



Extended corresponding states expressions for the changes in enthalpy, compressibility factor and constant-volume heat capacity at vaporization



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ABSTRACT

By analyzing data for the vapor pressure curve of 121 fluids considered by the National Institute of Standards and Technology (NIST) program RefProp 9.1, we find that the first and the second derivatives with respect to reduced temperature (T_r) of the natural logarithm of the reduced vapor pressure at the acentric point ($T_r = 0.7$) show a well defined behavior with the acentric factor ω . This fact is used for checking some well-known vapor pressure equations in the extended Pitzer corresponding states scheme. In this scheme, we then obtain analytical expressions for the temperature dependence of the enthalpy of vaporization and the changes in the compressibility factor and the constant-volume heat capacity along the liquid–vapor coexistence curve. Comparisons with RefProp 9.1 results are presented for argon, propane and water. Furthermore, very good agreement is obtained when comparing with experimental data of perfluorobenzene and perfluoro-*n*-heptane.

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1. Introduction

The vapor pressure equation for a pure fluid gives the relation between saturation pressure p_σ and temperature T from the triple to the critical point along the liquid–vapor phase boundary σ . The form of this equation is one of the most fascinating unsolved problems in physics. Perhaps, it is the equation for which a larger number of proposals have been made. The only two informations that thermodynamics provides about it concern to its first temperature derivative, the so-called Clapeyron–Clausius equation,

$$p'_\sigma(T) \equiv \frac{dp_\sigma}{dT} = \frac{\Delta_v \bar{H}}{T(\bar{V}^g - \bar{V}^l)}, \quad (1)$$

and to its second temperature derivative, the so-called Yang–Yang equation [1],

$$p''_\sigma(T) \equiv \frac{d^2 p_\sigma}{dT^2} = \frac{\bar{C}_{v2}^g - \bar{C}_{v2}^l}{T(\bar{V}^g - \bar{V}^l)}, \quad (2)$$

where $\Delta_v \bar{H}$ is the molar enthalpy of vaporization, \bar{V}^g and \bar{V}^l are the vapor (g) and liquid (l) molar volumes at saturation, and \bar{C}_{v2}^g and \bar{C}_{v2}^l

are the two-phase vapor and liquid molar heat capacities at constant volume.

Equations (1) and (2) are exact thermodynamic relations, and they can be rewritten in different convenient forms that involve the natural logarithm of the vapor pressure as a function of the temperature. One of these forms for equation (1) is

$$\frac{d \ln p_\sigma}{dT} = \frac{\Delta_v \bar{H}}{RT^2 \Delta_v Z}, \quad (3)$$

where Z is the compressibility factor defined as $p_\sigma \bar{V}/RT$, R being the gas constant, and therefore $\Delta_v Z = Z^g - Z^l$ is the change in the compressibility factor associated to vaporization. On the other hand, taking into account the relationship

$$\frac{d^2 \ln p_\sigma}{dT^2} = -\left(\frac{d \ln p_\sigma}{dT}\right)^2 + \frac{1}{p_\sigma} \frac{d^2 p_\sigma}{dT^2}, \quad (4)$$

and using equations (2) and (3) one obtains

$$\frac{d^2 \ln p_\sigma}{dT^2} = -\left(\frac{\Delta_v \bar{H}}{RT^2 \Delta_v Z}\right)^2 + \frac{\Delta_v \bar{C}_v}{RT^2 \Delta_v Z}, \quad (5)$$

where $\Delta_v \bar{C}_v = \bar{C}_{v2}^g - \bar{C}_{v2}^l$. In terms of the reduced variables $T_r \equiv T/T_c$ and $p_r \equiv p_\sigma/p_c$, with T_c and p_c being the temperature and the pressure of the critical point, equation (3) becomes

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$$\frac{d \ln p_r}{dT_r} = \frac{\Delta_v \bar{H}_r}{T_r^2 \Delta_v Z} \quad (6)$$

where $\Delta_v \bar{H}_r \equiv \Delta_v \bar{H}/RT_c$ is the reduced enthalpy of vaporization, while equation (5) becomes

$$\frac{d^2 \ln p_r}{dT_r^2} = -\frac{1}{T_r^4} \left(\frac{\Delta_v \bar{H}_r}{\Delta_v Z} \right)^2 + \frac{1}{T_r^2} \frac{\Delta_v \bar{C}_v^*}{\Delta_v Z} \quad (7)$$

where $\Delta_v \bar{C}_v^* \equiv (\bar{C}_{v2}^g - \bar{C}_{v2}^l)/R$. If one knows the temperature dependence of the right-hand side of equations (6) or (7), integrations of these equations yield the vapor pressure curve. For example, by assuming a constant ratio $\Delta_v \bar{H}_r/\Delta_v Z$ and imposing that $p_r = 1$ at $T_r = 1$, integration of equation (6) leads to the so-called Clausius–Clapeyron (CC) equation,

$$\ln p_r = A \left(1 - \frac{1}{T_r} \right), \quad (8)$$

where the parameter A can be obtained from a known point in the vapor–pressure curve.

The two-parameter corresponding-states principle (CSP) states that fluids at equal reduced pressure and temperature should behave identically [2]. If the CSP were true, the parameter A in equation (8) should take the same value for all fluids. Guggenheim [3] proposed a value of $A \approx 5.4$ by fitting experimental vapor pressure data for a small number (seven) of nonpolar fluids. In order to extend the CSP to a wider range of fluids more parameters must be introduced in the corresponding-states correlations. In particular, in order to quantify the deviation of fluids with respect the two-parameter CSP predictions, Pitzer proposed in 1955 a third parameter ω , named *acentric factor* and defined as [4,5]

$$\omega \equiv -1.0 - \log_{10} p_r \quad \text{at} \quad T_r = 0.7, \quad (9)$$

Although the acentric factor was originally introduced to represent the nonsphericity (acentricity) of a molecule, nowadays it is used as a measure of the complexity of a molecule with respect to its size/shape and polarity and it is tabulated for many fluids [6]. Fluids with nearly $\omega = 0$ are called *simple* fluids (e.g., the seven Guggenheim’s fluids). The Pitzer three-parameter CSP states that fluids with the same value of ω should behave identically at equal reduced pressure and temperature. We note that the acentric factor can be used to introduce the so-called acentric point given by $T = 0.7T_c$ and $p_\sigma = 10^{-(1+\omega)} p_c$.

In the Pitzer CSP theory, a vapor–pressure equation has the form

$$\ln p_r = f(T_r; \omega), \quad (10)$$

with $f(1; \omega) = 0$. Furthermore, taking into account definition (9), the function $f(T_r; \omega)$ must satisfy the condition

$$f(0.7; \omega) = -(1 + \omega) \ln 10, \quad (11)$$

in order to be self-consistent at the acentric point. Recently [7] we have checked condition (11) for testing some vapor–pressure equations often used for estimating the vapor pressure of a large variety of fluids. In this work, we analyze the behavior of the first and second derivatives with respect the reduced temperature of $\ln p_r$ at the acentric point, i.e., the functions

$$f'(0.7; \omega) \equiv \left(\frac{d \ln p_r}{dT_r} \right)_{T_r=0.7} \quad (12)$$

and

$$f''(0.7; \omega) \equiv \left(\frac{d^2 \ln p_r}{dT_r^2} \right)_{T_r=0.7}. \quad (13)$$

In particular, by using vapor–pressure data for the 121 fluids reported by the NIST program RefProp 9.1 [8], we find that both

$f'(0.7; \omega)$ and $f''(0.7; \omega)$ show a well defined behavior with the acentric factor ω . This information can be used for testing vapor pressure equations or for obtaining adjustable coefficients appearing in them. On the other hand, in this work we also analyze the behavior of the reduced enthalpy of vaporization

$$\Delta_v \bar{H}_{r\omega} \equiv \Delta_v \bar{H}_r(T_r = 0.7), \quad (14)$$

the change in the compressibility factor

$$\Delta_v Z_\omega \equiv \Delta_v Z(T_r = 0.7), \quad (15)$$

and the change in the heat capacity at constant volume

$$\Delta_v \bar{C}_{v\omega}^* \equiv \Delta_v \bar{C}_v^*(T_r = 0.7), \quad (16)$$

at the acentric point. We find that $\Delta_v \bar{H}_{r\omega}$ is almost linearly correlated with ω while the ω -dependence of $\Delta_v Z_\omega$ and $\Delta_v \bar{C}_{v\omega}^*$ is well explained from $\Delta_v \bar{H}_{r\omega}$, $f'(0.7; \omega)$ and $f''(0.7; \omega)$. Finally, the obtained equations are used for predicting the effect of temperature on the reduced enthalpy of vaporization and on the changes in the compressibility factor and the constant-volume heat capacity during vaporization. We compare the obtained equations with NIST data for argon, propane and water and also with experimental data of perfluorobenzene and perfluoro-*n*-heptane, with very good agreement.

2. Checking vapor–pressure equations at the acentric point

The first temperature derivative of the natural logarithm of the vapor pressure at the acentric point, equation (12), can be obtained from equation (6),

$$f'(0.7; \omega) = \frac{\Delta_v \bar{H}_{r\omega}}{0.7^2 \Delta_v Z_\omega}, \quad (17)$$

with $\Delta_v \bar{H}_{r\omega}$ and $\Delta_v Z_\omega$ defined by equations (14) and (15), respectively. Figure 1(a) shows a plot of $f'(0.7; \omega)$ vs. ω . Symbols correspond to data obtained from RefProp 9.1 and equation (17) for the 121 substances listed in table 1. One can see that $f'(0.7; \omega)$ increases with ω in a practically linear way.

At this point it is important to remark that RefProp 9.1 is a computer program that uses the most accurate equations of state and models available for calculating a large number of properties for the 121 pure fluids included in the program [8]. Therefore, the results obtained from RefProp are not experimental data and, in some particular cases, are subjected to deviations that can be ascribed to the equation of state considered for the fluid. Nonetheless, in most cases RefProp 9.1 gives very accurate results that can be used to test the extended corresponding states expressions derived in this work.

The second temperature derivative of the natural logarithm of the vapor pressure at the acentric point, equation (13), can be obtained from equation (7)

$$f''(0.7; \omega) = -\frac{1}{0.7^4} \left(\frac{\Delta_v \bar{H}_{r\omega}}{\Delta_v Z_\omega} \right)^2 + \frac{1}{0.7^2} \frac{\Delta_v \bar{C}_{v\omega}^*}{\Delta_v Z_\omega}. \quad (18)$$

Figure 1(b) shows a plot of $f''(0.7; \omega)$ vs. ω . Symbols correspond to data obtained from RefProp 9.1 and equation (18). One can see that $f''(0.7; \omega)$ decreases with ω in a practically linear way. In figure 1(b) one can observe that the result for heavy water (filled square) clearly deviates from the observed trend for $f''(0.7; \omega)$. This behavior is related to a deviation in the RefProp 9.1 result of $\Delta_v \bar{C}_{v\omega}^*$ for heavy water (See Section 4 and figure 2(c)).

By taking as reference the acentric point, the CC vapor–pressure equation (8) becomes the well-known result [9,7,10]

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