

On the Clausius–Clapeyron Vapor Pressure Equation

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To provide the temperature dependence of the saturated pressure, P , of a fluid along the liquid–vapor coexistence curve, most chemistry and physics textbooks use the Clausius–Clapeyron equation (1–8)

$$\ln \frac{P}{P_0} = A \left(\frac{1}{T_0} - \frac{1}{T} \right) \quad (1)$$

where P_0 and T_0 are the vapor pressure and the absolute temperature of a reference point in the coexistence curve and A is a constant characteristic of the substance. Equation 1 is usually derived from integration of the Clapeyron equation for vaporization,

$$\frac{dP}{dT} = \frac{\Delta_{\text{vap}}\bar{H}}{T(\bar{V}^{\text{v}} - \bar{V}^{\text{l}})} \quad (2)$$

under the following assumptions: (i) the molar enthalpy (latent heat) of vaporization is constant ($\Delta_{\text{vap}}\bar{H} \approx \text{constant}$), (ii) the molar volume of the liquid is negligible respect to the molar volume of the vapor ($\bar{V}^{\text{l}} \ll \bar{V}^{\text{v}}$), and (iii) the vapor behaves as an ideal gas ($\bar{V}^{\text{v}} \approx RT/P$). These are reasonably good approximations at low temperatures where the vapor pressure is small.

Surprisingly, the Clausius–Clapeyron equation, eq 1, is able to predict the vapor pressure of some fluids along the entire coexistence curve with good accuracy, even near the critical point where the approximations made for integration of eq 2 are not valid. To understand this fact it is convenient to use the compressibility factor $Z = P\bar{V}/RT$ and to rewrite the Clapeyron equation (eq 2) as

$$\frac{d \ln P}{d(1/T)} = - \frac{\Delta_{\text{vap}}\bar{H}}{R\Delta_{\text{vap}}Z} \quad (3)$$

where $\Delta_{\text{vap}}Z$ is the difference between the compressibilities of the vapor and liquid phases. Far enough from the critical point the above mentioned approximations hold, so that $\Delta_{\text{vap}}Z \approx 1$ and $\Delta_{\text{vap}}\bar{H} \approx \text{constant}$, and integration of eq 3 leads to eq 1. Furthermore, although $\Delta_{\text{vap}}\bar{H}$ and $\Delta_{\text{vap}}Z$ are dependent on the temperature, owing to a compensating effect, the ratio $\Delta_{\text{vap}}\bar{H}/\Delta_{\text{vap}}Z$ in eq 3 is constant for some substances over the entire temperature range from the triple point to the critical point. Then, by assuming that the right-hand side of eq 3 is constant, integration of this equation, by using the critical point as reference, yields (9)

$$\ln P_{\text{r}} = b \left(1 - \frac{1}{T_{\text{r}}} \right) \quad (4)$$

where $P_{\text{r}} = P/P_{\text{c}}$ and $T_{\text{r}} = T/T_{\text{c}}$, with P_{c} and T_{c} being the critical pressure and the critical temperature, respectively, and b is a constant characteristic of the substance. Although eqs 1 and 4 provide the natural logarithm of the vapor pressure as a linear function of $1/T$, we remark that they have been obtained by using different approximations.

For a given substance, the value of the parameter b in eq 4 can be calculated by fitting a set of experimental vapor pres-

sure data between the triple point temperature and the critical temperature. In particular, Guggenheim proposed the empirical equation (10–12)

$$\ln P_{\text{r}} = 5.4 \left(1 - \frac{1}{T_{\text{r}}} \right) \quad (5)$$

on the basis of the study of the behavior of the vapor pressure of seven fluids: argon (Ar), krypton (Kr), xenon (Xe), carbon monoxide (CO), nitrogen (N₂), methane (CH₄), and oxygen (O₂). Equation 5 is usually considered as an example of the law of corresponding states: different fluids obey the same equation in terms of the reduced variables P_{r} and T_{r} . However, the value $b = 5.4$ was obtained for a particular set of *simple* fluids (those with zero or small molecular dipole moments), so that it does not have a universal character.

In this article we present a universal form for the Clausius–Clapeyron vapor pressure equation without an adjustable parameter. The proposed equation is based on the use of dimensionless variables reduced by using both triple point and critical point coordinates. This can be convenient, for example, to analyze the deviations of experimental vapor pressure data with respect to the Clausius–Clapeyron equation. In this context, we also propose a simple correction to the universal Clausius–Clapeyron equation consistent with the renormalization group theory of critical phenomena. The proposed vapor pressure equation contains only one empirical parameter that is calculated using the acentric point as reference. We then check whether the proposed equation provides a good prediction for the vapor pressure of the Guggenheim fluids and also of more complex fluids.

Universal Form of the Clausius–Clapeyron Equation

The liquid–vapor coexistence curve extends from the triple point to the critical point. Experimentally, near the critical point the main difficulties arise from the divergence of several properties, while near the triple point the difficulties arise from the measurement of low vapor pressures. In spite of these difficulties, triple point and critical point coordinates are tabulated for many fluids. If the triple point pressure, P_{t} , and the triple point temperature, T_{t} , are known, the triple point can be used, together with the critical point, as a reference in the study of vapor pressure equations. In particular, they can be used to calculate the parameter b in eq 4. By imposing that eq 4 passes through the triple point, one obtains

$$b = \frac{T_{\text{rt}} \ln P_{\text{rt}}}{T_{\text{rt}} - 1} \quad (6)$$

where $T_{\text{rt}} = T_{\text{t}}/T_{\text{c}}$, and $P_{\text{rt}} = P_{\text{t}}/P_{\text{c}}$ are the reduced triple point temperature and pressure, respectively. By substituting eq 6 into eq 4, one can rewrite the Clausius–Clapeyron equation as

$$\frac{T_{\text{r}} \ln P_{\text{r}}}{T_{\text{rt}} \ln P_{\text{rt}}} = \frac{1 - T_{\text{r}}}{1 - T_{\text{rt}}} \quad (7)$$

This equation suggests the definition of a dimensionless variable ϕ , related to both the reduced temperature and the reduced

vapor pressure by

$$\phi \equiv \frac{T_r \ln P_r}{T_{rt} \ln P_{rt}} \quad (8)$$

and a dimensionless temperature t by

$$t \equiv \frac{1 - T_r}{1 - T_{rt}} = \frac{T_c - T}{T_c - T_t} \quad (9)$$

The use of the new variables ϕ and t allows one to write the Clausius–Clapeyron equation, eq 7, in the simple form,

$$\phi = t \quad (10)$$

We note that, for any fluid, the values of the dimensionless temperature t range between the triple point value, $t_t = 1$, and the critical point value, $t_c = 0$. In a similar way, the dimensionless variable ϕ is normalized in the sense that its maximum value is reached at the triple point, $\phi_t \equiv \phi(1) = 1$, while its minimum value is reached at the critical point, $\phi_c \equiv \phi(0) = 0$. Thus, eq 10 can be considered as a universal form of the Clausius–Clapeyron equation not only because it does not depend on any adjustable parameter (in contrast to eq 4 that includes the parameter b), but also because variables ϕ and t range between 0 and 1 for all fluids.

Therefore, the (t, ϕ) diagram provides a universal framework to represent the whole coexistence curve, from the triple point (1, 1) to the critical point (0, 0), for any fluid. In this diagram one can appreciate the deviations of the experimental vapor pressure with respect to the Clausius–Clapeyron equation, eq 10. A plot of $\phi(t)$ versus t for the seven Guggenheim fluids is shown in Figure 1. The symbols are *experimental* values of $\phi(t)$ calculated from the vapor pressure data provided by the NIST program (13) for these fluids, whereas the solid line is the linear equation 10. The triple point and critical point coordinates used in the calculations are given in Table 1. From Figure 1, one can see that the Guggenheim fluids seem to verify eq 10 rather satisfactorily and that the larger deviations are presented by oxygen.

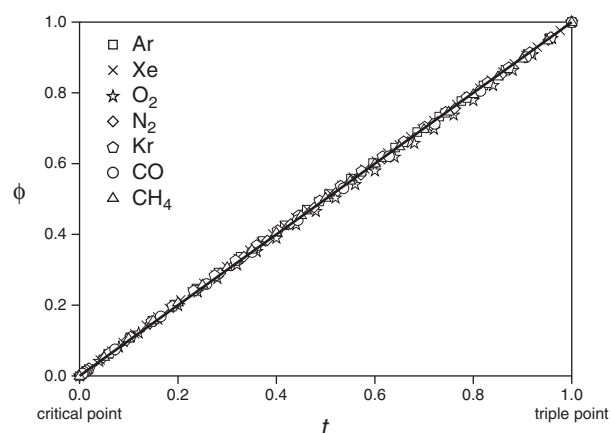


Figure 1. Dimensionless variable ϕ versus dimensionless temperature t for the Guggenheim fluids. The symbols represent NIST data (13) whereas the solid line represents the universal form of the Clausius–Clapeyron equation, eq 10.

To quantify the deviations between theory and the experimental vapor pressure data, we took $N = 99$ data for each substance between $t_0 = 0$ (critical point) and $t_{100} = 1$ (triple point) with $\Delta t \equiv t_i - t_{i-1} = 0.01$ ($i = 1, \dots, N$) and calculated the average absolute relative deviation (AARD)

$$\text{AARD} = \frac{100\%}{N} \sum_{i=1}^N \left| 1 - \frac{P_{ri}^{(\text{calc})}}{P_{ri}^{(\text{exp})}} \right| \quad (11)$$

where $P_{ri}^{(\text{calc})} = P_r(t_i)$ is the value calculated from the theoretical equation and $P_{ri}^{(\text{exp})}$ denotes the corresponding experimental value. Taking into account eq 9 one has $T_r = 1 - (1 - T_{rt})t$, so that in terms of the dimensionless temperature t the vapor pressure values provided by the Guggenheim equation, eq 5,

Table 1. Values of the Triple Point Coordinates, T_t and P_t , the Critical Point Coordinates, T_c and P_c , the Acentric Factor, ω , and the Reduced Triple Point Pressure, $P_{rt} = P_t/P_c^a$

| Fluid | T_t/K | P_t/Pa | T_c/K | P_c/MPa | ω | P_{rt} | c_1^b |
|--|----------------|-----------------|----------------|------------------|----------|-------------------------|-----------|
| Ar | 83.8058 | 68891 | 150.687 | 4.8630 | -0.00219 | 1.417×10^{-2} | 0.169443 |
| Xe | 161.4 | 81748 | 289.733 | 5.8420 | 0.00363 | 1.399×10^{-2} | 0.142974 |
| Kr | 115.77 | 73503 | 209.48 | 5.5250 | -0.0009 | 1.330×10^{-2} | 0.192579 |
| CO | 68.16 | 15537 | 132.86 | 3.4935 | 0.050 | 4.447×10^{-3} | -0.342360 |
| N ₂ | 63.151 | 12520 | 126.192 | 3.3958 | 0.0372 | 3.687×10^{-3} | -0.209027 |
| CH ₄ | 90.6941 | 11696 | 190.564 | 4.5992 | 0.01142 | 2.543×10^{-3} | 0.042520 |
| O ₂ | 54.361 | 146.28 | 154.581 | 5.0430 | 0.0222 | 2.901×10^{-5} | -0.779429 |
| NH ₃ | 195.495 | 6091.2 | 405.40 | 11.3330 | 0.25601 | 5.375×10^{-4} | -1.09325 |
| CF ₄ | 98.94 | 641.44 | 227.51 | 3.7500 | 0.1785 | 1.711×10^{-4} | -1.43601 |
| H ₂ O | 273.16 | 611.65 | 647.096 | 22.0640 | 0.3443 | 2.772×10^{-5} | -1.57911 |
| C ₂ HCl ₂ F ₃ | 166.0 | 4.2021 | 456.831 | 3.6618 | 0.28192 | 1.148×10^{-6} | -3.28415 |
| C ₁₀ H ₂₂ | 243.5 | 1.4042 | 617.7 | 2.1030 | 0.488 | 6.677×10^{-7} | -3.95301 |
| C ₇ H ₁₆ | 182.55 | 0.17549 | 540.13 | 2.7360 | 0.349 | 6.414×10^{-8} | -4.03830 |
| C ₆ H ₁₄ ^c | 120.6 | 0.000011162 | 497.7 | 3.0400 | 0.280 | 3.672×10^{-12} | -5.27889 |

^aData are taken from ref 13. The shaded region indicates the Guggenheim fluids. ^bThe last column shows the values of the parameter c_1 given by eq 36 and used in the vapor pressure eq 39. ^cThe chemical formula of 2-methylpentane is represented by the abbreviated form C₆H₁₄.

are calculated by

$$\ln P_r(t) = -5.4 \frac{(1 - T_{rt})t}{1 - (1 - T_{rt})t} \quad (12)$$

while, from eqs 8, 9, and 10, the vapor pressure values are calculated by

$$\ln P_r(t) = \frac{T_{rt}t}{1 - (1 - T_{rt})t} \ln P_{rt} \quad (13)$$

The AARDs for the seven Guggenheim fluids evaluated using eqs 12 and 13 are listed in Table 2. As can be seen, when eq 12 is used the AARD is less than a 2% for Ar, Xe, Kr, and CH₄ but it is significantly larger for N₂ (~8%), CO (~11%), and O₂ (~10%). However, when eq 13 is used the AARDs for all Guggenheim fluids are below a 2%, except for O₂, which reaches ~7%. These quantitative results are in agreement with the deviations observed in Figure 1.

Why does oxygen result in a deviation of experimental values of P_r , calculated with eq 13, larger than those observed for the six remaining Guggenheim fluids? To answer to this question it seems relevant to analyze what factors could influence such deviations. A first candidate is the so-called *acentric factor* (14–16) that is widely used to describe deviations of thermodynamic quantities from the law of corresponding states. This factor was defined by Pitzer as (17, 18)

$$\omega \equiv -1 - \log_{10} P_{r\omega} \quad (14)$$

where $P_{r\omega}$ is the reduced vapor pressure at a reduced temperature $T_r = 0.7$, that is, $P_{r\omega} = P_r(T_r = 0.7)$. The values of ω , taken from the NIST program (13), for the Guggenheim fluids are listed in Table 1. From these values and the values of the AARD given in Table 2 one could conclude that a fluid with a small value of ω presents small deviations between experimental values of P_r and the behavior prescribed by eq 13. However, this is not the case for oxygen with a value of ω smaller than those for N₂ and CO but with a larger

Table 2. Absolute Average Relative Deviation, AARD, of Vapor Pressure Predictions by Different Equations for the Fluids of Table 1

| Fluid | AARD | | |
|--|-------|-------|-------|
| | eq 12 | eq 13 | eq 39 |
| Ar | 1.94 | 1.49 | 1.11 |
| Xe | 1.51 | 1.45 | 1.15 |
| Kr | 1.96 | 1.64 | 1.18 |
| CO | 11.0 | 1.76 | 1.22 |
| N ₂ | 8.00 | 1.55 | 1.30 |
| CH ₄ | 1.61 | 1.52 | 1.52 |
| O ₂ | 9.95 | 7.19 | 2.91 |
| NH ₃ | 103 | 6.56 | 1.01 |
| CF ₄ | 84.1 | 9.27 | 1.70 |
| H ₂ O | 297 | 12.2 | 1.41 |
| C ₂ HCl ₂ F ₃ | 550 | 26.0 | 1.60 |
| C ₁₀ H ₂₂ | 2330 | 31.1 | 0.69 |
| C ₇ H ₁₆ | 2100 | 33.5 | 1.53 |
| C ₆ H ₁₄ | 27500 | 46.5 | 2.83 |

NOTE: The shaded region indicates the Guggenheim fluids.

value of the AARD. A possible explanation for this can be found in the data reported in Table 1 for the triple point and critical point coordinates. These values are similar for the seven fluids except for the value corresponding to the triple point pressure for the oxygen, which is much smaller. Therefore, the second factor we consider in our analysis is the reduced triple point pressure, P_{rt} , as a measure of the *distance* between the triple point and the critical point. The values of P_{rt} for the Guggenheim fluids are reported in Table 1. One can see that this value for the oxygen is about two orders of magnitude smaller than the values for the remaining Guggenheim fluids. Thus, we conclude that the smaller the value of P_{rt} is, the larger the deviation of experimental P_r is with respect to value predicted by eq 13 or, equivalently, by eq 10.

To check the suggested influence of ω and P_{rt} on the AARD we now consider a new set of seven fluids not studied by Guggenheim: ammonia (NH₃), refrigerant R14 (CF₄), water (H₂O), refrigerant R123 (C₂HCl₂F₃), decane (C₁₀H₂₂), heptane (C₇H₁₆), and 2-methylpentane (C₆H₁₄). A plot of $\phi(t)$ versus t for these fluids is shown in Figure 2. The *experimental* values of

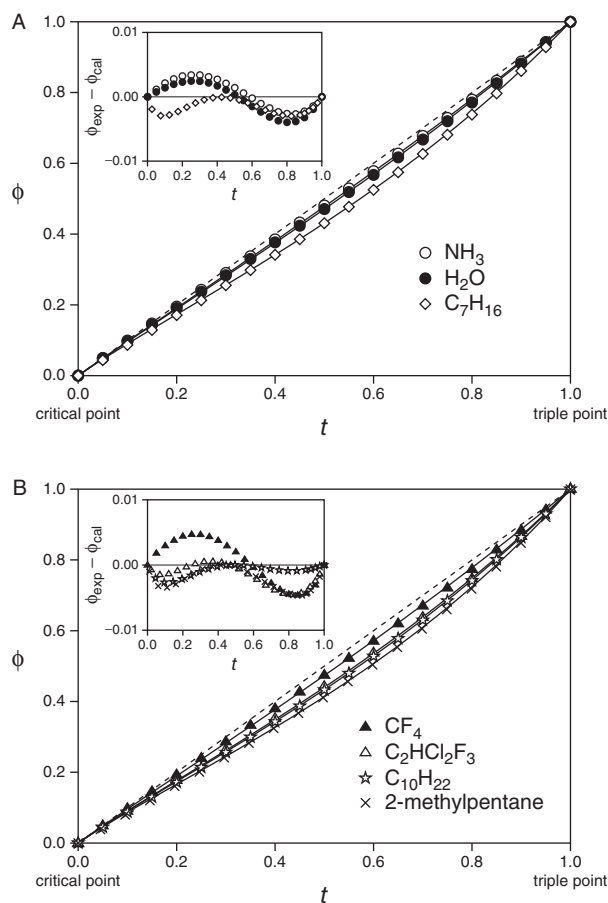


Figure 2. Dimensionless variable ϕ versus dimensionless temperature t for (A) ammonia, water, and heptane and (B) CF₄, C₂HCl₂F₃, decane, and 2-methylpentane. The symbols represent NIST data (13), the dashed lines represent the Clausius–Clapeyron equation, eq 10, and the solid lines represent eq 39 with values of parameter c_1 calculated from the acentric factor (see Table 1). The insets show the difference $\phi_{\text{exp}} - \phi_{\text{cal}}$, where the subscripts exp and cal represent the NIST data and the corresponding calculated values.

$\phi(t)$ were calculated from the vapor pressure data provided by the NIST program (13) for the fluids using the triple point and critical point coordinates given in Table 1. From Figure 2, one can see that the experimental values of $\phi(t)$ deviate appreciably from the linear eq 10 (dashed lines in Figure 2). Now (see Table 2) eq 12 predicts vapor pressures with an AARD between ~84% for CF_4 to ~27500% for 2-methylpentane, thus indicating that these seven fluids are not Guggenheim fluids in the sense that the value of 5.4 in eq 5 does not fit the experimental vapor pressure data for the fluids. However, eq 13 predicts vapor pressures with an AARD between 6.6% for ammonia to ~46.5% for 2-methylpentane, in agreement with the deviations observed in Figure 2. The values of ω and P_{rt} for these fluids are also reported in Table 1. One can see that, in general, the ability of the Clausius–Clapeyron equation in the form eq 10 (or eq 13) to predict vapor pressures increases as the acentric factor decreases and the reduced triple point pressure increases, improving in all cases the predictions of the Guggenheim equation, eq 5 (or eq 12). But it should be remarked that while the Guggenheim equation, eq 5, only needs T_c and P_c as input data, eq 10 also needs T_t and P_t as input data.

A Simple Correction to the Clausius–Clapeyron Equation

From definitions eqs 8 and 9, the natural logarithm of the vapor pressure can be written in terms of the dimensionless temperature t as

$$\ln P_r = \frac{T_{\text{rt}} \ln P_{\text{rt}}}{1 - (1 - T_{\text{rt}})t} \phi(t) \quad (15)$$

where the function $\phi(t)$ must verify the conditions $\phi(0) = 0$ and $\phi(1) = 1$. Taking into account eq 10, the following expression is proposed for the dimensionless variable ϕ as a function of the dimensionless temperature t ,

$$\phi(t) = t f(t) \quad (16)$$

where the function $f(t)$ provides the deviation of the saturated vapor pressure with respect to the behavior predicted by the Clausius–Clapeyron equation, eq 10. Since $\phi(1) = 1$, $f(t)$ must verify the condition

$$f(1) = 1 \quad (17)$$

Furthermore, since $\phi(0) = 0$, $f(t)$ presents an indeterminate form $0/0$ at $t = 0$. Then, using the L'Hôpital rule one obtains

$$\lim_{t \rightarrow 0} f(t) = \lim_{t \rightarrow 0} \frac{\phi(t)}{t} = \phi'(0) \quad (18)$$

where $\phi'(t) = d\phi(t)/dt$. From definitions eqs 8 and 9, one has

$$\begin{aligned} \phi'(t) &= \frac{d\phi}{dT_r} \frac{dT_r}{dt} \\ &= -\frac{1 - T_{\text{rt}}}{T_{\text{rt}} \ln P_{\text{rt}}} \left(\ln P_r + T_r \frac{d \ln P_r}{dT_r} \right) \end{aligned} \quad (19)$$

Then, taking into account that at $t = 0$ (critical point) one has $T_r = 1$ and $P_r = 1$ and eqs 18 and 19 yield

$$f(0) = \phi'(0) = -\frac{(1 - T_{\text{rt}}) \alpha_c}{T_{\text{rt}} \ln P_{\text{rt}}} \quad (20)$$

where $\alpha_c = (dP_r/dT_r)_{T_r=1}$ is the so-called Riedel factor that gives the slope of the reduced vapor pressure curve $P_r(T_r)$ at the critical point (19, 20).

To propose a form for the deviation function $f(t)$ we write this function as

$$f(t) = f_t(t) + f_c(t) \quad (21)$$

where $f_t(t)$ describes the behavior in the vicinity of the triple point while $f_c(t)$ accounts for the behavior near the critical point. The contribution $f_t(t)$ can be formally expanded in powers of $(1 - t)$,

$$f_t(t) = a_0 + \sum_{i=1} a_i (1 - t)^i \quad (22)$$

On the other hand, the expression for $\phi(t)$ must incorporate the singular behavior of the vapor pressure near the critical point $t_c = 0$. Therefore, we propose the following series for the contribution $f_c(t)$ in eq 21

$$f_c(t) = b_0 + \sum_{i=1} b_i t^{n_i} \quad (23)$$

where the exponents n_i ($n_1 < n_2 < \dots$) must be consistent with extended thermodynamics scaling for the vapor pressure around the critical point (21). In particular, as one approaches the critical point, renormalization group theory establishes that the second derivative of the vapor pressure with respect to the temperature diverges following the scaling law (22)

$$\frac{d^2 P_r}{dT_r^2} \sim (1 - T_r)^{-\alpha} \quad (24)$$

where $\alpha = 0.11$ is the universal critical exponent for the heat capacity at constant volume. Since P_r and dP_r/dT_r remain finite at the critical point, scaling law, eq 24, implies that

$$\frac{d^2 \ln P_r}{dT_r^2} \sim (1 - T_r)^{-\alpha} \quad (25)$$

when T_r approaches 1 (critical point). Taking into account the condition of critical point, $\ln P_r = 0$ at $T_r = 1$, integrating eq 25 twice yields

$$\ln P_r = A_1(1 - T_r) + A_2(1 - T_r)^{2-\alpha} + \dots \quad (26)$$

near the critical point. On the other hand, near the critical point ($t = 0$) one can approach $\phi(t) \approx t f_c(t)$. Then, using eqs 15 and 23, near the critical point one can write

$$\ln P_r = T_{\text{rt}} \ln P_{\text{rt}} (b_0 t + b_1 t^{1+n_1} + \dots) \quad (27)$$

Since $t \sim (1 - T_r)$, comparison between eqs 26 and 27 shows that the leading critical exponent in series in eq 23 is $n_1 = 1 - \alpha$. Therefore, retaining only low-order terms in eqs 22 and 23, we can express the function $f(t)$ as

$$\begin{aligned} f(t) &= (a_0 + b_0) + b_1 t^{1-\alpha} + a_1(1 - t) + \dots \\ &= c_0 (1 + c_1 t^{1-\alpha} - c_2 t + \dots) \end{aligned} \quad (28)$$

where the parameters c_i can be easily obtained in terms of the parameters a_i and b_i . The series $(1 + c_1 t^{1-\alpha} - c_2 t + \dots)$ in eq 28

approaches the limit $(1 - c_1 t^{1-\alpha} + c_2 t)^{-1}$ if

$$\left| c_1 t^{1-\alpha} - c_2 t \right| \leq 1 \quad (29)$$

It will be found below that this convergence condition is satisfied for the fluids considered in this article. Using this approximation, eq 28 yields

$$f(t) = \frac{c_0}{1 - c_1 t^{1-\alpha} + c_2 t} \quad (30)$$

Using eq 30, from conditions eqs 17 and 20, the parameters c_0 , c_1 , and c_2 are related by

$$c_0 = 1 - c_1 + c_2 = \phi'(0) \quad (31)$$

where $\phi'(0)$ can be calculated from eq 20 in terms of the Riedel factor α_c . Unfortunately, α_c is not usually available in pedagogical literature. However, from Figures 1 and 2 one can see that $\phi(t)$ approaches the critical point, $t_c = 0$, with approximately the same slope as eq 10, that is, one can assume that

$$\phi'(0) \approx 1 \quad (32)$$

Taking into account eq 20, this approximation is equivalent to

$$\alpha_c \approx -\frac{T_{rt} \ln P_{rt}}{1 - T_{rt}} \quad (33)$$

Using approximation eq 32, from eq 31 one obtains that $c_0 = 1$ and $c_1 = c_2$. Considering these results in eq 30, the final form that we propose for $f(t)$ is

$$f(t) = \frac{1}{1 + c_1(t - t^{1-\alpha})} \quad (34)$$

We note that the approximations made in eq 28 to obtain eq 34 essentially reduce to equating $1 + x$ to $1/(1-x)$, where $x = c_1(t^{1-\alpha} - t)$, and this requires that c_1 be small enough. Higher-order terms in the expansion $1/(1-x)$ cannot be neglected as c_1 becomes larger.

By substituting eq 34 into eq 16, the final form for $\phi(t)$ is

$$\phi(t) = \frac{t}{1 + c_1(t - t^{1-\alpha})} \quad (35)$$

Equation 35 contains only one fluid-dependent parameter (c_1) that can be obtained from additional experimental vapor pressure data (other than triple or critical points coordinates). In this work we shall obtain c_1 by using the acentric point ($T_r = 0.7$, $P_r = P_{r\omega}$) as reference. Then, by imposing that $\phi(t)$ passes through this point, from eq 35 one obtains

$$c_1 = \frac{t_\omega - \phi_\omega}{\phi_\omega(t_\omega - t_\omega^{1-\alpha})} \quad (36)$$

where, using eq 9,

$$t_\omega = \frac{0.3}{1 - T_{rt}} \quad (37)$$

and, using eqs 8 and 14,

$$\phi_\omega = \frac{0.7 \ln P_{r\omega}}{T_{rt} \ln P_{rt}} = -\frac{(1 + \omega) 0.7 \ln 10}{T_{rt} \ln P_{rt}} \quad (38)$$

The values of the parameter c_1 calculated from eq 36 are given in Table 1 for the fluids considered in this article. From these values one can check the convergence condition eq 29. Since $c_1 = c_2$, eq 29 becomes $|c_1| \leq 1/\max|t^{1-\alpha} - t| \approx 23.3$ (with $\alpha = 0.11$). One can see that in all cases one verifies this condition.

Using eq 15, the vapor pressure values provided by eq 35 are calculated by

$$\ln P_r(t) = \frac{T_{rt} t}{\left[1 - (1 - T_{rt})t\right] \left[1 + c_1(t - t^{1-\alpha})\right]} \ln P_{rt} \quad (39)$$

The AARDs, calculated using eq 39 with values of the parameter c_1 reported in Table 1, are listed in Table 2 for the fluids considered here. One can see that the predictions of eq 39 (or eq 35) for vapor pressures improve the predictions of eq 13 (or eq 10) specially for oxygen and the seven non-Guggenheim fluids considered. This improvement can be seen in Figure 2 where we have plotted with solid lines the function $\phi(t)$ given by eq 35, with the respective values of c_1 reported in Table 1, for ammonia, CF_4 , water, $\text{C}_2\text{HCl}_2\text{F}_3$, decane, heptane, and 2-methylpentane. The small deviations between $\phi(t)$ obtained from the NIST data and $\phi(t)$ calculated from eq 35 are shown in the insets of Figure 2. We note that eq 35 requires the acentric factor ω as an additional input datum respect to eq 10, but it is able to significantly improve the prediction of vapor pressures even for substances such as 2-methylpentane with a low reduced triple point pressure.

To apply this method to an additional fluid one must proceed as follows: (i) consider T_r , P_r , T_c , P_c , and ω as input data; (ii) calculate the parameter c_1 from eqs 36–38; and (iii) use eq 39 to obtain the reduced vapor pressure as a function of the dimensionless temperature t .

Conclusions

At a pedagogical level, there are two main reasons for proposing the Clausius–Clapeyron equation to describe the temperature dependence of the saturated vapor pressure of a fluid: it is easy to derive and justify theoretically and it provides a good accuracy for many applications, particularly at small temperature ranges far from the critical point. Furthermore, Guggenheim showed that for some simple fluids one can use a corresponding states form of the Clausius–Clapeyron equation along the entire liquid–vapor coexistence curve. However, the Guggenheim equation can not be considered as a strictly universal equation because it contains an empirical parameter obtained from a fit to experimental vapor pressure data for seven simple fluids.

In this article, we have shown that by introducing two dimensionless variables reduced by using both triple point and critical point coordinates, the Clausius–Clapeyron equation can be written by means of a simple linear equation without any adjustable parameter. By analyzing the deviations of experimental vapor pressure data for fourteen fluids (the seven considered by Guggenheim and other seven taken from the NIST program) with respect to such universal form, we have proposed a vapor

pressure equation that satisfies some conditions that make it useful for practical pedagogical applications: (i) it has a simple analytical form containing only one fluid-dependent parameter; (ii) it is consistent with the renormalization group theory of critical phenomena; and (iii) it provides a good reproducibility of experimental vapor pressure values over the entire liquid-vapor coexistence curve for a wide variety of fluids.

Acknowledgment

We gratefully acknowledge financial support from the Ministerio de Educación y Ciencia of Spain under Grants FIS2005-05081 FEDER and FIS2006-03764 FEDER.

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