J. Chem. Thermodynamics 68 (2014) 193–198

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

# Some empirical rules concerning the vapor pressure curve revisited

S. Velasco, J.A. White [*]

*Departamento de Física Aplicada, Universidad de Salamanca, 37008 Salamanca, Spain*
*IUFFyM, Universidad de Salamanca, 37008 Salamanca, Spain*

ARTICLE INFO

*Article history:*
Received 22 July 2013
Received in revised form 10 September 2013
Accepted 11 September 2013
Available online 20 September 2013

*Keywords:*
Vapor pressure curve
Saturation properties
Acentric factor
Claussius–Clapeyron equation

ABSTRACT

A form for the Clausius–Clapeyron vapor-pressure equation is obtained in the Pitzer corresponding states scheme. This equation allows one to rewrite the well-known Trouton, Guldberg, van Laar and Guggenheim rules in terms of the acentric factor $\omega$. The original forms of these empirical rules are recovered for some particular values of $\omega$. The proposed rules are checked by analyzing National Institute of Standards and Technology (NIST) data on the liquid-vapor coexistence curve for 105 fluids. These rules have been also analyzed by using the well-known Ambrose–Walton (AW) vapor pressure equation.

## 1. Introduction

In 1873, van der Waals proposed an equation of state (EOS) capable of describing qualitatively the liquid-vapor phase transition, including the critical point. An important byproduct of this equation was the corresponding states principle (CSP): if temperature, pressure and density are reduced by the critical parameters, all fluids satisfy the same EOS. Subsequently, many works were devoted to check this principle. Some of these works provided useful empirical rules relating quantities of the vapor pressure curve, such as the enthalpy of vaporization, the normal boiling point and the critical point. Perhaps the most popular rules in thermodynamics, physical chemistry and chemical engineering literature are, chronologically, Trouton, Guldberg, van Laar and Guggenheim rules.

In 1884, Trouton [1] found that for many fluids the molar entropy of vaporization at the normal boiling point $\Delta_v\bar{S}_b$, i.e. the ratio between the molar enthalpy of vaporization $\Delta_v\bar{H}_b$ and the normal boiling temperature $T_b$, is approximately constant,

$$\Delta_v\bar{S}_b = \frac{\Delta_v\bar{H}_b}{T_b} \approx 21\ \text{cal mol}^{-1}\ \text{K}^{-1} \approx 88\ \text{J mol}^{-1}\ \text{K}^{-1}, \tag{1}$$

or, in dimensionless form,

$$\frac{\Delta_v\bar{S}_b}{R} = \frac{\Delta_v\bar{H}_b}{RT_b} \approx 10.5, \tag{2}$$

where $R$ is the gas constant. Wisniak [2] pointed out that a similar relation was obtained analytically by Pictet in 1876 and empirically by Ramsay in 1877. In the present work equation (2) is named as Trouton's rule.

In 1890, Guldberg [3] noted that the normal boiling temperature $T_b$ of a fluid is approximately two-thirds of the critical temperature $T_c$,

$$\frac{T_b}{T_c} \approx \frac{2}{3}. \tag{3}$$

Guldberg proposed this relation after examining 64 fluids, mainly carbon and inorganic compounds. Also in 1890, Guye [4] reached a similar conclusion after comparing the ratio $T_b/T_c$ for 75 substances, providing a mean value of 0.645 for this ratio. In 1916, Lorenz [5] gave the value of 0.64 as the average $T_b/T_c$ ratio for 137 substances. In the present work equation (3) is named as Guldberg's rule.

In 1918, after examining data of 50 inorganic compounds and 58 organic ones, van Laar [6] proposed that the ratio $T_c/T_b$ can be obtained from

$$\frac{T_c}{T_b} = \frac{\log_{10} p_c}{f_s} + 1, \tag{4}$$

where $p_c$ is the critical pressure given in atm and $f_s$ a constant, having an average value of 2.9. In modern form, equation (4) can be rewritten as

$$h_b = \frac{T_{br} \ln p_{br}}{T_{br} - 1} \approx 2.9 \ln 10 \approx 6.7, \tag{5}$$

---

[*] Corresponding author at: Departamento de Física Aplicada, Universidad de Salamanca, 37008 Salamanca, Spain. Tel.: +34 923294436; fax: +34 923294584.
*E-mail address:* white@usal.es (J.A. White).

0021-9614/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jct.2013.09.014

where $T_{br} = T_b/T_c$ and $p_{br} = p_b/p_c$ with $p_b = 1\ \text{atm} = 101.325$ kPa. Equation (5), here named as van Laar's rule, states that the so-called Miller factor $h_b$ [7, 8] is approximately constant.

In 1945, Guggenheim [9] pointed out that in order to verify the CSP the normal boiling temperature $T_b$ should be replaced by the temperature $T_s$ at which the vapor pressure reaches 1/50th of the critical value, i.e. $p(T_s) = p_s = p_c/50$. Then, by examining data for seven *ideal* fluids (argon, krypton, xenon, nitrogen, oxygen, carbon monoxide, and methane) proposed the empirical relations

$$\frac{T_s}{T_c} \approx 0.58, \tag{6}$$

and

$$\frac{\Delta_v \bar{S}_s}{R} = \frac{\Delta_v \bar{H}_s}{RT_s} \approx 9.05, \tag{7}$$

where $\Delta_v \bar{S}_s$ and $\Delta_v \bar{H}_s$ are the molar entropy and molar enthalpy of vaporization at $T_s$, respectively. Equation (6) is here named as the first Guggenheim rule, while equation (7) is here named as the second Guggenheim rule.

We remark that not all fluids obey these rules exactly, so that a lot of modifications have been proposed in the literature in order to apply these rules with predicting purposes for different groups of substances [10, 11]. Although most of these modifications are based on the difference of molecular structure and molecular bonding, to date, there is not a clear physical theory neither to understand these rules nor to explain deviations for different fluids. In this paper, we propose a semi-empirical route, based on the Pitzer extension of the CSP, in order to both propose a simple fluid-dependent correction to these rules and obtain the constant values of equations (2)–(7) as particular cases.

## 2. The Clausius–Clapeyron equation in the Pitzer corresponding states scheme

The temperature dependence of the saturated pressure, $p$, of a fluid along the liquid-vapor coexistence curve is described by the Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta_v \bar{H}}{T\Delta_v \bar{V}}, \tag{8}$$

where $\Delta_v \bar{H}$ is the molar enthalpy of vaporization and $\Delta_v \bar{V} = \bar{V}^v - \bar{V}^l$ is the difference between the molar volumes of saturated vapor (v) and saturated liquid (l). Equation (8) is an exact thermodynamic relation, and it is has been rewritten in different, more convenient forms that involve the natural logarithm of the vapor pressure as a function of the temperature. One of these forms was proposed by Waring [12, 13]

$$\frac{d\ln p}{d(1/T)} = -\frac{\Delta_v \bar{H}}{R\Delta_v Z}, \tag{9}$$

where $Z$ is the compressibility factor defined as $p\bar{V}/RT$. If one knows the temperature dependence of $\Delta_v \bar{H}$ and $\Delta_v Z$, integration of equation (9) allows one to obtain the natural logarithm of the vapor pressure curve as a function of the temperature. By plotting $\ln p$ vs $1/T$, one approximately finds for many fluids a linear behavior from the triple point to the critical point. This suggests to define an apparent value of the ratio, $\Delta_v \bar{H}/\Delta_v Z$, by

$$\frac{d\ln p}{d(1/T)} = -\frac{1}{R}\left(\frac{\Delta_v \bar{H}}{\Delta_v Z}\right)^{\text{app}} = \text{const.} \tag{10}$$

Comparing equations (9) and (10) one has

$$\Delta_v \bar{H}(T) = \left(\frac{\Delta_v \bar{H}}{\Delta_v Z}\right)^{\text{app}} \Delta_v Z(T), \tag{11}$$

that can be used to calculate the molar enthalpy of vaporization at a given temperature, $\Delta_v \bar{H}(T)$, in terms of $\Delta_v Z(T)$, or vice versa.

By taking the critical point as reference, integration of equation (10) leads to the Clausius–Clapeyron equation,

$$\ln p_r = \frac{1}{RT_c}\left(\frac{\Delta_v \bar{H}}{\Delta_v Z}\right)^{\text{app}}\left(1 - \frac{1}{T_r}\right), \tag{12}$$

where $p_r = p/p_c$ and $T_r = T/T_c$. By fitting experimental vapor pressure data for the above mentioned seven *ideal* fluids, Guggenheim [14] proposed the vapor pressure equation

$$\ln p_r = 5.3\left(1 - \frac{1}{T_r}\right) \quad (0.55 < T_r < 1), \tag{13}$$

i.e., equation (12) with a value of $(\Delta_v \bar{H}/\Delta_v Z)^{\text{app}} = 5.3RT_c$. Two remarks can be made about equation (13). First, by assuming that at $T_s$ one verifies $\bar{V}^l_s \ll \bar{V}^v_s$ and that the vapor behaves as an ideal gas, $\bar{V}^v_s \approx RT_s/p_s$, then $\Delta_v Z_s \approx 1$, and equation (13) is consistent with equations (6) and (7) ($9.05 \times 0.58 \approx 5.25$). Second, it is a CSP equation, i.e. it does not contain any fluid characteristic parameter.

The CSP provided a nice and useful unified description of the thermodynamic behavior of fluids. Pitzer [15] and later Guggenheim [9] stated its statistical-mechanics basis. The CSP fluids are composed of nonpolar spherical molecules with similar intermolecular interactions. Noble gases are paradigmatic CSP fluids. By analyzing vapor pressure data for noble gases, Pitzer found that $p_r = 0.1$ at $T_r = 0.7$. Then, taking noble gases as a reference, he defined the acentric factor [16, 17]

$$\omega \equiv -1 - \log_{10} p_r \quad \text{at } T_r = 0.7, \tag{14}$$

as a measure of the deviation of a fluid with respect to the CSP behavior. Fluids with nearly $\omega = 0$ are called *simple* fluids. Although the acentric factor was originally introduced to represent the acentricity or nonsphericity of a molecule, nowdays 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 substances [18].

In general, in the Pitzer corresponding-states scheme, a vapor pressure equation has the form

$$\ln p_r = f(T_r, \omega), \tag{15}$$

with $f(1, \omega) = 0$. Furthermore, taking into account definition (14), the function $f(T_r, \omega)$ must satisfy the condition

$$f(0.7, \omega) = -(1 + \omega)\ln 10, \tag{16}$$

in order to be self-consistent [19]. By applying condition (16) to the Clausius–Clapeyron (CC) equation (12), one obtains

$$\ln p_r = A(\omega)\left(1 - \frac{1}{T_r}\right), \tag{17}$$

with

$$A(\omega) = \frac{1}{RT_c}\left(\frac{\Delta_v \bar{H}}{\Delta_v Z}\right)^{\text{app}} = \frac{7\ln 10}{3}(1 + \omega). \tag{18}$$

In particular, for $\omega = 0$, equation (18) yields $A(0) = 7\ln 10/3 \approx 5.37$ and equation (17) becomes the empirical Guggenheim vapor pressure equation (13). Then, by applying equation (17) to the vapor pressure $p_{sr} = 1/50$ one obtains

$$T^{CC}_{sr}(\omega) = \frac{A(\omega)}{A(\omega) + \ln 50}, \tag{19}$$

that provides the ratio $T_s/T_c$ as a function of the acentric factor. In particular, for $\omega = 0$ equation (19) yields

$$T^{CC}_{sr}(0) = \frac{A(0)}{A(0) + \ln 50} = \frac{7\ln 10}{7\ln 10 + 3\ln 50} = 0.5787 \approx 0.58, \tag{20}$$