# Avoiding the Use of Critical Constants in Cubic Equations of State

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*A new way to define the two parameters a, b of the Redlich–Kwong equation of state without using the critical constants is introduced. First, the "shifted" covolume (b–c) of the Peneloux modification of the equation of state is estimated by group contributions (for a wide range of compounds); from it and one vapor pressure–liquid density pair, the covolume b is then determined. The attractive parameter a is derived, at any temperature, from the covolume and the compound vapor pressure. The proposed method makes it possible to treat substances whose critical constants are not known (heavy or thermally unstable compounds) by using one density value and the vapor pressure curve. Examples are given of vapor–liquid equilibrium calculations.*

## Introduction

Two-parameter, cubic equations of state (EOS) for the calculation of vapor-liquid equilibria (VLE) and physical properties have found wide application, due to their accuracy and simplicity. In particular, they require the knowledge of the critical constants $T_c$, $P_c$ and the vapor pressure curves, from which pure compound parameters of the EOS can be determined.

For any compound, it is a usual practice to determine the values of the covolume $b$ and of the attractive parameter, at the critical temperature, by imposing the critical constraints (that is, that the first and second derivatives of pressure with volume be zero at the critical point), from which one obtains

$$b = \Omega_b (RT_c/P_c) \tag{1}$$

$$a(T_c) = a_c = \Omega_a (R^2 T_c^2/P_c), \tag{2}$$

where $\Omega_a$, $\Omega_b$ are constants, depending on the EOS. In particular, for the Redlich–Kwong EOS, which will be used here, $\Omega_b = 0.08664$, $\Omega_a = 0.42748$.

The covolume is usually assumed constant, while the attractive parameter is fitted to the compound vapor pressure curve, in order to ensure the best results in VLE calculations. It is normal practice to write $a(T)$ as a product of the critical value $a(T_c)$ and a correction factor $\alpha(T_r)$, which can be determined in two ways, at any temperature:

(a) Through an expression $\alpha(T_r)$, whose coefficients for each substance have been determined by regression of experimental vapor pressures. A popular expression for hydrocarbons is (Soave, 1972)

$$\alpha = \left[1 + m(\omega)\left(1 - \sqrt{T_r}\right)\right]^2 \tag{3}$$

where $\omega$ is the compound acentric factor and $m(\omega)$ is a universal function, typical of the EOS considered.

(b) Alternately, when the temperature is below the compound critical temperature, $\alpha$ can be determined directly from the experimental vapor pressure by a procedure that has been described by Soave (1986); it implies the calculation of the ratio $(P_r^{\text{sat}}/T_r)$ and from it, by a universal function, the ratio $(\alpha/T_r)$, wherefrom $\alpha$. This procedure avoids any vapor pressure regression and the errors involved in it, but of course it cannot be applied beyond the critical temperature.

In any case, all the data needed for any pure compound are its critical constants $T_c$, $P_c$ and its vapor pressure curve.

In spite of the very limited information required, this can still be a problem for substances that decompose before reaching their critical temperature; it is the case of heavy hydrocarbons (more than, say, $C_{12}$, although for $n$-alkanes up

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to $n$-eicosane critical constants have been measured by sophisticated techniques) and, more frequently, organic polar substances. So far, the lack of their critical constants has prevented their treatment by cubic EOSs.

The purpose of this work is to investigate how to avoid the use of critical constants in cubic EOSs. The results will show that this is possible, by the use of group contributions.

## Which Parameters Are Really Needed?

The procedure just outlined to determine component parameters requires the knowledge of the critical constants $T_c$ and $P_c$; now we show that their separate values are not needed, but only their ratio $(T_c/P_c)$, if the vapor pressure curve is known.

To prove that, let us consider a typical cubic EOS, such as the Redlich–Kwong one, in the enhanced version proposed by Peneloux (Peneloux et al., 1982), who introduced a volume shift $c$ to improve its volumetric behavior:

$$P = \frac{RT}{v+c-b} - \frac{a(T)}{(v+c)(v+c+b)} = RT\left(\frac{1}{v+c-b} - \frac{a}{RTb}\cdot\frac{b}{(v+c)(v+c+b)}\right). \quad (4)$$

Both $b$ and $c$ are assumed to be constant, as usual; the covolume $b$ can be expressed by Eq. 1, the volume shift $c$ by the following:

$$c = \delta R\left(\frac{T_c}{P_c}\right), \quad (5)$$

where $\delta$ is a constant, which is determined from one experimental liquid density.

As a third parameter, the ratio $(a/RTb)$ is taken, which, according to Eqs. 1 and 2, is given by:

$$\frac{a}{RTb} = \frac{\Omega_a}{\Omega_b}\frac{\alpha}{T_r}. \quad (6)$$

In terms of dimensionless variables, Eq. 4 can be rewritten as

$$(Z+C)^3 - (Z+C)^2 + B(Z+C)\left(\frac{A}{B} - 1 - B\right) - \frac{A}{B}B^2 = 0, \quad (7)$$

where

$$Z = \frac{Pv}{RT} \quad (8)$$

$$A = \frac{aP}{R^2T^2} = \alpha(T)\Omega_a\frac{P_r}{T_r^2} = \frac{\alpha(T)}{T_r}\Omega_a\frac{P}{T}\frac{T_c}{P_c} \quad (9)$$

$$B = \frac{bP}{RT} = \Omega_b\frac{P_r}{T_r} = \Omega_b\frac{P}{T}\frac{T_c}{P_c} \quad (10)$$

$$C = \frac{cP}{RT} = \delta\frac{T_c}{P_c}\frac{P}{T} \quad (11)$$

$$\frac{A}{B} = \frac{\Omega_a}{\Omega_b}\frac{\alpha}{T_r}. \quad (12)$$

Now, it has been shown (Soave, 1986) that, for any two-parameter cubic EOS, the group $(\alpha/T_r)$ is a direct, universal function of (it can be directly determined from) the ratio $P_r/T_r$ at saturation:

$$\frac{\alpha}{T_r} = f_{\mathrm{EOS}}\left(\frac{P_r^{\mathrm{sat}}}{T_r}\right) \quad (13)$$

with:

$$\frac{P_r^{\mathrm{sat}}}{T_r} = \left(\frac{P^{\mathrm{sat}}}{T}\right)\left(\frac{T_c}{P_c}\right), \quad (14)$$

where only the $(T_c/P_c)$ ratio is involved. According to the equations just reported, the same is true for all parameters contained by Eq. 7.

We can then conclude that, in addition to the vapor pressure curve, only the $(T_c/P_c)$ ratio, that is, the covolume, is required in order to use the Redlich–Kwong equation of state being considered.

While vapor pressures are usually well known, even for heavy or thermally unstable compounds, the problem of how to evaluate the covolume remains. We shall see below that, unlike the critical constants, it can be estimated accurately by the use of group contributions.

## Prediction of the Covolume by Using Group Contributions

Figure 1 plots the covolumes of $n$-alkanes $C_5$ to $C_{16}$, calculated by Eq. 1 for the Redlich–Kwong EOS and expressed as deviations from the straight line connecting $C_5$ and $C_{16}$ values, against the number of carbon atoms. Values of critical constants are from TRC tables (1989). Covolumes $b$ do not stay on a straight line: to evidence their curvature, their deviations (residuals) from the straight line connecting the two extreme points are reported. Therefore, unfortunately, covolumes cannot be estimated through group contributions; Elbro et al. (1991) tried to express the liquid volumes through group contributions, but the results were not satisfactory.

The results are much better with the differences $(b-c)$, which can be considered, according to Eq. 4, as the "shifted" covolume. In fact, when Eq. 4 is rearranged as

$$(v+c) - b = \frac{RT(v+c)(v+c+b)}{P(v+c+b)(v+c) + \alpha(T)a_c} \quad (15)$$

and the limit is taken for $P \to \infty$, one obtains

$$\lim_{P\to\infty}(v+c-b) = 0 \qquad \text{that is,} \qquad \lim_{P\to\infty} v = b - c. \quad (16)$$

As it can be seen from Eqs. 1 and 5, as well as in the expression of $(b-c)$:

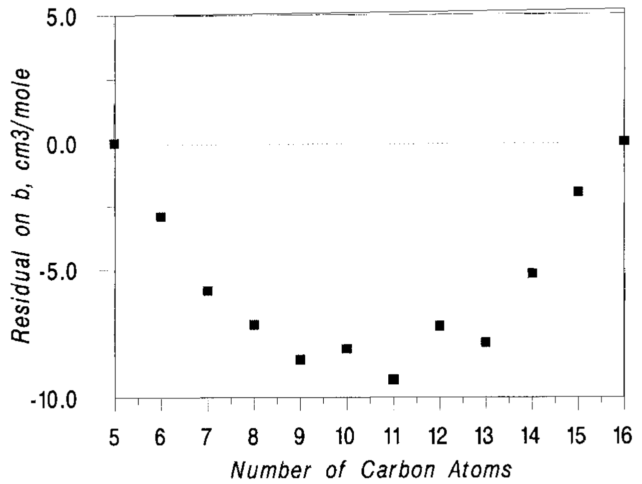

**Figure 1.** **Covolumes *b* for *n*-alkanes expressed as deviations from the straight line connecting $C_5$ and $C_{16}$ values.**

$$(b-c)=(\Omega_b-\delta)\frac{RT_c}{P_c}, \qquad (17)$$

only the $(T_c/P_c)$ ratio is involved.

The calculation of $(b-c)$ is relatively simple and requires only the critical constants and a pair of liquid density and vapor pressure values, at the same temperature. The procedure can be summarized as:

- Calculate the covolume $b$ by Eq. 1.
- Determine the ratio $(\alpha/T_r)$ from $(P_r^{sat}/T_r)$ (Soave, 1986) and from it the attractive parameter (Eq. 6).
- Solve the EOS (Eq. 4) and obtain $(v+c)$, whence the volume shift $c$.

Data needed for calculations have been taken from TRC (1989), Reid et al. (1988), and Ambrose and Walton (1989).

Figure 2 shows the residuals of $(b-c)$, that is, the deviations from the straight line connecting the two extreme points, for the $n$-alkane series considered in Figure 1. They are now situated accurately along a straight line. Therefore, group contributions can be determined for the $CH_2$ and $CH_3$ groups, from the slope and the intercept of the straight line, respectively.

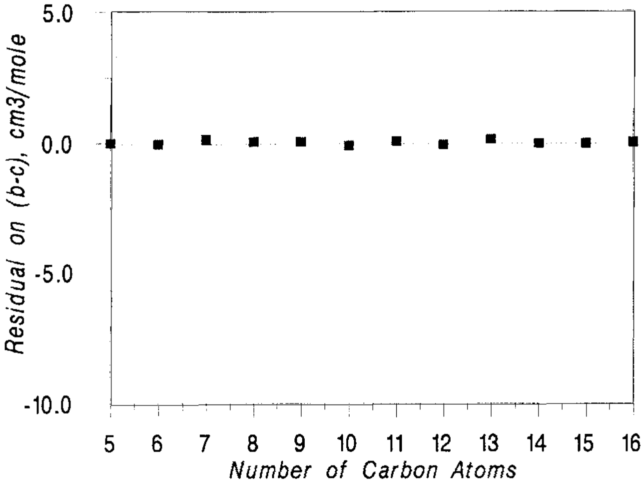

**Figure 2.** **" Shifted" covolumes (*b* − *c*) for *n*-alkanes expressed as deviations from the straight line connecting $C_5$ and $C_{16}$ values.**

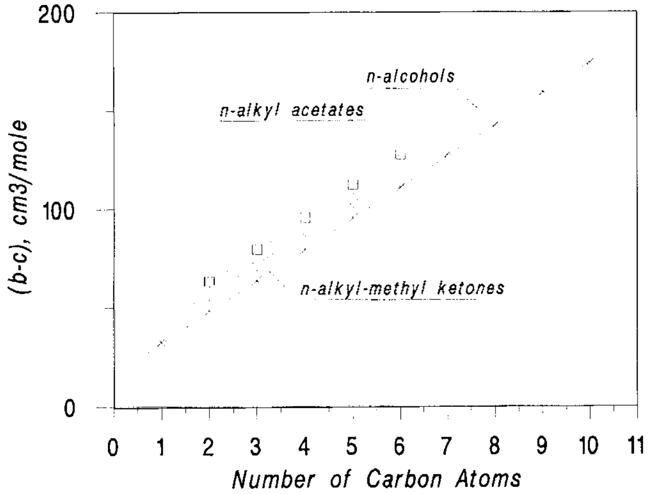

**Figure 3.** **" Shifted" covolumes (*b* − *c*) for some series of organic compounds.**

A similar behavior was observed with other organic compounds. Figure 3 shows the values of $(b-c)$ for some series of organic compounds formed by a non-alkyl functional group linked to $n$-alkyl chains: there is always a linearity with respect to the number of carbon atoms, thus confirming the previous results.

So, by regressing $(b-c)$ values calculated as just outlined, a table of group contributions was determined, which is shown in Table 1. Note that for each value, a quality index is also reported in the last column, to show its reliability: class A indicates a small standard deviation from the average, class B stands for either some dispersion or limited database for calculation, and class C denotes larger errors in the reproduction of $(b-c)$. More details about the regression procedure are given in Appendix A.

It is noteworthy that $(b-c)$ values are insensitive to the temperature as long as it remains below the atmospheric boiling point: Figure 4 shows the temperature dependence of $(b-c)$ for some typical compounds. For heavier compounds, the choice was then to use the commonly available density at 20°C. This was not possible for light compounds. A better choice in this case could be the liquid density at the boiling point, but it led to values of $(b-c)$ less perfectly aligned with those determined for heavier compounds. For that reason, only data of compounds boiling over 20°C were used to determine the group contributions of Table 1.

As an example of the application of the group contributions of Table 1 for the prediction of "shifted" covolumes $(b-c)_{GC}$, the results for a number of significant compounds are shown in Table 4.

## Determining $T_c/P_c$ and $\delta$ from $(b-c)$

Once a table of group contributions is available, the value of $(b-c)$ of any compound can be estimated from its molec-

**Table 1. Values of Group Contributions (GC) to the "Shifted" Covolume**

| Main Group | Subgroup | GC $cm^3/mol$ | Class |
|---|---|---|---|
| $CH_2$ Aliphatics (not cyclic) | $CH_3$ | 20.88 | A |
| | $CH_2$ | 15.93 | A |
| | CH | 10.25 | A |
| | C | 5.12 | A |
| ACH Aromatics | ACH | 12.33 | A |
| | AC | 6.90 | A |
| C = C Alkenes | $\delta(=)$ | 5.59 | A |
| C ≡ C Alkynes | $\delta(\equiv)$ | 9.36 | B |
| $y CH_2$ Aliphatics cyclic | $\delta$(cyclic) | −0.792 | B |
| OH | OH Alcohol | 11.05 | A |
| | OH Phenol | 10.05 | A |
| —O— Ethers | —O— | 6.90 | B |
| —COO— | —COO— Esters | 21.95 | A |
| | HCOO—Formates | 27.13 | B |
| —COOH Acids | —COOH | 27.15 | C |
| C = O Ketones | C = O | 15.47 | B |
| —CHO Aldehydes | —CHO | 19.89 | C |
| —S— Mercaptans-Sulfides | —SH | 21.66 | A–B |
| | —S— | 16.37 | A–B |
| $NH_2$ Amines | $NH_2$ | 12.89 | A–B |
| | NH | 10.71 | A–B |
| | N | 6.12 | A–B |
| CL Chlorides | $—CL_1$ | 17.01 | B |
| | $—CL_2$ | 16.50 | B |
| | $—CL_3$ | 18.54 | B |

ular structure. Now the problem becomes: How can $b$ and $c$ be determined separately from their difference?

Again, it can be seen that one vapor pressure and one liquid density value are needed, at the same temperature (20°C preferably, but not necessarily). The procedure is given in detail in Appendix B. The calculation of $(T_c/P_c)$ is more complicated than the former one for $(b-c)$ and must be executed iteratively, but this is not really important, as it has to be applied only once for any compound. As a consequence, the value of the attractive parameter can also be obtained.

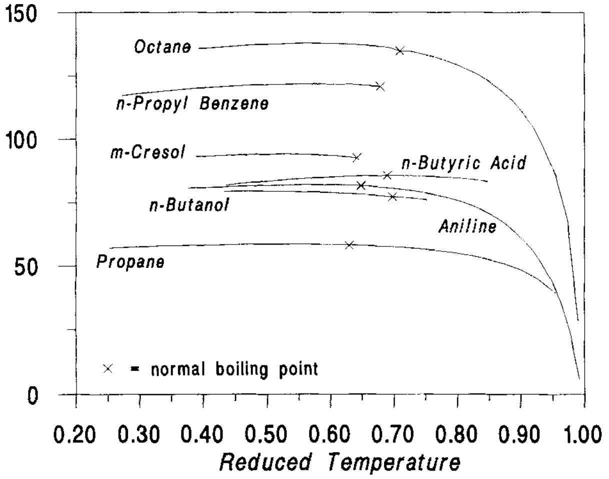

**Figure 4. Temperature dependence of "shifted" covolumes ($b-c$) for some compounds.**

**Table 2. Experimental (exp) vs. Predicted (GC) Values of $(T_c/P_c)$ Ratios**

| Name | $(T_c/P_c)_{exp}$ | $(T_c/P_c)_{GC}$ | Err% |
|---|---|---|---|
| *n*-Pentane | 13.94 | 13.86 | −0.57 |
| Isopentane | 13.62 | 13.90 | 2.06 |
| *n*-Octane | 22.87 | 22.95 | 0.35 |
| Cyclopentane | 11.35 | 11.43 | 0.70 |
| 1-Pentene | 13.18 | 13.02 | −1.21 |
| 2-Methyl-1-butene | 12.21 | 12.50 | 2.37 |
| 2-Methyl-2-butene | 12.30 | 12.88 | 4.71 |
| Benzene | 11.48 | 11.39 | −0.78 |
| Toluene | 14.40 | 14.76 | 2.50 |
| Ethylbenzene | 17.10 | 16.85 | −1.46 |
| *p*-Xylene | 17.55 | 18.20 | 3.70 |
| Methanol | 6.33 | 6.80 | 7.42 |
| Ethanol | 8.36 | 8.96 | 7.18 |
| 1-Propanol | 10.37 | 10.49 | 1.16 |
| 2-Propanol | 10.67 | 11.63 | 9.00 |
| *tert*-Butanol | 12.74 | 13.15 | 3.22 |
| Dimethyl sulfide | 9.10 | 9.04 | −0.66 |
| Diethyl sulfide | 14.07 | 14.24 | 1.21 |
| Ethyl mercaptan | 9.09 | 9.14 | 0.55 |
| Propionaldehyde | 10.39 | 9.92 | −4.52 |
| Acetone | 10.91 | 10.87 | −0.37 |
| Methylisopropyl ketone | 14.56 | 15.20 | 4.40 |
| Diethyl ketone | 15.20 | 14.30 | −5.92 |
| Isopropyl amine | 10.39 | 11.39 | 9.62 |
| *n*-Butyl-amine | 13.04 | 12.82 | −1.69 |
| Diethyl amine | 13.39 | 12.41 | −7.32 |
| Diethyl ether | 13.00 | 12.78 | −1.69 |
| Butyl methyl ether | 15.21 | 15.15 | −0.39 |
| Methyl *t*-butyl ether | 14.49 | 14.59 | 0.69 |
| Dipropyl ether | 17.52 | 18.58 | 6.05 |

The calculation procedure of component parameters $A$, $B$, $C$ from their $T_c/P_c$ ratio and vapor pressure is given by Eqs. 9 to 14. Mixture parameters are then calculated by the proper mixing rules.

It is thus possible to apply the cubic EOS to calculate thermodynamic properties and phase equilibria of pure compounds and mixtures, at any temperature and pressure, provided that the vapor pressure of components whose critical constants are not available is known.

## Validation of the Proposed Method

In Table 2 a first comparison is given between experimental and calculated $(T_c/P_c)$ ratios. The agreement is in general only fair, but a more significant validation can be set by comparing the values of experimental properties and those calculated with both predicted and true (that is, derived from experimental $T_c$ and $P_c$) component parameters.

### *Pure compounds*

In this case, we have considered the prediction of pure compound heats of vaporization, which are closely connected to thermal properties such as enthalpy and entropy. Starting from the general equation (Smith and Van Ness (1987)):

$$\frac{h-h_{id}}{RT} = Z - 1 - \frac{1}{RT}\int_{\infty}^{v}\left[P - T\left(\frac{\partial P}{\partial T}\right)_v\right]dv, \qquad (18)$$

**Table 3. Calculation of Enthalpy of Vaporization at the Normal Boiling Point for Significant Groups***

| Family | RMSD%(Crit) | RMSD%(GC) | ΔRMSD% |
|---|---|---|---|
| Alkanes | 0.95 | 0.93 | 0.02 |
| Alkenes | 1.68 | 1.63 | 0.05 |
| Aromatics | 0.51 | 0.47 | 0.04 |
| Alcohols | 2.04 | 1.95 | 0.09 |
| Ethers | 1.08 | 1.04 | 0.03 |
| Ketones | 1.88 | 1.89 | −0.01 |
| Amines | 2.09 | 2.05 | 0.04 |
| Sulfides | 0.67 | 0.72 | 0.05 |

*RMSD% Using Experimental Critical Constants (Crit) and with Group Contributions (GC).

$$\frac{h-h_{id}}{RT}=Z-1+T\cdot\frac{d(A/B)}{dT}\ln\left(1+\frac{B}{Z+C}\right),\qquad(19)$$

whence

$$\frac{\Delta h_v}{RT}=(Z^V+C)-(Z^L+C)+T_r\cdot\frac{d(A/B)}{dT_r}\cdot\left[\ln\left(1+\frac{B}{Z^V+C}\right)-\ln\left(1+\frac{B}{Z^L+C}\right)\right],\qquad(20)$$

where $(Z^V+C)$ and $(Z^L+C)$ are obtained by solving Eq. 7 and the derivative of $A/B$ is calculated from that of the vapor pressure, according to Eq. 13:

$$T_r\left(\frac{d(A/B)}{dT_r}\right)=\frac{\Omega_a}{\Omega_b}\frac{df_{\text{EOS}}}{d(P_r/T_r)}\left(\frac{dP_r^{\text{sat}}}{dT_r}-\frac{P_r^{\text{sat}}}{T_r}\right).\qquad(21)$$

Table 3 shows the percent root-mean-square deviation of the heats of vaporization at the atmospheric boiling points, calculated for various classes of compounds with the RK EOS and parameters $A$, $B$, $C$ both predicted with the proposed group contributions method and calculated from experimental critical constants. In all cases, parameters $A/B$ and their derivatives were determined directly from experimental vapor pressures. Experimental heats of vaporization were taken from the books of Majer and Svoboda (1985) and of Wilhoit and Zwolinski (1971).

It can be seen that both routes give acceptable results and that very similar values are obtained both with experimental and with predicted critical constants, thus proving that the prediction of parameters does not introduce any further inaccuracy.

### *Mixtures*

To show some potentials of the proposed method when dealing with mixtures, the correlation of experimental binary VLE data was considered: the RK EOS, with component parameters either calculated from experimental critical constants or predicted from group contributions, was applied. In both cases pure component $A/B$ ratios were determined directly from experimental vapor pressures.

For hydrocarbon mixtures the classic mixing rules were applied:

$$A=\sum_i\sum_j x_ix_j(1-k_{ij})(A_iA_j)^{1/2}\qquad(22)$$

$$B=\sum_i x_iB_i,\qquad(23)$$

with $k_{12}=k_{21}$ as the only adjustable parameter.

For mixtures containing polar components requiring more than one adjustable parameter, Vidal's mixing rules were used (Huron and Vidal, 1979), which are based on Eq. 23 and

$$\frac{A}{B}=\sum_i x_i\left(\frac{A_i}{B_i}-\frac{\ln\gamma_i^\infty}{\ln 2}\right).\qquad(24)$$

The infinite pressure activity coefficients $\gamma_i^\infty$ in Eq. 24 were calculated by the two-parameters NRTL equation:

$$\ln\gamma_i^\infty=x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2+\frac{\tau_{12}G_{12}}{(x_1G_{12}+x_2)^2}\right]\qquad(25)$$

$$G_{ij}=\exp(-\chi_{ij}\tau_{ij})\qquad(26)$$

$$\tau_{ij}=\frac{S_{ij}}{T}\quad\text{with}\quad\chi_{ij}=\chi_{ji}=0.30.\qquad(27)$$

In all cases, $P-T-x-y$ curves resulting from correlations, with either true or predicted component parameters, were practically overlapping; again, it is concluded that the use of group contributions did not introduce any further inaccuracy over the classic procedure. Experimental VLE data were compiled by Gmehling et al. (1980–1988).

Figures 5 to 8 show the results of VLE data correlations for various systems. In many cases, the critical constants of components were not available and their parameters had to be predicted from group contributions. Particularly, Figure 5 refers to a system where the classic mixing rules are suitable for data reduction.

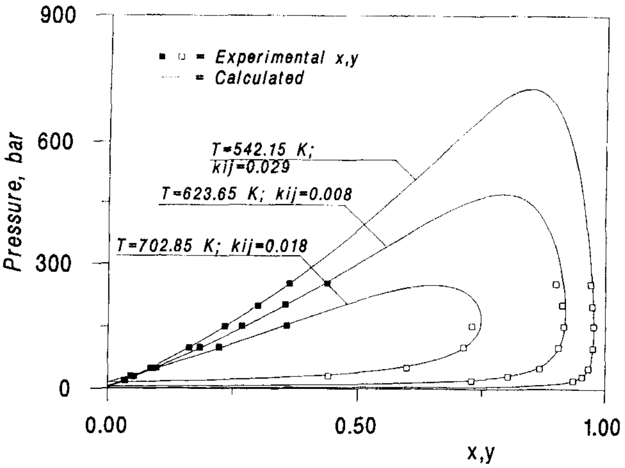

**Figure 5. System methane/diphenylmethane; $P-x-y$ diagram at three temperatures calculated with classic mixing rules; group contributions used for diphenylmethane only.**

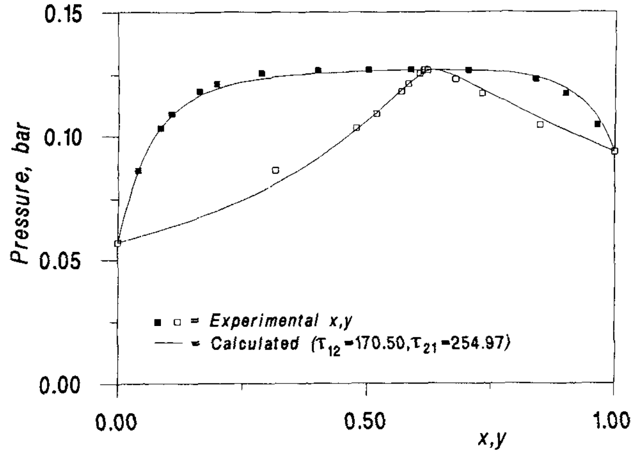

**Figure 6. System *n*-methylaniline/1,2-ethanediol; $P-x-y$ diagram at $T=393.15$ K with Huron-Vidal mixing rules; group contributions used for both components.**

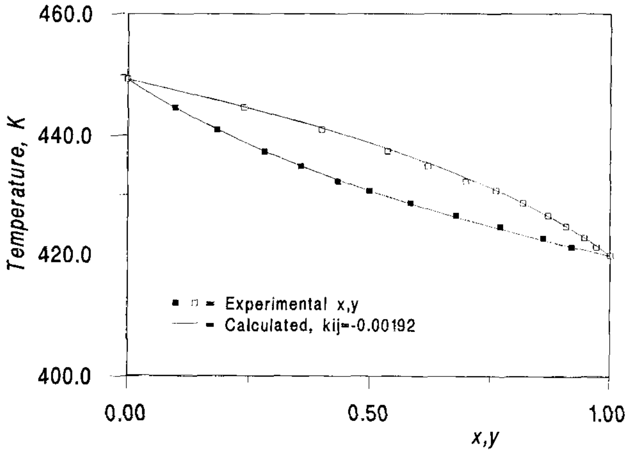

**Figure 8. System hexanoic acid/octanoic acid; $T-x-y$ diagram at $P=0.133$ bar with classical mixing rules; group contributions used for both components.**

The systems presented in Figures 6 and 7 are characterized by stronger interactions and require nonclassic mixing rules. Pure compound parameters have always been predicted by group contributions.

Finally, in Figure 8 an example of how the proposed method can handle mixtures of fatty acids is reported; in this case, classic mixing rules with one adjustable parameter worked fine.

## Conclusion

An original procedure has been developed that allows the treatment by a cubic equation of state of compounds whose critical constants are not available, due to the occurrence of decomposition before reaching their critical temperature.

The only limitation left by the proposed method is the need of vapor pressures of such components. This requirement is common to the activity-coefficient route and is not a serious drawback.

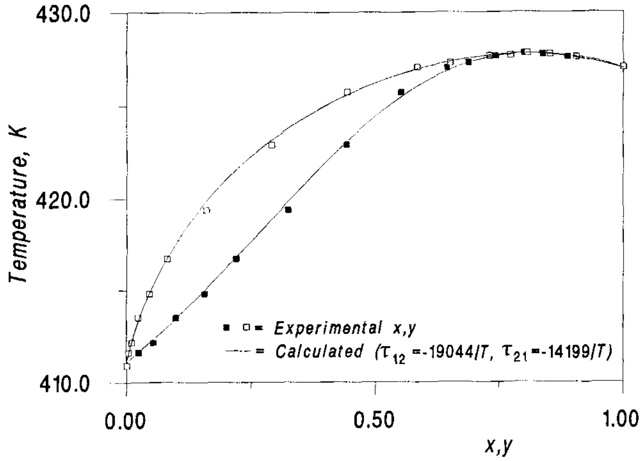

**Figure 7. System *p*-methylacetophenone/*m*-cresol; $T-x-y$ diagram at $P=0.133$ bar with Huron-Vidal mixing rules; group contributions used for both components.**

A table of group contributions for the calculation of the "shifted" covolume $(b-c)$ has been derived for many functional groups.

The proposed procedure has been validated by comparing calculated and experimental thermodynamic properties of pure compounds (heats of vaporization) and binary mixtures (vapor–liquid equilibria). The results obtained are generally satisfactory and comparable to those calculated using experimental critical constants, when available.

In conclusion, the application of equations of state has been extended to compounds whose critical constants are not known, and thus allows their treatment at conditions unattainable by classic calculation methods. One alternate procedure in such cases could be that based on activity coefficients, which, however, cannot be applied at near-critical conditions and require particular, less rigorous procedures in the presence of supercritical components, or dissolved gases.

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## Notation

$f$ = generic function (Eq. 13)
$G$ = binary interaction parameter of the NRTL equation
$h$ = molar enthalpy
$\Delta h$ = molar enthalpy of vaporization
$k$ = binary interaction parameter of the classic mixing rules
$R$ = universal gas constant
$S$ = binary parameter in the NRTL equation
$T$ = temperature
$x$ = mole fraction
$Z$ = compressibility factor
$\tau$ = binary parameter in the NRTL equation
$\chi$ = binary constant in the NRTL equation

### *Superscripts and subscripts*

$L$ = liquid phase
$V$ = vapor phase
$C$ = critical variables
$i$ = component index
$id$ = ideal gas
$j$ = component index
$r$ = reduced variables
$v$ = constant volume

## Literature Cited

Ambrose, D., and J. Walton, "Vapour Pressures up to Their Critical Temperatures of Normal Alkanes and 1-Alkanols," *Pure Appl. Chem.*, **61**, 1935 (1989).

Elbro, H. S., A. Fredenslund, and P. Rasmussen, "Group Contribution Method for the Prediction of Liquid Densities as a Function of Temperature for Solvents, Oligomers, and Polymers," *Ind. Eng. Chem. Res.*, **30**, 2576 (1991).

Gmehling, J., U. Onken, W. Arlt, P. Grenzheuser, U. Weidlich, B. Kolbe, and J. Rarey-Nies, *Vapor-Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Ser., Frankfurt, Germany (1980–1988).

Huron, M., and J. Vidal, "New Mixing Rule in Simple Equations of State for Representing Vapour-Liquid Equilibria of Strongly Non-Ideal Mixtures," *Fluid Phase Equil.*, **3**, 255 (1979).

Majer, V., and V. Svoboda, *Enthalpies of Vaporization of Organic Compounds*, Chemical Data Series No. 32, Blackwell, Oxford (1985).

Peneloux, A., E. Rauzy, and R. Freze, "A Consistent Correction for Redlich-Kwong-Soave Volumes," *Fluid Phase Equil.*, **8**, 7 (1982).

Reid, R., J. M. Prausnitz, and B. Poling, *The Properties of Gases and Liquids*, McGraw-Hill, New York (1988).

Smith, J. M., and H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 4th ed., Chap. 14, McGraw-Hill, New York (1987).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Soave, G., "Direct Calculation of Pure-Compound Vapour Pressures through Cubic Equation of State," *Fluid Phase Equil.*, **31**, 203 (1986).

TRC, "Thermodynamic Tables," Thermodynamics Research Center, Texas A&M Univ., College Station (1989).

Wilhoit, R. C., and B. Zwolinski, *Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds*, Texas A&M Univ. College Station (1971).

## Appendix A: Data Reduction for Determining Values of Group Contributions for ($b$-$c$)

The regression of experimental values of $(b-c)$, that is, values calculated from experimental $T_C$ and $P_C$, was performed sequentially, one group after another, starting from alkanes, for which accurate measurements of the critical constants are available for a large number of compounds. The objective function in the fitting procedure was:

$$obf = \sqrt{\frac{1}{Nc}\sum_{j=1}^{Nc} \mathrm{err}_j^2}, \tag{A1}$$

where $Nc$ is the number of compounds considered and $\mathrm{err}_j$ is calculated from:

$$\mathrm{err}_j = \frac{[(b-c)_{\mathrm{GC}} - (b-c)_{\mathrm{true}}]}{(b-c)_{\mathrm{true}}}. \tag{A2}$$

As a first step, the group contributions of $CH_2$ and $CH_3$ were determined by minimizing the objective function with respect to $n$-alkanes from $C_5$ to $C_{16}$. Then, contributions for CH and C were regressed in the same way on data of branched alkanes (from $C_5$ to $C_9$).

The determination of all the other contributions was performed one functional group at a time, by applying the known contributions of alkyl groups.

We note that the proposed procedure leads to smaller errors when the volume of the considered group is small with respect to that of the whole molecule where the group is present.

With reference to Table 2, we observe that alkenes, alkynes, and cycloalkanes were characterized by introducing an additional contribution, corresponding to the specific functionality: in this way the number of groups could be minimized.

A comparison between true and calculated covolumes $(b-c)$ is given in Table 4 for many compounds.

## Appendix B: Procedure for Determining $b$ and $c$ Separately from ($b$-$c$) and One Vapor Pressure-Liquid Density Pair

The rationale of the procedure reported below is that the value of $(a/RTb)$ obtained from the known vapor pressure and the assumed value of $b$:

$$\frac{a}{RTb} = \frac{\Omega_a}{\Omega_b} f_{\mathrm{EOS}}\left(\frac{P^{\mathrm{sat}}}{T}\frac{T_c}{P_c}\right), \tag{B1}$$

where

$$\frac{T_c}{P_c} = \frac{b}{\Omega_b R}, \tag{B2}$$

must be consistent with the EOS.

$$\frac{P}{RT} = \frac{1}{v+c-b} - \left(\frac{a}{RTb}\right)\frac{b}{(v+c)(v+c+b)}, \tag{B3}$$

where $v$ is the experimental liquid volume at the pressure $P$ (such as the atmospheric pressure), and the volume shift $c$ is given by

$$c = b - (b-c) \tag{B4}$$

with known $(b-c)$.

As a consequence, the value of $b$ is the only unknown. A possible solving procedure is the following:

**Table 4. True (Derived from Experimental $T_c$ and $P_c$) vs. Calculated (GC) Values of $(b-c)$***

| Reg Sub | Name | $(b-c)_{\text{true}}$ | $(b-c)_{\text{GC}}$ | Err% |
|---|---|---|---|---|
| $CH_3$, $CH_2$ | *n*-Pentane | 89.36 | 89.55 | −0.22 |
| $CH_3$, $CH_2$ | *n*-Decane | 169.30 | 169.20 | 0.06 |
| $CH_3$, $CH_2$ | *n*-Pentadecane | 249.42 | 248.85 | 0.23 |
| CH | 3-Methyl-pentane | 104.57 | 104.75 | −0.17 |
| CH | 2,3-Dimethyl-hexane | 135.39 | 135.88 | −0.36 |
| C | 2,2-Dimethyl-hexane | 137.52 | 136.43 | 0.80 |
| CH, C | 2,2,3-Trimethyl-butane | 119.62 | 119.77 | −0.13 |
| $\delta(=)$ | 1-Hexene | 100.45 | 100.44 | −0.01 |
| $\delta(=)$ | 1-Decene | 164.40 | 164.16 | −0.15 |
| $\delta(=)$ | 2-Methyl-2-pentene | 98.94 | 99.53 | 0.59 |
| $\delta(=)$ | 1,3-Pentadiene trans | 79.34 | 78.74 | −0.76 |
| $\delta(\equiv)$ | 1-Butyne | 61.42 | 61.54 | 0.20 |
| $\delta(\equiv)$ | 1-Pentyne | 77.04 | 77.47 | 0.55 |
| ACH | Benzene | 73.85 | 73.98 | 0.17 |
| ACH, AC | *n*-Propylbenzene | 121.02 | 121.29 | 0.22 |
| ACH, AC | *m*-Xylene | 105.40 | 104.88 | −0.50 |
| ACH, AC | 1,3,5-Trimethyl-benzene | 120.60 | 120.33 | −0.22 |
| $\delta$(cycl.) | Cyclopentane | 75.84 | 75.69 | −0.20 |
| $\delta$(cycl.) | Methyl-cyclohexane | 107.18 | 106.03 | −1.09 |
| $\delta$(cycl.) | 1,1,2-Trimethyl-cyclohexane | 120.68 | 121.84 | −0.08 |
| —O— | Diethyl ether | 80.34 | 80.52 | 0.22 |
| —O— | Butyl-methyl ether | 96.34 | 96.45 | 0.12 |
| —O— | Methyl-tert-butyl ether | 95.73 | 95.54 | −0.20 |
| —OH alcohol | 1-Butanol | 79.57 | 79.72 | 0.19 |
| —OH alcohol | 2-Methyl-1-butanol | 94.71 | 94.92 | 0.22 |
| —OH alcohol | 2-Hexanol | 110.54 | 110.85 | 0.28 |
| —OH alcohol | 1-Heptanol | 127.61 | 127.51 | −0.08 |
| C=O | Acetone | 57.31 | 57.23 | −0.13 |
| C=O | Methyl-ethyl ketone | 72.77 | 73.16 | 0.53 |
| C=O | Methyl-*n*-propyl ketone | 88.93 | 89.09 | 0.17 |
| C=O | Ethyl-propyl ketone | 104.08 | 105.02 | 0.89 |
| —COO— | Ethyl acetate | 79.56 | 79.64 | 0.09 |
| —COO— | Ethyl propionate | 95.35 | 95.57 | 0.23 |
| —COO— | Ethyl butyrate | 111.94 | 111.50 | −0.39 |
| —COOH | Propyl formate | 79.98 | 79.87 | −0.14 |
| —OH phenol | Phenol | 79.07 | 78.60 | −0.60 |
| —OH phenol | *m*-Cresol | 93.50 | 94.05 | 0.58 |
| —OH phenol | 2,5-Xylenol | 109.51 | 109.50 | −0.01 |
| $—CL_1$ | 1,2-Dichloroethane | 65.71 | 65.88 | 0.26 |
| $—CL_2$, $—CL_3$ | Pentachloroethane | 103.45 | 103.99 | 0.52 |
| —CL1 | 1-Chlorobutane | 84.27 | 85.68 | 1.64 |
| $—NH_2$ | *n*-Butyl amine | 81.22 | 81.56 | 0.42 |
| $—NH_2$ | *o*-Toluidine | 96.45 | 96.89 | 0.45 |
| $—NH_2$ | *p*-Toluidine | 97.42 | 96.89 | −0.55 |
| —NH— | Dipropyl amine | 116.27 | 116.19 | −0.06 |
| —NH— | Dibutyl amine | 147.94 | 148.05 | 0.07 |
| N | Triethyl amine | 116.39 | 116.55 | 0.14 |
| —COOH | Propionic acid | 64.37 | 63.96 | −0.65 |
| —COOH | *n*-Butyric acid | 82.66 | 79.89 | −3.47 |
| —CHO | Acetaldehyde | 41.10 | 40.77 | −0.80 |
| —CHO | *n*-Butyraldehyde | 71.51 | 72.63 | 1.54 |
| —S— | Dimethyl sulfide | 58.03 | 58.13 | 0.18 |
| —S— | Diethyl sulfide | 90.24 | 89.99 | −0.27 |
| —SH | Methyl mercaptan | 42.48 | 42.54 | 0.14 |
| —SH | Ethyl mercaptan | 58.57 | 58.47 | −0.17 |

*First column (reg sub) reports the structure of fitted subgroups.

- Assume initially $b=(b-c)$
- Calculate $(T_c/P_c)$ with Eq. B2 and $(a/RTb)_1$ with Eq. B1
- From Eq. B3 calculate a second value of $(a/RTb)$:

$$\left(\frac{a}{RTb}\right)_2=\left(\frac{1}{v+c-b}-\frac{P}{RT}\right)\frac{(v+c)(v+c+b)}{b} \qquad \text{(B5)}$$

and the error $(a/RTb)_2-(a/RTb)_1$

- Adjust accordingly the assumed value of $b$
- Calculate $c$ from Eq. B4
- Repeat the whole procedure until convergence is achieved.

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