Program calculates critical properties

João F Gomes

Available at: https://works.bepress.com/joao_gomes/27/
Program calculates critical properties

Methods of estimating the true critical properties of gas mixtures and a BASIC computer program to do the calculations are given.

J. F. P. Gomes, OPPI, Lisbon, Portugal

Knowledge of critical properties of substances is essential for much chemical engineering design, namely for designing compression and refrigeration units. In this article some methods of estimating the true critical properties of mixtures are presented with a BASIC computer program to avoid tedious calculations. These techniques are limited to hydrocarbon mixtures or to mixtures of hydrocarbons with CO₂, H₂S, CO and the permanent gases.

Although many correlations and techniques exist for estimating critical properties of binary gaseous mixtures from their individual properties, uncertainty occurs when they are applied to mixtures containing more than two components. The most used of these techniques are modified equations of state for mixtures and corresponding-states methods, in which the estimation of pseudocritical constants for mixtures is done.

Such constants are necessary if one is to use corresponding-states correlations to estimate mixture P-V-T or derived properties. However, these pseudocritical constants often differ considerably from the true critical points for mixtures.

Estimation techniques for the latter can be evaluated by comparison with experimental data; for the former, evaluation is indirect since the pseudocritical state does not exist in a physical sense.

Mixture critical temperatures: The true mixture critical temperature is usually not a linear mole-fraction average of the pure-component critical temperatures as referred by Reid et al.¹ Li² has suggested that if the composition is expressed as

\[ \theta_j = y_j V_{cj} \sum_i y_i V_n \]  

(1)

the true mixture critical temperature can be estimated by

\[ T_{cr} = \sum_i \theta_j T_{cj} \]  

(2)

Where \( y_j \) = mole fraction of component \( j \), \( V_{cj} \) = critical volume of \( j \), \( T_{cj} \) = critical temperature of \( j \), \( T_{cr} \) = true mixture critical temperature.

Other correlations were developed to estimate \( T_{cr} \), but this one is easier to use, and unless one of the components is a nonhydrocarbon, it is slightly accurate.³

Mixture critical volumes: Only very few experimental values are available for this property. Thus the range and accuracy of estimation methods are not clearly established yet. The Chueh and Prausnitz correlation,⁴ modified by Schick and Prausnitz⁵ seems to be one of the most accurate.

The mixture critical volume is given by the following equation:

\[ V_{cr} = \sum_j \phi_j V_{cj} + \sum_i \sum_j \phi_i \phi_j v_{ij} \]  

(3)

Where

\[ \phi_j = y_j V_{cj}^{2/3} / \sum_i y_i V_i^{2/3} \]  

(4)

\( v_{ij} \) is an interaction parameter such that \( v_{ii} = 0 \) and \( v_{ij} \) (\( i \neq j \)) can be estimated by the following set of equations:

\[ \Psi = A + B \delta_c + C \delta_c^2 + D \delta_c^3 + E \delta_c^4 \]  

(5)

\[ \Psi = 2 v_{ij} (V_a + V_b) \]  

(6)

\[ \delta_c = (V_{a2} - V_{b2}) (V_{a3} + V_{b3}) \]  

(7)

The five coefficients referred in equation (5) are given only for few binary mixtures⁶ and only when 0 ≤ δc ≤ 0.5. Even for several binaries these coefficients are equal to zero, and no values have been proposed yet for mixtures containing more than two components. In this paper we will assume that \( v_{ij} (i \neq j) = 0 \).

Some cases where tested for binary mixtures and it was found that this technique introduces an error which is always less than 5%.

Mixture critical pressure: The dependence of mixture
From these equations it becomes evident that estimation of critical properties involves tedious calculations if more than two components are considered, especially when calculating the mixture critical pressure interaction parameters.

\[ P_{cr} \left( RT_{cr} / (V_{cr} - b_n) \right) = (a_m / T_{cr}^{0.5}) V_{cr} (V_{cr} + b_n) \]  

where \( T_{cr} \) and \( V_{cr} \) are calculated from the methods described earlier.

The mixture coefficients for determining \( P_{cr} \) are defined as follows

\[ b_m = \sum_j y_j b_j = \sum_j (y_j \Omega_j R T_j / P_j) \]

\[ a_m = \sum_j \sum_k y_j y_k a_{jk} \]

with

\[ \Omega_j = 0.0867 - 0.0125 \omega_j + 0.011 \omega_j^2 \]

\[ a_{ij} = \Omega_{ij} R^2 T_{ij}^{0.5} / P_i \]

\[ a_{ij} = (\Omega_{ij} + \Omega_{ij} R T_{ij}^{0.5} (V_{ij} + P_j y_j)^4 (0.291 - 0.04(\omega_i + \omega_j)) \]

\[ T_{ij} = (1 - k_{ij}) (T_i T_j)^{1/2} \]

\[ \Omega_j = (R T_j / V_j b_j - P_j) P_j V_j (V_j + b_j) / (R T_j)^2 \]

The interaction parameter, \( k_{ij} \), ranges from 0.1 to 0.01 but is only tabulated for binary systems. Here we will assume an average value of 0.055 for \( k_{ij} \).

Spencer et al.\(^4\) reported that the average deviation between \( P_{cr} \) and experimental values is usually 2 atm, which is a very small error.

**Construction of a computer program**: From the above equations it becomes evident that estimation of critical properties involves tedious calculations if more than two components are considered, especially when calculating the mixture critical pressure interaction parameters. Thus, a computer program was constructed using BASIC language to perform all these calculations. The program is rather simple and does not need much memory so it can be used in current pocket calculators. A listing of the program is shown in Table 1.

**Testing the computer program**: The computer program was tested for two binary gaseous mixtures, and the results were compared with experimental values, where available.

\[ \text{(1) Mixture of ethane and benzene which contains 39.2 mole percent ethane. The true critical pressure and temperature are reported to be 83.8 atm and 225.9°C.} \]

Properties of the pure components were obtained from Reference 1 and the results obtained from the program are:

\[ T_{cr} = 219.8°C \quad P_{cr} = 76.2 atm \quad V_{cr} = 224.9 \text{ g/cm}^3 \]

Thus, errors are calculated as follows:

\[ \text{Error}_{T} = (\text{(219.8 – 225.9)/225.9}) \times 100 = -2.7\% \]

\[ \text{Error}_{P} = (\text{(76.2 – 83.8)/83.8}) \times 100 = -9.1\% \]

\[ \text{(2) Standard air mixture (21} \% \text{ O}_2, 79\% \text{ N}_2). \text{ The true critical pressure and temperature are: 37.2 atm and 132.3 K.} \]

Again, properties of the pure components were obtained from Reference 1 and the results obtained from the program are:

\[ T_{cr} = 131.3 \text{ K} \quad P_{cr} = 42.7 \text{ atm} \quad V_{cr} = 86.5 \text{ g/cm}^3 \]

And errors become:

\[ \text{Error}_{T} = (\text{(131.3 – 132.3)/132.3}) \times 100 = -0.75\% \]

\[ \text{Error}_{P} = (\text{(42.7 – 37.2)/37.2}) \times 100 = +14\% \]

The program will be tested for gaseous mixtures containing more than two components as soon as literature data becomes consistent. Meanwhile, it seems to be a useful tool for quick estimates of critical properties, and it is believed that the error in the estimation of critical pressure should not exceed 15% for systems with more than two components, especially when hydrocarbon mixtures are considered.

**Literature Cited**


**The author**

João Fernando Pereira Gomes is director of OPPI consulting engineers in Lisbon, Portugal. Prior experience includes assistant lecturer with Lisbon Technical University and research assistant with the Portuguese National Institute for Scientific Research and the Portuguese National Laboratories for Industrial and Engineering Research. Mr. Gomes holds a BS degree in chemical engineering from Lisbon Technical University, and is a member of the Portuguese Institution of Engineers, the Portuguese Chemical Society and the Combustion Institute. He is also the author of several scientific papers.
TABLE 1—Program listing

10 REM CALCULATION OF CRITICAL PROPERTIES OF GAS MIXTURES
20 REM BY J.F.GOMES, 1986
30 REM
40 PRINT "CALCULATION OF CRITICAL PROPERTIES OF GAS MIXTURES"
50 PRINT
60 PRINT "NUMBER OF COMPOUNDS IN THE GAS MIXTURE="
70 INPUT N
80 FOR I = 1 TO N
90 PRINT "COMPOND ",I
100 PRINT "CRITICAL TEMP. (K) ; CRITICAL PRESSURE (atm) ; CRITICAL VOLUME (cm3/mol) ; ACENTRIC FACT"
110 INPUT TC(I),PC(I),VC(I),GM(I)
120 NEXT I
130 PRINT "MOLECULAR WEIGHT (g/mol) ; MOLAR FRACTION "
140 PRINT "INPUT PH(I),X(I)
150 PRINT
160 PRINT "CALCULATION OF AVERAGE MOLECULAR WEIGHT"
170 THM = 0
180 FOR I = 1 TO N
190 H = X(I) * PH(I)
200 THM = THM + H
210 NEXT I
220 PRINT "AVERGA MOLECULAR WEIGHT = ",THM/100
230 PRINT "CALCULATION OF AVERAGE CRITICAL TEMPERATURE"
240 UP = 0
250 FOR I = 1 TO N
260 F = X(I) * VC(I)
270 UP = UP + F
280 NEXT I
290 FOR I = 1 TO N
300 PI(I) = X(I) * VC(I) / UP
310 NEXT I
320 R = F(I) / VC(I)
330 NEXT I
340 PRINT "CALCULATION OF CRITICAL VOLUME OF MIXTURE"
350 V = 0
360 FOR I = 1 TO N
370 R = X(I) * (VC(I) ^ (2 / 3))
380 V = V + R
390 NEXT I
400 NEXT I
410 N = F(I) * VC(I)
420 VCT = VCT + N
430 NEXT I
440 PRINT "CALCULATION OF CRITICAL VOLUME OF GAS MIXTURE (g/cm3) = ",VCT
450 REM CALCULATION OF CRITICAL PRESSURE OF GAS MIXTURE
460 PRINT "CALCULATION OF CRITICAL PRESSURE OF GAS MIXTURE"
470 FOR I = 1 TO N
480 GM(I) = 0.8847 * GM(I) + 0.0125 * GM(I) + 0.011 * GM(I) ^ 2
490 B(I) = GM(I) + B(I) = 0.284 * TC(I) / PC(I)
500 M(I) = (B(I) * TC(I) ^ 2) / (VC(I) - B(I)) - PC(I)
510 MA(I) = MA(I) * PC(I) / VC(I) * VC(I) / (M(I) + B(I)) + (B(I) - 2) / (0.045 * TC(I)) ^ 2
520 NEXT I
530 BM = B
540 FOR I = 1 TO N
550 BM = X(I) * B(I)
560 BM = BM + 80
570 NEXT I
580 FOR I = 1 TO N
590 PRINT "TR(I,J) = 0.89 + SQR (TC(I) * TC(J))"
600 PRINT "NEXT I"
610 PRINT "NEXT J"
620 PRINT "NEXT I"
630 FOR I = 1 TO N
640 FOR J = 1 TO N
650 AR(I,J) = (CM(I) + MA(J)) * 0.284 * (TR(I,J) ^ 1.5) * (VC(I) / VC(J)) / (4 * (0.0291 - 0.04 * (GM(I) + GM(J))))
660 PRINT "NEXT J"
670 PRINT "NEXT I"
680 PRINT "NEXT J"
690 PRINT "NEXT I"
700 PRINT "NEXT J"
710 N = 1 TO N
720 N = MA(I) * 0.284 ^ 2 + TC(I) ^ 2.5 / PC(I)
730 PRINT "NEXT I"
740 PRINT "NEXT J"
750 PRINT "NEXT I"
760 PRINT "NEXT J"
770 PCM = 0.284 * TC(I) / (VC(1) - BM) - (B / (VC(I) + BM) - SQR (TC(I)))
780 PRINT "CRITICAL PRESSURE OF GAS MIXTURE = ",PCM
790 END