# SINTEF

# Memo

# UNIFAC excess gibbs mixing rules

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# Contents

## 1 Introduction

The UNIFAC (*UNI*QUAC *F*unctional-group *A*ctivity *C*oefficients) model [5], is a group contribution model, and a further development of the UNIQUAC model [1]. Being a group contribution model, it accounts for molecular groups like C-$H_2$ and C-$H_3$, that can be thought upon as monomers in a polymer.

The UNIFAC excess Gibbs mixing rule have found application in the predictive SRK, PSRK [8], model, and VTPR [3]. It is also used as the universal mixing rule (UMR) [17] togther with t-mPR [11, 2]. The combined model is denoted UMR-PR.

## 2 UNIFAC model

The UNIFAC model [5] is given as follows,

$$\frac{A^{\mathrm{R}}}{RT} = \frac{A^{\mathrm{E}}}{RT} - \frac{A^{\mathrm{E}}}{RT_0} = -\sum_i^{\mathrm{NC}} n_i \sum_k^{\mathrm{NG}} v_k^i Q_k (\Lambda_k - \Lambda_k^i). \tag{1}$$

The symbols and formalism of Michelsen [13] is used. $A^{\mathrm{E}}/(RT_0)$ is the combinatorial term and is described in a later sub section. It is assumed that $A^{\mathrm{E}} = G^{\mathrm{E}}$.

The different symbols are defined as follows,

$$\Lambda_k = \ln \sum_j^{\mathrm{NG}} \Theta_j \tilde{E}_{jk}, \tag{2}$$

$$\Lambda_k^i = \ln \sum_j^{\mathrm{NG}} \Theta_j^i \tilde{E}_{jk}, \tag{3}$$

$$\tilde{E}_{jk} = \exp\left(-\frac{\tilde{U}_{jk}}{RT}\right), \tag{4}$$

$$\Theta_j = \frac{Q_j \sum_l^{\mathrm{NC}} n_l v_j^l}{\sum_l^{\mathrm{NC}} n_l \sum_m^{\mathrm{NG}} v_m^l Q_m}, \tag{5}$$

$$\Theta_j^i = \frac{Q_j v_j^i}{\sum_k^{\mathrm{NG}} v_k^i Q_k}. \tag{6}$$

Here $Q_k$ is the group surface area of group $k$, and $v_k^i$ is the number of groups $k$ in molecule $i$. Both $Q_k$ and $v_k^i$ are constants. $\tilde{U}_{jk}$ is the interaction energy per unit surface area of the $j - k$ group interaction. $\tilde{U}_{jk}$ can be a constant, or a temperature function.

### 2.1 Differentials

Differentiating 1 with respect to $n_\alpha$ we get,

$$\frac{1}{RT} \frac{\partial A^{\mathrm{R}}}{\partial n_\alpha} = \frac{A_\alpha^{\mathrm{R}}}{RT} = -\sum_k^{\mathrm{NG}} v_k^\alpha Q_k (\Lambda_k - \Lambda_k^\alpha) - \sum_i^{\mathrm{NC}} n_i \sum_k^{\mathrm{NG}} v_k^i Q_k \frac{\partial \Lambda_k}{\partial n_\alpha}. \tag{7}$$

Michelsen [13, Chap. 5,Eq. 56] show that

$$\sum_i^{NC} n_i \sum_k^{NG} v_k^i Q_k \frac{\partial \Lambda_k}{\partial n_\alpha} = \sum_j^{NG} v_j^\alpha Q_j \left( \sum_k^{NG} \frac{\Theta_j \tilde{E}_{jk}}{\sum_l^{NG} \Theta_l \tilde{E}_{lk}} - 1 \right). \tag{8}$$

But since second differentials are required, it do not help much for the compositional differentials. Using

$$\Lambda_k = \ln \sum_j^{NG} \Theta_j \tilde{E}_{jk} = \ln \sum_l^{NC} n_l \sum_j^{NG} v_j^l Q_j \tilde{E}_{jk} - \ln \sum_l^{NC} n_l \sum_m^{NG} v_m^l Q_m, \tag{9}$$

we get

$$\frac{\partial \Lambda_k}{\partial n_\alpha} = \frac{\sum_j^{NG} v_j^\alpha Q_j \tilde{E}_{jk}}{\sum_l^{NC} n_l \sum_j^{NG} v_j^l Q_j \tilde{E}_{jk}} - \frac{\sum_m^{NG} v_m^\alpha Q_m}{\sum_l^{NC} n_l \sum_m^{NG} v_m^l Q_m}. \tag{10}$$

Differentiating 7 further with respect to $n_\beta$ we get,

$$\frac{A_{\alpha\beta}^{R}}{RT} = -\sum_k^{NG} Q_k \left( v_k^\alpha \frac{\partial \Lambda_k}{\partial n_\beta} + v_k^\beta \frac{\partial \Lambda_k}{\partial n_\alpha} \right) - \sum_i^{NC} n_i \sum_k^{NG} v_k^i Q_k \frac{\partial^2 \Lambda_k}{\partial n_\alpha \partial n_\beta}, \tag{11}$$

$$= -\sum_k^{NG} Q_k \left( v_k^\alpha \frac{\partial \Lambda_k}{\partial n_\beta} + v_k^\beta \frac{\partial \Lambda_k}{\partial n_\alpha} \right) - \sum_k^{NG} \left( \sum_i^{NC} n_i v_k^i \right) Q_k \frac{\partial^2 \Lambda_k}{\partial n_\alpha \partial n_\beta}. \tag{12}$$

Differentiating Equation 10 we get the second differential of $\Lambda_k$,

$$\frac{\partial^2 \Lambda_k}{\partial n_\alpha \partial n_\beta} = -\frac{\left( \sum_j^{NG} v_j^\alpha Q_j \tilde{E}_{jk} \right) \left( \sum_j^{NG} v_j^\beta Q_j \tilde{E}_{jk} \right)}{\left( \sum_l^{NC} n_l \sum_j^{NG} v_j^l Q_j \tilde{E}_{jk} \right)^2} + \frac{\left( \sum_m^{NG} v_m^\alpha Q_m \right) \left( \sum_m^{NG} v_m^\beta Q_m \right)}{\left( \sum_l^{NC} n_l \sum_m^{NG} v_m^l Q_m \right)^2}. \tag{13}$$

We immediately see that 13 give a symmetric matrix of the second differentials.
   Differentiating 1 with respect to $T$ we get,

$$\frac{\partial \left( \frac{A^R}{RT} \right)}{\partial T} = -\sum_i^{NC} n_i \sum_k^{NG} v_k^i Q_k \left( \frac{\partial \Lambda_k}{\partial T} - \frac{\partial \Lambda_k^i}{\partial T} \right), \tag{14}$$

$$\frac{\partial^2 \left( \frac{A^R}{RT} \right)}{\partial T^2} = -\sum_i^{NC} n_i \sum_k^{NG} v_k^i Q_k \left( \frac{\partial^2 \Lambda_k}{\partial T^2} - \frac{\partial^2 \Lambda_k^i}{\partial T^2} \right). \tag{15}$$

Here,

$$\frac{\partial \Lambda_k}{\partial T} = \frac{\sum\limits_l^{NC} n_l \sum\limits_j^{NG} v_j^l Q_j \frac{\partial \tilde{E}_{jk}}{\partial T}}{\sum\limits_l^{NC} n_l \sum\limits_j^{NG} v_j^l Q_j \tilde{E}_{jk}}, \tag{16}$$

$$\frac{\partial \Lambda_k^i}{\partial T} = \frac{\sum\limits_j^{NG} Q_j v_j^i \frac{\partial \tilde{E}_{jk}}{\partial T}}{\sum\limits_j^{NG} Q_j v_j^i \tilde{E}_{jk}}, \tag{17}$$

$$\frac{\partial^2 \Lambda_k}{\partial T^2} = \frac{\sum\limits_l^{NC} n_l \sum\limits_j^{NG} v_j^l Q_j \frac{\partial^2 \tilde{E}_{jk}}{\partial T^2}}{\sum\limits_l^{NC} n_l \sum\limits_j^{NG} v_j^l Q_j \tilde{E}_{jk}} - \left(\frac{\partial \Lambda_k}{\partial T}\right)^2, \tag{18}$$

$$\frac{\partial^2 \Lambda_k^i}{\partial T^2} = \frac{\sum\limits_j^{NG} Q_j v_j^i \frac{\partial^2 \tilde{E}_{jk}}{\partial T^2}}{\sum\limits_j^{NG} Q_j v_j^i \tilde{E}_{jk}} - \left(\frac{\partial \Lambda_k^i}{\partial T}\right)^2. \tag{19}$$

$$\tag{20}$$

Differentiating Equation 7 we get

$$\frac{\partial \left(\frac{A_\alpha^R}{RT}\right)}{\partial T} = -\sum\limits_k^{NG} v_k^\alpha Q_k \left(\frac{\partial \Lambda_k}{\partial T} - \frac{\partial \Lambda_k^\alpha}{\partial T}\right) - \sum\limits_k^{NG} \left(\sum\limits_i^{NC} n_i v_k^i\right) Q_k \frac{\partial^2 \Lambda_k}{\partial n_\alpha \partial T}. \tag{21}$$

The cross differential of $\Lambda_k$ is found by differentiating Equation 10 with respect to $T$,

$$\frac{\partial^2 \Lambda_k}{\partial n_\alpha \partial T} = \frac{\sum\limits_j^{NG} v_j^\alpha Q_j \frac{\partial \tilde{E}_{jk}}{\partial T}}{\sum\limits_l^{NC} n_l \sum\limits_j^{NG} v_j^l Q_j \tilde{E}_{jk}} - \frac{\left(\sum\limits_j^{NG} v_j^\alpha Q_j \tilde{E}_{jk}\right)\left(\sum\limits_l^{NC} n_l \sum\limits_j^{NG} v_j^l Q_j \frac{\partial \tilde{E}_{jk}}{\partial T}\right)}{\left(\sum\limits_l^{NC} n_l \sum\limits_j^{NG} v_j^l Q_j \tilde{E}_{jk}\right)^2}. \tag{22}$$

## 2.2 The combinatorial term

The combinatorial term is comprised of a Flory-Huggins (FH) and a Staverman-Guggenheim (SG) contribution,

$$G^{E,comb} = G^{E,FH} + G^{E,SG}, \tag{23}$$

$$G^{E,FH} = \sum_i x_i \ln \frac{\phi_i}{x_i}, \tag{24}$$

$$G^{E,SG} = \frac{z}{2} \sum_i x_i q_i \ln \frac{\theta_i}{\phi_i}. \tag{25}$$

Where $z = 10$,

$$\phi_i = \frac{x_i r_i}{\sum\limits_j x_j r_j}, \tag{26}$$

$$\theta_i = \frac{x_i q_i}{\sum\limits_j x_j q_j}. \tag{27}$$

$$\tag{28}$$

$r_i$ and $q_i$ are molecule paramaters and non of the parameters are temperature dependent. $r_i$ is the molecular van der Waals volume and $q_i$ is the molecular van der Waals surface area. They are calculated from the group paramaters as follows,

$$r_i = \sum\limits_k^{\text{NG}} v_k^i R_k, \tag{29}$$

$$q_i = \sum\limits_k^{\text{NG}} v_k^i Q_k. \tag{30}$$

$$\tag{31}$$

### 2.2.1 Differentials of the Flory-Huggins combinatorial term

Writing Equation 24 as a function of mole numbers, we get,

$$G^{\text{E,FH}} = \sum\limits_i^{\text{NC}} n_i \left( \ln \phi_i - \ln n_i + \ln \sum\limits_j^{\text{NC}} n_j \right), \tag{32}$$

$$= \sum\limits_i^{\text{NC}} n_i \left( \ln n_i r_i - \ln \sum\limits_j^{\text{NC}} n_j r_j - \ln n_i + \ln \sum\limits_j^{\text{NC}} n_j \right) = \sum\limits_i^{\text{NC}} n_i \ln r_i - n \ln \sum\limits_j^{\text{NC}} n_j r_j + n \ln n. \tag{33}$$

Differentiating $G^{\text{E,FH}}$ with respect to $n_\alpha$ we get,

$$G_\alpha^{\text{E,FH}} = \ln r_\alpha - \ln \sum\limits_j^{\text{NC}} n_j r_j + \ln \sum\limits_j^{\text{NC}} n_j + 1 - \frac{r_\alpha \sum\limits_i^{\text{NC}} n_i}{\sum\limits_j^{\text{NC}} n_j r_j}, \tag{34}$$

$$= \ln r_\alpha - \ln \sum\limits_j^{\text{NC}} n_j r_j + \ln n + 1 - \frac{n r_\alpha}{\sum\limits_j^{\text{NC}} n_j r_j}, \tag{35}$$

$$= \ln \left( \frac{n r_\alpha}{\sum\limits_j^{\text{NC}} n_j r_j} \right) + 1 - \frac{n r_\alpha}{\sum\limits_j^{\text{NC}} n_j r_j} \tag{36}$$

$$= \ln \left( \frac{\phi_\alpha}{x_\alpha} \right) + 1 - \frac{\phi_\alpha}{x_\alpha} \tag{37}$$

Differentiating 35 with respect to $n_\beta$ we get,

$$G_{\alpha\beta}^{\text{E,FH}} = -\frac{r_\alpha + r_\beta}{\sum\limits_j^{\text{NC}} n_j r_j} + \frac{1}{n} + \frac{n r_\alpha r_\beta}{\left( \sum\limits_j^{\text{NC}} n_j r_j \right)^2}. \tag{38}$$

### 2.2.2 Differentials of the Staverman-Guggenheim combinatorial term

Writing Equation 25 as a function of mole numbers, we get,

$$G^{\text{E,SG}} = \frac{z}{2} \sum_i^{\text{NC}} n_i q_i \left( \ln \theta_i - \ln \phi_i \right), \tag{39}$$

$$= \frac{z}{2} \sum_i^{\text{NC}} n_i q_i \left( \ln \frac{q_i}{r_i} - \ln \sum_j^{\text{NC}} n_j q_j + \ln \sum_j^{\text{NC}} n_j r_j \right). \tag{40}$$

Differentiating $G^{\text{E,SG}}$ with respect to $n_\alpha$ we get,

$$G_\alpha^{\text{E,SG}} = \frac{z}{2} q_\alpha \left( \ln \frac{q_\alpha}{r_\alpha} - \ln \sum_j^{\text{NC}} n_j q_j + \ln \sum_j^{\text{NC}} n_j r_j - 1 + \frac{r_\alpha \sum_i^{\text{NC}} n_i q_i}{q_\alpha \sum_j^{\text{NC}} n_j r_j} \right), \tag{41}$$

$$= \frac{z}{2} q_\alpha \left( -\ln \left( \frac{r_\alpha \sum_j^{\text{NC}} n_j q_j}{q_\alpha \sum_j^{\text{NC}} n_j r_j} \right) - 1 + \frac{r_\alpha \sum_i^{\text{NC}} n_i q_i}{q_\alpha \sum_j^{\text{NC}} n_j r_j} \right), \tag{42}$$

$$= \frac{z}{2} q_\alpha \left( \ln \left( \frac{\theta_\alpha}{\phi_\alpha} \right) - 1 + \frac{\phi_\alpha}{\theta_\alpha} \right). \tag{43}$$

Differentiating 41 with respect to $n_\beta$ we get,

$$G_{\alpha\beta}^{\text{E,SG}} = \frac{z}{2} \left( -\frac{q_\alpha q_\beta}{\sum_j^{\text{NC}} n_j q_j} + \frac{q_\alpha r_\beta + q_\beta r_\alpha}{\sum_j^{\text{NC}} n_j r_j} - \frac{r_\alpha r_\beta \sum_i^{\text{NC}} n_i q_i}{\left( \sum_j^{\text{NC}} n_j r_j \right)^2} \right). \tag{44}$$

### 2.2.3 Comparing to combinatorial activity coefficient of Fredenslund et al.

Fredenslund et al. [5] uses the following expression for the activity combinatorial coefficient,

$$\ln \gamma_c = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j^{\text{NC}} x_j l_j, \tag{45}$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1). \tag{46}$$

Inserting for $l_i$ in the last term of Equation 45, we get,

$$\frac{\phi_i}{x_i} \sum_j^{\text{NC}} x_j l_j = \frac{z \phi_i}{2 x_i} \left( \sum_j^{\text{NC}} x_j r_j - \sum_j^{\text{NC}} x_j q_j \right) - \frac{\phi_i}{x_i} \left( \sum_j^{\text{NC}} x_j r_j - 1 \right), \tag{47}$$

$$= \frac{z}{2} \left( r_i - \frac{q_i \phi_i}{\theta_i} \right) - r_i + \frac{\phi_i}{x_i}. \tag{48}$$

Inserting Equation 48 and Equation 46 into Equation 45 we get,

$$\ln \gamma_c = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} + \frac{z}{2} q_i \left( \ln \frac{\theta_i}{\phi_i} - 1 + \frac{\phi_i}{\theta_i} \right). \tag{49}$$

We see that

$$\ln \gamma_c = G_\alpha^{\text{E,FH}} + G_\alpha^{\text{E,SG}}. \tag{50}$$

## 3  UMR-PR model

The UMR-PR model is developed by Voutsas et al [17], and uses the UNIFAC mixing rules together with a volume translated Peng-Robinson EOS, t-mPR [2].

UMR-PR applies the following covolume mixing rule,

$$b = \sum_i \sum_j x_i x_j b_{ij}, \tag{51}$$

$$b_{ij} = \left[ \frac{b_i^{\frac{1}{s}} + b_j^{\frac{1}{s}}}{2} \right]^s, \tag{52}$$

with $s = 2$.

UMR-PR ignores the Flory-Huggins contribution, Equation 24, of the combinatorial term, Equation 23.

UMR-PR uses the original temperature independent UNIFAC parameters published by Hansen et al [7] and Dortmund Data Bank, Wittig et al [18].

Data source: `https://en.wikipedia.org/wiki/UNIFAC`

`http://www.ddbst.com/unifacga.html`

`http://www.aim.env.uea.ac.uk/aim/info/UNIFACgroups.html`

The volume correction temperature differentials used in UMR is not continous. This might be a good reason not to use the model.

### 3.1  t-mPR model

t-mPR [2] is an extension of the t-PR [11] to mixtures.

The t-mPR model take the following form,

$$P = \frac{RT}{V + t - b} - \frac{a}{(V + t)(V + t + b) + b(V + t - b)}, \tag{53}$$

where,

$$t = t(\boldsymbol{x}, T) = \sum_i x_i t_i(T). \tag{54}$$

We see that by introducing $\tilde{V} = V + t$, the relations for this equation of state can be related to the standard Peng-Robinson equation of state. The translation is slightly more complicated than the Pénéloux [14] volume shift, due to the temperature dependency, and the lack of correction to the covolume.

## 4  PSRK model

PSRK [8] uses SRK with Mathias-Copeman $\alpha$-correlation [12], and a UNIFAC excess Gibbs energy model.

The zero pressure limit, Equation 55, is used when including the mixing rules into the SRK EOS. $h_{\mathrm{PSRK}}(\beta_0) = 0.64663$ is used.

The zero pressure limit is used when including the excess Gibbs energy into the equation of state,

$$\frac{a}{RTb} = \sum_i x_i \frac{a_i}{RTb_i} - \frac{1}{h(\beta_0)} \left( \sum_i x_i \ln \frac{b}{b_i} + \frac{G^{\mathrm{E}}}{RT} \right), \tag{55}$$

where $h(\beta_0)$ is a constant that depend on the EOS. We have $h_{\text{PR}}(\beta_0) = 0.53$.

> Implement terms additional to the infinite pressure terms? - Or ignore?

The linear mixing of the covolume is used in PSRK,

$$b = \sum_i x_i b_i. \tag{56}$$

Parameters: [10, 8, 9, 4, 6]

# 5 VTPR model

The Volume-Translated-Peng-Robinson (VTPR) EOS [3], uses a constant volume correction for each component. The correction in volume therefore don't depend on temperature. The Twu, Bluck, Cunningham and Coon $\alpha$-correlation [16] is used.

For the excess Gibbs energy, the UNIFAC model is used without the combinatorial term, Equation 23. The infinite pressure limit is used when including the activity coefficient model into the EOS.

Covolume mixing uses Equation 52 with $s = 4/3$.

Parameters: [15]

# 6 The general mixing rule for the covolume

The general mixing rules for the covolume take the following form,

$$nB = n^2 b = \sum_i \sum_j n_i n_j b_{ij}, \tag{57}$$

$$b_{ij}^{\frac{1}{s}} = (1 - l_{ij}) \frac{b_i^{\frac{1}{s}} + b_j^{\frac{1}{s}}}{2}. \tag{58}$$

Where $l_{ij}$ is assumed constant, symmetric, and have a default value of zero.

Differentiating and manipulating Equation 57, $B_i$ and $B_{ij}$ become,

$$nB_i = = 2 \sum_j n_j b_{ij} - B, \tag{59}$$

$$nB_{ij} = = 2 b_{ij} - B_i - B_j. \tag{60}$$

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