

Estimation of the critical constants of heavy hydrocarbons for their treatment by the Soave–Redlich–Kwong equation of state

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Abstract

Expressions were derived for the estimation of the critical constants of C_{7+} hydrocarbons from their normal boiling point and specific gravity at 60°F. Experimental critical temperatures were reproduced closely, while the critical pressures were adjusted to reproduce the boiling points at both 10 and 760 mm Hg by the Soave–Redlich–Kwong (SRK) equation of state. The proposed method ensures a greater accuracy in predicting heavy hydrocarbons' vapor pressures below their normal boiling points, with respect to using critical constants estimated by the common literature methods. The developed equations can be applied to hydrocarbons with normal boiling points from 90° to 525°C. © 1998 Elsevier Science B.V.

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1. Introduction

The calculation of vapor–liquid equilibria by an equation of state (EoS) requires as a first condition an accurate estimation of pure-component vapor pressures. For a cubic, two-parameter EoS, this depends on its ability to describe correctly the temperature dependence of the attractive parameter. In particular, for nonpolar compounds like hydrocarbons, we shall use the simple equation which was proposed by this author for the Redlich–Kwong EoS [1] and is frequently applied to other cubic EoSs also:

$$\alpha(T_r) = a(T)/a(T_c) = \left\{ 1 + m \left(1 - \sqrt{T_r} \right) \right\}^2 \quad (1)$$

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The parameter m can be (although it is not necessary) expressed as a function of the acentric factor ω [1]:

$$m = 0.48 + 1.574\omega - 0.176\omega^2 \quad (2)$$

Let us define the combination of the Redlich–Kwong EoS and Eqs. (1) and (2) as the Soave–Redlich–Kwong (SRK) EoS.

The calculation of vapor pressures of nonpolar compounds, especially heavy ones, by the SRK EoS (or any cubic EoS using Eq. (1)) yields usually unsatisfactory results, due to two reasons, mainly: (1) The inaccuracy of the assumed critical constants, which for heavy compounds are not known experimentally, but must be estimated with empirical expressions (Winn [2], Kesler and Lee [3], Riazi and Daubert [4], Twu [5]), which were obtained by correlation of data of light hydrocarbons and are applied outside their field of validity; (2) A further inaccuracy is due to Eq. (1) itself, whose trend is correct in a limited temperature range, namely over the normal boiling temperature. Below it, the calculated vapor pressures diverge rapidly from the experimental ones with decreasing the temperature.

In a comprehensive test, about 120 hydrocarbons C_{7+} were considered. Their critical constants were estimated by one of the above quoted methods. The acentric factors were adjusted to reproduce the normal boiling points (a normal practice with heavy hydrocarbons or petroleum cuts, whose normal boiling point (nbp) is often the only available vapor pressure), and the saturation temperatures were calculated by the SRK EoS at the pressure of 10 mm Hg and compared with the reference values from an available compilation (Zwolinski, Wilhoit [6]). The rms deviations ranged from 1.93°C (with critical constants calculated according to Twu [5]) to 4.90°C (Winn [2]), corresponding to average errors on the vapor pressures well over 10%. With all methods the errors were particularly serious for the n -alkanes over C_{20} .

A simple correction of the expressions for the critical constants to better reproduce their experimental values is not sufficient when using the SRK EoS, owing to the distortions caused by Eq. (1). To compensate for them, it is proposed here to adjust one critical constant (namely, the critical pressure), so as to force the SRK EoS to pass through two points of the vapor pressure curve: the nbp and another low-pressure one.

A typical example of the improvements obtainable is shown in Fig. 1 for n -dodecane. The first curve was calculated using the experimental values of the critical constants and the acentric factor: the calculated vapor pressures are just acceptable over the nbp, but below it they tend to diverge excessively. After adjusting the acentric factor to reproduce the nbp (second curve), the results were even worsened in the low range. Finally, the critical pressure was adjusted from the experimental value (18.17 bars) to 17.73 bars (–2.4%) together with the acentric factor, to reproduce at the same time the nbp and the saturation temperature at 10 mm Hg. That caused a marked improvement of the calculated vapor pressures in the whole range (third curve), with the only exception of the temperatures close to the critical one, which anyway for higher hydrocarbons are outside the range of normal operation. Such improvements were found for all examined compounds.

The proposed procedure thus replaces the true (often estimated) critical pressure by a value derived from vapor pressure data. This is an important advantage, as comprehensive vapor pressure compilations are available from the literature for heavy hydrocarbons also.

The whole procedure which will be followed consists of: (1) deriving (or selecting) an expression for the estimate of the critical temperature of hydrocarbons from their normal boiling point and

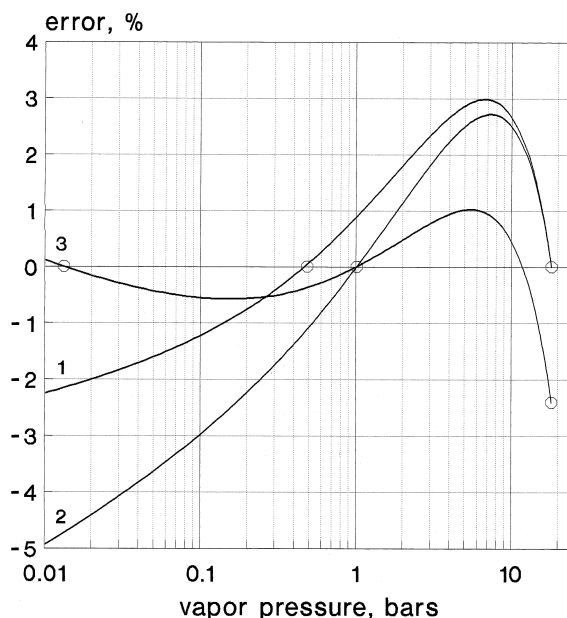


Fig. 1. Errors on *n*-dodecane vapor pressures from 0.01 bars to the critical pressure. Curve no. 1: true acentric factor; curve 2: acentric factor fitted to the nbp; curve 3: acentric factor and critical pressure fitted to the nbp and the saturation temperature at 10 mm Hg.

specific gravity at 60°F (15.5°C); (2) determining a comprehensive set of critical pressures from the estimated critical temperatures and the saturation temperatures at 10 and 760 mm Hg; (3) correlating the critical pressures towards the normal boiling points and specific gravities.

Considering the plenty and the extended range of the available data of *n*-alkanes, hence the possibility to predict accurately their critical constants, the equations for the prediction of the critical constants were divided into two parts: a first one to estimate the critical constants and the specific gravity of *n*-alkanes from their normal boiling point, and a second one for a correction term from the difference between the specific gravity and that of the reference *n*-alkane. Such approach was followed by Twu [5] and proved more accurate than a direct prediction.

2. Normal boiling point of *n*-alkanes as a function of the number of carbon atoms

A relationship between the nbp and the number of C atoms was determined preliminarily, to smooth the nbp values of *n*-alkanes given by Zwolinski and Wilhoit [6]. A first analysis showed that they are well aligned up to C₃₀, with the exception of C₁₈ and C₁₉. Between C₃₀ and C₃₁, there was a discontinuity which obliged to reject the following data.

The remaining values (*n*-alkanes C₇ to C₁₇ and C₂₀ to C₃₀) could be correlated accurately (root mean square deviation 0.06°C, see Table 1 for details) by the equation:

$$\ln(1063.98 - T_b) = 6.972 - 0.118n_C^{2/3} \quad (3)$$

Table 1

Experimental and calculated (Eq. (3)) normal boiling points of *n*-alkanes

n_C	Reference values by Zwolinski and Wilhoit [6]	Eq. (3)	Difference
7	98.43	98.40	−0.03
8	125.68	125.69	0.01
9	150.82	150.85	0.02
10	174.15	174.19	0.03
11	195.93	195.95	0.02
12	216.32	216.33	0.00
13	235.47	235.48	0.01
14	253.58	253.53	−0.05
15	270.68	270.58	−0.10
16	286.86	286.74	−0.12
17	302.02	302.08	0.06
20	343.8	343.83	0.0
21	356.5	356.49	0.0
22	368.6	368.61	0.0
23	380.1	380.21	+0.1
24	391.3	391.34	0.0
25	401.9	402.01	+0.1
26	412.2	412.27	+0.1
27	422.2	422.12	−0.1
28	431.6	431.61	0.0
29	440.8	440.74	−0.1
30	449.6	449.54	−0.1
			rms: 0.059
18	316.3	316.67	+0.4
19	329.9	330.57	+0.7
31	459.	458.03	−1.
32	468.	466.22	−2.
33	476.	474.12	−2.
34	483.	481.76	−1.
35	491.	489.14	−2.
36	498.	496.27	−2.
37	505.	503.17	−2.
38	512.	509.86	−2.
39	518.	516.33	−2.
40	525.	522.59	−2.

When compared to other similar expressions from the literature (Tsonopoulos [7]; Teja et al. [8]; Marano and Holder [9,10]), Eq. (3) yields similar, but more accurate results. It will be used from here on, to generate smoothed values of the nbp of the *n*-alkanes C_7 to C_{40} .

3. Critical temperature of *n*-alkanes

Experimental critical temperature data are restricted to below *n*-eicosane. The critical temperature of higher *n*-alkanes can only be estimated by one of the empirical expressions from the literature

(Ambrose [11]; Tsonopoulos [7]; Teja et al. [8]; Marano and Holder [9,10]), which were determined by correlation of the available data and yield diverging results for higher hydrocarbons (more than 40° of spread for $n\text{-C}_{40}$).

A (hopefully) more consistent and more practical expression was determined by connecting the critical temperature to the nbp directly. The starting point was the observation that literature expressions for T_b and T_c have similar forms, of the type:

$$\ln(a_1 - T_{b,c}) = a_2 - a_3 n_C^{a_4} \quad (4)$$

If the exponents in the equations for T_b and T_c are the same (an exponent 2/3 is used in fact in most literature expressions), a simple expression is obtained:

$$\ln(c_1 - T_c) = c_2 \ln(c_4 - T_b) - c_3 \quad (5)$$

where the coefficients c_1 and c_4 were assumed to be equal, to force the $T_b:T_c$ ratio to tend to the unity with $n_C \rightarrow \infty$, in agreement with Ambrose [11]:

$$\ln(c_1 - T_c) = c_2 \ln(c_1 - T_b) - c_3 \quad (6)$$

Eq. (6) was applied to correlate the critical temperatures of n -alkanes C_7 to C_{18} . The same values selected for their work by Teja et al. [8] were used, excepting C_{16} and C_{17} , for which the data by Ambrose and Walton [12] were preferred. The boiling temperatures were generated by Eq. (3). The following equation was obtained:

$$\ln(939.63 - T_{c0}) = 1.5062 \ln(939.63 - T_b) - 3.5626 \quad (7)$$

which reproduces the selected data with a residual rms deviation of 0.13 K (0.019%), mainly due to the dispersion and rounding-off of the data (see Table 2). Eq. (7) gives a unit limit of the $T_b:T_c$ ratio for $n_C \rightarrow \infty$ and should be preferred to the above quoted literature equations, because it allows a direct calculation of the critical constants of n -alkanes from their boiling points and ensures a better confidence in the extrapolation to high boiling points. The values given by Eq. (7) for heavy

Table 2
Experimental and calculated (Eq. (7)) critical temperatures of n -alkanes

n_C	Rosenthal and Teja [13]	Ambrose and Walton [12]	Anselme et al. [14]	Ambrose and Tsonopoulos [15]	Teja et al. [8]	Selected values	Eq. (7)
7	540.3	540.15	539.8	540.2	540.1	540.1	540.17
8	568.8	568.95	568.6	568.7	568.7	568.7	568.72
9	594.7	594.9	594.5	594.6	594.6	594.6	594.40
10	617.9	617.65	617.5	617.7	617.7	617.7	617.66
11	638.4	638.85	639.0	639.	638.8	638.8	638.86
12	658.8	658.65	658.2	658.	658.4	658.4	658.26
13	676.0	676.	675.8	675.	675.9	675.9	676.10
14	691.8	693.	693.0	693.	692.3	692.3	692.54
15	707.5	708.	708.4	708.	707.8	707.8	707.75
16	722.4	722.	723.0	723.	722.6	722.	721.9
17	735.9	735.	735.3	736.	735.6	735.	734.97
18	747.7	746.	745.8	747.	747.2	747.2	747.19
19		758.					758.59
20		769.					769.24

n-alkanes lie anyway in the same range of the other literature equations. Table 2 shows a comparison of the calculated critical temperatures of *n*-alkanes C_7 – C_{20} with the most recent experimental data.

4. Critical pressure of *n*-alkanes

The critical pressures of *n*-alkanes (or better, their adjusted values for a better prediction of the vapor pressures by the SRK EoS) were determined from the normal boiling points at 10 and 760 mm Hg (10 mm is the lower limit of application of the Antoine equations reported by Zwolinski and Wilhoit [6]; besides, it is important to have a fixed value for the second pressure, to avoid any scattering of the critical pressures).

Like the normal boiling points, also the temperatures at 10 mm reported by Zwolinski and Wilhoit [6] were slightly dispersed. The two temperature sets looked closely connected (see Table 1) by the equations, originally proposed for C_{20+} only (Kudchadker and Zwolinski [16]):

$$\log_{10} P \text{ (mm Hg)} = A - \frac{B}{T + C} \quad (8)$$

$$B = 3.53813T_b - 9.77736 \cdot 10^{-5}T_b^2 - 6.66695 \cdot 10^{-7}T_b^3 \quad (9)$$

$$C = -4.49159 \cdot 10^{-2}T_b - 2.68408 \cdot 10^{-4}T_b^2 - 5.18608 \cdot 10^{-8}T_b^3 \quad (10)$$

$$A = \log_{10}(760) + B/(C + T_b) \quad (11)$$

so it was decided to apply Eqs. (8)–(11) to generate smoothed values of the saturation temperatures at 10 mm Hg of all *n*-alkanes from C_7 on.

At this point any reference to the number of carbon atoms, hence to real compounds, had disappeared, since the *n*-alkanes taken as a reference are now defined by their nbp only. For the sake of uniformity, it was thus decided to assume evenly spaced values of the normal boiling points, from 370 K (C_7) to 800 K (C_{40}), generating for each of them the corresponding critical temperature with Eq. (7) and the saturation temperature at 10 mm Hg with Eqs. (8)–(11).

Then, the critical pressures were determined for each T_c , T_b , t_{10} set, according to the procedure described in Appendix A.

The calculated critical pressures were finally correlated very accurately (rms error 0.03% on the critical pressures, or 0.02°C on the saturation temperatures at 10 mm) by the following equation:

$$\ln P_{c0} = -8.5702 + 7.477(100/T_b)^3 + 1.7968 \ln(1054.9 - T_b) \quad (12)$$

Note that for $n_c \rightarrow \infty$, T_b , $T_c \rightarrow 939.63$ K and $P_c \rightarrow 0.969$ bars, while according to Eq. (7) it should be 1 atm. Such small difference was neglected anyway, considering that the limit $n_c \rightarrow \infty$ is beyond the range of validity of the proposed method and that imposing a correct limit to P_c would have decreased the accuracy of Eq. (12) in the normal range.

Eqs. (7) and (12) give the critical constants of an *n*-alkane having a known nbp. For other hydrocarbons, a correction term should be added to them. Calculation experience showed that corrections can be related to the difference between the specific gravity of the hydrocarbon and that of the corresponding *n*-alkane (specific gravity is often the only known property in addition to the boiling point).

5. Specific gravity of *n*-alkanes

The values of *n*-alkane specific gravities at 60°F are available in the API Project 44 compilations up to $n_c = 40$. From hexadecane on, their values are extrapolated below the melting point. That is not important, as the *n*-alkane used as a reference is a fictitious compound with a given nbp (of course, the final equation set, when applied to real *n*-alkanes, should ensure a correct prediction of their vapor pressures).

To make the correlation of the specific gravities with respect to the boiling points easier, they were expressed by means of the Watson *K* factor:

$$K = (1.8T_b)^{1/3}/S \quad (13)$$

The data of *n*-alkanes C_7 – C_{40} were reproduced within the fourth decimal figure by the equation:

$$K_0 = 11.7372 + 3.336 \cdot 10^{-3}T_b - \frac{976.3}{T_b} + \frac{3.257 \cdot 10^5}{T_b^2} \quad (14)$$

whence, according to Eq. (13), the specific gravity S_0 .

6. Critical temperature of other hydrocarbons

The deviation of the critical constants from those of *n*-alkanes is often expressed as a function of their specific gravities. This is an oversimplification, but the specific gravity of a hydrocarbon or a petroleum fraction is often the only available property, together with its nbp.

Fig. 2 plots the difference of the critical constants of about 40 hydrocarbons from those (calculated by Eq. (7)) of the *n*-alkanes of equal normal boiling point, with respect to the difference of specific gravities (Eq. (14) for the *n*-alkanes). From Fig. 2 we can draw some conclusions: (1) for each class of compounds (alkanes or aromatic hydrocarbons), there is a rough proportionality between $(T_c - T_{c0})$ and $(S - S_0)$; (2) considering the scattering of the points, no higher-degree correlation is possible; (3) the proportionality factor depends on the compound class (aromatic or not), i.e., as a first approximation, from the specific gravity; (4) the boiling point does not seem to affect the dependence of $(T_c - T_{c0})$ from $(S - S_0)$. In conclusion, the correlation to be found is of the type:

$$[(T_c - T_{c0}) \text{ or } T_c/T_{c0}] = f(S) \cdot [(S - S_0) \text{ or } S/S_0] \quad (15)$$

It must be considered now that, excluding *n*-alkanes, the experimental critical temperatures from the literature do not go beyond hydrocarbons C_{10} . Any expression found, when applied to heavier compounds, might give anomalous values of the critical pressures. It was thus preferred to determine both expressions for T_c and P_c at the same time. The procedure followed was:

- assume any two functions for T_c and P_c
- assume a set of coefficients of the two functions
- For each hydrocarbon:
- calculate T_c and P_c
- determine the value of the acentric factor that reproduces the normal boiling point

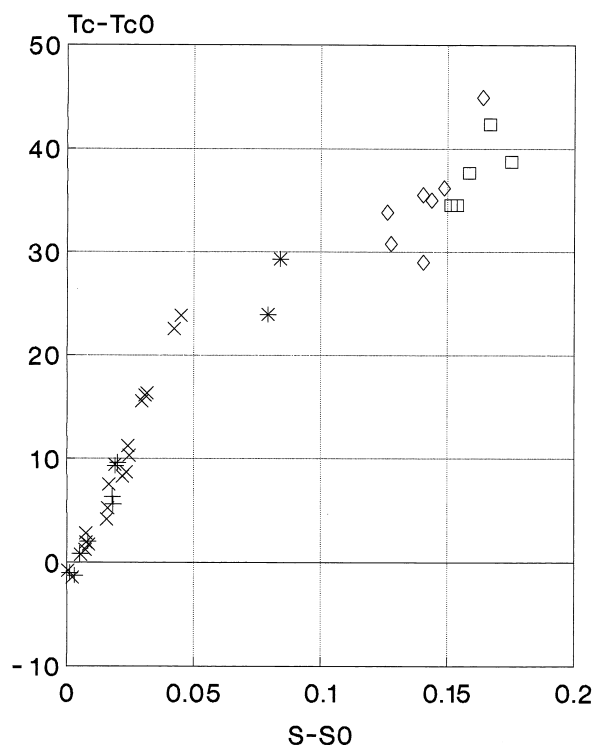


Fig. 2. Deviations ($T_c - T_{c0}$) from the critical temperatures of the n -alkane with the same normal boiling point, with respect to the differences ($S - S_0$) of the specific gravities at 60°F. Crosses: i -alkanes C_7 ; rotated crosses: i -alkanes C_8 ; stars: cycloalkanes C_7 ; squares: aromatics C_7 – C_8 ; diamonds: aromatics C_9 – C_{10} .

- calculate the saturation temperature at 10 mm Hg with the SRK EoS
- collect into a single objective function the (weighted) errors on the critical temperatures (when available) and on the temperatures at 10 mm Hg
- adjust the coefficients of the two equations to minimize the objective function
- modify the analytical forms of the two functions to find their combination giving the absolute minimum of the objective functions

The final results depend on the relative weight given to the errors on T_c and t_{10} ; a good compromise was to use for Δt_{10} a double weight than for T_c . With such assumption, the following expressions resulted:

$$\frac{T_c}{T_{c0}} = 1 + \left(5.40 - \frac{9.41}{S} + \frac{4.41}{S^2} \right) (S - S_0) \quad (16)$$

$$\ln(P_c/P_c^0) = 2.60(S - S_0) \quad (17)$$

(no further improvement was found by adding other terms to Eq. (17), or by adding the nbp as a second variable in the right-hand members.

The above functions gave a rms error of 2.47°C on the critical temperatures and 0.71°C on the saturation temperatures at 10 mm Hg. Such results are much better than using critical constants

Table 3

Overall errors on critical temperatures and saturation temperatures at 10 mm Hg. Calculations by the SRK EoS with critical constants estimation by proposed and literature methods

	ΔT_c (°C)	Δt_{10} (°C)
Winn [2]	6.20	4.90
Kesler and Lee [3]	4.84	3.13
Riazi and Daubert [4]	4.69	2.85
Twu [5]	4.46	1.93
This work	2.47	0.71

estimated by other methods from the literature, as summarized in Table 3 for about 50 critical temperatures and 120 points at 10 mm Hg. In particular, as shown in Table 4, the errors given for heavy *n*-alkanes by the proposed method do not exhibit any particular trend, unlike the other methods.

NB: The results of Tables 3 and 4 were obtained by using for *n*-alkanes also the complete set of Eqs. (7), (12), (14), (16) and (17) (as it is correct), and referring for all hydrocarbons to the data reported by Zwolinski and Wilhoit [6].

Table 4

Errors (°C) on the saturation temperatures at 10 mm Hg of *n*-alkanes C₇ to C₃₀, as calculated by literature methods and the proposed method

n_c	Kesler and Lee [3]	Winn [2]	Twu [5]	Riazi and Daubert [4]	This work
7	−0.45	0.76	0.22	−1.45	0.10
8	−0.04	1.29	0.39	−1.46	0.25
9	0.05	1.45	0.22	−1.74	0.06
10	0.36	1.81	0.28	−1.74	0.06
11	0.63	2.12	0.32	−1.72	0.00
12	1.04	2.59	0.56	−1.46	0.12
13	1.20	2.79	0.52	−1.41	−0.09
14	1.74	3.40	0.88	−0.90	0.06
15	2.14	3.90	1.16	−0.44	0.11
16	2.47	4.34	1.34	−0.01	0.03
17	3.67	5.67	2.42	1.36	0.85
18	4.51	6.68	3.17	2.44	1.31
19	4.83	7.18	3.40	3.05	1.25
20	2.27	4.86	0.79	0.88	−1.68
21	4.33	7.15	2.79	3.34	0.00
22	4.71	7.80	3.12	4.19	0.01
23	5.00	8.38	3.38	4.99	−0.06
24	5.38	9.09	3.75	5.95	−0.01
25	5.76	9.80	4.12	6.93	0.03
26	6.11	10.50	4.44	7.91	0.02
27	6.52	11.31	4.87	9.03	0.12
28	6.73	11.90	5.07	9.93	−0.02
29	7.09	12.67	5.44	11.04	0.02
30	7.31	13.34	5.70	12.06	−0.03

7. Conclusions

A set of equations (Eqs. (7), (12), (14), (16) and (17)) was developed, for the estimation of the critical constants of hydrocarbons from their normal boiling point and specific gravity at 60°F (15.5°C). The predicted values are particularly suited for an accurate calculation of the pure-compound vapor pressures and the vapour–liquid equilibria of their mixtures by the SRK equation of state.

Appendix A. Determination of the critical pressure from the vapor pressure at two different temperatures

Data:

–critical temperature T_c (K);

–vapor pressures P_1 , P_2 (bars) at the temperatures T_1 , T_2 (K).

Calculation basis: SRK EoS; Eqs. (1) and (2) for α .

The procedure is enumerated below.

(1) Calculate the reduced temperatures $T_{r1} = T_1/T_{c1}$, $T_{r2} = T_2/T_{c2}$.

(2) Assume a tentative value of the acentric factor ω ; it can be estimated from the vapor pressure data, basing on the assumption of a straight $\ln(P_r)$, $1/T_r$ line:

$$\log_{10}(P) = \log_{10}(P_c) + \frac{7}{3}(1 + \omega)\left(1 - \frac{1}{T_r}\right) \quad (\text{A1})$$

whence

$$\omega = \frac{\log_{10}(P_2/P_1)}{\frac{7}{3}\left(\frac{1}{T_{r1}} - \frac{1}{T_{r2}}\right)} \quad (\text{A2})$$

Calculate the corresponding tentative value of m with Eq. (2).

Calculate the values of α at the temperatures T_1 , T_2 with Eq. (1):

$$\alpha_1 = \left[1 + m(1 - \sqrt{T_{r1}})\right]^2 \quad (\text{A3})$$

$$\alpha_2 = \left[1 + m(1 - \sqrt{T_{r2}})\right]^2 \quad (\text{A4})$$

and the corresponding values α_1/T_{r1} and α_2/T_{r2} .

From each α/T_r determine the corresponding value of P_r/T_r at saturation, by direct procedure (Soave [17]), and the corresponding P_r values.

Adjust properly the assumed acentric factor and repeat the above procedure until the ratio $P_{r2}:P_{r1}$ is equal to $P_2:P_1$.

Finally, from P_{r1} or P_{r2} determine the critical pressure $P_c = P/P_r$.

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