

Letter to the Editor

The editors have received a letter from one of our readers, Dr. van Poolen. He points out that a recent publication by H. Grine and H. Madani (hthp 51, 39–61, 2022) contains an inconsistency.

Dr. van Poolen has provided detailed step-by-step calculations highlighting the error and its consequences. These calculations are available upon request, but are too lengthy to be reproduced here.

Instead, we have decided to summarize his letter and his findings in the following, together with the author's (H. Grine) reply.

LETTER TO THE EDITOR

“Dear Editor of the HTHP Journal:

As an affiliate for many years with the Fluid Properties Group at the National Institute of Science and Technology in Boulder, CO, I am intrigued by the paper “Method for prediction of liquid-vapor critical points in binary mixtures: geometrical-EOS model“, published in *High Temperatures High Pressures*, Vol 51, pp. 39–61. It appears to be a simple, innovative method to correlate binary mixture critical data.

My interest led me to do some calculations within which several issues arose.

The method in the paper has promise but needs a thorough scrutiny by the authors so that interested parties can make sense of and subsequently use the method and equations presented. The ability to reproduce results of the author's is a necessary prelude to using the method confidently. Detailed calculations supplied by the authors for the correlation attempt above would be valuable.

Lambert Van Poolen, Ph.D., Loveland, CO”

Calculation

In eqn (10) of the aforementioned paper, the authors define a linear relationship between pressure and temperature:

$$P_L = AT_L + B \quad (10)$$

This implies that the coefficient A has the dimension $[A] = \frac{\text{pressure}}{\text{temperature}}$ and the dimension of B is $[B] = \text{pressure}$.

From the orthogonality condition the authors derive their eqn (11):

$$T_L = \frac{1}{A^2 + 1} (AP_c + T_c - AB) \quad (11)$$

This equation cannot be correct since A and hence A^2 is not dimensionless, but “1” is.

In fact, the correct equation is:

$$T_L = \frac{1}{2} \left(\frac{P_c}{A} + T_c - \frac{B}{A} \right) \quad (11a)$$

In order to find out the impact of this correction, Dr. van Poolen recalculated one data point for the binary system Ethane-Propane, taken from Table 5 of the paper, namely for mole fraction 0.5807. In doing so, he followed the procedure described in the paper. As EOS, he choose the Soave-Redlich-Kwong (SRK) EOS. His result is shown in Table 1 below, and compared with the experimental data point and the calculation by Grine and Madani.

As can be seen, the critical temperature calculated by using the corrected equation (11a) is shifted to higher temperatures by about 20 K, and the relative deviation from the experimental value (337.91 K) is now about 6%.

TABLE 1

Critical Temperature and Critical Pressure for the System Ethane-Propane at Mole Fraction $x = 0.580$. Comparison of experimental data with original calculation by Grine and Madani and revised calculation by van Poolen.

	Experiment	Grine & Madani	van Poolen
Critical Temperature [K]	337.91	338.36	358.96
Critical Pressure [MPa]	5.030	5.003	5.236

AUTHOR'S REPLY

I have gone through Van Poolen's letter to which I send my best regards ... He has adopted another method in his reductionist calculations which is

correct and can be published in another article. As for our calculations, they are also correct and accurate, because we have followed another methodology to estimate the critical points;

From equations (1) and (4) we have:

$$P_L = AT_L + B \quad (1)$$

$$P_c = \frac{T_{c2} - T_{c1}}{P_{c1} - P_{c2}} T_c + P_L - \frac{T_{c2} - T_{c1}}{P_{c1} - P_{c2}} T_L \quad (4)$$

Then:

$$\frac{T_{c2} - T_{c1}}{P_{c2} - P_{c1}} T_L = P_c - P_L + \frac{T_{c2} - T_{c1}}{P_{c2} - P_{c1}} T_c \quad (4a)$$

Replacing (1) in (4a); with $\frac{T_{c2} - T_{c1}}{P_{c2} - P_{c1}} = \frac{1}{A}$; we obtained:

$$\frac{1}{A} T_L = P_c - AT_L - B + \frac{1}{A} T_c \quad (4b)$$

Or:

$$(1 + A^2) T_L = AP_c + T_c - AB \quad (4c)$$

Finally we arrived to the equation (11)

$$T_L = \frac{1}{A^2 + 1} [AP_c + T_c - AB] \quad (11)$$

For his observation about the units, I answer them as I have answered the same problem that has been discussed before; from the mathematical condition of perpendicularity (Mathematical theorem) we arrive at equation (4).

From this condition we can replace the ratio $\frac{T_{c2} - T_{c1}}{P_{c1} - P_{c2}}$ by $\frac{P_c - P_L}{T_c - T_L}$:

This removes the problem of units. Also the pressure P on the line (NM) is given by the linear relationship: $P(T) = AT + B$, while on the curved line (NM) the critical pressure is given at least in polynomial of second degree (or one of the equations of state) i.e.:

$$P_c(T) = \bar{A}T^2 + \bar{B}T + C \quad (12)$$

So equations (4), (25), (31), (35), (37) and (38) are correct and the unit for each equation is the unit of pressure.

In addition:

By applying Pythagoras's theorem on the two adjacent triangles; NCL and LCM (Figure 1) we find:

$$\frac{T_L - T_c}{P_c - P_L} = \frac{P_{c2} - P_{c1}}{T_{c2} - T_{c1}} = A \quad (13)$$

We can write the equation (11) as:

$$T_L = \frac{1}{A.A+1} [AP_c + T_c - AB] \quad (14)$$

The dimensional analysis gives:

$$[T_L] = \left[\frac{1}{\frac{[P] \cdot [T]}{[T] \cdot [P]} + 1} \right] \left[\frac{[T]}{[P]} \cdot [P] + [T] - \frac{[T]}{[P]} \cdot [P] \right] = [T] \quad (14a)$$

H. Grine,
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