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Calculation and Prediction of Thermodynamic Properties of Non-Electrolyte Mixtures with a New *quasi*-Chemical Approximation

Rolf Lacmann* and **Andrea Stäudte**

Institut für Physikalische und Theoretische Chemie, Technische Universität Carolo-Wilhelmina, D-38092 Braunschweig, Germany

Summary. Using the old, modified TASQUAC model [1–3], only small negative excess entropies of mixing can be described with model assumptions. Intra- and intermolecular vibrations and the rotation of molecules are also not considered. In this work, therefore, a new relationship for the interaction energy with an enthalpy (Δh) and an entropy parameter (Δs) in the *quasi*-chemical approximation is suggested. The exact solution for the *quasi*-chemical equilibrium in the two-component mixture is given, and a new model for describing and predicting phase equilibria in multi-component systems S-TASQUAC is developed. We examined the possibilities of using S-TASQUAC to predict VLE data and compared the results of binary systems to the results of other known models of liquid mixtures (Wilson, NRTL, UNIQUAC). The results of the calculated data demonstrate the usability of S-TASQUAC as a qualified tool to describe and predict phase equilibria.

Keywords. Theory; Methods of calculation; Vapour-liquid equilibria; *quasi*-chemical approximation; *Gibbs* free energy parameter.

Berechnung und Vorhersage von thermodynamischen Eigenschaften von Nichtelektrolyt-Mischungen mittels einer neuen *quasi*-chemischen Näherung

Zusammenfassung. Bei Verwendung des alten, modifizierten TASQUAC-Modells [1–3] können nur kleine negative Zusatz-Mischungsentropien näherungsweise beschrieben werden. Intra- und intermolekulare Schwingungen sowie die Rotation der Moleküle bleiben unberücksichtigt. In dieser Arbeit wurde daher eine neue From der Betrachung der Wechselwirkungsenergien, gekennzeichnet durch einen Enthalpie-(Δh) und einen Entropieparameter (Δs), vorgeschlagen. Die exakte Lösung für das quasi-chemische Gleichgewicht in einem Zweikomponentengemisch wird hergeleitet und ein neues Modell für die Beschreibung und die Vorhersage von Phasengleichgewichten in Mehrkomponentensystemen wird entwickelt. Es wird die Möglichkeit untersucht, S-TASQUAC für die Vorhersage von VLE-Daten zu verwenden. Anschließend werden die für binäre Gemische erhaltenen Ergebnisse mit denen anderer bekannter Modelle (Wilson, NRTL, UNIQUAC) für Flüssigkeitsgemische verglichen. Die Resultate beweisen, daß S-TASQUAC gut geeignet ist, um Phasengleichgewichte zu beschreiben bzw. vorherzusagen.

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* Corresponding author

Introduction

In designing chemical processes for the separation of fluid mixtures, chemical engineers must frequently estimate the liquid-phase activity coefficients of multi-component systems. There are many methods for estimating multi-component properties, provided information on the binary subsystem is available in the form of binary parameters determined from a least-squares analysis of binary data.

A few predictive methods use the *quasi*-chemical theory by *Barker* [4] and *Guggenheim* [5] to describe thermodynamic excess functions (ΔH^{E}, ΔG^{E}, ΔS^{E}, $\Delta\mu^{\mathrm{E}}$). With this quasi-chemical model, only small negative excess entropies of mixing can be given, because by assumption of specific interaction compared with the statistical arrangement of molecules a higher order is created. In many real mixtures, positive values for ΔS^{E} arise which can be explained by association, complex formation, or preferential orientation, but cannot be described satisfyingly with the existing *quasi*-chemical theory. The vibration and rotation of molecules, which are influenced by surrounding molecules, is also not considered. Therefore, this method should be expanded.

Theory

The *quasi*-chemical theory is used frequently to describe thermodynamic excess functions (ΔH^{E}, ΔG^{E}, ΔS^{E}, $\Delta\mu^{\mathrm{E}}$). The mathematical relations are given as

$$\frac{N_{\mathrm{AB}}^2}{N_{\mathrm{AA}} \cdot N_{\mathrm{BB}}} = 4 \cdot \exp\left(-2 \cdot \Delta W_{\mathrm{AB}}/kT\right) = 4 \cdot \eta_{\mathrm{AB}} \tag{1}$$

$$Z \cdot N_{\mathrm{A}} = N_{\mathrm{AB}} + 2 \cdot N_{\mathrm{AA}} \tag{2}$$

$$Z \cdot N_{\mathrm{B}} = N_{\mathrm{AB}} + 2 \cdot N_{\mathrm{BB}} \tag{3}$$

N_{AB}, N_{AA}, and N_{BB} are the number of AB, AA and BB contacts in a mixture of N_{A} molecules of type A and N_{B} molecules of type B. The molecules are located on lattice sites in a lattice with the coordination number Z.

Equation (1) is the relation for the number of AB, AA, and BB contacts at equilibrium in a binary system; the factor 4 is obtained from the square of the symmetry factor σ of the contacts. The interchange energy ΔW_{AB} is given by Eq. (4):

$$\Delta W_{\mathrm{AB}} = \bar{U}_{\mathrm{AB}} - \frac{\bar{U}_{\mathrm{AA}} + \bar{U}_{\mathrm{BB}}}{2} \tag{4}$$

$\bar{U}$ is the potential energy between two molecules at equilibrium. Ideal mixtures are defined by $\Delta W_{\mathrm{AB}} = 0$ and $\eta_{\mathrm{AB}} = 1$. The system of equations of equilibrium (1) and contact site balances (2), (3) can be solved analytically for a binary system:

$$N_{\mathrm{AB}} = Z \cdot N \cdot x_{\mathrm{A}} \cdot x_{\mathrm{B}} \cdot \left(\frac{2}{1+\beta}\right) \tag{5}$$

with x_{A}, x_{B} = mole fractions, $N = N_{\mathrm{A}} + N_{\mathrm{B}}$, and

$$\beta = \left(1 + 4 \cdot x_{\mathrm{A}} \cdot x_{\mathrm{B}} \cdot (\eta_{\mathrm{AB}}^{-1} - 1)\right)^{1/2} \tag{6}$$

The heat of mixing is given by

$$\Delta H^{\mathrm{E}} = N_{\mathrm{AB}} \cdot \Delta W_{\mathrm{AB}} \tag{7}$$

Integration of Eq. (7) with respect to the reciprocal temperature leads to the following expression of the excess *Gibbs* free energy [6].

$$\begin{aligned}\Delta G^{\mathrm{E}} &= T \cdot \int_0^{1/T} \Delta H^{\mathrm{E}}\, d\left(\frac{1}{T}\right) = T \cdot \Delta W_{\mathrm{AB}} \cdot \int_0^{1/T} N_{\mathrm{AB}} d\left(\frac{1}{T}\right)\\ &= \frac{R \cdot T \cdot Z}{2} \cdot \left[x_{\mathrm{A}} \cdot \ln \frac{\beta - 1 + 2x_{\mathrm{A}}}{x_{\mathrm{A}} \cdot (\beta + 1)} + x_{\mathrm{B}} \cdot \ln \frac{\beta - 1 + 2x_{\mathrm{B}}}{x_{\mathrm{B}} \cdot (\beta + 1)}\right]\\ &= \bar{N}_{\mathrm{AB}} \cdot \Delta W_{\mathrm{AB}}\end{aligned} \tag{8}$$

The activity coefficients can be calculated as

$$\gamma_{\mathrm{i}} = \left[\frac{\beta - 1 + 2x_{\mathrm{i}}}{x_{\mathrm{i}} \cdot (\beta + 1)}\right]^{Z/2} \tag{9}$$

$\bar{N}_{\mathrm{AB}}$ is the average number of *AB* contacts in the reciprocal temperature range from 0 to 1/*T*.

$$\bar{N}_{\mathrm{AB}} = \int_0^{1/T} \frac{N_{\mathrm{AB}}\, d\frac{1}{T}}{1/T} \tag{10}$$

ΔS^{E} can be obtained through

$$\Delta S^{\mathrm{E}} = \left(\frac{\Delta H^{\mathrm{E}} - \Delta G^{\mathrm{E}}}{T}\right) = \frac{\Delta W_{\mathrm{AB}}}{T} \cdot (N_{\mathrm{AB}} - \bar{N}_{\mathrm{AB}}) \tag{11}$$

ΔS^{E} is a pure configurational entropy and smaller than zero. The value for $|T \cdot \Delta S^{\mathrm{E}}|$ is therefore much smaller than $|\Delta H^{\mathrm{E}}|$ or $|\Delta G^{\mathrm{E}}|$.

The critical temperature of phase separation is given by

$$\Delta T_{\mathrm{c}} = \frac{\Delta W_{\mathrm{AB}}}{k \cdot Z \cdot \ln(Z/(Z-2))} \tag{12}$$

The system of equilibrium equations (1) and contact site balances (2), (3) can only be solved iteratively for mixtures with three or more components. The *quasi*-chemical theory is only an approximation for the number of contacts; therefore it is permitted to use a *Taylor* series approximation which can be solved analytically. The *Taylor* series can use the ideal mixtures $\eta_{\mathrm{AB}} = 1$ as starting point. This formalism (TASQUAC) also allows the derivation of a group contribution method (GTASQUAC) [7].

Many real mixtures show values for $T \cdot \Delta S^{\mathrm{E}}$ which are larger than zero and larger than those calculated with the *quasi*-chemical theory in its present form. Therefore, this method should be expanded. In many cases, ΔW_{AB} is treated as temperature dependent. For example, the form $\Delta W_{\mathrm{AB}} = a_1 + a_2 \cdot (1 - T_0/T)$ was introduced by *Kehiaian et al.* [8]. The temperature dependence of ΔW_{AB} yields additional adjustable parameters. The equation allows one to take into account dispersion and dipole interactions. The temperature dependence of dipole interactions is proportional to the reciprocal temperature: $U_{\text{DP-DP}} \sim 1/T$ [9].

The factor $4 \cdot \eta$ in Eq. (1) can be regarded as a *quasi*-chemical equilibrium constant which can be expressed as

$$\begin{aligned} \ln K &= -\Delta G^0/RT = -\Delta g^0/kT \\ &= \ln 4 - 2 \cdot \Delta W_{\mathrm{AB}}/kT \end{aligned} \tag{13}$$

with $\Delta g^0 = \Delta h^0 - T \cdot \Delta s^0, \Delta h^0 = 2 \cdot \Delta W_{\mathrm{AB}}, \Delta s^0 = k \cdot \ln \sigma^2 = k \cdot \ln 4,$ and the symmetry factor σ.

This fulfills formally the general thermodynamic relation between equilibrium constant and *Gibbs* free energy, but it does not cause a deviation from the ideal mixtures for $\Delta W_{\mathrm{AB}} = 0$. This starting point is not valid for inter- and intramolecular vibration and rotations of a molecule. These properties are influenced by neighbouring molecules of the same or different type, especially in the liquid phase. To take into account these interactions, we extended Eq. (1) [10] to

$$\frac{N_{\mathrm{AB}}^2}{N_{\mathrm{AA}} \cdot N_{\mathrm{BB}}} = 4 \cdot \exp(-2 \cdot \Delta g_{\mathrm{AB}}/kT) = 4 \cdot \eta_{\mathrm{AB}}^{\mathrm{G}} = 4 \cdot \eta_{\mathrm{AB}}^{\mathrm{H}} \cdot \eta_{\mathrm{AB}}^{S} \tag{1a}$$

In this way, $\ln K = \ln 4 + \ln \eta_{\mathrm{AB}}^{\mathrm{G}} = -\Delta G^0/RT$ is a real equilibrium constant with a real *Gibbs* free energy. Δg_{AB} is given by two parameters, Δh_{AB} and Δs_{AB}, which are defined analogous to ΔW_{AB} in Eq. (4)

$$\Delta h_{\mathrm{AB}} = \bar{U}_{\mathrm{AB}} - \frac{\bar{U}_{\mathrm{AA}} + \bar{U}_{\mathrm{BB}}}{2}, \Delta s_{\mathrm{AB}} = s_{\mathrm{AB}} - \frac{s_{\mathrm{AA}} + s_{\mathrm{BB}}}{2} \tag{4a}$$

The Δs_{AB} parameter can be regarded as a vibrational and rotation interaction; Δh_{AB} and Δs_{AB} are temperature independent.

The partition function for vibration Z_{v} with high temperature can be written as $Z_{\mathrm{v}} = k \cdot T/h \cdot v$; for the *quasi*-chemical equilibrium we therefore have to introduce

$$\frac{Z_{\nu\mathrm{AB}}^2}{Z_{\nu\mathrm{AA}} \cdot Z_{\mathrm{vBB}}} = \frac{v_{\mathrm{AA}} \cdot v_{\mathrm{BB}}}{v_{\mathrm{AB}} \cdot v_{\mathrm{BA}}}$$

v_{AA} is the vibration of molecule A with a neighbouring molecule A, and v_{AB} is the vibration of molecule A with a neighbouring molecule B. For all vibration frequencies, we get

$$\Delta s = k \cdot \ln\left(\prod v_{\mathrm{A_iB}} \cdot \prod v_{\mathrm{B_iA}} / \left(\prod v_{\mathrm{A_iA}} \cdot \prod v_{\mathrm{B_iB}}\right)\right)$$

Döge, *Arndt*, *Buhl*, and *Bettermann* [11] have shown that the *Raman* band shape, the full width at half-height, and the maximum frequency of the v_1 bands of CH_3I and $CDCl_3$ in the mixture depend on the particular concentration. The same quantities were examined for the CH-vibration of CH_2I_2 and CCl_4 by *Moser*, *Asenbaum*, and *Döge* [12].

The contact site balances (Eqs. (2), (3)) stay unchanged. So we get

$$N'_{\mathrm{AB}} = Z \cdot N \cdot x_{\mathrm{A}} \cdot x_{\mathrm{B}} \cdot \left(\frac{2}{\beta' + 1}\right) \tag{5a}$$

with

$$\beta' = \left(1 + 4 \cdot x_A \cdot x_B \cdot \left(\frac{1}{\eta_{AB}^H \cdot \eta_{AB}^S} - 1\right)\right)^{1/2} \tag{6a}$$

The heat of mixing, the excess *Gibbs* free energy, and the activity coefficient are now given as

$$\Delta H^{E'} = N'_{AB} \cdot \Delta h_{AB} = Z \cdot N \cdot x_A \cdot x_B \cdot \left(\frac{2}{\beta' + 1}\right) \cdot \Delta h_{AB} \tag{7a}$$

$$\Delta G^{E'} = \frac{R \cdot T \cdot Z}{2} \cdot \left(x_A \cdot \ln \frac{\beta' - 1 + 2x_A}{x_A \cdot (\beta' + 1)} + x_B \cdot \ln \frac{\beta' - 1 + 2x_B}{x_B \cdot (\beta' + 1)}\right) \tag{8a}$$

$$\gamma'_i = \left(\frac{\beta' - 1 + 2x_i}{x_i \cdot (\beta' + 1)}\right)^{Z/2} \tag{9a}$$

$\Delta S^{E'}$ can be calculated as shown in Eq. (12):

$$\Delta S^{E'} = \frac{\Delta H^{E'} - \Delta G^{E'}}{T} \tag{11a}$$

$\Delta S^{E'}$ now consists of two parts. The first part depends on the contact number:

$$\Delta S_1^{E'}(\Delta s_{AB}) = N'_{AB}(\eta_{AB}^G) \cdot \Delta s_{AB}.$$

The second part depends on the configuration and is only a function of η_{AB}^G.ΔS_{config}^E vanishes for $\Delta h_{AB} = T \cdot \Delta s_{AB}$ $(\Delta g_{AB} = 0, \eta_{AB}^G = 1)$ because ΔS_{config}^E is only a function of η_{AB}^G. In this case, the number of AB contacts in a real mixture equals the number of contacts in a mixture with a statistical distribution of AB contacts ($N'_{AB} = Z \cdot N \cdot x_A \cdot x_B, \beta'$ in Eq. (5a) $= 1$).

Equation (8a) corresponds to these conditions. The critical temperature of phase separation is obtained through

$$\begin{aligned} \frac{\Delta g_{AB}}{k \cdot T_c} &= \frac{\Delta h_{AB} - T_c \cdot \Delta s_{AB}}{k \cdot T_c} = Z \cdot \ln \frac{Z}{Z - 2} \\ T_c &= \frac{\Delta h_{AB}}{k \cdot Z \cdot \ln(Z/(Z-2)) + \Delta s_{AB}} \end{aligned} \tag{12a}$$

Tables 1 and 2 show the results of $\eta_{AB}^G, \beta', \Delta G^{E'}/R \cdot T \cdot Z, \Delta S^{E'}/R \cdot Z$, and $\Delta H^{E'}/R \cdot T \cdot Z$ for different combinations of $\Delta h_{AB}/kT$ and $\Delta s_{AB}/k$ at $x_A = 0.5$. The results of three special cases are shown below

1) $\Delta h_{AB}/kT = \Delta s_{AB}/k \to \eta_{AB}^G, \beta' = 1; \Delta G^{E'} = 0, \Delta H^{E'} = -T \cdot \Delta S^{E'}$
2) $\Delta h_{AB}/kT = 0 \to \Delta H^{E'} = 0,\ \Delta G^{E'} = -T \cdot \Delta S^{E'}$
3) $\Delta s_{AB}/k = 0 \to \eta_{AB}^G = \eta_{AB},\ \beta = \beta'; |T \cdot \Delta S^{E'}| \ll \Delta H^{E'}, \Delta G^{E'}; \Delta S^{E'} < 0$

As in the original *quasi*-chemical theory, only binary systems can be calculated analytically. The modification of TASQUAC using the modified interaction parameter (mod. TASQUAC) can avoid this disadvantage and can be used for the development of a group contribution method. Results with Eqs. (7a), (8a), (9a), and (11a) will be presented together with results of the S-TASQUAC calculations for binary systems.

S-TASQUAC

For the analytical calculation of contact numbers of multi-component systems [13], the contact numbers are approximated by a *Taylor* series:

$$N_{\mathrm{AB}} = N^{*}_{\mathrm{AB}} + \sum_{\mathrm{CD}} \left(\left(\frac{\partial N_{\mathrm{AB}}}{\partial \eta^{G}_{\mathrm{CD}}} \right)^{*} \cdot (\eta^{G}_{\mathrm{CD}} - 1) + \frac{1}{2} \cdot \sum_{\mathrm{EF}} \left(\frac{\partial^{2} N_{\mathrm{AB}}}{\partial \eta^{G}_{\mathrm{CD}} \partial \eta^{G}_{\mathrm{EF}}} \right)^{*} \cdot (\eta^{G}_{\mathrm{CD}} - 1) \cdot (\eta^{G}_{\mathrm{EF}} - 1) \right) \tag{14}$$

The starting point of development of a *Taylor* series is at $\Delta g_{\mathrm{AB}} = 0$. For the differentials in Eq. (14) we derived analytical X-functions [14, 15] depending on the concentration where $\bar{Z}$ is the mean coordination number of mixture

$$N^{*}_{\mathrm{AB}} = \bar{Z} \cdot N \cdot X^{\mathrm{AB}} \tag{15}$$

$$\left(\frac{\partial N_{\mathrm{AB}}}{\partial \eta^{G}_{\mathrm{CD}}} \right)^{*} = \bar{Z} \cdot N \cdot X^{\mathrm{AB}}_{\mathrm{CD}} \tag{16}$$

$$\left(\frac{\partial^{2} N_{\mathrm{AB}}}{\partial \eta^{G}_{\mathrm{CD}} \partial \eta^{G}_{\mathrm{EF}}} \right)^{*} = \bar{Z} \cdot N \cdot X^{\mathrm{AB}}_{\mathrm{CD,EF}} \tag{17}$$

$$\bar{Z} = x_{\mathrm{A}} \cdot Z_{\mathrm{A}} + x_{\mathrm{B}} \cdot Z_{\mathrm{B}} \tag{18}$$

$\bar{Z} \cdot N/2$ is the total number of hetero-contacts in the mixture. If $\bar{Z} \cdot N$ is placed outside the parentheses, N_{AB} in a mixture with any number of components is given by

$$N_{\mathrm{AB}} = \bar{Z} \cdot N \cdot \left(X^{\mathrm{AB}} + \sum_{\mathrm{CD}} \left(X^{\mathrm{AB}}_{\mathrm{CD}} \cdot (\eta^{G}_{\mathrm{CD}} - 1) + \frac{1}{2} \cdot \sum_{\mathrm{EF}} X^{\mathrm{AB}}_{\mathrm{CD,EF}} \cdot (\eta^{G}_{\mathrm{CD}} - 1) \cdot (\eta^{G}_{\mathrm{EF}} - 1) \right) \right) \tag{19}$$

For the heat of mixing defined by Eq. (7a) we get

$$\Delta H^{E} = \bar{Z} \cdot N \cdot \sum_{\mathrm{AB}} \left(X^{\mathrm{AB}} + \sum_{\mathrm{CD}} \left(X^{\mathrm{AB}}_{\mathrm{CD}} \cdot (\eta^{G}_{\mathrm{CD}} - 1) + \frac{1}{2} \cdot \sum_{\mathrm{EF}} X^{\mathrm{AB}}_{\mathrm{CD,EF}} \cdot (\eta^{G}_{\mathrm{CD}} - 1) \cdot (\eta^{G}_{\mathrm{EF}} - 1) \right) \right) \cdot \Delta h_{\mathrm{AB}} \tag{20}$$

The excess Gibbs free energy $\Delta \mathrm{G}^{\mathrm{E}}$ is determined by integration of ΔH^{E} according to Eq. (8). The X-functions depend only on the mole fractions and remain constant. Therefore, the $\eta^{G}(T)$-functions have only to be integrated, and ΔG^{E} can be written as

$$\Delta G^E_{\text{S-TASQUAC}} = \bar{Z} \cdot N \cdot \sum_{\text{AB}} \left(X^{\text{AB}} \cdot \left(\Delta h_{\text{AB}} - T \cdot \Delta s_{\text{AB}} \right.\right.$$
$$+ \sum_{\text{CD}} \left(X^{\text{AB}}_{\text{CD}} \cdot \left(\Delta h_{\text{AB}} \cdot \Theta^G_{\text{CD}} - T \cdot \Delta s_{\text{AB}} \cdot \sigma_{\text{CD}} \right.\right.$$
$$\left.\left.\left.\left. + \frac{1}{2} \cdot \sum_{\text{EF}} X^{\text{AB}}_{\text{CD,EF}} \cdot \left(\Delta h_{\text{AB}} \cdot \Theta^G_{\text{CD,EF}} - T \cdot \Delta s_{\text{AB}} \cdot \sigma_{\text{CD,EF}} \right) \right) \right) \right) \right) \tag{21}$$

with the temperature functions Θ^G_{CD}, $\Theta^G_{\text{CD,EF}}$ and the entropy functions σ_{CD}, $\sigma_{\text{CD,EF}}$

$$\Theta^G_{\text{CD}} = T \cdot \int_0^{1/T} (\eta^G_{\text{CD}} - 1)\, \mathrm{d}\left(\frac{1}{T}\right) = \frac{\eta^S_{\text{CD}} \cdot (\eta^H_{\text{CD}} - 1)}{\ln \eta^H_{\text{CD}}} - 1 \tag{22}$$

$$\Theta^G_{\text{CD,EF}} = T \cdot \int_0^{1/T} (\eta^G_{\text{CD}} - 1) \cdot (\eta^G_{\text{EF}} - 1)\, \mathrm{d}\left(\frac{1}{T}\right) \tag{23}$$
$$= \frac{\eta^S_{\text{CD}} \cdot \eta^S_{\text{EF}} \cdot (\eta^H_{\text{CD}} \cdot \eta^H_{\text{EF}} - 1)}{\ln(\eta^H_{\text{CD}} \cdot \eta^H_{\text{EF}})} - \frac{\eta^S_{\text{CD}} \cdot (\eta^H_{\text{CD}} - 1)}{\ln \eta^H_{\text{CD}}} - \frac{\eta^S_{\text{EF}} \cdot (\eta^H_{\text{EF}} - 1)}{\ln \eta^H_{\text{EF}}} + 1$$

In relation to the expression of free excess enthalpy for temperature independent interchange energy the individual terms of zero, first, and second approximations must be corrected with the entropy term multiplied by the temperature. On the basis of zero approximation this can easily be shown. If the indefinite integration

$$T \cdot \int \Delta h_{\text{AB}} \mathrm{d}\left(\frac{1}{T}\right)$$

is carried out, the solution can be written as

$$\Delta h_{\text{AB}} + \text{const} \cdot T$$

According to the definition of new interchange energy, this constant should be $-\Delta s_{\text{AB}}$.

The entropy functions σ_{CD} and $\sigma_{\text{CD,EF}}$ for the first and second approximation were derived from a precise *quasi*-chemical solution. They are physically comprehensible, because the molecules are not arranged statistically for very high temperatures $T \to \infty$ anymore. Now, the number of molecule contacts is given by the entropy (η^s) alone.

$$\sigma_{\text{CD}} = \frac{\eta^S_{\text{CD}} - 1}{\ln \eta^S_{\text{CD}}} - 1 \tag{24}$$

$$\sigma_{\text{CD,EF}} = \frac{\eta^S_{\text{CD}} \cdot \eta^S_{\text{EF}} - 1}{\ln(\eta^S_{\text{CD}} \cdot \eta^S_{\text{EF}})} - \frac{\eta^S_{\text{CD}} - 1}{\ln \eta^S_{\text{CD}}} - \frac{\eta^S_{\text{EF}} - 1}{\ln \eta^S_{\text{EF}}} + 1 \tag{25}$$

The chemical potential is determined by solution of the differential $(\partial\Delta G^E/\partial N_\mathrm{K})_{T,P,N_L}$. For this purpose, the X-functions alone are differentiated; from them, the Y-functions are derived, because the X-functions contain N_K explicitly, and the $\eta^G(T)$ and η^S terms remain constant. Now, the chemical potential of each component K is given by:

$$\begin{aligned}\Delta\mu_\mathrm{K}^{E,\mathrm{S-TASQUAC}} = Z_K \cdot \sum_\mathrm{AB} \Bigg(& {}_\mathrm{K}Y^\mathrm{AB} \cdot (\Delta h_\mathrm{AB} - T \cdot \Delta s_\mathrm{AB}) \\ & + \sum_\mathrm{CD} \Bigg({}_\mathrm{K}Y_\mathrm{CD}^\mathrm{AB} \cdot \left(\Delta h_\mathrm{AB} \cdot \Theta_\mathrm{CD}^G - T \cdot \Delta s_\mathrm{AB} \cdot \sigma_\mathrm{CD}\right) \\ & + \frac{1}{2} \cdot \sum_\mathrm{EF} {}_\mathrm{K}Y_\mathrm{CD,EF}^\mathrm{AB} \cdot (\Delta h_\mathrm{AB} \cdot \Theta_\mathrm{CD,EF}^G - T \cdot \Delta s_\mathrm{AB} \cdot \sigma_\mathrm{CD,EF})\Bigg)\Bigg)\end{aligned} \tag{26}$$

$$\text{with} \quad {}_\mathrm{K}Y = \left(\frac{\partial(N \cdot X)}{\partial N_K}\right)_{N_\mathrm{L}} \tag{27}$$

The mole fraction functions X and Y have been explained in detail in a previous paper [15].

Instead of mole fractions, coordination fractions were introduced to describe the asymmetrical course of mixing functions and to take into account the different sizes and shapes of components.

$$\kappa_\mathrm{K} = \frac{Z_\mathrm{K} \cdot x_\mathrm{K}}{\sum_\mathrm{K} Z_\mathrm{K} \cdot x_\mathrm{K}} \tag{28}$$

Z_K is the coordination number of a component and is calculated using Eq. (28a) where $A_{\mathrm{W},Bondi}$ is the surface area of components determined by the *Bondi* method [18] (cf. Table 3).

$$Z_\mathrm{K} = \frac{A_{\mathrm{W},Bondi}}{A_\mathrm{WS}} \qquad A_\mathrm{WS} = 2.5 \cdot 10^8\,\mathrm{cm}^2 \cdot \mathrm{mol}^{-1} \tag{28a}$$

Now, employing the chemical potential, the activity coefficient is given by

$$\gamma_\mathrm{K}^\mathrm{S-TASQUAC} = \exp\left(\frac{\Delta\mu_\mathrm{K}^{E,\mathrm{S-TASQUAC}}}{k \cdot T}\right) \tag{29}$$

Analogous to the UNIQUAC model [16], the equations for ΔG^E and γ_K consist of two parts, a combinatorial (comb) and a residual (res) part.

$$\Delta G^E = \Delta G^E_\mathrm{S-TASQUAC,res} + \Delta G^E_\mathrm{comb} \tag{30}$$

$$\ln\gamma_\mathrm{K} = \ln\gamma_\mathrm{K}^\mathrm{S-TASQUAC,res} + \ln\gamma_\mathrm{K}^\mathrm{comb} \tag{31}$$

The combinatorial part describes the contribution of molecules with different sizes and shapes, whereas the residual part is due to intermolecular forces and is computed from the properties of mixtures. The combinatorial part can be expressed by the *Flory-Huggins* expression with the modification of *Kikic et al.* [17]. The volume fractions ϕ_K can now be calculated by using the volume increments of

Table 1. Model calculation results for η_{AB}^{G} and β' for different combinations of $\Delta h_{AB}/kT$ (0.0, ±0.1) and $\Delta s_{AB}/k$ (0.0, ±0.1) at $x_A = 0.5$

$\Delta h_{AB}/kT \rightarrow$ $\Delta s_{AB}/k$ ↓	−0.1	0.0	+0.1
−0.1	$\eta_{AB}^{G} = 1.00$ $\beta' = 1.00$	$\eta_{AB}^{G} = 0.82$ $\beta' = 1.11$	$\eta_{AB}^{G} = 0.67$ $\beta' = 1.22$
0.0	$\eta_{AB}^{G} = 1.22$ $\beta' = 0.91$	$\eta_{AB}^{G} = 1.00$ $\beta' = 1.00$	$\eta_{AB}^{G} = 0.82$ $\beta' = 1.11$
+0.1	$\eta_{AB}^{G} = 1.49$ $\beta' = 0.82$	$\eta_{AB}^{G} = 1.22$ $\beta' = 0.91$	$\eta_{AB}^{G} = 1.00$ $\beta' = 1.00$

Bondi [18] (cf. Table 3, normalization on volume of the standard segment $V_{W_s} = 15.17\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ [14]):

$$\ln \gamma_K^{\mathrm{comb}} = \ln\left(\frac{\phi_K}{x_K}\right) + 1 - \frac{\phi_K}{x_K} \tag{32}$$

$$\text{with} \quad \phi_K = \frac{r_K^{2/3} \cdot x_K}{\sum_L r_L^{2/3} \cdot x_L}, \; r_K = \frac{V_{\mathrm{w},\mathit{Bondi}}}{V_{\mathrm{WS}}}, \quad \text{and} \quad V_{\mathrm{WS}} = 15.17\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}. \tag{33}$$

The excess free enthalpy and activity coefficients of the S-TASQUAC model can now be written in the following form using the modifications discussed above:

$$\Delta G^E = \sum_K x_K \cdot \ln\left(\frac{\phi_K}{x_K}\right) + \Delta G^E_{\text{S-TASQUAC,res}} \tag{34}$$

$$\ln \gamma_K = \ln\left(\frac{\phi_K}{x_K}\right) + 1 - \frac{\phi_K}{x_K} + \frac{\Delta \mu^E_{\text{K,S-TASQUAC}}}{k \cdot T} \tag{35}$$

Table 2. Model calculation results for $\Delta G^{E'}/R \cdot T \cdot Z, \Delta H^{E'}/R \cdot T \cdot Z$, and $\Delta S^{E'}/R \cdot Z$ for different combinations of $\Delta h_{AB}/kT$ (0.0, ±0.1) and $\Delta s_{AB}/k$ (0.0, ±0.1) at $x_A = 0.5$

$\Delta h_{AB}/kT \rightarrow$ $\Delta s_{AB}/k$ ↓	−0.1	0.0	+0.1
−0.1	$\Delta G^{E'} = 0.0000$ $\Delta H^{E'} = -0.0250$ $T \cdot \Delta S^{E'} = -0.0250$	$\Delta G^{E'} = 0.0240$ $\Delta H^{E'} = 0.0000$ $T \cdot \Delta S^{E'} = -0.0240$	$\Delta G^{E'} = 0.0470$ $\Delta H^{E'} = 0.0230$ $T \cdot \Delta S^{E'} = 0.0250$
0.0	$\Delta G^{E'} = -0.0256$ $\Delta H^{E'} = -0.0262$ $T \cdot \Delta S^{E'} = -0.0006$	$\Delta G^{E'} = 0.0000$ $\Delta H^{E'} = 0.0000$ $T \cdot \Delta S^{E'} = 0.0000$	$\Delta G^{E'} = 0.0243$ $\Delta H^{E'} = 0.0238$ $T \cdot \Delta S^{E'} = -0.0005$
+0.1	$\Delta G^{E'} = -0.0524$ $\Delta H^{E'} = -0.0275$ $T \cdot \Delta S^{E'} = 0.0249$	$\Delta G^{E'} = -0.0256$ $\Delta H^{E'} = 0.0000$ $T \cdot \Delta S^{E'} = 0.0256$	$\Delta G^{E'} = 0.000$ $\Delta H^{E'} = 0.0250$ $T \cdot \Delta S^{E'} = 0.0250$

Table 3. Surface and volume values A_W and V_W and model parameters Z_K and r_K

	$10^{-9}A_W/\text{cm}^2\cdot\text{mol}^{-1}$	$V_W/\text{cm}^3\cdot\text{mol}^{-1}$	Z_K	r_K
Chloroform	6.03	43.54	24.12	2.87
Tetrachloromethane	7.28	52.34	29.12	3.45
Benzene	6.00	48.39	24.00	3.19
Chlorobenzene	7.11	57.80	28.44	3.81
Cyclohexane	8.10	61.44	32.40	4.05
Aniline	7.04	56.43	28.16	3.72
Toluene	7.42	59.47	29.68	3.92

Real System Calculations

The quality of the S-TASQUAC model can only be estimated by comparing its results with those of other models and experimental data. It is important to point out that the different models have different numbers of parameters that can be adjusted. The *Wilson* [17] and UNIQUAC models [16] require two parameters, whereas the NRTL model [20] uses three for each data set. The S-TASQUAC model only needs two parameters (Δh_{AB} and Δs_{AB}). For all models, these parameters were calculated from binary VLE data for *Wilson*, NRTL, and UNIQUAC to each separate data set, but for S-TASQUAC and old TASQUAC to all data sets of binary systems.

For fitting the general interchange parameter of the S-TASQUAC-model, the function

$$\min = \sum_{i=1}^{M_{\text{VLE}}} \frac{1}{N_\text{i}} \cdot \left(\frac{p_{\text{exp}} - p_{\text{calc}}}{p_{\text{exp}}}\right)^2 \tag{36}$$

with M_{VLE} = number of data sets and N_i = number of data points in a data set i is minimized by the NAG-routine E04FDF. The results of adjustment are summarized in Table 4.

With these parameters, the mean deviations in vapour composition, pressure, or temperature were calculated and compared with experimental results as shown in Tables 5 and 6. The VLE deviations of the models *Wilson*, NRTL, and UNIQUAC are taken from *Gmehling et al.* [21]. All deviations were determined in the same way:

$$\text{Mean} \quad \delta X = \frac{1}{N} \cdot \sum_{i=1}^{N} |X_{\text{calc}} - X_{\text{exp}}| \quad X = p, T, y \tag{37}$$

For a better comparison and because of the low pressure data (see VLE data), all deviations were calculated without taking real-gas corrections into account. We checked the influence of real-gas behaviour with the subroutines PHIS and BIJS [22], but the influence is (as expected) quite weak. The mean deviation for the exact solution (Eqs. (7a), (8a), (9a)) and the S-TASQUAC approximation (Eqs. (20), (21), (26)) are nearly the same. Therefore, only the S-TASQUAC values are given.

Table 4. General binary interchange parameters from VLE data for a temperature dependent description of $\Delta g_{\mathrm{AB}}/k = \Delta h_{\mathrm{AB}}/k - T\Delta s_{\mathrm{AB}}/k$ [10]

Component A	Component B	M_{VLE}	$\Delta h_{\mathrm{AB}}k^{-1}/K$	$10^3\Delta s_{\mathrm{AB}}k^{-1}$
Benzene	Cyclohexane	28	13.18	24.81
Benzene	Hexane	32	12.12	18.09
Benzene	Toluene	25	19.21	50.61
Benzene	Chlorobenzene	5	1.95	3.35
Benzene	Aniline	10	15.97	21.61
Tetrachloromethane	Chloroform	6	3.23	3.93
Tetrachloromethane	Cyclohexane	8	1.80	1.26
Tetrachloromethane	Toluene	5	7.89	23.37
Cyclohexane	Toluene	13	12.00	25.14
Cyclohexane	Chlorobenzene	2	9.88	14.17
Cyclohexane	Aniline	4	38.95	51.63
Cyclohexane	Hexane	14	4.72	12.35
Toluene	Aniline	4	25.74	44.40
Hexane	Chlorobenzene	3	14.73	25.18

Comparing the new model to the other ‘‘local composition’’-models shows that S-TASQUAC provides better results and is of the same quality as the description of liquid-vapour equilibrium. It should be mentioned that for the *Wilson*, NRTL, and UNIQUAC models the parameters were fitted individually with one set of parameters for each data set (M_{VLE} parameter sets), but in the case of TASQUAC and S-TASQUAC, respectively, one set of parameters was fitted to all data sets. A further important result is also that for mixtures containing components with dipole moment or aromatics the agreement between experimental and calculated values is two to three times better with S-TASQUAC than with *Wilson*, NRTL, and UNIQUAC. Compounds with dipole moment and aromatics have favoured orientations with mutually energetic linking. Such an orientation means an additional order. When two liquids are mixing, one is disturbed by the addition of foreign molecules. As a result, the excess entropy increases over ideal value, because a disorder is produced during the mixing process. Such positive excess entropies could be described with the S-TASQUAC-model. Another advantage of the new model is the quick implementation of thermodynamic calculations.

Finally, the predictive power of the S-TASQUAC model was examined. For that purpose, we have investigated four ternary systems whose thermodynamic excess functions were calculated solely from parameters obtained from the adjustment of binary VLE data. These results were compared to those of the old TASQUAC-model (see Table 7). In the case of the systems hexane-benzene chlorobenzene and hexane-cyclohexanebenzene, S-TASQUAC is superior (factor 2–3). The results for the other ternary mixtures are of the same quality.

The S-TASQUAC formalism allows the development of a group contribution method. We will publish this new S-GTASQUAC model in the following paper. The software can be obtained from the corresponding author.

Table 5. Results of a selection of mixtures (isothermal data sets) and comparison with different models

Component A	Component B	Ref.	Parameters were fitted to each data set						Parameters were fitted to all data sets			
			Wilson		NRTL		UNIQUAC		TASQUAC		S-TASQUAC	
			δp/mmHg	δy	δp/mmHg	δy	δp/mmHg	δy	δp/mmHg	δy	δp/mmHg	δy
Chloroform	Tetrachloromethane	[21a]	0.81	0.0025	0.82	0.0025	0.81	0.0025	0.62	0.0032	0.55	0.0031
Benzene	Cyclohexane	[21b]	1.17	0.0020	1.18	0.0017	1.18	0.0017	1.07	0.0038	1.12	0.0038
Benzene	Aniline	[21c]	8.73	0.0015	8.60	0.0015	8.70	0.0015	4.25	0.0013	4.89	0.0012
Toluene	Aniline	[21d]	1.44	0.0023	1.44	0.0024	1.45	0.0024	1.48	0.0023	1.81	0.0019
Tetrachloromethane	Toluene	[21e]	1.13	0.0011	1.08	0.0011	1.15	0.0011	0.76	0.0018	0.58	0.0014
Cyclohexane	Toluene	[21f]	0.39	0.0036	0.40	0.0035	0.39	0.0036	0.56	0.0052	0.53	0.0040
Tetrachloromethane	Cyclohexane	[21g]	1.90	0.0039	1.90	0.0039	1.90	0.0039	1.44	0.0049	1.70	0.0048
Cyclohexane	Chlorobenzene	[21h]	2.62	0.0053	2.63	0.0053	2.61	0.0053	2.82	0.0051	1.69	0.0063

Table 6. Results of a selection of mixtures (isobaric data sets) and comparison with different models

Component A	Component B	Ref.	Parameters were fitted to each data set						Parameters were fitted to all data sets			
			Wilson		NRTL		UNIQUAC		TASQUAC		S-TASQUAC	
			$\delta T/K$	δy	$\delta T/K$	δy	$\delta T/K$	δy	$\delta T/K$	δy	$\delta T/K$	δy
Chloroform	Tetrachloromethane	[21a]	0.08	0.0014	0.09	0.0013	0.08	0.0014	0.08	0.0030	0.06	0.0031
Benzene	Cyclohexane	[21b]	0.10	0.0016	0.10	0.0016	0.10	0.0016	0.12	0.0025	0.13	0.0025
Benzene	Aniline	[21c]	1.51	0.0119	1.50	0.0117	1.45	0.0121	1.26	0.0134	1.51	0.0224
Cyclohexane	Toluene	[21f]	0.15	0.0075	0.15	0.0075	0.14	0.0076	0.17	0.0049	0.16	0.0059
Tetrachloromethane	Cyclohexane	[21g]	0.27	0.0030	0.25	0.0031	0.26	0.0030	0.17	0.0040	0.15	0.0059
Cyclohexane	Chlorobenzene	[21h]	1.68	0.0174	1.64	0.0174	1.54	0.0174	1.07	0.0128	0.76	0.0093

Table 7. Description of ternary mixtures with the TASQUAC and S-TASQUAC models (prediction of binary VLE data)

System	TASQUAC		S-TASQUAC	
	$\delta T/K$	δy	$\delta T/K$	δy
Benzene-cyclohexane-toluene [21i]	3.73	0.0225	3.78	0.0224
Hexane-benzene-chlorobenzene [21j]	0.54	0.0176	0.36	0.0162
Hexane-cyclohexane-benzene [21k]	0.61	0.0081	0.23	0.0046

System	TASQUAC		S-TASQUAC	
	δp/mmHg	δy	δp/mmHg	δy
Benzene-cyclohexane-aniline [21l]	13.79	0.0063	13.82	0.0061
Hexane-cyclohexane-benzene [21k]	9.11	0.0133	3.64	0.0039

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List of Symbols and Abbreviations

A_W	surface of a molecule
G	*Gibbs* free energy
g	*Gibbs* free molar energy
Δg_{AB}	*Gibbs* free energy parameter for the S-TASQUAC-model
H	enthalpy
h	molar enthalpy
Δh_{AB}	enthalpy parameter for the S-TASQUAC-model
K	equilibrium constant for the number of contact pairs
k	*Boltzmann* constant
M_{VLE}	number of VLE data sets
N	total number of molecules
N_I	number of data points
N_K	number of molecules of type K
N_{AB}	number of contacts between molecules of component A and B
p	pressure
r	volume parameter
S	entropy
s	molar entropy
Δs_{AB}	entropy parameter for the S-TASQUAC-model
T	temperature
V_W	volume of a molecule
W	interchange energy
x	liquid-phase mole fraction
X	concentration function

y	vapour-phase mole fraction
Y	concentration function
Z	coordination number
$\bar{Z}$	mean coordination number
Θ_{KL}	temperature function
β, β'	function for the calculation of contact numbers in a binary mixture (exact *quasi*-chemical solution)
γ	activity coefficient
δ	deviation
$\eta^G = \exp\left(\frac{-2 \cdot \Delta g_{AB}}{k \cdot T}\right)$	interchange parameter (dimensionless) for S-TASQUAC model
$\eta^H = \exp\left(\frac{-2 \cdot \Delta h_{AB}}{k \cdot T}\right)$	enthalpy parameter (dimensionless) for the S-TASQUAC-model
$\eta^S = \exp\left(\frac{2 \cdot \Delta s_{AB}}{k}\right)$	entropy parameter (dimensionless) for the S-TASQUAC-model
κ_{K}	coordination fraction of component K
μ_{K}	chemical potential
v	vibration frequency
ϕ	volume fraction
σ	symmetry number
σ_{KL}	entropy function of the S-TASQUAC-model
NRTL	*N*on *R*andom *T*wo *L*iquids
TASQUAC	*T*aylor *S*eries *A*pproximation of *Quasi*-*C*hemical Equilibrium
S-TASQUAC	Entropy-TASQUAC
G-TASQUAC	*G*roup contribution TASQUAC
UNIQUAC	*Uni*versal *Quasi*-*C*hemical
VLE	*V*apour-*L*iquid *E*quilibrium

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