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LETTER TO THE EDITOR

On an old basic form for vapor pressure equations

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In a recent SHORT COMMUNICATION, Mohammadzadeh and Zahedi proposed a vapor pressure equation for pure substances based on a graphical method [1]:

$$P^n = A_{MZ}\log T + B_{MZ} \quad (1)$$

where P is the vapor pressure, T is the given temperature and A_{MZ} and B_{MZ} are constants. The exponent n is assumed to have the following form:

$$n = \ln(T_c/T_b)/\ln(P_c/P_b) \quad (2)$$

where T_c and P_c are the critical temperature and pressure, respectively and T_b is the normal boiling point temperature. P_b is the atmospheric pressure (=0.101325 MPa) that is introduced by the author in order to remove the non-SI unit "atm."

Eq. (1), however, is not a new one. In 1964 with a paper entitled "A New Basic Form for Vapor Pressure Equations," Hall reported a model centered on the discovery that under a constant latent heat the volume change in vaporization can be described with a simple function of pressure [2]. This relation substitutes into the Clapeyron equation to give a form that can be integrated. The resulting simple model is:

$$P^A = B\log T + C \quad (3)$$

where A, B and C are constants and Eq. (1) is the same as Eq. (3).

We'd like to call Eq. (3) the "Hall equation" and Eqs. (1) and (2) together the "Mohammadzadeh-Zahedi-Hall model" or "MZH model" in short since what Mohammadzadeh and Zahedi actually did was add the empirical relation, Eq. (2).

The MZH model may not be used for the purpose of extrapolation to the low temperature region. It is clear that the term on the left-hand side of Eq. (1) must be positive; therefore, the MZH model has inherent limitation such that:

$$T > 10^{-B_{MZ}/A_{MZ}} \quad (4)$$

As an example, A_{MZ}=2.9406 and B_{MZ}=−5.9507 for propane [1] so that T>105.6 K, but the triple point is as low as 85±3 K [3]. Unless we take alternative measures, it is very likely that the MZH model and even the original Hall model are only applicable within a limited range of temperatures from the critical point to a certain minimum temperature that may not be defined because of the inequality of Eq. (4). This limitation was not discussed by Mohammadzadeh and Zahedi [1].

Since Eq. (2) was given with no explanation about its development, it is worthwhile to examine its validity. We used Eq. (5), which is equivalent to Eq. (3), to correlate the data of 67 substances (49 organics and 18 inorganic fluids) from the NIST Chemistry Webbook [3] for the entire vapor-liquid saturation range from the critical point to the minimum point or the triple point.

$$\ln P_r = \alpha\ln(1+\beta\ln T_r) \quad (5)$$

where α=1/A and $\beta = \{(P_b/P_c)^{1/\alpha} - 1\}/\ln(T_b/T_c)$. We set the critical point and the normal boiling point as the two reference points and then minimized the RMS (root mean square) deviation. This procedure is equivalent to optimizing the value of one variable A in Eq. (3). The average AAD (average absolute deviation) was found to be 4.02%. Fig. 1 shows the correlation between A_{OPT}, the optimized value, and n from the MZH model. We observed that the correlation between the two variables seems questionable because most of the points are located away from the diagonal line as in Fig. 1.

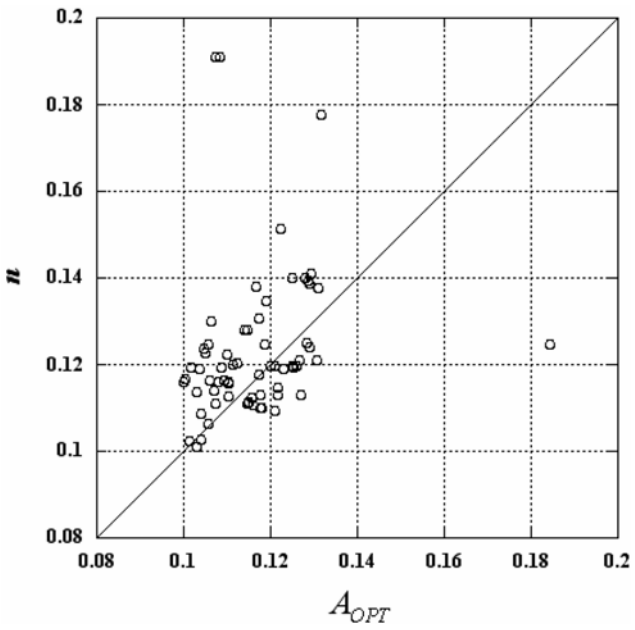

Fig. 1. Correlation between A_{OPT} and n. Most of the points are off the diagonal line. One point is not shown for He with n> 0.2.

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Table 1. Performance comparison of the three vapor pressure models

Model (year)	AAD[a]	Number of adjustable parameters[b]	Note
Hall (1964) [2]	4.02%	1	A=adjustable parameter
MZH (2008) [1]	5.61%	0	A=n (see Eq. (2))
This work (2010)	4.32%	0	A=4/35[c]

[a]Average value for 49 organics and 18 inorganic fluids
[b]The critical point and the normal boiling point are used as the two reference points, reducing the number of parameters by two
[c]The fraction approximates 0.11575 which is the average value of A_{OPT} for 67 substances

Thus, we correlated the data again, simply fixing A=4/35, which is close to 0.11575, the average value of A_{OPT} for 67 substances, to get an average AAD of 4.32%. This compares with an average AAD of 5.61% using the MZH model as summarized in Table 1. Eq. (5) with α=35/4 that is more accurate on the average and simpler than the MZH model must be a good example to doubt the validity of Eq. (2).

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