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New basis functions for the representation of vapor pressure data

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ABSTRACT

In this work, Wagner's formulation and methodology for the representation of vapor pressure data have been extended by using new basis functions, obtained by analytical integration of Clausius–Clapeyron equation assuming a Watson like formulation for the heat of vaporization. The proposed rational base functions are more flexible and lead to higher accuracy in data fitting, comparing favorably to Wagner's equations. Even for a few components, a general pattern has not been identified, and, as clearly mentioned by Wagner, it is mandatory to use stepwise regression in order to retain the most relevant terms for a given number of parameters; this is required by the increased flexibility of the proposed function basis.

1. Introduction

Up to 1973, most empirical vapor pressures equations were obtained by integration of the Clapeyron equation

$$\frac{d\log(P^{sat})}{dT}=\frac{\Delta H_{vap}(T)}{RT^2\Delta Z_{vap}} \tag{1}$$

assuming

- an ideal gas phase behavior,
- that the volume of the liquid is much smaller than the volume of the vapor,
- that the latent heat of vaporization could be expressed as a polynomial of temperature.

The first two assumptions reduce the Clapeyron equation to the Clausius–Clapeyron equation

$$\frac{d\log(P^{sat})}{dT}\approx\frac{\Delta H_{vap}(T)}{RT^2} \tag{2}$$

and, using the third assumption, Eq. (1) writes

$$\frac{d\log(P^{sat})}{dT}=\sum_{j=0}^{j=n}a_jT^{j-2} \tag{3}$$

and integration leads to

$$\log(P^{sat})=b_0+\frac{b_1}{T}+b_2\log(T)+\sum_{j=3}^{j=n}b_jT^{j-2} \tag{4}$$

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F	basis functions
H	enthalpy
P	pressure
R	universal gas constant
T	temperature
W	Lambert function
Z	compressibility factor

Greek letters

Φ	Lerch transcendent function
τ	$1 - T_r$

Subscripts

b	boiling point
c	critical
r	reduced
vap	vaporization

Superscript

sat	saturation

Switching to reduced coordinates, after rearrangements and introducing $\tau = 1 - T_r$, Eq. (4) can write

$$\log(P_r^{sat}) = c_0 \frac{\tau}{1-\tau} + c_1 \log(1-\tau) + \sum_{j=2}^{j=n} c_j \tau^{j-1} \tag{5}$$

In 1973, in two key papers [1,2], Wagner proposed to represent the logarithm of the reduced vapor pressure on the basis of 27 potential terms

$$\log(P_r^{sat}) = \frac{\sum_{j=1}^{j=21} n_j \tau^{(j-3)/2} + n_{22}\log(\tau) + n_{23}(1-\tau)^{\delta} + n_{24}(1-\tau)^2 \log(1-\tau) + n_{25}\tau(1-\tau)^{\delta} + n_{26}\log(\beta_1 - \tau) + n_{27}((\beta_2 - \tau)/\beta_2 \tau)\log(\beta_2 - \tau)}{1-\tau} \tag{6a}$$

It must be noticed that, except if parameters δ, β_1, β_2 are a priori assigned fixed values, even on the logarithmic basis, this model is not linear with respect to its parameters. This model contains most of the terms used in traditional vapor pressure equations plus, in particular, a polynomial in $\tau^{1/2}$. In practice, this basis reduced quickly later to the first summation

$$\log(P_r^{sat}) = \frac{\sum_{j=1}^{j=21} c_j \tau^{(j-3)/2}}{1-\tau} \tag{6b}$$

According to Wagner, the most relevant terms must be selected using a stepwise linear regression technique but, currently, the most popular used forms are

$$\log({P_r}^{sat}) = \frac{c_1\tau + c_2\tau^{3/2} + c_3\tau^{5/2} + c_4\tau^5}{1-\tau} \tag{7}$$

and

$$\log({P_r}^{sat}) = \frac{c_1\tau + c_2\tau^{3/2} + c_3\tau^{3} + c_4\tau^6}{1-\tau} \tag{8}$$

In this first paper [1], Wagner showed that the introduction of a polynomial in $\tau^{1/2}$ leads to the fact that, with $\alpha = (T/P)dP/dT$, at the critical point, the derivatives $d\alpha/dT$ and d^2P/dT^2 correctly approach unlimited values while any form of Eq. (5) would incorrectly lead to finite values.

Applied entirely, Wagner's methodology systematically leads, and from very far away, to the best representation of vapor pressure data for any given number of adjustable parameters (four parameters are the most typical; five parameters were used for some components (i.e., water [1], oxygen [3]). In fact, one can say that Wagner's formulation is, from decades, the key reference for vapor pressure data fitting [4]; very many papers refer to the intrinsic qualities of Wagner's approach [5–8], to mention only few.

However, if Wagner's formulation is used (Eq. (6b)), a back calculation of what looks like a heat of vaporization in Eq. (2) leads to

$$T_r^2 \frac{d[\log(P_r^{sat})]}{dT_r} = -\frac{1}{2}\sum_{j=1}^{j=21} c_i \tau^{(j-5)/2}[(i-3) - (i-5)\tau] = \sum_{j=1}^{j=23} d_i \tau^{(j-5)/2} \tag{9}$$

In the right-hand side of Eq. (9), when approaching the critical point, the first four terms tend to infinity, the fifth term is a constant and all remaining terms tend to zero. The summation should then start at $j = 5$ and not $j = 1$; the same conclusion is reached considering that the Riedel factor [9], defined by the value of $d\log(P_r)/d\log(T_r)$ at the critical point, must have a finite value.