CH_2O$
	CH–O	27	0.6908	0.468	Diisopropyl ether:	$4CH_3$, 1CH, 1CH–O
15 "CNH"	CH_3NH	32	1.4337	1.244	Dimethylamine:	$1CH_3$, $1CH_3NH$
	CH_2NH	33	1.2070	0.936	Diethylamine:	$2CH_3$, $1CH_2$, $1CH_2NH$
	CHNH	34	0.9795	0.624	Diisopropylamine:	$4CH_3$, 1CH, 1CHNH
19 "CCN"	CH_3CN	41	1.8701	1.724	Acetonitrile:	$1CH_3CN$
	CH_2CN	42	1.6434	1.416	Propionitrile:	$1CH_3$, $1CH_2CN$

†H. K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, *IEC Research*, vol. 30, pp. 2352–2355, 1991.

considered identical with respect to group interactions. Therefore parameters characterizing group interactions are identified with pairs of *main* groups. Parameter values a_{mk} for a few such pairs are given in Table G.2.

The UNIFAC method is based on the UNIQUAC equation, for which the activity coefficients are given by Eq. (G.7). When applied to a solution of groups, Eqs. (G.8) and (G.9) are written:

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right) \tag{G.13}$$

$$\ln \gamma_i^R = q_i\left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k}\right)\right] \tag{G.14}$$

Table G.2: UNIFAC–VLE Interaction Parameters, a_{mk}, in kelvins†

		1	3	4	5	7	9	13	15	19
1	CH2	0.00	61.13	76.50	986.50	1318.00	476.40	251.50	255.70	597.00
3	ACH	−11.12	0.00	167.00	636.10	903.80	25.77	32.14	122.80	212.50
4	ACCH2	−69.70	−146.80	0.00	803.20	5695.00	−52.10	213.10	−49.29	6096.00
5	OH	156.40	89.60	25.82	0.00	353.50	84.00	28.06	42.70	6.712
7	H2O	300.00	362.30	377.60	−229.10	0.00	−195.40	540.50	168.00	112.60
9	CH2CO	26.76	140.10	365.80	164.50	472.50	0.00	−103.60	−174.20	481.70
13	CH2O	83.36	52.13	65.69	237.70	−314.70	191.10	0.00	251.50	−18.51
15	CNH	65.33	−22.31	223.00	−150.00	−448.20	394.60	−56.08	0.00	147.10
19	CCN	24.82	−22.97	−138.40	185.40	242.80	−287.50	38.81	−108.50	0.00

†H. K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, *IEC Research*, vol. 30, pp. 2352–2355, 1991.

The quantities J and L are still given by Eqs. (G.10) and (G.11). In addition, the following definitions apply:

$$r_i = \sum_k \nu_k^{(i)} R_k \tag{G.15}$$

$$q_i = \sum_k \nu_k^{(i)} Q_k \tag{G.16}$$

$$e_{ki} = \frac{\nu_k^{(i)} Q_k}{q_i} \tag{G.17}$$

$$\beta_{ik} = \sum_m e_{mi} \tau_{mk} \tag{G.18}$$

$$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j} \tag{G.19}$$

$$s_k = \sum_m \theta_m \tau_{mk} \tag{G.20}$$

$$\tau_{mk} = \exp\frac{-a_{mk}}{T} \tag{G.21}$$

Subscript i identifies a species, and j is a dummy index running over all species. Subscript k identifies subgroups, and m is a dummy index running over all subgroups. The quantity $\nu_k^{(i)}$ is the number of subgroups of type k in a molecule of species i. Values of the subgroup parameters R_k and Q_k and of the group interaction parameters a_{mk} come from tabulations in the literature. Tables G.1 and G.2 show a few parameter values; the number designations of the complete tables are retained.[4]

The equations for the UNIFAC method are presented here in a form convenient for computer programming. In the following example we run through a set of hand calculations to demonstrate their application.

Example G.1

For the binary system diethylamine(1)/n-heptane(2) at 308.15 K, find γ_1 and γ_2 when $x_1 = 0.4$ and $x_2 = 0.6$.

Solution G.1

The subgroups involved are indicated by the chemical formulas:

$$CH_3 - CH_2NH - CH_2 - CH_3\ (1) / CH_3 - (CH_2)_5 - CH_3\ (2)$$

[4]H. K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, IEC Research, vol. 30, pp. 2352–2355, 1991.

The following table shows the subgroups, their identification numbers k, values of parameters R_k and Q_k (from Table G.1), and the numbers of each subgroup in each molecule:

	k	R_k	Q_k	$\nu_k^{(1)}$	$\nu_k^{(2)}$
CH_3	1	0.9011	0.848	2	2
CH_2	2	0.6744	0.540	1	5
CH_2NH	33	1.2070	0.936	1	0

By Eq. (G.15)

$$r_1 = (2)(0.9011) + (1)(0.6744) + (1)(1.2070) = 3.6836$$

Similarly,

$$r_2 = (2)(0.9011) + (5)(0.6744) = 5.1742$$

In like manner, by Eq. (G.16),

$$q_1 = 3.1720 \qquad \text{and} \qquad q_2 = 4.3960$$

The r_i and q_i values are molecular properties, independent of composition. Substituting known values into Eq. (G.17) generates the following table for e_{ki}:

	e_{ki}	
k	$i = 1$	$i = 2$
1	0.5347	0.3858
2	0.1702	0.6142
33	0.2951	0.0000

The following interaction parameters are found from Table G.2:

$$a_{1,1} = a_{1,2} = a_{2,1} = a_{2,2} = a_{33,33} = 0 \text{ K}$$
$$a_{1,33} = a_{2,33} = 255.7 \text{ K}$$
$$a_{33,1} = a_{33,2} = 65.33 \text{ K}$$

Substitution of these values into Eq. (G.21) with $T = 308.15$ K gives

$$\tau_{1,1} = \tau_{1,2} = \tau_{2,1} = \tau_{2,2} = \tau_{33,33} = 1$$
$$\tau_{1,33} = \tau_{2,33} = 0.4361$$
$$\tau_{33,1} = \tau_{33,2} = 0.8090$$

Application of Eq. (G.18) leads to the values of β_{ik} in the following table:

	β_{ik}		
i	$k = 1$	$k = 2$	$k = 33$
1	0.9436	0.9436	0.6024
2	1.0000	1.0000	0.4360

Substitution of these results into Eq. (G.19) yields:

$$\theta_1 = 0.4342 \qquad \theta_2 = 0.4700 \qquad \theta_{33} = 0.0958$$

and by Eq. (G.20),

$$s_1 = 0.9817 \qquad s_2 = 0.9817 \qquad s_{33} = 0.4901$$

The activity coefficients may now be calculated. By Eq. (G.13),

$$\ln \gamma_1^C = -0.0213 \qquad \text{and} \qquad \ln \gamma_2^C = -0.0076$$

and by Eq. (G.14),

$$\ln \gamma_1^R = 0.1463 \qquad \text{and} \qquad \ln \gamma_2^R = 0.0537$$

Finally, Eq. (G.7) gives:

$$\gamma_1 = 1.133 \qquad \text{and} \qquad \gamma_2 = 1.047$$