# Getting a Handle on Advanced Cubic Equations of State

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Understanding the strengths and limitations of a cubic equation of state (CEOS) is key to selecting the right one for your flowsheet simulation.

Engineers must often perform complex phase-equilibria calculations to model systems typically found in the refining and chemical industries. Cubic equations of state (CEOS) are currently the equations of state considered most applicable for such calculations. This article focuses on the enhancements made to the CEOS that are considered industry-wide standards and points out the strengths and limitations of these CEOS and their mixing rules.

The Soave modification of the Redlich-Kwong (SRK) equation *(1)* has been very successful in extending the applicability of CEOS to systems that contain non-polar and slightly polar components. However, Soave-type CEOS that use the van der Waals mixing rules have difficulty handling the phase behavior of polar systems. Numerous efforts have been made to develop mixing rules and EOS models for "associating" fluids. The modern approach of combining CEOS with excess Helmholtz or Gibbs energy models is one example. With so many EOS and mixing rules available, it is no wonder that chemical engineers have difficulty selecting an appropriate thermodynamic method for the simulation of their flowsheets. This article addresses questions frequently asked at the inception of flowsheet simulation, namely, "Which equation of state do I use?" and, "What mixing rules should be selected for my system?"

## Twu-Sim-Tassone CEOS

A general two-parameter CEOS can be represented by the equation:

$$P = \frac{RT}{v-b} - \frac{a}{(v+ub)(v+wb)} \tag{1}$$

There are two parameters, *a* and *b*. Generally, there are two ways to evaluate them. One is to fit the parameters to experimental data, usually the vapor pressure and liquid density. The other is to derive the parameters from the critical con-

straints by setting the first and second derivatives of the pressure, with respect to volume, equal to zero at the critical point. Since cubic equations of state do not represent *PVT* behavior well, particularly near the critical region, the use of a CEOS to predict liquid densities results in large errors. This is one of the inherent limitations of any CEOS. Using regression to force-fit the EOS to liquid density by regression not only fails to satisfy the critical constraints, but also sacrifices the ability of the EOS to predict *K*-values, and also leads to an over estimation of critical temperature and critical pressure.

However, the critical constraints induce a constant value of the critical compressibility factor, $Z_c$, for all components. The $Z_c$ for real fluids is known from experiment to be generally smaller than that predicted from the CEOS. Thus, predicted liquid densities differ considerably from their experimental values. SRK, Peng-Robinson (PR), and TST equations of state *(2, 3)* predict a constant $Z_c$, equal to 0.3333, 0.3074 and 0.2962 for all substances, respectively. The value of $Z_c$ obtained from TST is closest to the real value of $Z_c$ for most substances.

The constants *u* and *w* are EOS-dependent. Twu et. al. *(2, 3)* propose a methodology to find a CEOS that predicts liquid densities for heavy hydrocarbons and polar components better than the SRK or PR equations. For the TST equation, $u = -0.5$ and $w = 3.0$. For the SRK equation, $u = 0$, $w = 1$. For the PR equation, $u = -0.4142$ and $w = 2.4141$. SRK is the equation of choice for predicting the liquid density for methane and PR is best for *n*-pentane up to *n*-heptane; and TST is superior for *n*-octane and higher carbon numbers, as well as for polar components. Another special feature of the CEOS is that while it typically under-predicts liquid density, this shortcoming may be corrected by volume translation without affecting the *K*-value calculation *(4)*.

Although the ability to accurately predict liquid-density varies from one CEOS to the next, no single equation has an advantage over another in terms of its modeling accuracy as

long as the same alpha function (for pure-component vapor pressure correlation) and the same mixing rules (for mixture-property correlation) are used *(5)*. *Since the ability of any CEOS to predict phase equilibria of mixtures depends on the alpha function and the mixing rule, these two elements will be the focus of the remainder of this article.*

## Alpha functions for cubic equations of state

The accurate prediction of *K*-values from any CEOS requires an equally accurate prediction of pure-component vapor pressures, which depends on the development of an appropriate alpha function $\alpha(T)$. The first CEOS to be successfully applied to the calculation of thermodynamic properties for the vapor phase was the modified form of the van der Waals equation by Redlich and Kwong *(6)*, who incorporated temperature dependence into the *a* term:

$$P = \frac{RT}{v-b} - \frac{a/T^{0.5}}{v(v+b)} \tag{2}$$

The success of the Redlich-Kwong (RK) equation stimulated numerous researchers to propose various correlations for improving the prediction of vapor pressure. Wilson *(7)* first introduced a general form of temperature dependence of the *a* parameter in the RK equation in 1964:

$$a(T) = \alpha(T)a_c \tag{3}$$

where $a_c$ is the value of *a* at the critical point. In 1966, Wilson *(8)* expressed $\alpha(T)$ as a function of the reduced temperature, $T_r = T/T_c$, and the acentric factor $\omega$ as follows:

$$\alpha(T) = T_r + (1.57 + 1.62\omega)(1 - T_r) \tag{4}$$

However, since the error of predicted vapor pressure from Eq. 4 is quite large, Wilson's function did not find widespread use. The $\alpha(T)$ function that did find its way into the mainstream was proposed by Soave in 1972. He developed a linear equation for $\alpha$ as a function of temperature by plotting $\alpha^{0.5}$ against $T_r^{0.5}$ at a constant $\omega$:

$$\alpha(T) = (1 + m(1 - T_r^{0.5}))^2 \tag{5}$$

The *m* parameter is obtained by forcing the equation to reproduce vapor pressures for light hydrocarbons corresponding to $C_1$ through $C_{10}$ at $T_r = 0.7$, and is correlated as a function of $\omega$:

$$m = 0.480 + 1.57\omega - 0.176\omega^2 \tag{6}$$

Soave's development of Eqs. 5 and 6 represented a great step forward in the practical application of CEOS. The Soave $\alpha(T)$, (or Eq. 5) defined as a function of both $T_r$ and $\omega$, is good for predicting the vapor pressures of hydrocarbons at temperatures above their normal boiling points, but not at conditions above the critical point, since the function does not decrease mono-

## Nomenclature

| | |
|---|---|
| *a, b* | = CEOS parameters |
| $a^*, b^*$ | = reduced parameters of *a* and *b* |
| *A* | = Helmholtz energy |
| $c_1, c_2, c_3$ | = constants in $\alpha(T)$ function (Eq. 14, 15) |
| $C_1$ | = constant at infinite pressure |
| $C_r$ | = constant at zero pressure |
| $C_{v0}$ | = function at zero pressure |
| *G* | = Gibbs energy |
| $k_{ij}, k_{ij}$ | = binary interaction parameter |
| $l_{ij}$ | = binary interaction parameter |
| *m* | = parameter in Soave's equation for $\alpha(T)$, Eq. 5 |
| *n* | = parameter in Soave's expanded equation for $\alpha(T)$, Eq. 7 |
| *L, M, N* | = parameters in the Twu $\alpha$ function |
| *P* | = pressure |
| *R* | = ideal gas constant |
| *r* | = constant reduced liquid volume at zero-pressure |
| *T* | = temperature |
| *u, w* | = CEOS constants |
| *v* | = molar volume |
| $v_0^*$ | = reduced liquid volume at zero pressure |
| *V* | = total volume |
| $x_i$ | = mole fraction of component *i* in liquid phase |
| *Z* | = compressibility facto |

*Greek letters*

| | |
|---|---|
| $\alpha$ | = CEOS alpha function |
| $\delta$ | = parameter used to define $\tau$ |
| $\omega$ | = acentric factor |
| $\tau$ | = parameter used in TST excess Gibbs energy model |

*Subscripts*

| | |
|---|---|
| 0 | = zero pressure |
| $\infty$ | = infinite pressure |
| *c* | = critical property |
| *i, j ,k* | = property of component *i, j, k* |
| *ij, ji* | = interaction property between components *i* and *j* |
| *ik, ki* | = interaction property between components *i* and *k* |
| *r* | = reduced property |
| *vdw* | = van der Waals |

*Superscripts*

| | |
|---|---|
| * | = reduced property |
| *E* | = excess property |
| (0) and (1) | = denotes value of $\alpha$ when $\omega = 0$ and $\omega = 1$ |

†*Any consistent set of units is acceptable.*

tonically with increasing temperature.

Another shortcoming of Soave's $\alpha(T)$ function is that the calculated vapor pressures tend to diverge from the experimental ones at low temperatures. Therefore, Soave proposed a new $\alpha(T)$ function to improve vapor-pressure prediction by expanding Eq. 5 as follows *(9)*:

$$\alpha(T) = 1 + m(1 - T_r) + n(1 - T_r^{0.5})^2 \tag{7}$$

where *m* and *n* are obtained by correlating vapor-pressure values generated by the Lee-Kesler EOS:

$$m = 0.484 + 1.515\omega - 0.44\omega^2 \tag{8}$$
$$n = 2.756m - 0.700 \tag{9}$$

| Table 1. | | | | |
|---|---|---|---|---|
| | $T_r \leq 1$ | | $T_r > 1$ | |
| α Parameter | $\alpha^{(0)}$ | $\alpha^{(1)}$ | $\alpha^{(0)}$ | $\alpha^{(1)}$ |
| L | 0.544000 | 0.544306 | 0.379919 | 0.0319134 |
| M | 1.01309 | 0.802404 | 5.67342 | 1.28756 |
| N | 0.935995 | 3.10835 | −0.200000 | −8.000000 |

The $L$, $M$ and $N$ databank of the generalized alpha function for Eqs. 11 and 12 with the Soave-Redlich-Kwong EOS for subcritical and supercritical conditions.

| Table 2. | | | | |
|---|---|---|---|---|
| | $T_r \leq 1$ | | $T_r > 1$ | |
| α Parameter | $\alpha^{(0)}$ | $\alpha^{(1)}$ | $\alpha^{(0)}$ | $\alpha^{(1)}$ |
| L | 0.272838 | 0.625701 | 0.373949 | 0.0239035 |
| M | 0.924779 | 0.792014 | 4.73020 | 1.24615 |
| N | 1.19764 | 2.46022 | −0.200000 | −8.000000 |

The $L$, $M$ and $N$ databank of the generalized alpha function for Eqs. 11 and 12 with the Peng-Robinson EOS for subcritical and supercritical conditions.

| Table 3. | | | | |
|---|---|---|---|---|
| | $T_r \leq 1$ | | $T_r > 1$ | |
| α Parameter | $\alpha^{(0)}$ | $\alpha^{(1)}$ | $\alpha^{(0)}$ | $\alpha^{(1)}$ |
| L | 0.196545 | 0.704001 | 0.358826 | 0.0206444 |
| M | 0.906437 | 0.790407 | 4.23478 | 1.22942 |
| N | 1.26251 | 2.13086 | −0.200000 | −8.000000 |

The $L$, $M$ and $N$ databank of the generalized alpha function for Eqs. 11 and 12 with the Twu-Sim-Tassone EOS for subcritical and supercritical conditions.

Unfortunately, the accuracy of predicting vapor pressure from Soave's new $\alpha(T)$ was no better than the original one, and consequently, was never accepted for application. Numerous investigators have tried to improve Soave's alpha function by either altering the parameters or adding extra terms. But as long as the same or a similar form of the alpha function is used, and the same approach as Soave is applied (*i.e.*, plotting $\alpha^{0.5}$ vs. $T_r^{0.5}$), the function's inherent weakness will not be overcome.

### Better vapor pressure prediction

Twu et. al. *(10, 11)* developed a new methodology to improve the accuracy of the vapor-pressure prediction from a CEOS. They found that the alpha function is a linear function of the acentric factor at a constant reduced temperature.

$$\alpha = \alpha^{(0)} + \omega(\alpha^{(1)} - \alpha^{(0)}) \qquad (10)$$

$$\alpha^{(0)} = T_r^{N^{(0)}(M^{(0)}-1)} e^{L^{(0)}(1-T_r^{N^{(0)}M^{(0)}})} \qquad (11)$$

$$\alpha^{(1)} = T_r^{N^{(1)}(M^{(1)}-1)} e^{L^{(1)}(1-T_r^{N^{(1)}M^{(1)}})} \qquad (12)$$

The superscripts (0) and (1) in Eqs. 10, 11 and 12 are consistent with the definition of the acentric factor at $\omega = 0$ and $\omega = 1$, respectively. In other words, these two alpha functions are forced to pass through the saturated vapor pressure at $T_r = 0.7$ for $\omega = 0$ and $\omega = 1$, respectively.

Twu et. al. used the latest data from the DIPPR *(12)* databank to generate the values of $\alpha^{(0)}$ and $\alpha^{(1)}$ for SRK, PR and TST cubic equations of state. Tables 1–3 show the $L$, $M$, and $N$ values used with Eqs. 11 and 12 for SRK, PR and TST CEOS, respectively. The advantage of having a linear acentric factor is that one can reliably extrapolate its value for heavy hydrocarbons. The new generalized $\alpha(T)$ function for SRK, PR and TST, in Eqs. 10–12, allows the accurate prediction of vapor-pressure data from the triple point to the critical point for light or heavy hydrocarbons using any of these EOS.

Although the Twu alpha function mentioned above works very well for non-polar components, it is generally not suitable for polar components. In an attempt to resolve this difficulty, Soave *(13)* presents a two-parameter alpha function:

$$\alpha(T) = 1 + (1 - T_r)(m + n/T_r) \qquad (13)$$

where $m$ and $n$ are empirical constants that are fitted to the vapor pressure of the component of interest, and are not related to previously mentioned $m$ and $n$ constants. Eq. 13 fits vapor pressure quite well, but the function can become nega-

tive at high temperatures. Since the alpha function represents the attractive forces, it is physically incorrect for it to be negative. Mathias *(14)* and Mathias and Copeman *(15)* proposed $\alpha(T)$ functions similar to Soave's (Eq. 5). Mathias' $\alpha(T)$ function is expressed as:

$$\alpha(T) = (1 + c_1(1 - T_r^{0.5}) + c_2(1 - T_r)(0.7 - T_r^{0.5}))^2 \qquad (14)$$

while Mathias and Copeman's $\alpha(T)$ function takes the form:

$$\alpha(T) = (1 + c_1(1 - T_r^{0.5}) + c_2(1 - T_r^{0.5})^2 + c_3(1 - T_r^{0.5})^3)^2 \qquad (15)$$

Both functions increase with increasing temperature at the supercritical region. To overcome this difficulty, a second correlation for the $\alpha(T)$ function at temperatures higher than the $T_c$ is often required. However, using a second correlation creates a discontinuity in these alpha functions at the critical point and produces deviations in the predicted enthalpies.

Melhem et. al. *(16)* proposed a similar, but logarithmic form of $\alpha(T)$:

$$\alpha(T) = \exp[1 + c_1(1 - T_r^{0.5}) + c_2(1 - T_r^{0.5})]^2 \qquad (16)$$

The accuracy of vapor pressure regressed from this model is not as good as that for the other functions mentioned above.

Twu *(17)* derived $\alpha(T)$ from a probability distribution:

$$\alpha(T) = T_r^{N(M-1)} e^{L(1-T_r^{NM})} \qquad (17)$$

Eq. 17 has three parameters, $L$, $M$ and $N$, which, unlike those in Tables 1–3, are unique for each component and are determined from the regression of pure-component vapor-pressure data. The authors have set up databanks for $L$, $M$ and $N$ for a

wide range of components, which can be obtained by contacting the authors directly. Twu's $\alpha(T)$ function has been found to be more accurate than other $\alpha(T)$ functions found in literature for predicting vapor pressures for polar and non-polar components at temperatures ranging from the triple point to the critical point. Using the component-dependent parameters, the accuracy of reproducing the vapor pressure from Eq. 17 is within experimental error given in DIPPR.

Twu's $\alpha(T)$ function has some unique features. Fluids such as hydrogen exhibit a maximum alpha at low temperatures (about 19 K). Twu's $\alpha(T)$ function accurately describes this behavior and is the only function so far that shows this maximum at low temperature. In addition, it is continuous at the critical point for all components and extrapolates very well to supercritical conditions without exhibiting abnormal characteristics, such as increasing with increasing temperature.

Due to the accuracy and wide temperature range of application of the advanced Twu $\alpha(T)$ functions (Eqs. 10, 11, 12 and 17) for predicting vapor pressures when used in the SRK, PR and TST equations of state, these equations have been selected for use in the SRK, PR and TST models as follows. For petroleum fractions and components that do not have vapor-pressure data available, Eqs. 10, 11 and 12 should be used. For all components that do have vapor-pressure data available, Eq. 17 can be used.

## van der Waals mixing rules

In addition to using an appropriate $\alpha(T)$ function for the accurate prediction of vapor pressure, the ability of a CEOS to correlate and predict phase equilibria of mixtures depends strongly upon the mixing rule applied. The most commonly used method to extend equations of state to a non-polar mixture is to use the van der Waals one-fluid mixing rules:

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}\left(1 - k_{ij}\right) \tag{18}$$

$$b = \sum_i \sum_j x_i x_j\left[\frac{1}{2}\left(b_i + b_j\right)\right] \tag{19}$$

where $k_{ij}$ is the binary interaction parameter that is obtained from the regression of vapor-liquid equilibrium data. The van der Waals mixing rules are capable of accurately representing vapor-liquid equilibria using only one binary-interaction parameter for non-polar or slightly polar systems. However, many mixtures of interest in the chemical industry contain strongly polar or associating components. One way to modify the van der Waals mixing rules so that they can better describe polar systems is to use the asymmetric $k_{ij}$ for the $a$ parameter, as developed by Twu et. al. (17):

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}\left(1 - k_{ij}\right) +$$
$$\sum_i x_i\left[\sum_j x_j \left(a_i a_j\right)^{1/6}\left(k_{ji} - k_{ij}\right)^{1/3}\right]^3 \tag{20}$$

Eq. 20 has two adjustable parameters, $k_{ij}$ and $k_{ji}$. Generally, they are not equal. The use of an asymmetric definition of $k_{ij}$ in the van der Waals mixing rule of Eq. 20 is similar to the asymmetric parameters $A_{ij}$ and $A_{ji}$ used in the excess Gibbs energy ($G^E$) mixing rule of the NRTL model. If $k_{ij} = k_{ji}$, Eq. 20 reduces to the van der Waals mixing rule (Eq. 18).

The modified van der Waals mixing rule (Eq. 20) provides accurate correlation of complex mixtures, including highly non-ideal systems that previously could only be correlated by activity-coefficient models. However, Eq. 20 no longer satisfies the second virial coefficient.

## Huron-Vidal infinite-pressure mixing rules

Since the van der Waals mixing rules are applicable only to mixtures whose excess Gibbs energy can be approximated by the regular solution theory, quite a few new mixing rules have been recently developed based on appropriate excess energy models. Huron and Vidal (18) successfully formulated a new EOS parameter $a$ by assuming that the excess Gibbs energy at infinite pressure, $G^E_\infty$, which is derived from a CEOS, is equal to $G^E$ derived from a liquid-activity-coefficient model. They also assumed that the liquid volume at infinite pressure equals the EOS co-volume, $b$. The Huron-Vidal derivation led to the following equation for $a^*$:

$$a^* = b^*\left[\sum_i x_i \frac{a_i^*}{b_i^*} + \frac{1}{C_1}\left(\frac{G^E_\infty}{RT}\right)\right] \tag{21}$$

The parameters $a^*$ and $b^*$ in Eq. 21 are defined as:

$$a^* = Pa/R^2T^2 \text{ and } b^* = Pb/RT \tag{21a, b}$$

The Huron-Vidal approach uses the conventional linear mixing rule for the $b$ parameter:

$$b = \sum_i \sum_j x_i x_j\left[\frac{1}{2}\left(b_i + b_j\right)\right] \tag{22}$$

The $C_1$ in Eq. 21 is a constant, and is defined as:

$$C_1 = -\frac{1}{(w-u)}\ln\left(\frac{1+w}{1+u}\right) \tag{23}$$

where $u$ and $w$ are EOS-dependent constants used to represent a particular two-parameter CEOS. For example, $u = -0.5$ and $w = 3.0$ for the TST CEOS.

Although Huron and Vidal presented their model more than two decades ago, their mixing rule is not widely used due to lack of parameters available in literature for the excess Gibbs energy at infinite pressure and the inability to accurately describe non-polar hydrocarbon mixtures and to satisfy the quadratic composition dependence of the second virial coefficient.

## Wong-Sandler infinite-pressure mixing rules

The Huron-Vidal approach requires the excess volume, $V^E$, to be zero and EOS parameter $b$ to be calculated via a linear mixing rule. To allow the use of a different mixing rule for parameter $b$, Wong and Sandler (19) developed a model equating

the excess Helmholtz energy at infinite pressure from a CEOS to excess Helmholtz energy calculated from an activity coefficient model, and they constrained the EOS parameters $a$ and $b$ to satisfy the second-virial-coefficient condition:

$$a^* = b^* \left[ \sum_i x_i \frac{a_i^*}{b_i^*} + \frac{1}{C_1} \left( \frac{A_\infty^E}{RT} \right) \right] \qquad (24)$$

$$b = \frac{\sum_i^n \sum_j^n x_i x_j \left( b_{ij} - \frac{a_{ij}}{RT} \right)}{1 - \frac{a^*}{b^*}} \qquad (25)$$

The Wong-Sandler model introduced a binary interaction parameter, $k_{ij}$ to correct the assumption that the excess Helmholtz free energy at infinite pressure can be approximated by the excess Gibbs free energy at low pressure:

$$b_{ij} - \frac{a_{ij}}{RT} = \frac{1}{2} \left[ \left( b_i - \frac{a_i}{RT} \right) + \left( b_j - \frac{a_j}{RT} \right) \right] \left( 1 - k_{ij} \right) \qquad (26)$$

Wong and Sandler demonstrated that parameters in the activity coefficient models correlated at low temperatures can be used to extrapolate to higher temperatures. Michelsen and Heidemann [20] suggest that this success is fortuitous.

In an effort to reduce the Wong-Sandler mixing rules to the conventional van der Waals mixing rules, Orbey and Sandler [21] modify the $G^E$ model of NRTL differently. Consequently, the mixing rules used in their model cannot employ the NRTL parameters reported in the DECHEMA Chemistry Data Series.

### Twu-Coon infinite-pressure mixing rules

Twu and Coon [22] used a van der Waals mixture as a reference to derive the mixing rules for their EOS. These mixing rules re-define $a$ and $b$ as:

$$a^* = b^* \left[ \frac{a_{vdw}^*}{b_{vdw}^*} + \frac{1}{C_1} \left( \frac{A_\infty^E}{RT} - \frac{A_{\infty\, vdw}^E}{RT} \right) \right] \qquad (27)$$

$$b^* = \frac{b_{vdw}^* - a_{vdw}^*}{1 - \left[ \frac{a_{vdw}^*}{b_{vdw}^*} + \frac{1}{C_1} \left( \frac{A_\infty^E}{RT} - \frac{A_{\infty\, vdw}^E}{RT} \right) \right]} \qquad (28)$$

$C_1$ in Eqs. 27 and 28 is defined in Eq. 23. The asymmetric van der Waals mixing rule is applied to the $a_{vdw}$ parameter, and the linear mixing rule is used for the $b_{vdw}$ parameter:

$$a_{vdw} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \left( 1 - k_{ij} \right) +$$

$$\sum_i x_i \left[ \sum_j x_j \left( a_i a_j \right)^{1/6} \left( k_{ji} - k_{ij} \right)^{1/3} \right]^3 \qquad (29)$$

$$b_{vdw} = \sum_i \sum_j x_i x_j \left[ \frac{1}{2} \left( b + b_j \right) \right] \qquad (30)$$

Subscript $vdw$ in $A_{\infty\, vdw}^E$ in Eqs. 27 and 28 denotes that the properties are evaluated from the CEOS using the van der Waals mixing

rule for its $a$ and $b$ parameters as given by Eqs. 29 and 30.

The Twu-Coon mixing rules reduce to the van der Waals mixing rules if $A_\infty^E = A_{\infty\, vdw}^E$. It is extremely desirable that the composition-dependent mixing rules reduce to the classical mixing rules because the latter work very well for non-polar systems. The use of asymmetric parameters, $k_{ij}$ and $k_{ij}$, improves the accuracy of the reproduction of the liquid-activity coefficients. Although it may be more accurate to simply refit the $G^E$ parameters in the mixing rules instead of introducing two new parameters, $k_{ij}$ and $k_{ij}$, to match the results of the activity coefficient model, doing so would sacrifice the extrapolation ability of the infinite-pressure approach. Furthermore, the original idea of using directly published parameters for activity coefficient models in the equation of state will be lost.

### Twu-Sim-Tassone infinite-pressure mixing rules

It is a challenge to find a general expression for $A_\infty^E$ that can be simplified to $A_{\infty\, vdw}^E$ in the Twu-Coon infinite-pressure mixing rules (Eqs. 27 and 28). As mentioned previously, Orbey and Sandler modified the $G^E$ model of NRTL to a different form to reduce the Wong-Sandler mixing rules to the conventional van der Waals mixing rules. Twu et. al. [23] developed a new excess Gibbs energy function, which reduces to the van der Waals one-fluid mixing rule (Eqs. 18 and 19). The incorporation of this new excess Gibbs function into a CEOS allows the Twu-Coon infinite-pressure mixing rules to smoothly transition to the conventional van der Waals one-fluid mixing rules. A general multi-component equation for a liquid activity coefficient model is proposed by Twu et. al. [23] for incorporation in the infinite-pressure mixing rules:

$$\frac{G^E}{RT} = \sum_i^n x_i \frac{\sum_j^n x_j \tau_{ji} G_{ji}}{\sum_k^n x_k G_{ki}} \qquad (31)$$

Eq. 31 appears to be similar to the NRTL equation, but there is a fundamental difference between them. NRTL assumes $A_{ij}$, $A_{ij}$, and $\alpha_{ij}$ are the parameters of the model, but the TST excess Gibbs energy model assumes $\tau_{ij}$ and $G_{ij}$ are the binary-interaction parameters. More importantly, any appropriate temperature-dependent function can be applied to $\tau_{ij}$ and $G_{ij}$. For example, to obtain the NRTL model, $\tau_{ij}$ and $G_{ij}$ are calculated as usual from the NRTL parameters $A_{ij}$, $A_{ij}$ and $\alpha_{ij}$:

$$\tau_{ij} = A_{ij}/T \qquad (32)$$

$$G_{ij} = \exp[-\alpha_{ij}\tau_{ij}] \qquad (33)$$

In this way, the NRTL parameters reported in the DECHEMA Chemistry Data Series can be used in Eqs. 32 and 33, and both the NRTL model and the TST model (Eq. 31) are equally accurate for use in phase equilibrium calculations.

Eq. 31 reduces to the conventional van der Waals mixing rules when the following expressions are used for $\tau_{ij}$ and $G_{ij}$:

$$\tau_{ij} = (\delta_{ij} b_i)/2 \qquad (34)$$

$$G_{ji} = b_j/b_i \qquad (35)$$

where:

$$\delta_{ij} = -\frac{C_1}{RT}\left[\left(\frac{\sqrt{a_i}}{b_i} - \frac{\sqrt{a_j}}{b_j}\right)^2 + 2k_{ij}\frac{\sqrt{a_i}}{b_i}\frac{\sqrt{a_j}}{b_j}\right] \qquad (36)$$

Eqs. 34 and 35 are expressed in terms of the CEOS parameters $a_i$ and $b_i$ and the binary interaction parameter $k_{ij}$. Substituting Eqs. 34 and 35 into Eq. 31, the excess Gibbs free energy of the van der Waals fluid is obtained. Subsequently, Eqs. 27 and 28 reduce to the classical van der Waals one-fluid mixing rules (Eqs. 18 and 19). The discussion above demonstrates that Eq. 31 is more generic than NRTL. Both the NRTL and van der Waals fluid models are special cases of the excess Gibbs free energy function expressed in Eq. 31.

The TST infinite-pressure mixing rules are represented by Eqs. 27–36 and can be used to model van der Waals fluids and highly non-ideal mixtures. One can choose the appropriate expressions for $\tau_{ij}$ and $G_{ij}$ from Eqs. 34 and 35 for binary pairs that are best described by the van der Waals one-fluid mixing rules, while Eqs. 32 and 33 can be used for pairs that behave non-ideally.

## Twu(*v*) zero-pressure mixing rules

There are generally three approaches for developing excess Helmholtz energy mixing rules for CEOS: the infinite-pressure mixing-rule approach *(18, 19, 22, 29)*; the zero-pressure approach *(3, 24–29)*; and the no-reference-pressure approach *(30)*, which will not be discussed here. There is a fundamental difference behind these approaches: The infinite-pressure approach assumes the excess Helmholtz energy to be independent of pressure, whereas the zero-pressure and the no-reference-pressure approaches assume that the reduced liquid volume is either constant or the same as that calculated from a CEOS using the van der Waals mixing rule for its *a* and *b* parameters.

As mentioned, the infinite-pressure approach introduces binary interaction parameters to correct the assumption of the constant excess Helmholtz energy, but it is still unable to accurately reproduce the incorporated liquid activity coefficients. To correct this shortcoming, Twu et. al. *(28)* developed the following zero-pressure mixing rules:

$$a^* = b^*\left[\frac{a^*_{vdw}}{b^*_{vdw}} + \frac{1}{C_{v_0}}\left(\frac{A^E_\infty}{RT} - \frac{A^E_{\infty vdw}}{RT}\right)\right] \qquad (37)$$

$$b^* = \frac{b^*_{vdw} - a^*_{vdw}}{1 - \left[\frac{a^*_{vdw}}{b^*_{vdw}} + \frac{1}{C_{v_0}}\left(\frac{A^E_\infty}{RT} - \frac{A^E_{\infty vdw}}{RT} - \ln\left(\frac{b_{vdw}}{b}\right)\right)\right]} \qquad (38)$$

Eqs. 37 and 38 are labeled as Twu(*v*) mixing rules. The parenthetic *v* parameter signifies that the mixing rule is volume-de-

pendent. Also, the EOS *a* and *b* parameters, denoted as $a_{vdw}$ and $b_{vdw}$, are evaluated from the van der Waals mixing rules without using binary interaction parameters:

$$a_{vdw} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \qquad (39)$$

$$b_{vdw} = \sum_i \sum_j x_i x_j \left[\frac{1}{2}\left(b_i + b_j\right)\right] \qquad (40)$$

$C_{v0}$ is a function of reduced liquid volume at zero pressure, or $v_0^* = v_0/b$:

$$C_{v_0} = -\frac{1}{(w-u)}\ln\left[\frac{v_0^* + w}{v_0^* + u}\right]_{vdw} \qquad (41)$$

The zero-pressure liquid volume $v_0^*{}_{vdw}$ is calculated from the TST CEOS using the van der Waals mixing rule for *a* and *b*, setting pressure equal to zero and selecting the smallest root.

$$v_0^*{}_{vdw} = \frac{1}{2}\left\{\left(\frac{a^*}{b^*} - u - w\right) - \left[\left(u + w - \frac{a^*}{b^*}\right)^2 - 4\left(uw + \frac{a^*}{b^*}\right)\right]^{\frac{1}{2}}\right\} \qquad (42)$$

Eq. 42 has a root as long as the following condition is met:

$$\frac{a^*}{b^*} \geq (2 + u + w) + 2\sqrt{(u+1)(w+1)} \qquad (43)$$

In Eqs. 37 and 38, $A^E_0$ and $A^E_{0\,vdw}$ are the excess Helmholtz energies at zero pressure. As stated, subscript *vdw* in $A^E_{0\,vdw}$ denotes that the properties are evaluated from the CEOS using the van der Waals mixing rule (Eq. 39–40) for its *a* and *b* parameters.

There are numerous useful features present in the Twu(*v*) mixing rules, such as their ability to reduce to the van der Waals mixing rule when $A^E_0 = A^E_{0\,vdw}$. The mixing rules also satisfy the quadratic composition dependence of the second virial coefficient boundary condition. But most importantly, the Twu(*v*) mixing rules are density dependent in an explicit form, which allows them to reproduce, almost exactly, the incorporated $G^E$ model (Eq. 31). The mixing rules provide excellent agreement between experimental data and VLE predictions over a wide range of temperatures and pressures using the information contained only in this $G^E$ model.

The mixing rule for parameter *b* defined in Eq. 38 satisfies the quadratic composition dependence of the second virial coefficient. Alternatively, the conventional linear mixing rule (Eq. 19) could be chosen to solve for *b*, in which case the quadratic composition dependence of the second virial coefficient would be ignored. The mixing rule — either with or without the second virial coefficient constraint — has little effect on the phase equilibrium prediction *(28)*.

## Twu(*r*) zero-pressure mixing rules

The Twu(*v*) mixing rules (Eqs. 37 and 38) are density-de-

pendent through the function $C_{v0}$. $C_{v0}$, as defined by Eq. 41, is calculated from $v_0^{*}{}_{vdw}$, which is defined in Eq. 42. Solving for $C_{v0}$ via Eq. 42 can cause problems when Eq. 42 has no real root. This may occur when the inequality in Eq. 43 is not satisfied. In such cases, one must extrapolate to find $v_0^{*}$. However, by eliminating the need to calculate $v_0^{*}$ from the EOS, one can assume that the zero-pressure liquid volume of the van der Waals fluid, $v_0^{*}{}_{vdw}$, is a constant, defined here as $r$:

$$v_0^{*}{}_{vdw} = r \tag{44}$$

Substituting Eq. 44 into Eq. 41 yields:

$$C_{v_0} = -\frac{1}{(w-u)} \ln\left[\frac{r+w}{r+u}\right] \tag{45}$$

The symbol $C_r$ is used to replace $C_{v0}$ to signify that $C_r$ is a

constant — *i.e.*, no longer a density-dependent function. Eqs. 37 and 38 then become:

$$a^{*} = b^{*}\left[\frac{a^{*}_{vdw}}{b^{*}_{vdw}} + \frac{1}{C_r}\left(\frac{A^{E}_{\infty}}{RT} - \frac{A^{E}_{\infty vdw}}{RT} - \ln\left(\frac{b_{vdw}}{b}\right)\right)\right] \tag{46}$$

$$b^{*} = \frac{b^{*}_{vdw} - a^{*}_{vdw}}{1 - \left[\frac{a^{*}_{vdw}}{b^{*}_{vdw}} + \frac{1}{C_r}\left(\frac{A^{E}_{\infty}}{RT} - \frac{A^{E}_{\infty vdw}}{RT} - \ln\left(\frac{b_{vdw}}{b}\right)\right)\right]} \tag{47}$$

Eqs. 46 and 47 are called the volume-independent Twu mixing rules, expressed as Twu($r$) to differentiate them from the volume-dependent mixing rules, Twu($v$). The parameter ($r$) signifies that the Twu($r$) model is not a function of liquid density $v_0^{*}$. Rather, it depends on the selected value of $r$.

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$A^E_{0\ vdw}$ in Eqs. 46 and 47 can be derived from the EOS by assuming a fixed reduced liquid volume $r$ for a van der Waals fluid at zero pressure:

$$\frac{A^E_{0\ vdw}}{RT} = \sum_i x_i \ln\left(\frac{b_i}{b_{vdw}}\right) + C_r\left[\frac{a^*_{vdw}}{b^*_{vdw}} - \sum_i x_i \frac{a^*_i}{b^*_i}\right] \qquad (48)$$

Since $v^*_{0\ vdw}$ depends on the composition and mixture temperature, the assumption of constant $v^*_{0\ vdw}$ sacrifices, to some extent, the quality of the match between the EOS and the $G^E$ model. Nevertheless, this kind of simplification has major benefits. As previously mentioned, the rigorous zero-pressure mixing rules require the value of zero-pressure liquid volume at system temperature. However, high temperatures can result in low values of $a^*/b^*$, thereby violating Eq. 43 and making it impossible to find a liquid-volume root of the EOS at zero pressure. The simplification of the zero-pressure mixing rules obviates the need to calculate liquid volume at zero pressure and is one way to extend the range of the method.

The simplified Twu($r$) mixing rules given by Eqs. 46 and 47 are no longer a function of liquid density $v^*_0$. Rather, they depend only on the selected value of $r$. Therefore, the selection of an appropriate value of $r$ in the mixing rule is the key factor for improving the accuracy of VLE calculations. A universal value of $r = 1.18$, determined from the information of the incorporated $G^E$ model for SRK, has been recommended by Twu et. al. *(29)* for use in the phase equilibrium prediction for all systems.

## TST zero-pressure mixing rules

Once again, a problem exists in finding a general equation for $A^E_0$ to reduce to $A^E_{0\ vdw}$ in the Twu($r$) zero-pressure mixing rules. Twu et. al. *(23)* have developed a new excess Gibbs energy function, $G^E$ (Eq. 31) to allow the infinite-pressure mixing rules to transition smoothly to the van der Waals mixing rules. Twu et. al. *(3)* recently proposed a methodology to reduce the zero-pressure mixing rules to the van der Waals mixing rules. Since the excess Helmholtz energy is less pressure-dependent than the excess Gibbs energy, Twu et. al. assume that the excess Helmholtz energy of the van der Waals fluid at zero pressure given by Eq. 48 can be approximated by the excess Helmholtz energy of the van der Waals fluid at infinite pressure.

$$\frac{A^E_{0\ vdw}}{RT} = \frac{A^E_{\infty\ vdw}}{RT} = C_1\left[\frac{a^*_{vdw}}{b^*_{vdw}} - \sum_i x_i \frac{a^*_i}{b^*_i}\right] \qquad (49)$$

This approximation permits the use of the versatile liquid $G^E$ model given by Eq. 31 in the zero-pressure mixing rule, to reduce Eq. 31 to the van der Waals mixing rule.

To correct the approximation that the excess Helmholtz energy of a van der Waals fluid at zero pressure equals the excess Helmholtz energy of the van der Waals fluid at infinite pressure, the authors use the binary interaction parameter, $k_{ij}$ to the van der Waals mixing rule for its $a$ parameter, $a_{vdw}$:

$$a_{vdw} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}\ (1 - k_{ij}) \qquad (50)$$

Alternatively, the binary interaction parameter, $l_{ij}$, can be introduced to the van der Waals mixing rule for its $b_{vdw}$:

$$b_{vdw} = \sum_i \sum_j x_i x_j \left[\frac{1}{2}(b_i + b_j)\right](1 - l_{ij}) \qquad (51)$$

The TST zero-pressure mixing rules are represented by Eqs. 31, 46, 47, 49, 50 and 51. The parameter $k_{ij}$ or $l_{ij}$ is derived from reported parameters of the activity coefficient model instead of additional data or a correlation. Since $k_{ij}$ or $l_{ij}$ in Eq. 50 or 51 requires no additional data or regression, the TST mixing rule essentially has the same number of parameters as the incorporated liquid activity model.

In conclusion, incorporating an excess Helmholtz energy mixing rule into any CEOS, such as the TST, PR or SRK using the Twu alpha function will produce accurate results during phase equilibrium calculations. Engineers can select any one of these equations of state without having to worry about discrepancies in the outcomes as long as the same $A^E$ mixing rule and the same alpha function are used. The TST equation of state is the preferred choice for polymer systems because it provides a more-accurate liquid-density prediction, which is quite important for polymer solutions.

If an EOS method is selected for calculations, one would likely pick from TST, PR or SRK. Then, the user should choose the most-appropriate Twu et. al. alpha function and the most advanced TST excess energy mixing rules for an accurate prediction of phase equilibrium for systems containing either nonpolar and/or polar components. The TST method allows the

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