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Kontogeorgis, Georgios; Coutsikos, Philippos

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Thirty Years with EoS/G^E Models—What Have We Learned?

Georgios M. Kontogeorgis* and Philippos Coutsikos

Centre for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800, Lyngby, Denmark

ABSTRACT: Thirty years of research and the use of EoS/G^E mixing rules in cubic equations of state are reviewed. The most popular approaches are presented both from the derivation and application points of view and they are compared to each other. It is shown that all methods have significant capabilities but also limitations which are discussed. A useful approach is presented for analyzing the models by looking at the activity coefficient expression derived from the equations of state using various mixing rules. The size-asymmetric systems are investigated in detail, and an explanation is provided on how EoS/G^E mixing rules should be developed so that such asymmetric mixtures are adequately represented.

1. INTRODUCTION

Approximately 30 years have passed since the publication of the Huron−Vidal mixing rule.[1] Since then numerous models have appeared which can be classified under the so-called EoS/G^E terminology. These models are mixing rules for the energy (and covolume) parameters of cubic equations of state (EoS) by incorporating an activity coefficient model, often a local composition (LC) model like Wilson,[2] NRTL,[3] UNIQUAC,[4] or UNIFAC.[5] The objective with the use of EoS/G^E models is two-fold. First of all, these mixing rules have enhanced dramatically the range of applicability of cubic EoS to include high pressure vapor−liquid equilibria VLE (and sometimes other types of phase equilibria) for mixtures of compounds of wide complexity and asymmetry in size and energies. An additional objective is, sometimes, to reproduce at low pressures the incorporated activity coefficient models, thus permitting the use of existing interaction parameters of local composition models, including group contribution models (UNIFAC). In brief, the EoS/G^E mixing rules, proposed over the last 30 years, combine the "advantages" (but also often carry along the shortcomings) of cubic EoS and of the LC activity coefficient models incorporated. In some cases, however these mixing rules may result in superior EoS models, compared to the EoS and g^E models used in their derivation (although this may be coincidental). Nevertheless, the starting point of **many but not all** EoS/G^E mixing rules is the equality of excess Gibbs energies (g^E) or the excess Helmholtz energies (a^E) from the cubic EoS and the external activity coefficient model (denoted as M), such as a LC model. This equality is stated at some suitable reference pressure P:

$$\left(\frac{g^E}{RT}\right)^{EoS}_P = \left(\frac{g^E}{RT}\right)^M_P \tag{1a}$$

$$\left(\frac{a^E}{RT}\right)^{EoS}_P = \left(\frac{a^E}{RT}\right)^M_P \tag{1b}$$

The g^E and a^E expressions from Soave−Redlich−Kwong (SRK)[6] and Peng−Robinson (PR),[7] the two cubic EoS which are widely used today in practice, are shown in Table 1. For

comparison, the expressions from the van der Waals[8] EoS are also given. The expressions shown in Table 1 require no mixing rules as they are derived from the fundamental equations:

$$\frac{g^E}{RT} = \ln \varphi - \sum_i x_i \ln \varphi_i = \sum_i x_i \ln \gamma_i \tag{2a}$$

$$\frac{a^E}{RT} = \frac{g^E}{RT} - \frac{PV^E}{RT} \tag{2b}$$

Moreover, the expressions of Table 1 are written in such a form so that the contributions related to excess entropy (S^E), excess volume (V^E), and excess internal energy (U^E) are identified since:

$$\frac{g^E}{RT} = -\frac{S^E}{R} + \frac{PV^E}{RT} + \frac{U^E}{RT} \tag{3a}$$

$$\frac{a^E}{RT} = \frac{g^E}{RT} - \frac{PV^E}{RT} = -\frac{S^E}{R} + \frac{U^E}{RT} \tag{3b}$$

Under some conditions, eq 1 can be solved with respect to the energy parameter and a mixing rule can be derived. The most known reference pressures which have led to widely used mixing rules are **the infinite pressure and the zero pressure**. The infinite pressure was the assumption used by Huron and Vidal[1] starting from eq 1a and 13 years later it was also used by Wong and Sandler[9] based on eq 1b. The zero reference pressure was introduced by Mollerup[10] and Michelsen[11,12] and leads to one exact formulation (under some assumptions) and to useful general but "approximate zero" reference pressure mixing rules like MHV1, MHV2 (modified Huron−Vidal first and second order) by Dahl and Michelsen,[13] and the PSRK (predictive SRK) model by Gmehling and co-workers.[14] There have been also presented useful EoS/G^E models which are not derived directly from eqs 1a or 1b. One of the most successful

Table 1. g^E and a^E Expressions from Three Cubic Equations of State

equation of state	g^E	a^E
vdW[8]	$\left(\sum_i x_i \ln\left(\dfrac{V_i - b_i}{V - b}\right)\right) + \dfrac{P}{RT}\left(V - \sum_i x_i V_i\right) + \left(\dfrac{1}{RT}\left(\sum_i x_i \dfrac{a_i}{V_i} - \dfrac{a}{V}\right)\right)$	$\left(\sum_i x_i \ln\left(\dfrac{V_i - b_i}{V - b}\right)\right) + \left(\dfrac{1}{RT}\left(\sum_i x_i \dfrac{a_i}{V_i} - \dfrac{a}{V}\right)\right)$
SRK[6]	$\left(\sum_i x_i \ln\left(\dfrac{V_i - b_i}{V - b}\right)\right) + \dfrac{P}{RT}\left(V - \sum_i x_i V_i\right) + \left(\dfrac{1}{RT}\left[\sum_i x_i \dfrac{a_i}{b_i}\ln\left(\dfrac{V_i + b_i}{V_i}\right) - \dfrac{a}{b}\ln\left(\dfrac{V+b}{V}\right)\right]\right)$	$\left(\sum_i x_i \ln\left(\dfrac{V_i - b_i}{V - b}\right)\right) + \left(\dfrac{1}{RT}\left[\sum_i x_i \dfrac{a_i}{b_i}\ln\left(\dfrac{V_i + b_i}{V_i}\right) - \dfrac{a}{b}\ln\left(\dfrac{V+b}{V}\right)\right]\right)$
PR[7]	$\left(\sum_i x_i \ln\left(\dfrac{V_i - b_i}{V - b}\right)\right) + \dfrac{P}{RT}\left(V - \sum_i x_i V_i\right) + \left(\dfrac{1}{RT2\sqrt{2}}\left[\sum_i x_i \dfrac{a_i}{b_i}\ln\left(\dfrac{V_i + (1+\sqrt{2})b_i}{V_i + (1-\sqrt{2})b_i}\right) - \dfrac{a}{b}\ln\left(\dfrac{V + (1+\sqrt{2})b}{V + (1-\sqrt{2})b}\right)\right]\right)$	$\left(\sum_i x_i \ln\left(\dfrac{V_i - b_i}{V - b}\right)\right) + \left(\dfrac{1}{RT2\sqrt{2}}\left[\sum_i x_i \dfrac{a_i}{b_i}\ln\left(\dfrac{V_i + (1+\sqrt{2})b_i}{V_i + (1-\sqrt{2})b_i}\right) - \dfrac{a}{b}\ln\left(\dfrac{V + (1+\sqrt{2})b}{V + (1-\sqrt{2})b}\right)\right]\right)$

such models is LCVM (linear combination of Vidal and Michelsen mixing rules) proposed in 1994 by Tassios and co-workers.[15] LCVM and other models in this family were introduced in order to solve some problems of the previously presented approaches, especially for size-asymmetric mixtures like gases with heavy hydrocarbons. In our view, LCVM is the last one of the models offering a significant advance in the topic of EoS/G^E mixing rules. This does not mean that there are no other successful EoS/G^E approaches—indeed there are many and they will be discussed in this review. We feel, however, that most successful EoS/G^E mixing rules can be categorized as those following the infinite or zero reference pressure assumption and those **not** having a specific reference pressure (like LCVM), which were developed having especially the asymmetric systems in mind. Finally, it may be expected that any EoS and any g^E model could be combined in the EoS/G^E mixing rules. This is **partially true** but there are exceptions (both theoretical and practical ones), as will be explained later.

In the 30 years that have elapsed since the Huron–Vidal mixing rules, much has been learned on the capabilities and limitations of the EoS/G^E mixing rules. The scientific interest is significant (see Table 2) but it has somewhat declined over the recent years. This is partly attributed to the fact that we have now a rather mature technology with significant potential, impressive results, though, regrettably, also some serious theoretical and practical limitations.

These limitations have become the source of intense discussions in the scientific community and have possibly led

Table 2. Citations of Major EoS/G^E Developments (Source: Web of Science, 11/7/2011)[a]

article	citations	citations/year
Huron and Vidal, 1979[1]	538	16
Michelsen, exact, 1990[11]	256	12
Dahl and Michelsen, 1990 (MHV1, MHV2)[13]	226	11
Gmehling, 1991 (PSRK)[14]	305	15
Wong and Sandler, 1992[9]	496	25
LCVM (Tassios, 1994)[15]	154	9

[a]In the PPEPPD conferences 1995 and 1998 (as published in *Fluid Phase Equilibria*, volumes 116−117 and 158−160) about 20 articles are published related to EoS/G^E mixing rules, while fewer than 10 are published in the subsequent PPEPPD conferences 2001, 2004, 2007, and 2010. Similar trends are observed in other conferences, for example, ESAT.

to some misconceptions and misunderstandings. It is the purpose of this review to outline the capabilities and limitations of the major EoS/G^E approaches, when compared against experimental data and when compared against each other and the theory used in their derivation. The review reflects the authors' own opinion, which may not always coincide with the developers' point of view. Section 2 discusses the five major approaches previously mentioned (Huron−Vidal, Wong− Sandler, "exact" zero reference pressure, approximate zero reference pressure and LCVM). Some of their numerous variations will also be presented. In this section, mostly VLE (original scope of these models) including gas solubilities will be discussed (from the application point of view), while

Table 3. The Five Major EoS/G^E Approaches. Note That $\alpha = a/(bRT)$

method	SRK	PR
Huron−Vidal[1]	$\dfrac{a}{b} = \sum_i x_i \dfrac{a_i}{b_i} - \dfrac{g^{E,\infty}}{\ln 2}$ $b = \sum_i x_i b_i$	$\dfrac{a}{b} = \sum_i x_i \dfrac{a_i}{b_i} - \dfrac{g^{E,\infty}}{0.6232}$ $b = \sum_i x_i b_i$
exact[2,11] zero reference pressure $u_0 = V/b$ at $P = 0$	$\left(\dfrac{g^E}{RT}\right)_0^M = \sum_i x_i \ln\left(\dfrac{b_i}{b}\right) + q^e(\alpha) - \sum x_i q_i^e(\alpha_i)$ $q^e(\alpha) = -1 - \ln(u_0 - 1) - \alpha \ln\left(\dfrac{u_0 + 1}{u_0}\right)$ $b = \sum_i x_i b_i{}^a$	$\left(\dfrac{g^E}{RT}\right)_0^M = \sum_i x_i \ln\left(\dfrac{b_i}{b}\right) + q^e(\alpha) - \sum x_i q_i^e(\alpha_i)$ $q(\alpha) = -1 - \ln(u_0 - 1) - \dfrac{\alpha}{2\sqrt{2}} \ln\left(\dfrac{u_0 + (1+\sqrt{2})}{u_0 + (1-\sqrt{2})}\right)$ $b = \sum_i x_i b_i{}^a$
approximate zero reference pressure models[13,14]	$\alpha = \dfrac{1}{q_1}\left(\dfrac{g^{E,M}}{RT} + \sum_i x_i \ln\left(\dfrac{b}{b_i}\right)\right) + \sum_i x_i \alpha_i$ $q_1 = -0.593$ (MHV1)[13] $q_1 = -0.64663$ (PSRK)[14] $q_1\left(\alpha - \sum_i x_i \alpha_i\right) + q_2\left(\alpha^2 - \sum_i x_i \alpha_i^2\right) = \left(\dfrac{g^{E,M}}{RT}\right) + \sum_i x_i \ln\left(\dfrac{b}{b_i}\right)$ $q_1 = -0.4783,\ q_2 = -0.0047$ $b = \sum_i x_i b_i{}^a$	$\alpha = \dfrac{1}{q_1}\left(\dfrac{g^{E,M}}{RT} + \sum_i x_i \ln\left(\dfrac{b}{b_i}\right)\right) + \sum_i x_i \alpha_i$ $q_1 = -0.53$ (PR) $q_1\left(\alpha - \sum_i x_i \alpha_i\right) + q_2\left(\alpha^2 - \sum_i x_i \alpha_i^2\right) = \left(\dfrac{g^{E,M}}{RT}\right) + \sum_i x_i \ln\left(\dfrac{b}{b_i}\right)$ $q_1 = -0.4347,\ q_2 = -0.003654$[116] $b = \sum_i x_i b_i{}^a$
Wong−Sandler[9]	$\dfrac{a}{b} = \sum_i x_i \dfrac{a_i}{b_i} - \dfrac{g^{E,M}}{\ln 2}$ $b = \dfrac{\sum_i \sum_j x_i x_j \left(b - \dfrac{a}{RT}\right)_{ij}}{1 + \dfrac{g^{E,M}}{\ln 2 RT} - \sum_i x_i \dfrac{a_i}{b_i RT}}$ For the cross-parameter there are different choices, for example, $\left(b - \dfrac{a}{RT}\right)_{ij} = \dfrac{\left(b_i - \dfrac{a_i}{RT}\right) + \left(b_j - \dfrac{a_j}{RT}\right)}{2}(1 - k_{ij})$	$\dfrac{a}{b} = \sum_i x_i \dfrac{a_i}{b_i} - \dfrac{g^{E,M}}{0.6232}$ $b = \dfrac{\sum_i \sum_j x_i x_j \left(b - \dfrac{a}{RT}\right)_{ij}}{1 + \dfrac{g^{E,M}}{0.6232 RT} - \sum_i x_i \dfrac{a_i}{b_i RT}}$ For the cross-parameter there are different choices, for example, $\left(b - \dfrac{a}{RT}\right)_{ij} = \dfrac{\left(b_i - \dfrac{a_i}{RT}\right) + \left(b_j - \dfrac{a_j}{RT}\right)}{2}(1 - k_{ij})$
LCVM[15]	$\alpha = \left(\dfrac{\lambda}{A_V} + \dfrac{1-\lambda}{A_M}\right)\left(\dfrac{g^{E,M}}{RT}\right) + \dfrac{1-\lambda}{A_M} \sum_i x_i \ln\left(\dfrac{b}{b_i}\right) + \sum_i x_i \alpha_i$ (the model has not been used with SRK) $b = \sum_i x_i b_i{}^a$	$\alpha = \left(\dfrac{\lambda}{A_V} + \dfrac{1-\lambda}{A_M}\right)\left(\dfrac{g^{E,M}}{RT}\right) + \dfrac{1-\lambda}{A_M} \sum_i x_i \ln\left(\dfrac{b}{b_i}\right) + \sum_i x_i \alpha_i$ $A_V = -0.623,\ A_M = q_1 = -0.52$ $\lambda = 0.36$ [original UNIFAC] $b = \sum_i x_i b_i{}^a$

^{a}Alternative mixing rules for the co-volume are possible.

other properties (LLE, solid−gas equilibria, thermal) will be briefly considered in section 3, where a comparative discussion and evaluation of all mixing rules will also be presented. The review closes with the conclusions and assessment of the status of EoS/G^E methodology, about 30 years after its conception.

2. CAPABILITIES AND LIMITATIONS OF THE FIVE MAJOR EOS/G^E APPROACHES

Table 3 presents the five major EoS/G^E approaches as applied to SRK and PR in **their usual form** (deviations from this form are explained in this section). We will present the Huron−Vidal and Wong−Sandler models first, due to their similarities

(infinite pressure models) and the zero reference pressure models will follow (exact and approximate versions). The section will end with a presentation of LCVM and related models.

2.1. The Huron−Vidal Approach. The starting point is eq 1a at infinite pressure where it can be assumed that the volume is equal to the covolume ($\lim_{P\to\infty} V = b$ and $\lim_{P\to\infty} V_i = b_i$). It can be easily shown that this assumption eliminates the excess entropy ($-S^E/R$) term of the g^E expression of cubic EoS like SRK and PR, which corresponds to the term reflecting size/ shape differences between the mixture components, the so-called "combinatorial/free-volume" term. The second assumption is that the linear mixing rule is used for the covolume

$(b = \sum_i x_i b_i)$, see Table 3, which eliminates the excess volume term at infinite pressure. Thus at infinite pressure:

$$\frac{g^{E,EoS,\infty P}}{RT} = \frac{U^{E,\infty}}{RT} = \frac{g^{E,res}}{RT} = \left(\frac{A_V}{RT}\left(\sum_i x_i \frac{a_i}{b_i} - \frac{a}{b}\right)\right)$$

$$= \frac{A_V}{RT}\left(\sum_i x_i \varepsilon_i - \varepsilon\right) \quad \varepsilon = \frac{a}{b}$$

$$A_V = 1 \quad (\text{vdW, van Laar})$$

$$A_V = \ln 2 \quad (\text{SRK})$$

$$A_V = 0.623 \quad (\text{PR}) \tag{4}$$

Equation 4, also shown in Table 3, is the Huron−Vidal mixing rule.[1] It is clear that the linear mixing rule for the covolume is used in its derivation and no other mixing rules for the covolume can be used in order to arrive to eq 4 when eq 1a is the starting point for the derivation.

Another important remark is that, in general, $g^{E,EoS,\infty P} \neq g^{E,EoS,low,P}$, thus the existing parameter tables from activity coefficient models which are obtained from low pressure data cannot be used in eq 4.

It is also quite interesting to note that since at infinite pressure $S^E = V^E = 0$ and $g^E = U^E$ then the $g^{E,EoS,\infty P}$ is essentially an "energetic" or "residual" (in the activity coefficient terminology) excess Gibbs energy contribution, and only such activity coefficient models should be used in connection with the Huron−Vidal approach. Examples of such models are NRTL and the residual part of UNIQUAC or UNIFAC.

Indeed, Huron and Vidal[1,26] combined SRK with NRTL and they presented excellent correlation results for the VLE of acetone/water, methanol/CO_2, methanol/propane, and other complex mixtures. The performance of SRK with the Huron−Vidal mixing rules is better than when SRK is used with the van der Waals one fluid mixing rules ($a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij}$, $b = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j b_{ij}$). Good predictions are also obtained for multicomponent VLE.

It should be noted that Huron and Vidal used an NRTL version which, under certain assumptions for the parameter values, can result in the vdW1f mixing rules for nonpolar compounds. In this way, the SRK EoS can be used for mixtures of polar and nonpolar compounds, using the classical interaction parameters in cross a_{12} or the Huron−Vidal parameters. This permits reusing the interaction parameter tables for k_{ij} (correction in the geometric mean rule for the cross energy parameter) available for SRK for mixtures with nonpolar compounds.

The Huron−Vidal mixing rule has been widely used both in academia and industry. It has been shown[16−20] (in its SRK/NRTL formulation) to be an excellent correlation tool even for highly complex VLE, LLE, and VLLE for a variety of mixtures including those containing water, alcohols, or glycols and hydrocarbons and for both binary and multicomponent mixtures. Parameters obtained from correlating binary data can be used to predict phase equilibria for multicomponent systems (see also the discussion in section 3).

Feroiu, Geana, and co-workers[21−24] have shown that SRK/Huron−Vidal coupled with the residual term of UNIQUAC and parameters obtained from infinite dilution data can correlate/predict CO_2-alcohols VLE and VLLE over extensive temperature ranges. It should be emphasized that for obtaining good results over broad temperature ranges, (linearly) temperature dependent interaction parameters are needed in the local composition model. Note that, in agreement to the previous discussion, the combinatorial term of UNIQUAC is dropped.

Vidal himself in a series of publications[25−27] proposed combining the Huron−Vidal mixing rule in SRK or PR using the residual term of UNIQUAC or UNIFAC, in the latter case for developing a predictive model. Of course, in both cases new interaction parameters (molecular or group ones) should be determined based on experimental data. Later, Soave and co-workers[28−34] continued this work proposing an SRK/Huron−Vidal model with the residual term of UNIFAC and applied the derived model (UNIFEST) with success to some polar mixtures containing ethers, alcohols, ketones, esters, and alkanes or light gases. More work was in progress[28,29] but to the knowledge of the authors this group contribution SRK/Huron−Vidal parameter table has not been completed (see, however, the discussion in section 3 and ref 98). In the first of these publications[28] Soave illustrated (Figure 3 of ref 28) that the combinatorial term of the external model (UNIFAC) should be dropped as "*calculations have shown that it causes an excessive decrease of volatility which cannot be compensated in mixtures of light and heavy hydrocarbons*".[28] The test system was ethane/octane at 25 °C. Soave[29] also mentioned that "*the combinatorial term produced over-specified coefficient values*".[29] We believe that these conclusions from Soave are correct and consistent with the derivation of the Huron−Vidal mixing rule, see eq 4, since the excess Gibbs energy at infinite pressure from the EoS only corresponds to its "energetic" or "residual" part. Thus, in the case of the Huron−Vidal mixing rule, eq 1a implies equating the energetic g^E from the EoS (right-hand side of eq 4) and from an explicit activity coefficient model.

We will further elucidate this point by looking at the activity coefficient equation derived from SRK using the Huron−Vidal and classical mixing rules. Following the discussion by Kontogeorgis and co-workers[16,35,37] and Sacomani and Brignole[36] we will analyze the Huron−Vidal mixing rule by looking at the activity coefficient equation, which unlike the g^E expression, depends on the mixing rule. To simplify things, we limit our discussion to infinite dilution conditions, zero values of the interaction parameters and binary systems. Under these conditions, and using the linear mixing rule for the covolume parameter, the expressions for the activity coefficient are for SRK with the various mixing rules given in eqs 5a−5d (note that ∞ indicates infinite dilution here).

SRK with vdW1f mixing rules:

$$\ln \gamma_1^\infty = \ln \gamma_1^{comb-FV} + \ln \gamma_1^{res}$$

$$= \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1 - \left(\frac{V_1 - b_1}{V_2 - b_2}\right)$$

$$+ \frac{a_1}{b_1 RT}\ln\frac{\left(1 + \frac{b_1}{V_1}\right)}{\left(1 + \frac{b_2}{V_2}\right)} + \frac{a_2}{b_2 RT}\left(\frac{V_1 b_2 - V_2 b_1}{V_2^2 + b_2 V_2}\right)$$

$$+ \frac{b_1}{RT}\left[\frac{\sqrt{a_2}}{b_2} - \frac{\sqrt{a_1}}{b_1}\right]^2 \ln\left(1 + \frac{b_2}{V_2}\right) \tag{5a}$$

SRK using the simplified mixing rule $a/b = \sum_i x_i a_i / b_i$ (this form of the equation corresponds to using only

the combinatorial/free-volume contribution of the cubic EoS):

$$\ln \gamma_1^\infty = \ln \gamma_1^{comb-FV} = \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1 - \left(\frac{V_1 - b_1}{V_2 - b_2}\right)$$

$$+ \frac{a_1}{b_1 RT} \ln \frac{\left(1 + \frac{b_1}{V_1}\right)}{\left(1 + \frac{b_2}{V_2}\right)} + \frac{a_2}{b_2 RT}\left(\frac{V_1 b_2 - V_2 b_1}{V_2^2 + b_2 V_2}\right) \tag{5b}$$

SRK using the Huron−Vidal mixing rule (using an external activity coefficient without or with an explicit combinatorial term):

$$\ln \gamma_1^\infty = \ln \gamma_1^{comb-FV} + \ln \gamma_1^{res}$$

$$= \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1 - \left(\frac{V_1 - b_1}{V_2 - b_2}\right) + \frac{a_1}{b_1 RT} \ln \frac{\left(1 + \frac{b_1}{V_1}\right)}{\left(1 + \frac{b_2}{V_2}\right)}$$

$$+ \frac{a_2}{b_2 RT}\left(\frac{V_1 b_2 - V_2 b_1}{V_2^2 + b_2 V_2}\right) + \left(\frac{-1}{A_V}\right) \ln\left(\frac{V_2 + b_2}{V_2}\right) \ln \gamma_1^{res,M} \tag{5c}$$

$$\ln \gamma_1^\infty = \ln \gamma_1^{comb-FV} + \ln \gamma_1^{res}$$

$$= \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1 - \left(\frac{V_1 - b_1}{V_2 - b_2}\right) + \frac{a_1}{b_1 RT}$$

$$\ln \frac{\left(1 + \frac{b_1}{V_1}\right)}{\left(1 + \frac{b_2}{V_2}\right)} + \frac{a_2}{b_2 RT}\left(\frac{V_1 b_2 - V_2 b_1}{V_2^2 + b_2 V_2}\right)$$

$$+ \left(\frac{-1}{A_V}\right) \ln\left(\frac{V_2 + b_2}{V_2}\right)(\ln \gamma_1^{comb,M} + \ln \gamma_1^{res,M}) \tag{5d}$$

where M is the external activity coefficient model such as NRTL. We use the symbol "res,M" to emphasize that only the residual term of an activity coefficient model or a purely energetic model should be used in the Huron−Vidal model. Nevertheless, if an activity coefficient model having both combinatorial and residual terms is used, then eq 5d applies.

By comparing eqs 5a−5c we can see that SRK with the Huron−Vidal mixing rule essentially modifies only the residual term of the equation of state (compared to the classical vdW1f mixing rule). This residual part is, for the vdW1f mixing rules, represented by the last bracketed term in eq 5a, which is a regular solution type term. In the case of SRK/Huron−Vidal this residual term is given by a local composition model (last term in eq 5c). The SRK EoS with the Huron−Vidal mixing rule has the same combinatorial-free volume term as SRK with the vdW1f mixing rules. It is thus clear that the performance of SRK/Huron−Vidal EoS coupled with NRTL cannot be identical to that of NRTL, especially for size-asymmetric systems, even at low pressures. This is because the EoS/G^E model contains a combinatorial term, while the explicit g^E model (NRTL) does not.

Following previous investigations[16,35−37] we can claim that the first term of eqs 5a and 5c (and the full eq 5b) is the combinatorial-free volume or size term of the EoS. It represents indeed the term that disappears at infinite pressure (if we set $V = b$ and $V_i = b_i$), exactly as the S^E and V^E terms vanish at infinite pressure. The regular solution terms in eq 5a or $\gamma^{res,M}$ in eq 5c which do not disappear at infinite pressure are the energy terms of the EoS. Having said that, how successfully do the well-known cubic EoS like SRK or PR represent nearly athermal mixtures with large size differences between the components which could provide a test for the combinatorial/free-volume term of cubic EoS ? Mixtures of alkanes offer an excellent such test as these are considered nearly athermal and, for example, ln $\gamma^{res,M}$ = 0 from UNIFAC for such systems. The results shown in refs 16 and 35−37 as well as some typical results given in Table 4 and Figure 1 illustrate that the combinatorial-free

Table 4. Percentage Absolute Deviation between Experimental and Calculated Activity Coefficients at Infinite Dilution for n-Butane and n-Heptane in Various Alkanes Using the PR EoS and Various Mixing Rules. For Comparison the Deviations with Original and Modified UNIFAC Combinatorials[5,112] Are Also Given

alkane	or.UNIFAC	mod.UNIFAC	PR−vdW1f, eq 6a ($k_{ij} = 0$)	PR-a/b or Vidal, eqs 6b or 6c	PR−Vidal, eq 6d (using or.UNIFAC in the external model)
		n-Butane			
20	39	16	27	0.6	46
22	41	17	32	1.1	50
24	40	13	44	2.0	51
28	43	13	54	2.5	58
32	45	11	68	5.3	63
36	46	10	83	9.3	67
average	42	13	51	3.5	56
		n-Heptane			
20	21	6.8	15	5.3	31
22	25	9.1	18	11.1	38
24	24	5.2	29	9.3	40
28	26	3.0	45	11.7	47
32	28	1.9	63	15.6	53
36	30	0.2	85	19.3	58
average	26	4.4	43	12	45

volume term of cubic EoS *does* provide qualitatively and in many cases even quantitatively correct results.

The results in Table 4 and Figure 1 are based on the Peng−Robinson equation of state for which the equations are similar to eqs 5a−5c:

PR with vdW1f mixing rules:

$$\ln \gamma_1^\infty = \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1 - \left(\frac{V_1 - b_1}{V_2 - b_2}\right) + \frac{a_1}{2\sqrt{2}\, b_1 RT}$$

$$\ln \frac{f(b_1, V_1)}{f(b_2, V_2)} + \frac{a_2}{b_2 RT}\left(\frac{V_1 b_2 - V_2 b_1}{V_2^2 + 2 b_2 V_2 - b_2^2}\right)$$

$$+ \frac{b_1}{2\sqrt{2}\, RT}\left[\frac{\sqrt{a_2}}{b_2} - \frac{\sqrt{a_1}}{b_1}\right]^2 \ln f(b_2, V_2) \tag{6a}$$
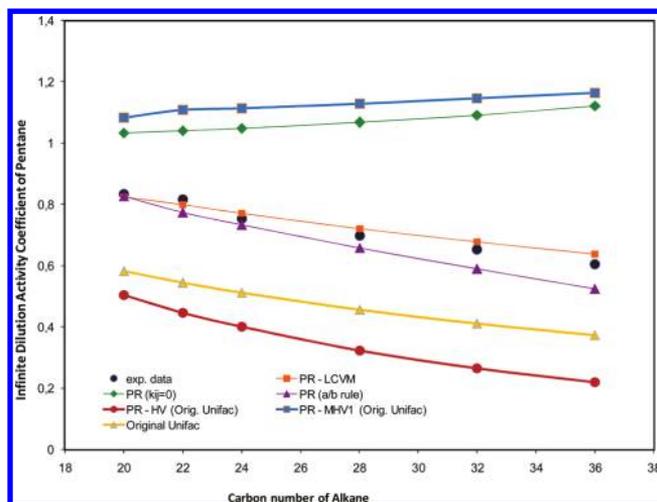
Figure 1. Experimental and predicted with PR and various mixing rules activity coefficients of pentane in alkanes of different chain length. The original UNIFAC[5] model is used in LCVM.

PR using the simplified mixing rule $a/b = \sum_i x_i a_i/b_i$:

$$\ln \gamma_1^\infty = \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1 - \left(\frac{V_1 - b_1}{V_2 - b_2}\right) + \frac{a_1}{2\sqrt{2}\, b_1 RT}$$
$$\ln \frac{f(b_1, V_1)}{f(b_2, V_2)} + \frac{a_2}{b_2 RT}\left(\frac{V_1 b_2 - V_2 b_1}{V_2^2 + 2b_2 V_2 - b_2^2}\right)$$

(6b)

PR using the Huron−Vidal mixing rule (using an external activity coefficient without or with an explicit combinatorial term):

$$\ln \gamma_1^\infty = \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1 - \left(\frac{V_1 - b_1}{V_2 - b_2}\right) + \frac{a_1}{2\sqrt{2}\, b_1 RT}$$
$$\ln \frac{f(b_1, V_1)}{f(b_2, V_2)} + \frac{a_2}{b_2 RT}\left(\frac{V_1 b_2 - V_2 b_1}{V_2^2 + 2b_2 V_2 - b_2^2}\right)$$
$$+ \left(\frac{-1}{A_V}\right)\left(\frac{\ln f(b_2, V_2)}{2\sqrt{2}}\right)\ln \gamma_1^{res,M}$$

(6c)

$$\ln \gamma_1^\infty = \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1 - \left(\frac{V_1 - b_1}{V_2 - b_2}\right) + \frac{a_1}{2\sqrt{2}\, b_1 RT}$$
$$\ln \frac{f(b_1, V_1)}{f(b_2, V_2)} + \frac{a_2}{b_2 RT}\left(\frac{V_1 b_2 - V_2 b_1}{V_2^2 + 2b_2 V_2 - b_2^2}\right)$$
$$+ \left(\frac{-1}{A_V}\right)\left(\frac{\ln f(b_2, V_2)}{2\sqrt{2}}\right)(\ln \gamma_1^{comb,M} + \ln \gamma_1^{res,M})$$

(6d)

In all the above cases:

$$f(b_i, V_i) = \left[\frac{V_i + (1 + \sqrt{2})b_i}{V_i + (1 - \sqrt{2})b_i}\right]$$

and the function $f(b_2, V_2)$ is the same as $f(b_1, V_1)$, with change of subscripts.

We note that the results with the cubic EoS combinatorial/ free-volume activity coefficient (or simply the a/b mixing rule)

are as good as those with the modified UNIFAC,[112] which is a very successful model for alkane mixtures. Moreover, the results are better than those with original UNIFAC. On the other hand, cubic EoS using the vdW1f mixing rules yield erroneous results which are even qualitatively wrong (positive deviations from Raoult's law). Equally poor results are obtained (last columns in Table 4; see also Figure 1) if, erroneously, the "full" UNIFAC model is used in the Huron−Vidal mixing rule i.e. use of eq 6d. A large overcorrection is resulted which yields activity coefficients exhibiting extreme negative deviations from Raoult's law. Although being qualitatively correct (negative deviations from Raoult's law), the results are in this case as poor as when the vdW1f mixing rules are used.

It is, thus, clear that inclusion of "additional" combinatorial free-volume terms would yield poorer results for alkanes. These "additional" terms appear in the SRK/Huron−Vidal model if we introduce a combinatorial term from an external activity coefficient model, that is, when we use eqs 5d or 6d. Including "erroneously" such an extra combinatorial term would eliminate the good performance of the combinatorial/free-volume part of the EoS. Moreover, this conclusion is in full agreement with the findings of Soave, Vidal, Feoiou et al., and others who have used the Huron−Vidal mixing rule using exclusively NRTL or the residual term of UNIQUAC or UNIFAC. The above analysis shows that especially for size-asymmetric systems, correlations of SRK/Huron−Vidal using Wilson or the full version of UNIQUAC or UNIFAC may not result in satisfactory results, even when interaction parameters are fitted to data.

It is interesting to note that the similarities between SRK and PR are not seen in the simpler van der Waals equation of state, for which the activity coefficient expressions at infinite dilution are shown in eqs 7a and 7b.

vdW with van der Waals one fluid mixing rules:

$$\ln \gamma_1^\infty = \ln \gamma_1^{comb-FV} + \ln \gamma_1^{res}$$
$$= \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1 - \left(\frac{V_1 - b_1}{V_2 - b_2}\right)$$
$$+ \frac{V_1}{RT}\left(\frac{\sqrt{a_1}}{V_1} - \frac{\sqrt{a_2}}{V_2}\right)^2$$

(7a)

vdW using the Huron−Vidal mixing rule:

$$\ln \gamma_1^\infty = \ln \gamma_1^{comb-FV} + \ln \gamma_1^{res}$$
$$= \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1 - \left(\frac{V_1 - b_1}{V_2 - b_2}\right) + \ln \gamma_1^{res,M}$$

(7b)

Upon comparing eq 7a with either 5a or 6a we can see that the vdW EoS generated activity coefficient does not include in the combinatorial-free volume contribution the following two terms, for example, for SRK

$$\frac{a_1}{b_1 RT}\ln\frac{\left(1 + \frac{b_1}{V_1}\right)}{\left(1 + \frac{b_2}{V_2}\right)} + \frac{a_2}{b_2 RT}\left(\frac{V_1 b_2 - V_2 b_1}{V_2^2 + b_2 V_2}\right)$$

This is an important omission. The vdW's combinatorial/ free-volume term (first three terms in eqs 7a and 7b) resembles

indeed activity coefficient models suitable for polymer solutions, like Flory–Huggins[113] or Entropic-FV.[114] However, using EoS-generated volumes, this term alone results to activity coefficients only slightly below unity for alkane mixtures. These activity coefficient values are in the right trend qualitatively in agreement to the experimental data (negative deviations from Raoult's law) but quantitatively they deviate significantly from the experimental values, as shown by Kontogeorgis et al.[38]

In conclusion, the Huron–Vidal mixing rule is an excellent correlative tool for low and high pressure VLE of complex systems and it is important to employ an energetic activity coefficient model in the mixing rule, for example, NRTL. The parameters must be refitted to data using the EoS and the mixing rule meaning that existing parameters cannot be used due to the infinite pressure assumption in the mixing rule derivation. There is another significant "double limitation". The derivation of eq 4 is based on the linear mixing rule for the covolume. This is indeed the most widely used mixing rule for the covolume in cubic EoS, and often good results are obtained. Moreover, using this combining rule, the combinatorial/free-volume contribution to the activity coefficient has the form of eqs 5 or 6, which results to satisfactory but *not perfect results* (for nearly athermal mixtures). The mixing rule for the covolume affects the liquid-phase properties especially for size-asymmetric systems and as shown by Kontogeorgis et al.[38] a single interaction parameter $[b_{ij} = ((b_i + b_j)/2))(1 - l_{ij})]$ can improve dramatically the results of cubic EoS (see also later, after eq 43). The l_{ij} parameter can effectively modify the combinatorial/free-volume contribution in the right direction and even adjust accordingly the energetic term of EoS, as the mixing rule for the covolume appears in all terms of cubic EoS-generated activity coefficients. Kontogeorgis et al.[38] showed for example that by using a single l_{ij} equal to about 0.02 accurate results are obtained with the PR EoS for mixtures of ethane with alkanes varying from decane to C44. The same is not possible with a single k_{ij} interaction parameter. However, the derivation of the Huron–Vidal mixing rule restricts the cubic EoS of the possibility of employing this extra degree of freedom, as a linear mixing rule for the covolume is imperative in its derivation. Moreover, the SRK using Huron–Vidal mixing rule violates the imposed by statistical thermodynamics quadratic composition dependency of the second virial coefficient:

$$B = \sum_i \sum_j x_i x_j B_{ij} \tag{8}$$

The second virial coefficient from cubic EoS like vdW, SRK, and PR is given as

$$B = b - \frac{a}{RT} \tag{9}$$

Even though cubic EoS do *not* give good second virial coefficients for pure compounds, it *might* be of interest to satisfy the theoretically correct limit of eq 8. Vidal[1,39] was aware of this limitation but he and others have stated that it is difficult to establish what importance should be attributed to this limitation and what is to gain by satisfying eq 8 for practical applications. Vidal[39] writes: "we have never observed practical problems attributable to this defect". Note that the classical vdW1f mixing rules *do* satisfy this theoretical limit. Wong and Sandler proposed in 1992[9] in a truly novel way a modification of the Huron–Vidal mixing rule which addresses several of its

limitations, permitting the use of existing interaction parameter databases, utilization of the extra degree of freedom by modifying the mixing rule for the covolume parameter and satisfaction of eq 8. Some other issues have been raised however. We discuss the Wong–Sandler mixing rule next.

2.2. The Wong–Sandler Mixing Rule. The Wong–Sandler mixing rule is, like Huron–Vidal, also based on the infinite reference pressure but with significant modifications compared to that in Huron–Vidal:

i First of all, the starting point is not eq 1a but eq 1b (at infinite pressure). Thus, by equating the excess Helmholtz energies, the excess volume term is eliminated (see eq 3b and Table 1).

ii Wong and Sandler assumed that the following is *approximately true*:

$$a^E_{model} \approx a^E_{\infty P} \approx a^E_{lowP} \approx g^E_{lowP} \tag{10}$$

The middle equality of the excess Helmholtz energy at infinite pressure with the excess Gibbs energy at low pressure is based in the empirical finding[40] of the relative insensitivity of the excess Helmholtz energy with pressure, whereas it is well-known that g^E is highly dependent on pressure. Wong et al.[42] justified also numerically this equality for the system methanol/benzene.

iii Having now the possibility for an additional degree of freedom, Wong and Sandler[9] choose to satisfy eq 8, thus:

$$\left(b - \frac{a}{RT}\right) = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \tag{11}$$

The Wong–Sandler mixing rule is derived from statements i–iii and eq 1b as follows. First, from statements i and ii, expressions identical to Huron–Vidal mixing rule are obtained (see also Table 3). In the case of Peng–Robinson we get

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{a^{E,\infty}}{0.6232} = \sum_i x_i \frac{a_i}{b_i} - \frac{g^{E,M}}{0.6232} \tag{12}$$

Substituting eq 12 in eq 11 we get, for the PR EoS,

$$b = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 + \frac{g^{E,M}}{0.6232RT} - \sum_i x_i \frac{a_i}{b_i RT}} \tag{13}$$

similar to SRK (see Table 3). So, the covolume parameter can be calculated from eq 13, and then the mixing rule for the energy parameter can be obtained from eq 12. In this way an excess Gibbs energy model with existing low-pressure obtained parameters $g^{E,M}$ can be in principle used. The Wong–Sandler mixing rule is defined by eqs 12 and 13 together with an expression for the cross virial coefficient. This last point is not a trivial issue and indeed, as explained later, the cross virial coefficient term plays a major role in the Wong–Sandler model. This is the case because of the uncertainty about which combining rule should be used for the cross virial coefficient. Moreover, Wong and Sandler[9] (and most subsequent investigators) have employed an interaction parameter k_{ij} in

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the model. The following choices for the cross virial coefficient have been reported:

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)}{2}(1 - k_{ij}) \quad (14a)$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{b_i + b_j}{2} - \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij}) \quad (14b)$$

(The possibility of using $k_{ij} = 0$ in eq 14a results in a linear mixing rule for the second virial coefficient, but this possibility has not been tested for the Wong–Sandler mixing rule).

Wong and Sandler[9] determined k_{ij} from experimental VLE data at one temperature and $x = 0.5$, while Orbey et al.[41,43] fitted k_{ij} to UNIFAC-obtained infinite dilution activity coefficients at $x = 0.5$, thus rendering the model fully predictive.

It is evident from the aforementioned discussion that, despite the apparent similarities, there are fundamental differences between the Huron–Vidal and Wong–Sandler approaches.

Great successes have been reported for the Wong–Sandler mixing rule. For example, Wong et al.[42] using van Laar as the g^E model with parameters estimated from low pressure data and $k_{ij} = 0.326$ predicted VLE for 2-propanol/water in the range 150–275 °C and up to 100 bar with excellent results. Similar very satisfactory results were obtained for acetone/pentane, ethanol/water, and other systems, using either NRTL or van Laar as the activity coefficient model incorporated. These examples, further verified and elaborated in subsequent publications, illustrate the key success of the Wong–Sandler mixing rule, namely to predict VLE using existing low pressure parameters from activity coefficient models over very extensive temperature and pressure ranges, thus extrapolating successfully far beyond g^E models alone could ever do on their own! Successful results have been obtained also for ternary and multicomponent VLE (and in some cases also VLLE), using binary system generated parameters. This great success made the Wong–Sandler mixing rules the object of many investigations from numerous researchers who applied the methodology also to liquid–liquid equilibria, excess enthalpies, solid–gas equilibria, even surfactants and polymers. Some of these applications are discussed in section 3.

Following the discussion with the Huron–Vidal mixing rule, the use of the "energetic" van Laar and NRTL models is consistent with the infinite pressure derivation of the model (as $S^E = 0$ in the model development). Still, the Wong–Sandler rule has been used even with UNIQUAC and UNIFAC which contain an external combinatorial term. This may be the cause of problems for size-asymmetric systems, as discussed below. Indeed, despite the significant success, there is a well-documented criticism regarding the Wong–Sandler mixing rules which mostly lies in the following four directions:

(1) Even if we do not consider the k_{ij} of eq 14 as an additional adjustable parameter but as a parameter that can be obtained from the incorporated g^E model, there is an uncertainty on how this parameter should be estimated, on which combining rule should be preferred for the cross second virial coefficient (eqs 14a or 14b or other) and on what *exactly* k_{ij} represents in the model (see also point 4 later). Can k_{ij} be estimated in a *reliable* way from cross second virial coefficient data?

(2) Equation 13 introduces a temperature dependent covolume parameter. Such temperature-dependent covolumes

are for good reasons avoided in cubic EoS, as discussed by Michelsen and Mollerup[44] and Satyro and Trebble.[45,46] This is because they may result in negative heat capacities at certain high pressure conditions. Thus, can the fulfillment of one correct physical behavior (eq 8) lead to unphysical behavior for another property?

(3) The good extrapolation capabilities of Wong–Sandler mixing rules *may not* necessarily be associated with the reproduction of the correct composition dependency of the mixture second virial coefficient. As Michelsen and Heidemann[47] showed, the PR/Wong–Sandler model results to rather large excess enthalpies which are closer to the experimental data compared to the values produced by the incorporated g^E model of the mixing rule. Can the extrapolation success of Wong–Sandler mixing rules be, as Heidemann,[48] writes "derived from this fortunate cancellation of errors?" We should point out, however, that Michelsen and Heidemann used the Wilson model in their analysis of the Wong–Sandler mixing rules. This is a g^E model with a combinatorial term (Flory–Huggins) and should not be preferred when an infinite reference pressure model is used. Their analysis would have been more convincing if, for example, the NRTL model was used instead.

(4) Coutsikos et al.[49] published a systematic investigation of the role of k_{ij} on the Wong–Sandler mixing rule and whether a unique k_{ij} value can be used. A summary of their results is provided in Table 5. They find that it is possible to use a single

Table 5. Summary of the Analysis of the Wong–Sandler (WS) Mixing Rule. Based on the Results from Coutsikos et al., 1995[49]

system (1)/(2)	ratio of covolumes b_1/b_2	ratio of infinite dilution activity coefficients	difference in percentage AAD in pressure between WS and gamma-phi approach	difference in vapor phase mole fraction × 100 between WS and gamma-phi approach
methanol/water	2.2	1.2	0.38	0.2
butane/methanol	1.8	0.6	2.9	10.4
hexane/C32	0.11	1.5		
butanol/water	4.3	13.1	2.9	18.1
hexanol/water	5.9	64.3	14.2	17.2

k_{ij} value and that PR/Wong–Sandler performs best for (size)symmetric systems. As the asymmetry increases (in either size or energy), for example, water/heavy alcohols or alkane mixtures, then one k_{ij} value cannot represent satisfactorily the phase behavior, and the k_{ij} should be considered composition dependent. Such dependency "destroys" the concept of this mixing rule. Moreover, they attribute this problem to the fact that k_{ij} must compensate for the errors introduced by the assumption $a_{\infty P}^E \approx a_{lowP}^E$ and conclude that this equality does *not* hold in the general case, especially for asymmetric systems. Thus, these authors make the bold statement that the basic assumption behind the Wong–Sandler mixing rule, that is, eq 10, fails for asymmetric systems. While their analysis is convincing the authors used UNIQUAC in their Wong–Sandler mixing rule. For this reason at least part of the problems seen for asymmetric systems, esp. when k_{ij} values must be fitted, could be related to the fact that a combinatorial term is used in the g^E model (UNIQUAC). This is not consistent with the infinite pressure derivation of the Wong–Sandler

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mixing rule. Again, as in point 3, the analysis would have been more convincing if the NRTL or van Laar models were used instead.

Finally, we should mention a practical problem of the Wong–Sandler mixing rule. As with Huron–Vidal, and the other models discussed later, parameters for gas-containing systems should be fitted separately in connection with these models. This is because such parameters are not available in activity coefficient models like NRTL and UNIFAC. Wong–Sandler rules have found so far **limited** applicability to gas-containing systems and extensive gas-containing tables are not available. Furthermore, the predictive approach of obtaining the k_{ij}-parameters (using UNIFAC) is not applicable to gas-containing systems.

2.3. The "Exact" Zero Reference Pressure Mixing Rule. The idea behind the use of the Wong–Sandler mixing rule was to use an external excess Gibbs energy model, $g^{E,M}$, with existing parameters obtained from low pressure phase equilibrium data. An alternative approach to using eq 1b as a starting point the way Wong and Sandler did is to start with eq 1a and use a zero reference pressure. This would always ensure reproduction of the incorporated g^E model when a mathematical solution can be obtained for the energy parameter. The zero reference pressure models appeared in early 90s, chronologically prior to the Wong–Sandler ones. The idea was put forward by Mollerup[10] and Heidemann and Kokal[50] but the mathematical problem was, essentially, solved in a tractable way by Michelsen,[11,12] who in 1990 presented the so-called "exact" model, shown in Table 3. This is an exact zero reference pressure mixing rule, ensuring full reproduction of the g^E model incorporated. Unfortunately, the mixing rule is implicit with respect to the energy parameter. Moreover, the mixing rule is not always obtainable, but only when a liquid solution is available at zero pressure, that is, for values above the limiting values shown in Table 3. This can be easily understood as illustrated here for SRK which at zero pressure and reduced variables ($\alpha = a/(bRT)$ and $u_0 = V/b$ at $P = 0$) is written as

$$\frac{1}{u_0 - 1} - \frac{\alpha}{u_0(u_0 + 1)} = 0 \tag{15}$$

The liquid volume solution at zero reference pressure is

$$u_0 = \frac{(\alpha - 1) - \sqrt{\alpha^2 - 6\alpha + 1}}{2} \tag{16}$$

but evidently it exists only for $\alpha_{lim} > 3 + 2\sqrt{2}$ (Table 3 gives the PR limiting value).

When the liquid volume at zero pressure does exist, then the fugacity coefficient from SRK,

$$\ln \varphi = \ln \frac{f}{P}$$
$$= -\ln\left[\frac{P(V - b)}{RT}\right] + \frac{PV}{RT} - 1 - \frac{a}{bRT}\ln\left(\frac{V + b}{V}\right) \tag{17a}$$

can be equivalently written as

$$\ln \frac{f_0}{P} - \ln b = q^e(\alpha)$$
$$= -1 - \ln(u_0 - 1) - \alpha \ln\left(\frac{u_0 + 1}{u_0}\right) \tag{17b}$$

Then, from the equation

$$\frac{g^E}{RT} = \ln \varphi - \sum_i x_i \ln \varphi_i = \ln \frac{f_0}{RT} - \sum_i x_i \ln \frac{f_{0,i}}{RT} \tag{18}$$

and using eq 1a, the expression for the mixing rule is obtained:

$$\left(\frac{g^E}{RT}\right)_0^M = \sum_i x_i \ln\left(\frac{b_i}{b}\right) + q^e(\alpha) - \sum x_i q_i^e(\alpha_i) \tag{19}$$

Michelsen[12] showed that SRK coupled with Wilson and eq 19 provided good results ensuring full reproduction of the Wilson results at low pressures.

It must be appreciated that eq 19:

- is mathematically correct at zero pressure without assumptions (other than the need for a liquid volume at zero pressure)
- ensures full reproduction of the g^E from the external activity coefficient model at zero pressure. Any g^E model can be used including models with or without combinatorial terms like Wilson, UNIQUAC or NRTL
- can be used with any low pressure activity coefficient models with existing interaction parameters obtained from low pressure VLE or other data, for example, the parameters available in the Dechema or UNIFAC tables can be used
- does not involve any assumption for the mixing rule for the covolume parameter; linear, quadratic, or other mixing rules for the covolume parameter can be used

There are limitations, however. Besides its nonanalytical character (need for iterative procedure for obtaining the energy parameter), unlike the Huron–Vidal and Wong–Sandler mixing rules, the serious practical limitation of the "exact mixing rule" is that it is not defined for reduced temperatures $T_r > 0.9$ due to the limiting value for the energy parameter mentioned above. This limitation essentially excludes gas solubilities. Since a very large number of high pressure systems where EoS using the EoS/G^E approach would be useful involve gas+polar (or nonpolar) compounds, excluding gas solubilities is an important practical limitation of the "Exact" mixing rule. A counter-argument (Michelsen, 2010, private communication) is that for such gas-containing systems, existing g^E models could not be used since these low pressure activity coefficient models do not have interaction parameters for gases. Such parameters for systems containing gases must be estimated using the EoS and the specific EoS/G^E mixing rule. Nevertheless, such estimation of interaction parameters cannot be done via eq 19 and this brought up the need for models like MHV1, MHV2, and PSRK which are discussed next. For reasons that will become clear later we will call these as "approximate zero reference pressure models".

2.4. The Approximate Zero Reference Pressure Models. To extend the applicability of the zero reference pressure approach to energy values lower than the limiting value mentioned above (after eq 16) and thus also to be able to use the zero reference pressure approach to gas-containing mixtures, approximations must be introduced. Dahl and Michelsen[13] noticed that the q-function of eq 17b can be approximated either as a first- or a second-order degree

equation with respect to the (reduced) energy parameter. In the linear case, if equation

$$q(\alpha) \approx q_o + q_1\alpha \tag{20a}$$

is introduced in eq 19, an explicit mixing rule is obtained, known as MHV1 (modified Huron–Vidal first order), due to its similarity to the Huron–Vidal mixing rule (see in Table 3):

$$\alpha = \frac{1}{q_1}\left(\frac{g^{E,M}}{RT} + \sum_i x_i \ln\left(\frac{b}{b_i}\right)\right) + \sum_i x_i\alpha_i \tag{20b}$$

or

$$\alpha = \frac{1}{q_1}\left(\frac{g^{E,M}}{RT} - \frac{g^{E,FH}}{RT}\right) + \sum_i x_i\alpha_i \tag{20c}$$

where the second term in parentheses is a Flory–Huggins (FH) type combinatorial term stemming from the equation of state and based on covolumes:

$$\frac{g^{E,FH}}{RT} = \sum_i x_i \ln\frac{b_i}{b} \tag{20d}$$

The significance of writing the MHV1 mixing rule in the equivalent form of eq 20b will be shown later.

If a quadratic equation for the q-function:

$$q(\alpha) \approx q_o + q_1\alpha + q_2\alpha^2 \tag{20e}$$

is combined with eq 19, the MHV2 mixing rule is obtained (modified Huron–Vidal second order):

$$q_1\left(\alpha - \sum_i x_i\alpha_i\right) + q_2\left(\alpha^2 - \sum_i x_i\alpha_i^2\right)$$
$$= \left(\frac{g^{E,M}}{RT}\right) + \sum_i x_i \ln\left(\frac{b}{b_i}\right) \tag{21}$$

The q_1 and q_2 values are obtained by fitting the $q - \alpha$ equation and thus these values depend on the EoS used and the range of fitting. Various proposals have been made. Dahl and Michelsen[13] proposed using for SRK $q_1 = -0.593$ fitted in the range $10 < \alpha < 13$ (or $8–18$ for MHV2). Gmehling[14] proposed again for SRK $q_1 = -0.64663$ fitted in the range $20 < \alpha < 25$. This has resulted to the so-called PSRK mixing rule. Slightly different values have been reported for other cubic EoS such as $q_1 = -0.53$ for PR.

It is instructive and helpful in the subsequent discussion to see that eq 20 (MHV1 and PSRK models) can be derived in an alternative way as shown by Mollerup,[10] Gmehling,[54] and Fischer[55] as well as by Sandler and co-workers.[51–53] This alternative derivation is based on the assumption of a constant packing fraction $u = V/b$ for all compounds and for the mixture. Recall that at infinite pressure the packing fraction is unity but for real fluids[10,54,55] we would expect that $V > b$ in most cases, with packing fractions on the order of $1.1–1.2$.

Consider, for example, SRK and the use of the packing fraction concept: the g^E shown in Table 1 can be written as

$$\frac{g^E}{RT} = \left(\sum_i x_i \ln\left(\frac{u_i - 1}{u - 1}\right) + \sum_i x_i \ln\frac{b_i}{b}\right) + \left(\frac{PV^E}{RT}\right)$$
$$+ \left[\sum_i x_i\alpha_i \ln\left(\frac{u_i + 1}{u_i}\right) - \alpha \ln\left(\frac{u + 1}{u}\right)\right] \tag{22}$$

Equation 22 can be simplified if we assume that the packing fraction of all compounds and of the mixture is the same. This appears to be a drastic assumption but at liquid-like conditions most compounds have similar packing fractions, as discussed by, among others, Fischer and Gmehling.[54,55] Under these conditions, eq 22 can be written as

$$\frac{g^E}{RT} = \sum_i x_i \ln\frac{b_i}{b} + A\left[\alpha - \sum_i x_i\alpha_i\right]$$
$$A = \ln\left(\frac{u}{u + 1}\right) \tag{23}$$

Equation 23 is remarkably similar to eq 20a and eq 20b and can be rearranged to read

$$\alpha = \frac{1}{A}\left(\frac{g^E}{RT} + \sum_i x_i \ln\left(\frac{b}{b_i}\right)\right) + \sum_i x_i\alpha_i \tag{24}$$

$$q_1 = A = \ln\left(\frac{u}{u + 1}\right) \tag{25}$$

Thus, eqs 20 and 23 or 24 are identical when q_1 and A are related as shown in eq 25. A similar expression is valid for PR. The relationship between q_1 and A provides an alternative way to estimate q_1 from the knowledge of the packing fraction value. Alternatively, the packing fraction values which correspond to previously published q_1 values can be calculated, for example, $q_1 = -0.593$[13] corresponds to $u = 1.234$ and $q_1 = -0.64663$[14] corresponds to $u = 1.1$. Other researchers such as Novenario et al.[56] proposed a value $u = 1.15$ for PR based on a large number of fluids and liquid volumes at 0.5, 1, and 2 bar. Tochigi et al.[57] have used in the MHV1 version a range of u-values for different liquids (calculated at $T_r = 0.4$), all being in the range $1.09–1.1$.

Numerous publications, for example, in references 13 and 58, have illustrated the success of approximate zero reference pressure models like MHV2 in reproducing low pressure data of the incorporated g^E model and most importantly in predicting high pressure VLE of polar mixtures like acetone/water and ethanol/water over very extensive temperature and pressure ranges (up to 700 K and 200 bar). The deviations reported[13] for five polar mixtures are less than 4% in pressure and 2 ($\times100$) in vapor phase mole fraction using MHV2 coupled with SRK and the Lyngby version of modified UNIFAC.[112] Very good results have also been reported for gas solubilities,[58] using estimated group contribution parameters for gases, also for multicomponent VLE.[59] In the PSRK model by Ghemling et al.[14,5460] the MHV1 mixing rule is combined with the Dortmund version of modified UNIFAC.[115]

Despite these successes, several limitations have been reported:

(1) The results are (or should) inevitably (be) bounded by how well the g^E model performs at low pressures. This means that in principle (if the mixing rule fully reproduces the g^E model incorporated) we should not expect better results than the g^E model used. For example, the EoS/G^E and the activity coefficient model incorporated should give very similar results for low pressure VLE and LLE. It is established that local composition models *do* exhibit problems in, for example, predicting multicomponent LLE for difficult systems like water−alcohol−hydrocarbons. These problems should be in principle inherited by the EoS/G^E models. Of course the same limitation is expected for the "exact" and the Wong−Sandler mixing rules as well.

(2) Approximate zero reference pressure models (and the "exact") do *not* satisfy the quadratic dependency for the second virial coefficient imposed by statistical mechanics if the linear mixing rule is used for the covolume, as often done. However, unlike the Huron−Vidal mixing rule, this assumption is not a necessary one in, for example, MHV1 and MHV2. One could have chosen to develop a mixing rule for the covolume which satisfies eq 8. This has been done for MHV1 by some researchers.[56,57,61,62] Tochigi et al.[61,62] have compared MHV1 coupled with either the linear mixing rule for the covolume or a mixing rule which satisfies eq 8. They found no difference in the two cases for the few systems tested under the assumption that k_{ij} (in eq 14a) is zero (which implies a linear mixing rule for the second virial coefficient).

(3) As shown by many investigators, for example, in refs 63, 64, and 92, MHV1, PSRK, and MHV2 perform **very poorly** for (size) asymmetric mixtures like those containing gases (N_2, CO_2, ethane, or methane) with hydrocarbons of different size. Even though a new interaction parameter is estimated, for example, for the group interaction $CO_2/-CH_2-$ (in the case of CO_2/alkanes), these investigations clearly show that **a single group parameter cannot describe gas solubilities over extensive size asymmetries.** The deviations are very high and increase systematically with increasing size difference of the mixture compounds (see also Figure 4). Boukouvalas et al.[15] and Gmehling[65] report that for ethane/dodecane the percentage deviation in pressure is about 12−14% with either PSRK or MHV2 but it increases to over 30% for ethane/eicosane and beyond. Similarly, for CO_2/alkanes, the deviations in pressure are higher than 30% for CO_2/eicosane and above. For methane/alkane mixtures, we have a similar picture. In this case, already for methane/nonane and beyond, the deviation in pressure is above 30% for MHV2 and in the case of PSRK for methane/hexadecane and beyond the deviation is also above 30%. These are very disappointing results for the approximate zero reference pressure models.

(4) It became soon apparent[15,63,64,92] that even for low pressure systems, such as mixtures of alkanes, the approximate zero reference pressure models do **not fully** reproduce the g^E model used in their derivation. The reproduction is satisfactory for mixtures of similar "size and energy" values, but as the asymmetry increases the reproduction of g^E and especially of the activity coefficient is very poor. This topic was analyzed by Kalospiros et al.[67] who showed that the difference between the g^E model (and the activity coefficient expression) obtained from the EoS using the EoS/G^E mixing rules and from the external g^E model (called here $g^{E,M}$) is

$$\Delta(\ln \gamma_i) = \ln \gamma_i - \ln \gamma_i^M$$

$$= -(\alpha - \bar{\alpha}_i)\left[\frac{dq^e(\alpha)}{d\alpha} - \frac{dq(\alpha)}{d\alpha}\right]$$

$$+ [q^e(\alpha) - q(\alpha)] - [q^e(\alpha_i) - q(\alpha_i)] \quad (26)$$

$$\Delta\left(\frac{g^E}{RT}\right) = \frac{g^E}{RT} - \frac{g^{E,M}}{RT}$$

$$= [q^e(\alpha) - q(\alpha)] - \sum_i x_i[q^e(\alpha_i) - q(\alpha_i)]$$

$$(27)$$

From eqs 26 and 27 it is clear that the results especially for the activity coefficients are very sensitive not only to the correct reproduction of the q function, but also its derivative with respect to the reduced energy parameter. Especially the reproduction of this derivative is very poor from the approximate zero reference pressure models. Kalospiros et al.[67] concluded that in terms of the EoS/G^E models, symmetric systems should be considered those with similar reduced energy values and only in this case can we expect good reproduction of the underlying g^E model. When the reduced energy values from the two compounds are different and especially as their difference increases, then we can expect poor reproduction of the $g^{E,M}$ by mixing rules like MHV1, MHV2, and PSRK. In reality, thus, we are talking about approximate zero reference pressure models, that is, the the actual reference pressure for these mixing rules (e.g., MHV1 and PSRK) is not exactly zero.[67]

The same conclusion can be reached in another way. Following Michelsen and Mollerup,[44] who start from the fundamental equation,

$$\frac{g^{E,P}}{RT} - \frac{g^{E,0}}{RT} = \int_0^P \frac{V^E}{RT} \, dP \quad (28)$$

it can be shown that at if we set P as infinite, then an almost exact expression can be obtained for the difference of g^E at infinite and zero pressure:

$$\frac{g^{E,\infty P}}{RT} - \frac{g^{E,0}}{RT} = \sum_i x_i \ln \frac{b}{b_i} - \sum_i x_i \ln \frac{\alpha}{\alpha_i} \quad (29)$$

This expression can be compared to the equivalent expression which is obtained from the difference of infinite pressure and approximate zero reference pressure models. In the case of SRK, the difference between the Huron−Vidal and MHV1 or PSRK mixing rules is

$$\frac{g^{E,\infty P}}{RT} - \frac{g^{E,approx0}}{RT} = -\ln 2\left(\alpha - \sum_i x_i\alpha_i\right)$$

$$- q_1\left(\alpha - \sum_i x_i\alpha_i\right) + \sum_i x_i \ln \frac{b}{b_i} \approx \sum_i x_i \ln \frac{b}{b_i}$$

$$(30)$$

(since the terms $-\ln 2$ and $-q_1$ almost cancel each other esp. for PSRK).

Upon comparing eqs 30, that is, the *approximate* difference between infinite and zero pressure models, and 29, which corresponds to a more or less exact difference between the g^E values at infinite and zero pressure, we see that the term

$$\sum_i x_i \ln \frac{\alpha}{\alpha_i}$$

is missing in eq 30. This term is eliminated or diminished when the reduced energies of the compounds are similar, which is in accordance to the terminology of "symmetric" systems of Kalospiros et al.[67] The inspection of eqs 29 and 30 provides thus an additional proof of the *approximate* zero reference pressure character of models like MHV1, PSRK, and the like.

Commenting on the four limitations discussed above, possibly little can be done about the first one, while the practical importance of the second limitation is somewhat unclear. On the other hand, limitations 3 and 4 are very important and appear interconnected, although we will see that this is not always the case. This has led to a number of models, starting with LCVM, which aim to extend the applicability of EoS/G^E mixing rules to asymmetric systems. This topic has led to many discussions in the literature both with respect to these models' capabilities and the explanation of their performance. We discuss in the coming section LCVM and some models which followed, and we present a general explanation of their performance for asymmetric systems.

2.5. LCVM and Related Models. The first model which addressed specifically the limitation of size-asymmetric systems is LCVM (linear combination of Vidal and Michelsen mixing rules) was proposed by Tassios and co-workers[15] in 1994. The authors have presented the LCVM mixing rule for the energy parameter of the PR EoS as

$$\alpha = \left(\frac{\lambda}{A_V} + \frac{1-\lambda}{A_M} \right)\left(\frac{g^{E,M}}{RT} \right) + \frac{1-\lambda}{A_M} \sum_i x_l \ln\left(\frac{b}{b_i} \right) + \sum_i x_i \alpha_i \tag{31}$$

with $A_V = -0.623$, $A_M = q_1 = -0.52$ and $\lambda = 0.36$ [original UNIFAC], is a universal value obtained from ethane/alkane VLE data. The translated PR and original UNIFAC are used, and the λ value depends on the specific choice of EoS and g^E model.

LCVM was criticized in the literature[41,47,48,51,52,54] due to its *apparent* empirical nature:

- The model cannot be derived from the usual starting point of EoS/G^E models, neither from eq 1a nor from eq 1b.
- Being a combination of infinite and approximate zero reference pressure models, it appears not to have a specific reference pressure itself. Thus it is uncertain whether a UNIFAC parameter table with parameters estimated based on low pressure data can be used.
- It contains an additional parameter, which though universal, seems to be connected to the specific cubic EoS and g^E model used by the authors, thus it is not certain that the mixing rule can be used with EoS and g^E models other than those employed in its development.
- The whole approach appears rather empirical, for example, why should this specific λ value be used? No theoretical explanation was originally offered.

Despite these limitations, Tassios and co-workers have shown in a series of publications[15,63,66−74] that the LCVM

model can be used highly successfully for size asymmetric systems such as methane, CO_2, nitrogen, H_2S, ethane with hydrocarbons of different sizes, as well as with polar compounds (alcohols, water, acids, etc), for predicting Henry's law constants, solid−gas equilibria, gas condensates and infinite dilution activity coefficients of mixtures containing alkanes. In addition, the results for polar (symmetric and asymmetric) high pressure systems are *at least* as good as those of MHV2 and the WS mixing rules. Other researchers[75] have also applied LCVM with success, for example, in high pressure wax formation for petroleum fluids. Soon it became apparent that the success of LCVM could not be attributed to coincidence or cancellation of errors. Some explanation should exist. Following the analysis presented by Kontogeorgis and co-workers,[16,37,76] further verified by Li et al.,[65] we briefly outline below a phenomenological explanation which can justify the success of both LCVM and several of the subsequent models.

First, it can be shown that LCVM can be written in a form equivalent to eq 31 as

$$\alpha = C_1\left(\frac{g^{E,M}}{RT} - \frac{C_2}{C_1}\frac{g^{E,FH}}{RT} \right) + \sum_i x_i \alpha_i \Rightarrow$$

$$\alpha = C_1\left[\left(\frac{g^{E,comb,M}}{RT} - \frac{C_2}{C_1}\frac{g^{E,FH}}{RT} \right) + \frac{g^{E,res,M}}{RT} \right] + \sum_i x_i \alpha_i \tag{32}$$

where

$$C_1 = \frac{\lambda}{A_V} + \frac{1-\lambda}{A_M}$$

$$C_2 = \frac{1-\lambda}{A_M}$$

$$A_V = -0.623, \quad A_M = -0.52$$

The FH combinatorial is given in eq 20d and for $\lambda = 0.36 \Rightarrow$ $C_2/C_1 = 0.68$ "comb" and "res" are the combinatorial and residual terms of the external activity coefficient model used, for example, UNIFAC.

The MHV1 model, eq 20, can also be written in a similar way when an external g^E model like UNIQUAC and UNIFAC is used which has separate combinatorial and residual terms:

$$\alpha = \frac{1}{q_1}\left(\frac{g^{E,M}}{RT} - \frac{g^{E,FH}}{RT} \right) + \sum_i x_i \alpha_i \Rightarrow$$

$$\alpha = \frac{1}{q_1}\left[\left(\frac{g^{E,comb,M}}{RT} - \frac{g^{E,FH}}{RT} \right) + \frac{g^{E,res,M}}{RT} \right] + \sum_i x_i \alpha_i \tag{33}$$

In most cases we can ignore the Staverman−Guggenheim contribution to the combinatorial term as it typically contributes little to the activity coefficient value, when physical values are used for the van der Waals volume and area. Then, the combinatorial contributions to the excess Gibbs energy from UNIQUAC/UNIFAC and the various versions of modified UNIFAC are expressed as the following:

Table 6. Percentage Absolute Deviation between Experimental and Calculated Activity Coefficients at Infinite Dilution for n-Butane and n-Heptane in Various Alkanes Using the PR EoS and the MHV1 and LCVM Mixing Rules. For Comparison the Deviations with Original and Modified UNIFAC Combinatorials[5,112] Are Also Given

alkane	Or.UNIFAC	Mod.UNIFAC	PR-MHV1 with Or.UNIFAC	PR-MHV1 with modified UNIFAC	PR-LCVM (PR-a/b rule)
			n-Butane		
20	39	16	39	98	0.9 (0.6)
22	41	17	50	120	0.6 (1.1)
24	40	13	64	150	5.8 (2.0)
28	43	13	77	187	5.3 (2.5)
32	45	11	95	234	7.0 (5.3)
36	46	10	113	285	8.4 (9.3)
average	42	13	73	179	4.7 (3.5)
			n-Heptane		
20	21	6.8	15	50	4.0 (5.3)
22	25	9.1	17	46	7.0 (11.1)
24	24	5.2	26	63	3.4 (9.3)
28	26	3.0	38	88	2.0 (11.7)
32	28	1.9	50	114	1.7 (15.6)
36	30	0.2	62	144	0.3 (19.3)
Average	26	4.4	35	83	3.1 (12.0)

Original UNIFAC/UNIQUAC

$$\frac{g^{E,comb,M}}{RT} = \sum_i x_i \ln \frac{r_i}{r} = \sum_i x_i \ln \frac{r_i}{\sum_i x_i r_i} \tag{34a}$$

Modified UNIFAC ($x = {}^2/_3$ for Lyngby version and $x = {}^3/_4$ for Dortmund version)

$$\frac{g^{E,comb,M}}{RT} = \sum_i x_i \ln \frac{r_i^x}{r^x} = \sum_i x_i \ln \frac{r_i^x}{\sum_i x_i r_i^x} \tag{34b}$$

Thus, it can be seen that the combinatorial terms from the external activity coefficient model, for example, eqs 34a and 34b, and from the FH-type one stemming from the EoS at the approximate zero reference pressure (eq 20c) are similar in functionality. But are they similar in magnitude as well? Ideally, and for the purpose of obtaining a purely energetic parameter especially when new interaction parameters are estimated, this "difference of combinatorial terms" from the EoS and from the external activity coefficient model should be zero. "The two combinatorials should cancel", as stated by Mollerup[10] more than 20 years ago. In this way, eq 1a, in the case of approximate zero reference pressure models, could be written as

$$\left(\frac{g^{E,comb,M}}{RT}\right) = \left(\frac{g^{E,comb,EoS}}{RT}\right)_{approx.zero}$$

$$= \left(\frac{g^{E,FH}}{RT}\right) = \sum_i x_i \ln\left(\frac{b_i}{b}\right) \tag{35a}$$

$$\left(\frac{g^{E,res,M}}{RT}\right) = \left(\frac{g^{E,res,EoS}}{RT}\right)_{approx.zero} \tag{35b}$$

Notice that in the case of Huron–Vidal and Wong–Sandler mixing rules, eqs 1a and 1b reduce essentially to eq 35b, as explained previously.

Unfortunately, as shown by Kontogeorgis and Vlamos[76] and by Li et al.[65] this "difference of combinatorials" does not cancel out. It is small for systems with similar asymmetry but as the size and

energy differences between the mixture components increase, then this difference of the combinatorial terms (i.e., the combinatorial contribution to the activity coefficient from EoS minus that from the external g^E model) increases as well, as shown in the above-mentioned publications.[76,65] In the same references[76,65] the following are also shown: (i) The LCVM with the correction factor $C_2/C_1 = 0.68$ minimizes the combinatorial difference between the FH term from the EoS and the original UNIFAC combinatorial. A correction factor $C_2/C_1 = 0.3$ (corresponding to λ equal to 0.7) minimizes again the combinatorials' difference when the combinatorial term of the modified UNIFAC is used. Interestingly, this λ-value for a modified UNIFAC has been already recommended by Boukouvalas et al.[15] in the original publication of LCVM (without explanation). (ii) PSRK with fitted van der Waals volume (r) parameters can also minimize the combinatorial difference between the combinatorial term in eq 34b and the FH term.

Additional evidence is provided by the results shown in Table 6 as well as Figures 2 and 3 for mixtures of alkanes with
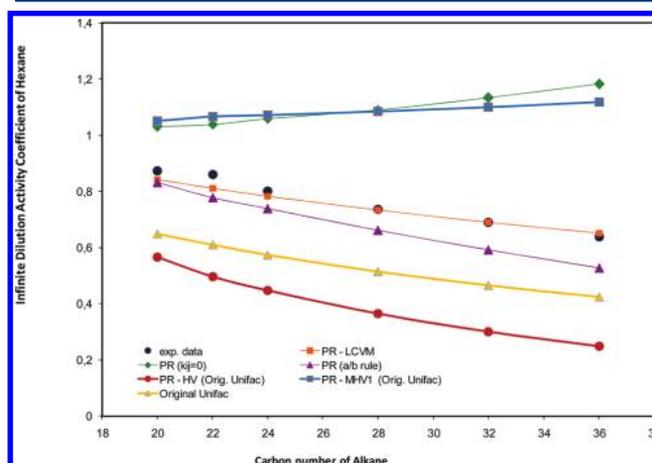

Figure 2. Experimental and predicted with PR and various mixing rules activity coefficients of hexane in alkanes of different chain length. The original UNIFAC[5] model is used in LCVM.

different chain length. These are the same systems as shown in Table 4 and in Figure 1 but now the results of MHV1 and
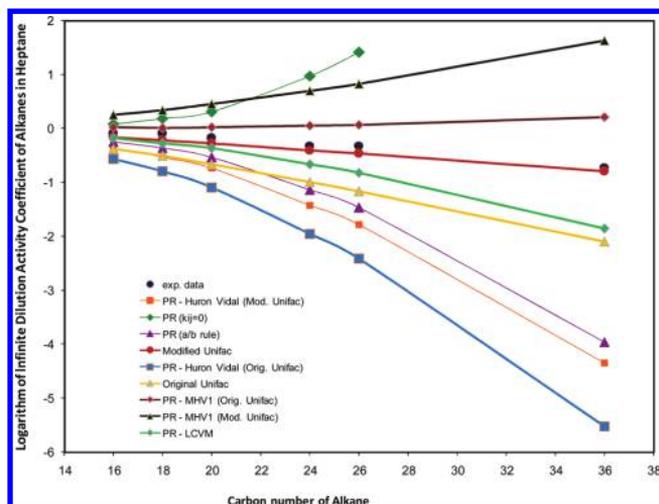
Figure 3. Experimental and predicted with PR and various mixing rules activity coefficients of heavy alkanes of different chain length in heptane. The logarithm of the infinite dilution activity coefficient is presented in order to best compare the various models. The original UNIFAC[5] model is used in LCVM. The modified UNIFAC of Larsen et al.[112] is used.
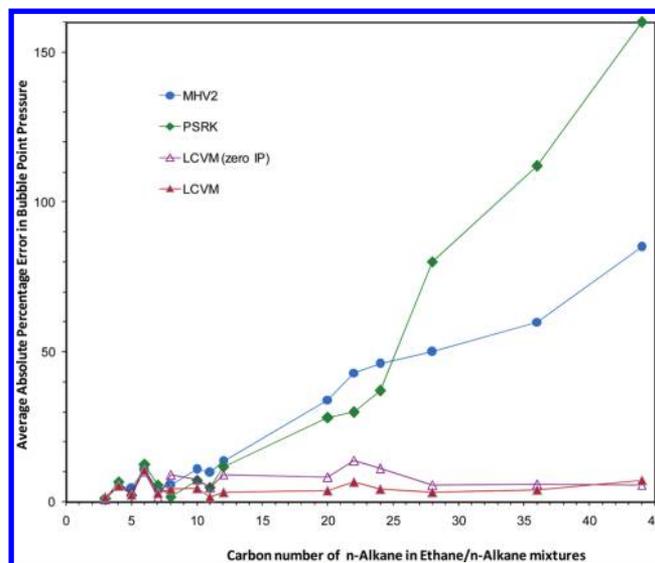

Figure 4. Vapor−liquid equilibrium calculations for ethane/alkane mixtures. Average absolute deviation between experimental and predicted bubble point pressures with the MHV2, PSRK and LCVM models (the latter with and without interaction parameters (zero IP)). The original UNIFAC[5] model is used in LCVM. Adapted from ref 15.

LCVM are also shown and are compared to those of explicit activity coefficient models (original and modified UNIFAC). The following can be observed: (i) None of the two EoS/G^E models reproduce the results of the activity coefficient model used in their derivations which are the original UNIFAC for LCVM and the modified UNIFAC for MHV1. (ii) MHV1 with an "additional to that of the EoS" combinatorial/free-volume term (the bracketed term in eq 39) performs very poorly. The results are as poor as those of the EoS using the vdW1f mixing rules, resulting to positive deviations from Raoult's law. (iii) LCVM eliminates approximately the double combinatorial, thus resulting to very good results as for these systems they are close to those obtained using the a/b mixing rule or equivalently the Huron−Vidal model. Notice that the results with LCVM are much better than those of the incorporated activity coefficient model (original UNIFAC) and comparable to modified UNIFAC, which is known to perform well for alkane mixtures. (iv) An extreme case of asymmetry is represented by activity coefficients of heavy alkanes in small ones, as shown for one example in figure 3.The results with PR/vdW1f are extremely poor. The other models show qualitatively correct results. Quantitatively LCVM performs best, followed by PR using the a/b rule.

LCVM and PSRK with Li et al.[65] parameters were shown to perform very well for size asymmetric systems, for example, ethane or CO_2 with alkanes of different sizes. Naturally, if the purpose of the EoS/G^E model is to reproduce the incorporated g^E model at low pressures and low asymmetries with existing parameters the difference between the two combinatorial terms will be small and play a very small role in the calculations. This explains why the problems of approximate zero reference pressure models remained unnoticed when MHV2 and PSRK were used, for example, for acetone/water, ethanol/water, or CO_2/methanol. What constitutes, however, the real problem of MHV1/MHV2/PSRK and similar models is the case of gas-containing mixtures such as methane, ethane, or CO_2 with alkanes, as shown in Figure 4. Then a new parameter must be fitted, for example, CO_2/CH_2, and subsequently used to predict phase behavior for all CO_2/alkane mixtures. This increasing

with size "combinatorials' difference" is added to the activity coefficient (and the EoS) making it essentially impossible for the regression to arrive to a single group parameter which can represent these mixtures of extensive asymmetries, as shown in the literature. When this combinatorials' difference is eliminated, as done, for example, in LCVM, the problem disappears and these models can indeed be used for asymmetric systems. It is worth noticing in Figure 4 that LCVM performs well for ethane/alkanes even in the absence of any interaction parameters. This is in essence identical in using only the combinatorial/free-volume term of the equation of state, in agreement to the previous discussion.

In agreement to these conclusions, more models appeared which in a similar way eliminate the "double combinatorial problem". It is worth mentioning the GCVM by Coniglio et al.[77] and the corrected Huron−Vidal (CHV) by Sandler:[52]

GCVM[77]

$$\alpha = C_1 \left(\frac{g^{E,M}}{RT} - \frac{C_2}{C_1} \frac{g^{E,FH}}{RT} \right) + \sum_i x_i \alpha_i \tag{36}$$

$$C_1 = \frac{1}{A_M} \qquad C_2 = \frac{1-\mu}{A_M}$$

$$A_M = -0.53, \quad \mu = 0.285$$

For PR and UNIFAC VLE the ratio is $C_2/C_1 = 0.715$

CHV[52]

$$\alpha = \frac{1}{C^*} \left(\frac{g^{E,M}}{RT} - (1-\delta) \frac{g^{E,FH}}{RT} \right) + \sum_i x_i \alpha_i \tag{37}$$

$$C^* = -0.6931$$

$$1 - \delta = 0.64 - 0.7$$

The above values for CHV have been proposed for original UNIFAC VLE. Similar values (around 0.715) have been suggested by Zhong and Masuoka.[78]

The similarity of eqs 36 and 37 to LCVM, eq 32, is striking! Even the correction coefficients are similar, illustrating further in agreement with the double combinatorial difference concept, that this correction coefficient is more related to which g^E model is used (e.g., original or modified UNIFAC) rather than which cubic EoS (since both SRK and PR at approximate zero reference pressure include the FH-type term).

An additional evidence of the above explanation on the role of the "double combinatorial" can be offered by looking at the activity coefficient equation from LCVM and the related models, for example, GCVM and CHV.

For CHV (and similarly also for the other models) using SRK, the infinite dilution activity coefficient of a compound in a binary system is

$$\ln \gamma_1^\infty = \ln \gamma_1^{comb-FV} + \ln \gamma_1^{res} = \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1$$

$$- \left(\frac{V_1 - b_1}{V_2 - b_2}\right) + \frac{a_1}{b_1 RT} \ln\frac{\left(1 + \frac{b_1}{V_1}\right)}{\left(1 + \frac{b_2}{V_2}\right)}$$

$$+ \frac{a_2}{b_2 RT}\left(\frac{V_1 b_2 - V_2 b_1}{V_2^2 + b_2 V_2}\right) + \left(\frac{-1}{C^*}\right)\ln\left(\frac{V_2 + b_2}{V_2}\right)$$

$$[\ln \gamma_1^{comb,M} - (1 - \delta)\ln \gamma_1^{FH}] + \left(\frac{-1}{C^*}\right)$$

$$\ln\left(\frac{V_2 + b_2}{V_2}\right)\ln \gamma_1^{res,M} \tag{38}$$

As compared to the expression under the same conditions for MHV1:

$$\ln \gamma_1^\infty = \ln \gamma_1^{comb-FV} + \ln \gamma_1^{res} = \ln\left(\frac{V_1 - b_1}{V_2 - b_2}\right) + 1$$

$$- \left(\frac{V_1 - b_1}{V_2 - b_2}\right) + \frac{a_1}{b_1 RT} \ln\frac{\left(1 + \frac{b_1}{V_1}\right)}{\left(1 + \frac{b_2}{V_2}\right)} + \frac{a_2}{b_2 RT}$$

$$\left(\frac{V_1 b_2 - V_2 b_1}{V_2^2 + b_2 V_2}\right) + \left(\frac{-1}{A_M}\right)\ln\left(\frac{V_2 + b_2}{V_2}\right)[\ln \gamma_1^{comb,M}$$

$$- \ln \gamma_1^{FH}] + \left(\frac{-1}{A_M}\right)\ln\left(\frac{V_2 + b_2}{V_2}\right)\ln \gamma_1^{res,M} \tag{39}$$

Upon comparing eqs 38 and 39 with eqs 5a−5c, we note that the residual term is the same as for the SRK/Huron−Vidal. Moreover, the combinatorial/free-volume terms of cubic EoS using the various mixing rules differ only by the bracketed terms in eqs 38 and 39 included in MHV1 and CHV. This is what we have indicated as the combinatorial terms' difference. Indeed, as can be expected based on what we discussed previously, if this combinatorials' difference is small, then the combinatorial/free-volume part of the cubic EoS performs quite well for athermal mixtures like for activity coefficients with alkane systems. As shown before, the combinatorial/free-volume of cubic EoS (SRK and PR) describes satisfactorily (at least qualitatively, often also quantitatively) the size/shape effects of alkane mixtures (in

this case, recall that the residual term is zero). For CHV, LCVM, and GCVM the bracketed terms (difference of combinatorials) are close to zero, while the corresponding bracketed term of MHV1 is not zero. Moreover, the combinatorials' difference in MHV1 increases with size asymmetry, thus explaining why MHV1 and related models result in unphysical high (even above unity) activity coefficients for alkane mixtures (see also the results in Table 6 and Figures 2 and 3).

It appears that LCVM, GCVM, CHV and related models obey in reality eq 35a, that is, they reproduce the $g^{E,comb}$ of the incorporated model, or in reality they "correct" the combinatorial activity coefficient of the incorporated g^E model. In this way the residual (energetic) term of EoS is allowed to "do the remaining job", that is, to describe phase behavior for complex mixtures using interaction parameters, either via existing (e.g., UNIFAC) or new interaction parameters (for gas-containing mixtures).

The approach of eliminating the "double combinatorial" has resulted in a new trend in the development of EoS/G^E models making them suitable also for asymmetric systems. Two more recent approaches have been developed which essentially rely on the same principle as outlined above.

The first approach by Gmehling and co-workers[79−87] is to develop a new type of PSRK as well as an EoS/G^E based on a translated PR (called VTPR) both of which eliminate the double combinatorial in eq 33 from the start. Thus, the resulting mixing rule resembles the one obtained at infinite pressure with two differences: the q_1 value corresponds to the zero reference pressure models and a nonlinear mixing rule is used for the covolume:

$$\alpha = \frac{1}{q_1}\left(\frac{g^{E,res,M}}{RT}\right) + \sum_i x_i \alpha_i$$

$$q_1 = -0.64663 \tag{40a}$$

(the above q_1 is for PSRK, for VTPR $q_1 = -0.53087$) with

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

$$b_{ij} = \left(\frac{b_i^{3/4} + b_j^{3/4}}{2}\right)^{4/3} \tag{40b}$$

Similarly, Voutsas et al.[88−91] proposed the UMR-PR model, an EoS/G^E mixing rule similar to VTPR but keeping the Staverman−Guggenheim (SG) part of the combinatorial term and they have used a slightly different expression for the covolume:

$$\alpha = \frac{1}{q_1}\left(\frac{g^{E,SG,M}}{RT} + \frac{g^{E,res,M}}{RT}\right) + \sum_i x_i \alpha_i$$

$$q_1 = -0.53 \tag{41a}$$

with

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

$$b_{ij} = \left(\frac{b_i^{1/2} + b_j^{1/2}}{2} \right)^2 \tag{41b}$$

It may appear somewhat surprising that the authors have *not* eliminated the *full* difference of the combinatorials but chose to keep part of the combinatorial contribution, the one that usually has the least effect. Otherwise the approach is similar to the one of Gmehling and co-workers for VTPR. Nevertheless, unlike VTPR, in the UMR-PR the existing UNIFAC parameters can be used. New parameters are fitted for the group interactions in VTPR.

A similar model to UMR-PR but coupled with SRK has been recently proposed by Chen et al.[92] using a $^2/_3$ exponent in the *b*'s in eq 41b. Equally satisfactory results as for UMR-PR are obtained for gas/alkanes.

The second approach is to introduce an l_{ij} parameter in the covolume combining rule and maintain the same form for the mixing rule for the energy parameter as for the approximate zero reference pressure models. For example, Gani and co-workers[64,92] used the MHV1 model with

$$b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}) \tag{42}$$

A constant $l_{ij} = 0.3$ could describe well a series of asymmetric systems of CO_2 and fatty acid esters.

The use of a combining rule differing from the linear one for the covolume and the role of l_{ij} (correction to the covolume mixing rule) may be significant, as discussed by Kontogeorgis et al.[38] They showed that using an $l_{ij} = 0.02$ (and $k_{ij} = 0$) PR can correlate ethane/alkanes using the vdW1f mixing rules very well.

The inspection of the general equation for the activity coefficient expression from cubic EoS provides some insight on the significance of the mixing rule for the covolume parameter. For PR,

$$\ln \gamma_i = \ln \left[\frac{V_i - b_i}{V - b} \right] + 1 - \left[\frac{V_i - \overline{b}_i}{V - b} \right]$$
$$+ \frac{\alpha_i}{2\sqrt{2}} \ln \left[\frac{V_i + (1 + \sqrt{2})b_i}{V_i + (1 - \sqrt{2})b_i} \right]$$
$$- \frac{\overline{\alpha}_i}{2\sqrt{2}} \ln \left[\frac{V + (1 + \sqrt{2})b}{V + (1 - \sqrt{2})b} \right]$$
$$+ \frac{\alpha(bV_i - V\overline{b}_i)}{V(V + b) + b(V - b)} \tag{43}$$

where

$$\alpha = \frac{a}{bRT}$$

$$\overline{b}_i = -b + 2 \sum_j x_j b_{ij}$$

$$\overline{a}_i = -a + 2 \sum_j x_j a_{ij}$$

$$\overline{\alpha}_i = \frac{a}{bRT} \left[\frac{\overline{a}_i}{a} + 1 - \frac{\overline{b}_i}{b} \right]$$

Equation 43 is simplified if a linear mixing rule is used for the covolume:

$$b = \sum_i x_i b_i$$

Then,

$$\ln \gamma_i = \ln \left[\frac{V_i - b_i}{V - b} \right] + 1 - \left[\frac{V_i - b_i}{V - b} \right]$$
$$+ \frac{\alpha_i}{2\sqrt{2}} \ln \left[\frac{V_i + (1 + \sqrt{2})b_i}{V_i + (1 - \sqrt{2})b_i} \right] - \frac{\overline{\alpha}_i}{2\sqrt{2}}$$
$$\ln \left[\frac{V + (1 + \sqrt{2})b}{V + (1 - \sqrt{2})b} \right] + \frac{\alpha(bV_i - Vb_i)}{V(V + b) + b(V - b)} \tag{44a}$$

$$\alpha = \frac{a}{bRT}$$

$$\overline{a}_i = -a + 2 \sum_j x_j a_{ij}$$

$$\overline{\alpha}_i = \frac{a}{bRT} \left[\frac{\overline{a}_i}{a} + 1 - \frac{b_i}{b} \right]$$

At infinite dilution, eq 44a can be written as

$$\ln \gamma_1^\infty = \ln \left[\frac{V_1 - b_1}{V_2 - b_2} \right] + 1 - \left[\frac{V_1 - (b_2 - 2b_{12})}{V_2 - b_2} \right]$$
$$+ \frac{a_1}{2\sqrt{2}\,b_1 RT} \ln \left[\frac{V_1 + (1 + \sqrt{2})b_1}{V_1 + (1 - \sqrt{2})b_2} \right]$$
$$+ \frac{a_2}{b_2 RT} \left(\frac{V_1 b_2 + V_2 b_2 - 2V_2 b_{12}}{V_2^2 + 2V_2 b_2 - b_2^2} \right)$$
$$- \frac{a_2}{\sqrt{2}\,b_2 RT} \left(\frac{a_{12}}{a_2} + \frac{1}{2} - \frac{b_{12}}{b_2} \right)$$
$$\ln \left[\frac{V_2 + (1 + \sqrt{2})b_2}{V_2 + (1 - \sqrt{2})b_2} \right] \tag{44b}$$

Upon comparing eqs 43 and 44, it can be seen that the mixing rule for the covolume parameter appears in *all* terms of the EoS expression for the activity coefficient. This may justify why the use of an l_{ij} or a combining rule other than the arithmetic mean for the covolume parameter can effectively "correct" both the combinatorial and the residual contributions of the equation of state.

3. DISCUSSION

A general discussion on the capabilities and limitations of EoS/G^E mixing rules is offered in this section, supported by some additional references. Table 7 shows a comparative presentation of the characteristics of some of the most well-known mixing rules.

The most important conclusions from the investigations on EoS/G^E mixing rules can be summarized as follows:

(1) Huron−Vidal mixing rules combined with a cubic EoS (SRK or PR) constitute an excellent fitting tool, both for correlating phase behavior (including LLE and VLLE) of mixtures of complex compounds and for predicting multiphase behavior for multicomponent mixtures. In particular the NRTL

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Table 7. Comparative presentation of some of the well-known EoS/G^E models (Y = yes, N = no)

mixing rule	can existing g^E model parameters be used ?	satisfying mixing rule for second virial coefficient	successful for size-asymmetric systems	full reproduction of incorporated g^E	extensive table/application for gas-containing systems
Huron−Vidal	N	N	Y (possibly- not clearly shown?)	N	N[a]
Wong Sandler	Y	Y	N (few applications)	N	N
MHV1/PSRK MHV2	Y	N (?)	N	N	Y
"Exact"	Y	N (?)	N	Y	N
LCVM	Y	N (?)	Y	N	Y
PSRK-new, VTPR	N	N	Y	N	Y

[a]The mixing rule has been used for gas-containing systems but no extensive parameter table or applications have been reported.

version proposed by Huron and Vidal which can be used together with the vdW1f mixing rules is very useful. Excellent results with SRK/HV have been presented recently even for highly associating mixtures like those containing water/hydrocarbons and multicomponent mixtures of water, glycols (MEG, TEG), and hydrocarbons (including methane) as well as for reservoir fluids with polar chemicals.[93−95,107,16] The results for these complex mixtures and others, for example, CO_2/water/dimethyl ether and mixtures with polar chemicals[16] (aniline, sulfolane) are satisfactory and comparable to those obtained with association models like those belonging to the SAFT family. Table 8 summarizes some results with SRK/Huron−Vidal and CPA for several binary and multicomponent mixtures containing polar compounds. Compared to SAFT-type approaches such as CPA and PC-SAFT, SRK/HV requires more adjustable parameters (at least three per binary, five if they are temperature-dependent) but nevertheless the performance for multicomponent systems is often satisfactory. Temperature-dependent interaction parameters are needed for demanding systems, for example, for describing the solubilities of all compounds over extensive temperature-ranges for CO_2−water−methane.[96] Still, association models also exhibit difficulties for such mixtures. The Huron−Vidal mixing rule has been recently combined with an association model (CPA) in order to improve the performance of the association model for water−acetic acid VLE.[97] It is important to emphasize that the most successful results with the SRK/Huron−Vidal model are obtained when a "purely energetic" activity coefficient model is used, for example, NRTL or the residual term of UNIQUAC, UNIFAC, or ASOG, as also illustrated recently by Soave[98] in a successful SRK/HV model using the residual term of the UNIFAC/ASOG models. We have demonstrated in section 2 that this choice of activity coefficient model is consistent with the Huron−Vidal derivation. It is of interest to state that the Huron−Vidal mixing rule is equivalent to the van der Waals one fluid mixing rule if a van Laar type g^E model is incorporated in the Huron−Vidal mixing rule. This issue has been discussed by Soave and Jaubert in recent publications.[98,160]

(2) A serious problem of most EoS/G^E approaches is their inability to reproduce the underlying activity coefficient model. This problem has been shown to be partially responsible for the problems of EoS/G^E approaches for size-asymmetric systems. Nevertheless, a full reproduction of a model like original UNIFAC would not do very good for alkane mixtures. As seen in Figures 1−3 and Tables 4 and 6 the combinatorial/free-volume term of cubic EoS performs actually better than UNIFAC's combinatorial term. In this way, it is more suitable for the EoS/G^E models to retain the combinatorial term of the

Table 8. Comparison between CPA and SRK/Huron−Vidal (SRK/HV) for Various Polar Systems.[a]

water/hydrocarbons VLLE (11 systems, C3−C10, BTEX, hexene and decene)		
concentration of	SRK/Huron−Vidal	CPA
water in liquid phase	41	7
hydrocarbon in liquid phase	24	30
water in vapor phase	6	4

MEG and TEG/hydrocarbons LLE (seven systems)		
concentration of	SRK/Huron−Vidal	CPA
hydrocarbon in glycol phase	3	7
glycol in hydrocarbon phase	27	8

MEG−water−aromatic HCs (benzene, toluene) LLE—two ternary systems at two temperatures (298, 323 K)				
	polar phase,		HC phase	
	SRK/Huron−Vidal	CPA	SRK/Huron−Vidal	CPA
MEG	2	2	47	16
water	1	1	23	12
HC	21	20	0	0

MEG−water−C1−C3 (283−311 K, 69−210 bar) VLE, and MEG−water−C1−toluene VLLE (275−323 K, 69 bar)						
	liquid phase or liquid HC		water phase		vapor phase	
	SRK/HV	CPA	SRK/HV	CPA	SRK/HV	CPA
MEG	18	8	0	0	135	17
water	13	12	0	0	30	27
methane	23	17	19	18	0	0
C3 or toluene	72	33	59	14	3	2

VLLE of MEG−water−C1−C3−toluene and MEG−water−C1−C3−C7 in the range 283−311 K and 69−205 bar.						
	liquid HC phase		water phase		vapor phase	
	SRK/HV	CPA	SRK/HV	CPA	SRK/HV	CPA
MEG	157	26	0	0	98	48
water	46	31	0	0	23	40
methane	18	8	32	35	0.5	0.7
propane	4	6	140	88	6	6
toluene or C7	10	8	>100	28	12	18

[a]The numbers are % AAD deviations between experimental and calculated mole fractions. From Folas, Ph.D. work[94] (adapted). CPA has one interaction parameter per binary, while SRK/HV has three binary interaction parameters. The multicomponent results are predictions and are based solely on binary interaction parameters estimated from binary data.

EoS itself (rather than of the external model) and this is what is done in LCVM and related models which perform successfully for size-asymmetric systems. As Kalospiros et al.[67] write: "it may be better to sacrifice the underlying g^E in order to obtain

overall good results". While we recognize that some may disagree with this, the capabilities of the combinatorial/free-volume term of the EoS support this statement.

(3) We have provided in section 2 several references and arguments which underline the importance of eliminating the double combinatorial term in the approximate zero reference pressure models so that the resulting EoS/G^E approaches can be used successfully for size-asymmetric systems. Indeed models like CHV and LCVM perform best for such systems. The literature is rich with such approaches, for example, Zhong and Masuoka[78] have proposed the following mixing rule:

$$\alpha = \frac{1}{q_1}\left((1+f)\frac{g^{E,M}}{RT} - \frac{g^{E,FH}}{RT}\right) + \sum_i x_i \alpha_i \qquad (45)$$

Although in eq 45 the correction factor is included in the external model term rather than in the FH term, the significance is the same and the average value reported ($f = 0.36$) is equivalent to the corrections factors used in the other models. Zhong and Masuoka[78] present also correlations of the f-parameter with the carbon number for some gas/alkane families.

Neau and co-workers[102,103] have recently proposed an EoS/G^E mixing rule which, though not clearly stated as such, again uses the principle of the elimination of the double combinatorial. They employ PR with a generalized (group-based) NRTL that includes a combinatorial term based on segment fractions (van der Waals volumes). This is identical with the combinatorial term that is included in the mixing rule they propose:

$$\alpha = \frac{1}{C}\left(\frac{g^{E,M}}{RT} - \sum_i x_i \ln\frac{r_i}{r}\right) + \sum_i x_i \alpha_i \qquad (46)$$

Thus, the two combinatorial terms are eliminated and the resulting model has the same combinatorial/free-volume term as the EoS itself. The resulting PR-NRTL is in essence a Huron–Vidal type mixing rule. Thus, while we agree with the authors' statement that the final model accounts for the entropic effects correctly this does not happen because of the new version of NRTL that the authors use. It is rather due to the elimination of the double combinatorial in eq 46. Neau et al.[99,100] show that their new model gives good results, which we expect that they will be similar to those of other EoS/G^E models with the same qualitative characteristics. It is interesting to note that their model can represent the minimum of the hydrocarbon solubility in water with temperature which, as it has been shown,[19] it can be also described by the Huron–Vidal mixing rule in general. A similar model presented earlier by the same authors[101–104] is again based on a variation of eq 46 using the generalized NRTL. In those earlier works MHV1 is used with covolumes which are estimated via the van der Waals volumes (instead of the critical properties). The result is again essentially an elimination of the double combinatorial. An additional indication for the "double combinatorial" problem for size-asymmetric systems can be extracted from the work of Lermite and Vidal[25,26] who used an MHV1 (constant-packing based) approach but (possibly inspired by the Huron–Vidal

mixing rule) kept only the residual term of UNIQUAC or UNIFAC, thus their mixing rule is

$$\alpha = \frac{1}{q_1}\left(\frac{g^{E,M,res}}{RT} - \frac{g^{E,FH}}{RT}\right) + \sum_i x_i \alpha_i \qquad (47)$$

New interaction parameters are fitted but, as might be expected, the results are not satisfactory for asymmetric gas-containing mixtures. This conclusion is again in agreement with the "double combinatorial" explanation. In this case we have a single "extra (to that of the EoS)" combinatorial term. It is the FH-term (originated from the constant packing fraction assumption) which is added to the combinatorial/free-volume term of EoS and results to an overcorrection of the combinatorial/free-volume term from the EoS. On the other hand, the same authors[27,39] used correctly in combination with the Huron–Vidal mixing rule:

$$\alpha = \frac{1}{q_1}\left(\frac{g^{E,M,res}}{RT}\right) + \sum_i x_i \alpha_i \qquad (48)$$

the residual term of UNIQUAC or UNIFAC. Equation 48 is the Huron–Vidal mixing rule and essentially also the mixing rule used in PSRK-new and VTPR. The results are satisfactory for a variety of mixtures including size-asymmetric ones (new parameters must be fitted but they can be group-based ones).

Finally, we should mention that PSRK-new, VTPR, and UMR-PR are quite similar models. All three models essentially eliminate the double combinatorial and use a different than the usual arithmetic mean mixing rule rule for the covolume parameter. As shown by Chen et al.,[79] the importance of this combining rule (eq 40b) over the arithmetic mean one is rather small and it is the elimination of the double combinatorial which is the main reason for the successful results for size-asymmetric systems. Voutsas (2010, private communication) verified that by indicating that the new combining rule for the covolume (eq 41b) is particularly important for polymeric systems, otherwise a linear mixing rule could as well be used. New parameters are regressed in VTPR while UMR-PR employs the existing UNIFAC interaction parameters.

There are many studies in the literature that indicate that combining rules other than the linear one for the covolume can result in improved results for polymer mixtures. For example, Zhong and Masuoka[105] used the simple form of SRK/Huron–Vidal shown in eq 48 without any residual term. This means that they used essentially the a/b mixing rule together with the Wong–Sandler mixing rule for the second virial coefficient, that is, eqs 11 and 14a. They showed (and it was verified by Louli and Tassios[106]) that excellent correlation results are obtained for polymer–solvent VLE using a single k_{ij} per system. The performance is better than with other mixing rules. The success was considered surprising in the articles by Zhong–Masuoka[105] and Louli–Tassios[106] but we believe it can be explained by the fact that the a/b mixing rule isolates and illustrates that the combinatorial/free volume contribution from cubic EoS is represented adequately, as shown by the results for mixtures with alkanes differing significantly in size (see Figures 1–3 and Tables 4 and 6).

(4) Liquid–liquid equilibrium studies using the EoS/G^E models have been presented by several authors[110,111,117–124] and particularly interesting are the investigations by Escobedo–Alvarado and Sandler[110] and Knudsen et al.[111] It is shown in these works that EoS/G^E mixing rules such as MHV2 and

Wong–Sandler, especially when combined with molecular-based local composition models (NRTL, UNIQUAC) can correlate well LLE of complex mixtures. The results are satisfactory for high pressure LLE based on low pressure obtained parameters. In this sense and also because of their better temperature dependency (which permits more successful extrapolations) EoS/G^E models are superior to the underlying g^E model.[110,122] For strongly hydrogen bonding systems, however, such as 2-butanol/water and 2-butoxyethanol/water a significant number of adjustable parameters is needed for describing the observed closed loop behavior and its dependency on temperature and pressure. Predictions for multi-component systems based solely on binary data are not satisfactory.[111]

(5) Compared to the large number of studies on phase behavior, relatively few investigations have been published for thermal properties (heat of mixing, heat capacities). Djordjevic et al.[136] in their review article discuss particularly the performance of several EoS/G^E mixing rules for enthalpies and heat capacities. Their most important conclusion is, that for all mixing rules, the need of temperature dependent adjustable parameters is crucial for describing accurately thermal properties. In general, as Ghosh[135] discusses, the excess enthalpies produced from the EoS/G^E mixing rules are more positive than those obtained from the incorporated activity coefficient models.

More specifically, both the PSRK and VTPR models have been tested to both enthalpies and heat capacities and qualitatively good results have been reported by Gmehling and co-workers,[79,81,82,84,86,87] especially for VTPR. This can be partially attributed to the good temperature dependency of the interaction parameters and the inclusion of thermal data in the UNIFAC parameter estimation. Deviations between 4 and 8% have been reported for the new PSRK of Chen et al.[79] for the excess enthalpies of alkanes with alkanes, ketones and methanol. Moreover, VTPR is shown to perform clearly better than PSRK for excess enthalpies for a wide range of families (alkanes+aromatics, alkanes+ketones, aromatics+ketones, esters+alkanes, esters+aromatics).

Good excess enthalpies have been presented with UMR-PR[89] for a few systems using temperature dependent interaction parameters. Detailed studies on excess enthalpies with the Wong–Sandler and MHV1 mixing rules have been presented by Sandler and co-workers,[125,126] Zhong and Masuoka,[127] and Ohta.[128] Zhong and Masuoka[127] showed that MHV1 cannot reproduce the excess enthalpies of the incorporated activity coefficient model but a modification similar to eq 45 performed much better both for asymmetric systems VLE and for excess enthalpies. Good excess enthalpies have been reported with this modified MHV1 model for a wide range of alcohol–hydrocarbon, alcohol–water, and alcohol–ketone systems. The results are comparable to those of modified UNIFAC. Ohta[128] compared MHV1 and Wong–Sandler rules and found acceptable and similar excess enthalpies (& VLE) for a number of systems, including a few ternary excess enthalpies, using temperature dependent parameters.

Sandler and co-workers[125,126] have also studied the MHV1 and Wong–Sandler mixing rules for excess enthalpies. They found[125] that, for four highly nonideal systems, the models can calculate VLE and excess enthalpies separately but not both. The best way to regress parameters for these models is by using simultaneously VLE and excess enthalpy data (and not any of this type of data alone). Especially excess enthalpy data are

useful for selecting the best set of adjustable parameters.[126] Moreover, they showed that simultaneous correlation of VLE and excess enthalpies at one temperature is possible but extrapolation at other temperatures did not result in accurate prediction of either VLE or excess enthalpies. Better results are obtained for less nonideal systems.[126] Because of the pressure dependency, the Wong–Sandler (and other mixing rules) should be preferred over the incorporated activity coefficient model for capturing the pressure dependency of thermal properties.

(6) Another application of EoS/G^E models is in the prediction of solid–gas equilibria. This is an important type of phase behavior, crucial in the design of supercritical fluid extraction. These systems are challenging due to the asymmetric nature of the gas and the solute, both in terms of molecular size and intermolecular forces but also because often the pure component properties (critical properties and vapor pressures) of solids are not available and their estimations e.g. from group contribution methods are not always reliable. An additional issue is the frequent need of cosolvents for increasing the solubility of the solute in the supercritical fluid, thus the modeling of supercritical fluid/cocolvent/solute is of importance. The MHV1, Huron–Vidal, Wong–Sandler, LCVM, and UMR-PR mixing rules have been used for solid–gas equilibrium calculations.[73,74,89,129−132]

The applications are not very extensive, mostly CO_2 with aromatic hydrocarbons, acids, and alcohols have been reported, and there is limited application to cosolvents (mostly for LCVM and UMR-PR). There are good correlative (semi-predictive) results and some researchers[129,130] have illustrated that an interaction parameter in the covolume is needed for obtaining good results. The WS-NRTL is also a good correlative tool,[131] applied also to mixed solids, but there is a need for high-interaction parameters in the case of cosolvents/complex solids.

One of the models applied to many solid–gas systems is LCVM. Good predictions are obtained for CO_2 mixtures with aromatic hydrocabrons, aliphatic acids, and some alcohols. Satisfactory results are also obtained in some cases for ternary systems with cosolvents, and LCVM can be used to some extent for predicting the enhancement and for cosolvent screening. However, the uncertainty on critical properties and vapor pressures of the solid may be significant, and poor results for very complex molecules, for example, naproxen and cholesterol are obtained.

It appears that the performance of EoS/G^E mixing rules for solid–gas systems is, despite the many efforts, at a preliminary level; most results are of semicorrelative value and no "real winner" among the various models can be identified.

(7) Many EoS/G^E models (Huron–Vidal, MHV1, PSRK, VTPR, Wong–Sandler, LCVM, UMR-PR) have been applied to polymers and an extensive reference list is available in a recent monograph.[16] In these applications, typically an activity coefficient suitable model for polymers, such as, Flory–Huggins[113] or Entropic-FV,[114] is used in the mixing rule. Most applications are concerned with vapor–liquid equilibria including Henry's law constants and gas solubilities. Good results are obtained for many polymers, which are comparable to those obtained by SAFT and other noncubic equations of state.[133] There are, however, two key issues which have not been fully understood and/or analyzed. The first is common for all equations of state applied to polymers, that is, not only the cubic ones. What is the "correct" or "best" way to estimate the

EoS parameters for polymers? Traditional methods (using critical and vapor pressure data) can apparently not be used, and a variety of approaches have been employed (see ref 16), but there is no consensus on which is the best approach for practical applications. The second issue is the use of mixing rule, which may be more important than which "polymer" activity coefficient model is actually implemented. In particular, it has been shown[105,106,134,150] that the a/b mixing rule (which we have discussed extensively in this work) has a great potential in describing polymer and other asymmetric mixtures over a wide range of temperatures and polymer molecular weights, either combined with the Wong−Sandler mixing rule or with the Berthelot rule for the cross association energy. It remains to be seen what it is the best way to use the a/b mixing rule for polymers and how it compares to other approaches.

Epilogue. This review of EoS/G^E models focused mostly on methodological aspects and less on applications. Detailed reviews of these mixing rules are offered in books[16,41,108] and extensive review articles[135−137] on cubic equations of state.

We mentioned in the beginning of the article that the interest in EoS/G^E models has somewhat declined during the last years, possibly due to their maturity. Indeed since Prausnitz et al.[155] so wisely predicted, almost 30 years ago, that advanced mixing rules will be in the future used for extending cubic EoS to complex mixtures, much has been done. Today, EoS/G^E mixing rules are available in commercial simulators[156,157] and they are extensively used in many industrial applications.[156−159] They are a "working worse", one of the most useful ones, of modern applied chemical engineering thermodynamics.

Nevertheless new applications of EoS/G^E mixing rules do appear, for example, on refrigerants,[138] fluorocarbons,[148] synthetic fluids,[149] multicomponent systems.[139,140] New developments have also appeared, for example, the promising one-parameter EoS/G^E model (based on Wong−Sandler mixing rule) proposed by Ioannidis and Knox[151,152] as well as theoretical investigations[153,154] which are, in general terms, in agreement to the findings of this review, for example, about the role of "double combinatorial". Moreover, the EoS/G^E models have inspired successful recent developments of group contribution methods for predicting the interaction parameter k_{ij} of the cross energy combining rule in the van der Waals one fluid mixing rules such as the method developed for PR by J.N. Jaubert and co-workers.[141−144] Finally, various approaches of implementing COSMO-RS in the EoS/G^E framework have recently appeared.[145−147] While it may be early to fully evaluate them, they may in the future extend the applicability of this successful quantum-chemistry method (one of the cornerstones of modern thermodynamics) to high pressures.

Despite the significant capabilities of EoS/G^E mixing rules, there are limitations pointed out over the years, some of which have found solutions but others are tightly connected to the incorporated (local composition) activity coefficient models. Already in 1993 Vidal[39] (see also ref 108) pointed out that asymmetric systems and VLLE for methanol/ethane (and related systems) are problems not addressed adequately by cubic EoS even with the EoS/G^E mixing rules. We feel and we have illustrated in this review that up-to-date EoS/G^E models can handle satisfactorily size-asymmetric systems. But we agree that complex multiphase equilibria is still only partially addressed by EoS/G^E mixing rules and the significant number of adjustable parameters may constitute a problem in some cases. For such complex systems, association theories such as SAFT and CPA often perform better.[16,108,109]

4. CONCLUSIONS

The significant knowledge accumulated over the last 30 years for the powerful EoS/G^E mixing rules for cubic equations of state has been reviewed. Models based on the infinite, zero, and no specific reference pressure have been presented, including derivation and assessment of their performance. A method to evaluate and compare mixing rules of cubic equations of state by looking at the activity coefficient expression derived from the equation has been utilized throughout this work. It has been shown that all EoS/G^E mixing rules have significant capabilities but also a number of limitations, beyond those stemming from the "base" models (EoS and activity coefficient) used in their derivation. First of all, it is illustrated that the Huron−Vidal mixing rules constitute an excellent correlation tool, capable of representing complex mixtures phase behavior, but an "energetic" activity coefficient model is consistent with the derivation, for example, NRTL or the residual term of UNIQUAC or UNIFAC. The resulting model, that is, the cubic EoS with Huron−Vidal mixing rules and NRTL is expected to be superior to NRTL even at low pressures, due to inclusion of the successful combinatorial/free-volume term from the cubic equation of state. Several of the limitations of the Huron−Vidal mixing rules are corrected in the Wong−Sandler mixing rule. However, it is not certain to what extent the assumptions of the Wong−Sandler mixing rule hold for asymmetric systems, whether the k_{ij} parameter is unique over the whole concentration range, and what implications the temperature dependent covolume parameter may have. We further show that mixing rules like MHV1 and PSRK are only approximate zero reference pressure models, and particularly for asymmetric systems they do not reproduce the incorporated activity coefficient model. This deficiency is partially connected to a significant problem of several of these mixing rules, namely their inability to provide good results for size-asymmetric systems, for example, gases with heavy alkanes. It is shown that LCVM and subsequently also other models like GCVM and CHV correct for these deficiencies by eliminating the "double combinatorial difference," that is, the difference between the Flory−Huggins term stemming from the EoS at approximate zero reference pressure and the combinatorial term from the incorporated activity coefficient model. This observation is consistent with the most recent generation of models like the new version of PSRK, VTPR, UMR-PR, and PR-NRTL all of which essentially eliminate the difference of the "two combinatorial terms".

In brief, all EoS/G^E approaches have significant capabilities and the most modern versions correctly solve for the problems of earlier approaches for asymmetric systems. The cubic EoS using the EoS/G^E mixing rules are in some respects superior than the incorporated activity coefficient model, because of the inclusion of the combinatorial/free-volume term and the temperature/pressure dependency of the EoS. This is especially the case for size-asymmetric systems and for enthalpies. Nevertheless, the performance of the final cubic equation of state should not be expected, for polar relatively symmetric systems, to be significantly superior to the underlying activity coefficient model. Associating mixtures and multiphase behavior especially for multicomponent systems represent the limit of these approaches and association models, for example, those belonging to the SAFT family are expected to perform

better for such difficult systems and with fewer adjustable parameters.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: gk@kt.dtu.dk.

Notes
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