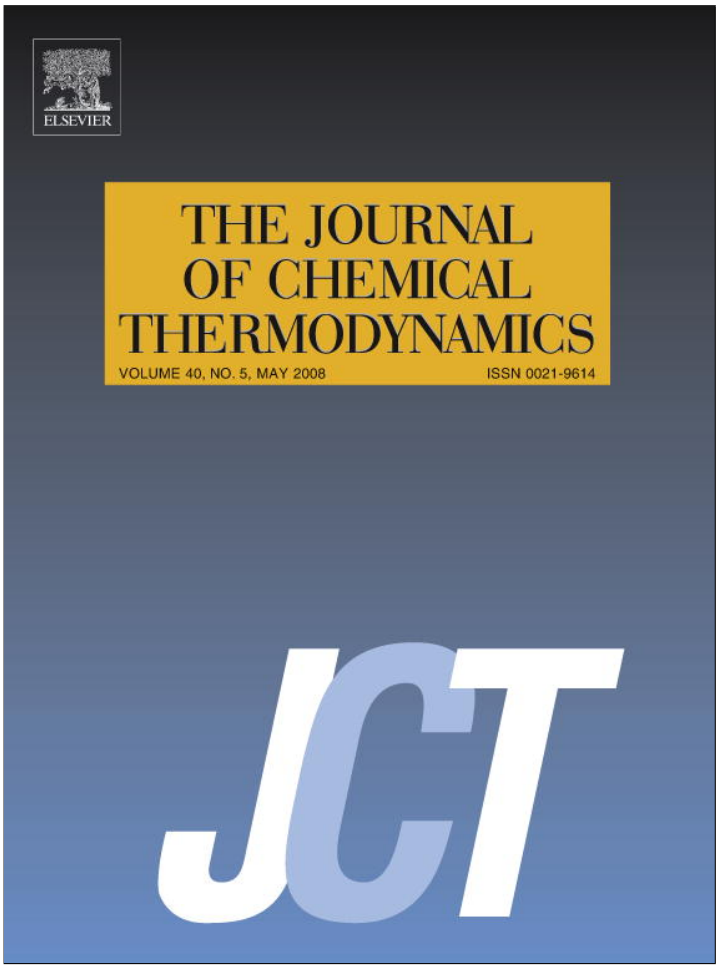

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A predictive vapor-pressure equation

S. Velasco [a], F.L. Román [a,b,*], J.A. White [a], A. Mulero [c]

[a] Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Salamanca, 37008 Salamanca, Spain
[b] Departamento de Física Aplicada, E.P.S. de Zamora, Universidad de Salamanca, 49022 Zamora, Spain
[c] Departamento de Física, Universidad de Extremadura, E-06071 Badajoz, Spain

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Abstract

A simple equation is presented for predicting the temperature dependence of the vapor-pressure of a pure substance along the entire (liquid + vapor) coexistence curve, from the triple point to the critical point. The proposed equation is based on the use of a dimensionless temperature reduced by using critical and triple point values, and of the Clausius–Clapeyron equation as a zeroth-order approximation. The pressure and temperature at the triple point, the normal boiling temperature, and the pressure and temperature at the critical point are required as input data. The proposed equation is verified for 53 fluids by using NIST data. These data are reproduced with an overall average deviation of 0.55%.

Keywords: Vapor-pressure; Vapor-pressure equations; Predictions; Riedel parameter; Pure substances

1. Introduction

Vapor-pressure equations try to provide the temperature dependence of the saturated pressure of a fluid along the (liquid + vapor) coexistence curve. Since the Clapeyron equation was proposed in 1834, there has been a plethora of vapor-pressure equations described for both correlating and predicting experimental data of pure fluids. Most of these equations are based on the corresponding-states principle, and give the natural logarithm of the reduced vapor-pressure, $P_r = P/P_c$, as a function of the reduced temperature, $T_r = T/T_c$, where P_c and T_c are the pressure and temperature at the critical point. An excellent summary of the main vapor-pressure equations proposed in the literature up to 1994 can be found in the paper by Xiang and Tan [1]. A discussion of those equations that seem to be most accurate for correlation and estimation can be found in reference [2]. We note, however, that several older proposals [3–7], and of course more recent ones [8–15], were not included in reference [2].

Perhaps, the most widely recognized predictive vapor-pressure equation is that proposed by Riedel in 1954 [16]. Riedel's equation consists of a part arising from the integration of the Clapeyron equation by assuming that the enthalpy of vaporization varies linearly with the temperature plus a corrective term proportional to the temperature raised to the sixth power. Using as input data, the normal boiling temperature, T_b, and the critical values, T_c and P_c, Riedel's equation is able to predict with a fair degree of accuracy the vapor-pressure of various classes of pure substances [17].

However, as is also the case for other predictive equations, Riedel's equation does not provide in general satisfactory accuracy in the very low pressure range, *i.e.*, close to the triple point. As has recently been pointed out by Vetere [18], the main problem in providing vapor pressures as a function of temperature perhaps lies in characterizing the vapor-pressure behavior of a substance in the very low temperature range. Experimentally, some methods to extrapolate results can be used [19,20], or heat capacities can be measured in this low temperature region and the

* Corresponding author. Address: Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Salamanca, 37008 Salamanca, Spain. Tel.: +34 923294436; fax: +34 923294584.
E-mail address: romanh@usal.es (F.L. Román).

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Clapeyron equation used to obtain the vapor-pressure behavior [21–23]. Theoretically, the simplest approach is to extrapolate the frequently used vapor-pressure equations to low temperatures [8,13,24]. Another possibility is to modify the original equation to improve its performance in predicting experimental data in the low pressure range [18,25]. If the triple point pressure is known with sufficient precision, a third possibility is to include the temperature, T_t, and the pressure, P_t, at the triple point as input data [3–6,8,14,15]. The present study will follow this third way.

Here, we propose a predictive vapor-pressure equation based on the use of both a dimensionless temperature t reduced by using the triple point and critical temperatures, and the Clausius–Clapeyron equation as a zeroth-order approximation to characterize the natural logarithm of the reduced vapor-pressure, $\ln P_r$, as a function of t. In particular, the proposed equation consists of the Clausius–Clapeyron equation times a corrective function of t given as the product of two polynomial terms constructed by requiring the vapor-pressure equation to pass through a number of reference points. By taking the triple and the normal boiling points as reference, the simplest form of the proposed equation contains only one unknown parameter that can be evaluated by imposing the same condition used in the original Riedel method: the equation presents an inflection point just at the critical point. While the Riedel equation is based only on the normal boiling temperature and the critical coordinates and contains two empirical parameters, the proposed equation also needs the triple point coordinates as additional input but does not require any empirical parameter.

In this paper, the reliability of the proposed equation in predicting vapor-pressure data are evaluated for 53 pure substances. These results are compared with those obtained from the Riedel equation by using its original parameters and with those obtained from the Riedel equation with parameters calculated by imposing that, like the proposed equation, it also passes through the triple point.

The paper is organized as follows. In Section 2, we present the original Riedel equation and another formulation of this equation by assuming that it passes through the triple point. In Section 3, we present the new equation. In Section 4, we present and compare the results of the three equations. Finally, Section 5 presents the main conclusions.

2. Riedel's equation

The Clapeyron equation provides the basis for the analysis of phase transitions. In particular, the Clapeyron equation for vaporization may be written as

$$\frac{\mathrm{d}\ln P_r}{\mathrm{d}T_r} = \frac{\Delta H_r}{T_r^2 \Delta Z}, \tag{1}$$

where $\Delta H_r = \Delta H/RT_c$ is the reduced enthalpy of vaporization, R the ideal gas constant, and ΔZ the difference between the compressibility factors of saturated vapor and saturated liquid.

Most proposed vapor-pressure equations come from integrating equation (1). In this context, Riedel proposed the form [16]

$$\ln P_r = A' - \frac{B'}{T_r} + C' \ln T_r + D' T_r^6, \tag{2}$$

where the first three terms arise from integration of equation (1) by assuming that $\Delta Z = 1$ and that ΔH_r varies linearly with T_r. The T_r^6 term is added to reduce the inaccuracies introduced by the above assumptions, especially in the high-pressure region. In equation (2), A', B', C', and D' are substance-dependent constants that are calculated by introducing the function

$$\alpha(T_r) \equiv \frac{\mathrm{d}\ln P_r}{\mathrm{d}\ln T_r} = T_r \frac{\mathrm{d}\ln P_r}{\mathrm{d}T_r} = \frac{\Delta H_r}{T_r \Delta Z}, \tag{3}$$

and imposing that equation (2) satisfies the following conditions: (1) it passes through the critical point [$T_r = 1$ and $P_r = 1$]; (2) it passes through the normal boiling point [$T_{br} = T_b/T_c$ and $P_{br} = 0.101325/P_c$, with P_c expressed in MPa]; and (3) it fits the experimental evidence that close to the critical point the function α is independent of the temperature (Plank–Riedel condition) [26]

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T_r}\right)_{T_r=1} = 0. \tag{4}$$

From these conditions one has

$$A' = -35Q, \quad B' = -36Q, \quad C' = 42Q + \alpha_c, \quad D' = -Q, \tag{5}$$

with $\alpha_c = \alpha(T_r = 1)$ given by

$$\alpha_c = -\frac{\psi_b Q - \ln P_{br}}{\ln T_{br}}, \tag{6}$$

$$\psi_b = -35 + \frac{36}{T_{br}} + 42 \ln T_{br} - T_{br}^6, \tag{7}$$

where Q is an unknown empirical parameter. By correlating the experimental vapor-pressure data for various pure compounds, Riedel proposed the following expression for the parameter Q:

$$Q = K_1(K_2 - \alpha_c), \tag{8}$$

with $K_1 = 0.0838$ and $K_2 = 3.758$. Substituting equation (8) into equation (6) one obtains

$$\alpha_c = \frac{K_1 K_2 \psi_b - \ln P_{br}}{K_1 \psi_b - \ln T_{br}}, \tag{9}$$

which yields α_c in terms of P_{br} and T_{br}. It should be noted that condition (4) is at odds with renormalization-group theory which predicts that $\mathrm{d}^2 P_r/\mathrm{d}T_r^2$ is indeterminate at the critical point [1]. However, as was remarked by Vetere [17] (following Ambrose [27]), "as far as correlation is concerned, whether or not an equation is analytic at the critical point is of no importance".

In 1991, Vetere [17] showed that the constant K_1 in equation (8) can be considered neither constant nor universal. He thus proposed using a substance-dependent value

for this constant in order to improve the predictions of Riedel's equation for the vapor-pressure of alcohols and acids. Very recently, Vetere [18] proposed for K_1 different linear T_r-dependent expressions for various families of compounds with similar physico-chemical properties in order to improve estimation with Riedel's equation in the very low pressure range, between the triple point and 1 mmHg.

We here also consider the Riedel equation, but assuming the condition that it passes through the triple point instead of using the empirical correlation (8). To this end, we write the Riedel equation (2) in the form

$$\ln P_r = A'' - \frac{B''}{T_r} + C'' \ln T_r + D'' T_r^6, \tag{10}$$

where A'', B'', C'', and D'' are evaluated by imposing the following four conditions on the equation: (1) it passes through the triple point; (2) it passes through the critical point; (3) it passes through the normal boiling point; and (4) it satisfies equation (4). From these conditions one can easily obtain that

$$A'' = -35Q', \quad B'' = -36Q', \quad C'' = 42Q' + \alpha_c, \quad D'' = -Q', \tag{11}$$

with

$$Q' = \frac{\ln P_{tr} \ln T_{br} - \ln P_{br} \ln T_{tr}}{\psi_t \ln T_{br} - \psi_b \ln T_{tr}}, \tag{12}$$

$$\alpha_c = -\frac{\psi_b Q' - \ln P_{br}}{\ln T_{br}} = -\frac{\psi_t Q' - \ln P_{tr}}{\ln T_{tr}}, \tag{13}$$

$$\psi_t = -35 + \frac{36}{T_{tr}} + 42 \ln T_{tr} - T_{tr}^6, \tag{14}$$

with $P_{tr} = P_t/P_c$ being the reduced triple point pressure, and where ψ_b is given by equation (7). Equation (10) needs the triple point coordinates as additional input but it does not require any empirical parameter. It can therefore be considered as a fully predictive version of the original Riedel equation.

The present work compares the original Riedel equation, equation (2), and the Riedel equation in the form (10). We shall denote the method based on the use of equation (2) by R1 (original Riedel's model), and that based on the use of equation (10) by R2 (Riedel's model with the triple point as reference).

3. Our proposal

Let us begin with the simplest approach to the vapor-pressure curve

$$\ln P_r^{(0)}(T_r) = A - \frac{B}{T_r}, \tag{15}$$

where A and B are substance-dependent constants. Equation (15) comes from integrating equation (1) assuming that the ratio $\Delta H_r/\Delta Z$ is constant, and is usually called the Clausius–Clapeyron equation. By imposing that $P_r^{(0)}(T_r)$ passes through the critical point, one has $B = A$, and equation (15) becomes

$$T_r \ln P_r^{(0)}(T_r) = A(T_r - 1), \tag{16}$$

where the constant A can be obtained from a known vapor-pressure value. For example, by choosing the triple point as reference one has

$$A = \frac{T_{tr} \ln P_{tr}^{(0)}}{T_{tr} - 1}, \tag{17}$$

which substituted into equation (16), leads to

$$\phi_0(t) \equiv \frac{T_r \ln P_r^{(0)}(T_r)}{T_{tr} \ln P_{tr}} = \frac{T_r - 1}{T_{tr} - 1} = 1 - t, \tag{18}$$

where we have introduced the dimensionless temperature

$$t = \frac{T - T_t}{T_c - T_t} = \frac{T_r - T_{tr}}{1 - T_{tr}}. \tag{19}$$

Equation (18) is a very simple, universal form of expressing the Clausius–Clapeyron equation along the whole (liquid + vapor) coexistence curve, from the triple point temperature, $t = 0$, to the critical temperature, $t = 1$. The dimensionless temperature (19) has been considered by several authors to correlate experimental data of the enthalpy of vaporization [28–30], the liquid saturation density [31], and the vapor-pressure [4,3,5,8,14,15] of several substances. It has also been used by us [32] to analyze the apparent universal behavior of some thermodynamic properties along the coexistence curve.

Equation (18) suggests the introduction of the variable

$$\phi(t) \equiv \frac{T_r \ln P_r}{T_{tr} \ln P_{tr}}, \tag{20}$$

to model the behavior of the vapor-pressure along the whole coexistence curve. We note that $\phi_0(t)$, given by equation (18), is the function $\phi(t)$ with reduced vapor-pressure given by the Clausius–Clapeyron equation (15). We also note that the values of $\phi(t)$ range between $\phi(0) = 1$, at the triple point, and $\phi(1) = 0$, at the critical point. Figure 1 shows the variation of $\phi(t)$ with t for three substances (water, R12, and 2-methylpentane) from the vapor-pressure data reported in the NIST program [33]. We have also plotted (dashed line) the Clausius–Clapeyron equation (18). One observes that the $\phi(t)$ *versus* t plot provides a universal framework in which to appreciate the deviations from the vapor-pressure data of the values predicted by the Clausius–Clapeyron equation. To analyze such deviations, we introduce the function

$$f(t) = \frac{\phi_0(t)}{\phi(t)} = \frac{1 - t}{\phi(t)}, \tag{21}$$

which is a bounded regular function along the whole coexistence curve verifying the boundary condition

$$f(0) = 1. \tag{22}$$

We note that $f(t)$ is well defined at the critical point where it takes the value

$$f(1) = -\frac{1}{\phi'(1)} = -\frac{T_{tr} \ln P_{tr}}{(1 - T_{tr})\alpha_c}, \tag{23}$$

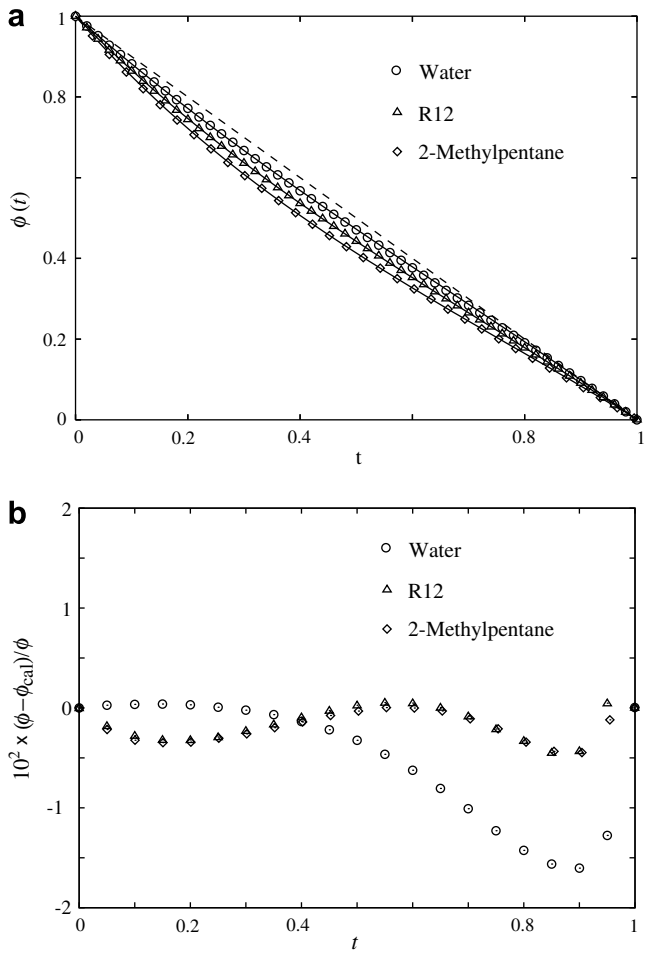

FIGURE 1. (a) Plot of function $\phi(t)$ *versus* reduced temperature t for water (circles), R12 (triangles), and 2-methylpentane (diamonds) using NIST data. The solid lines represent the predicted behavior using equation (32) whereas the dashed line represents the universal form of the Clausius–Clapeyron equation (18). (b) Relative deviations $10^2(\phi - \phi_{cal})/\phi$ *versus* reduced temperature t for water (circles), R12 (triangles), and 2-methylpentane (diamonds) using NIST data.

where $\phi'(t) = d\phi(t)/dt$ and α_c is the Riedel function (3) at the critical point.

Inspired by a proposition of Ledanois *et al.* [6], we now write $f(t)$ as the product of two polynomial terms

$$f(t) = f_1(t) f_2(t). \tag{24}$$

The first term $f_1(t)$ is the Lagrange interpolation polynomial of degree $n-1$

$$f_1(t) = \sum_{i=1}^{n} a_{i-1} t^{i-1}, \tag{25}$$

where the coefficients a_i are obtained by imposing that $\phi(t)$ passes through n reference points $(\phi_1, t_1), \ldots, (\phi_n, t_n)$ other than the critical point. The second term in equation (24), $f_2(t)$, is another polynomial that yields the best fit to the remaining known experimental data (not reference points). Since the conditions $f_2(t_i) = 1$ must be verified, we express this polynomial as

$$f_2(t) = 1 + \left[\prod_{i=1}^{n}(t - t_i)\right] \sum_{j=0}^{m} b_j t^j, \tag{26}$$

where the coefficients b_j are adjustable parameters.

Using only the triple and normal boiling points as reference (*i.e.*, with $t_1 = 0$ and $t_2 = t_b$), the interpolating polynomial (25) becomes

$$f_1(t) = 1 + a_1 t, \tag{27}$$

where

$$a_1 = \frac{1 - t_b - \phi_b}{t_b \phi_b} \tag{28}$$

with

$$t_b = \frac{T_{br} - T_{tr}}{1 - T_{tr}} \tag{29}$$

and

$$\phi_b = \frac{T_{br} \ln P_{br}}{T_{tr} \ln P_{tr}}. \tag{30}$$

In this case, the simplest form of the polynomial (26) is obtained for $m = 0$, for which

$$f_2(t) = 1 + b_0 t(t - t_b). \tag{31}$$

Then, taking into account equations (21), (24), (27), and (31), we obtain

$$\phi(t) = \frac{1 - t}{(1 + a_1 t)[1 + b_0 t(t - t_b)]}. \tag{32}$$

In the above equation, b_0 is the only unknown parameter and, for a given substance, it can be obtained from a fitting procedure. However, we can also determine b_0 by using the Plank–Riedel condition, equation (4). Indeed, condition (4) can be written as

$$\left(\frac{d^2 \ln P_r}{dT_r^2}\right)_{T_r=1} + \left(\frac{d \ln P_r}{dT_r}\right)_{T_r=1} = 0, \tag{33}$$

or, taking into account equations (19) and (20), as

$$\phi''(1) = (1 - T_{tr})\phi'(1), \tag{34}$$

where $\phi''(t) = d^2\phi(t)/dt^2$. Then, using equation (32), one obtains

$$b_0 = -\frac{1 - T_{tr} + (3 - T_{tr})a_1}{2(1 - t_b)a_1 + [5 - T_{tr} - (3 - T_{tr})t_b](1 + a_1)}. \tag{35}$$

Thus, equation (32) with the parameters a_1 and b_0 given by equations (28) and (35), respectively, provides a simple equation for the vapor-pressure along the whole coexistence curve. Application of equation (32) needs the reduced triple point constants P_{tr} and T_{tr}, and the reduced normal boiling temperature T_{br} as input data. Therefore, the proposed equation does not include any empirical parameter and can be considered as a fully predictive equation. In comparison with the method R1, the proposed equation needs two additional inputs (the triple point coordinates), but it uses the same inputs as the method R2.

In the present work, we have only compared the results of equation (32) with those of Riedel equations R1 and R2, omitting comparison with other well established equations. The main reason for this procedure lies in a recent work by Vetere [18] in which the author compares Riedel's equation with the predictive version of other well-known equations of the literature ([39–44], *etc.*) showing that the Riedel equation was probably the best, simplest choice among the considered vapor-pressure equations. Furthermore, since our result, equation (32), is a fully predictive equation, it should be compared with equations of the same kind.

TABLE 1
Critical pressure P_c, critical temperature T_c, reduced triple point temperature T_{tr}, reduced normal boiling temperature T_{br}, and the natural logarithm of the reduced triple point pressure P_{tr} for the substances considered in this work (data from NIST)

	P_c/MPa	T_c/K	T_{tr}	T_{br}	$\ln P_{tr}$	a_1	b_0
Cyclopropane	5.5689	398.30	0.68541	0.60675	−2.7881	0.069478	−0.087923
Propyne	5.6267	402.38	0.67846	0.61633	−3.0610	−0.0047272	−0.065571
R114	3.2516	418.83	0.65217	0.66077	−3.6077	0.055656	−0.10318
Neon	2.6786	44.492	0.55205	0.60919	−4.1211	−0.039367	−0.090051
Argon	4.8630	150.69	0.55612	0.57935	−4.2569	0.0086271	−0.10640
Xenon	5.8420	289.73	0.55707	0.56967	−4.2692	0.013360	−0.10668
Krypton	5.5255	209.48	0.55265	0.57156	−4.3198	0.0096061	−0.10691
2,2-Dimethylpropane	3.1963	433.74	0.59160	0.65166	−4.5030	0.069754	−0.12935
R116	3.0477	293.03	0.59072	0.66567	−4.7608	0.076111	−0.13486
R41	5.8970	317.28	0.55156	0.61468	−5.3155	0.060126	−0.13374
Carbon monoxide	3.4982	132.86	0.51302	0.61448	−5.4168	0.052168	−0.14482
Nitrogen	3.3958	126.19	0.50044	0.61300	−5.6030	0.039849	−0.14420
Hydrogen sulfide	8.9987	373.10	0.50308	0.57049	−5.9581	0.090204	−0.15400
Methane	4.5992	190.56	0.47593	0.58599	−5.9744	0.022408	−0.14097
Cyclohexane	4.0750	553.64	0.50479	0.63920	−6.6537	0.13367	−0.18323
Benzene	4.9012	562.05	0.49586	0.62847	−6.9289	0.14706	−0.18851
R125	3.6179	339.17	0.50865	0.66356	−7.1241	0.14548	−0.19211
R115	3.1584	353.10	0.49210	0.66330	−7.2706	0.11764	−0.18895
R113	3.3923	487.21	0.48630	0.65831	−7.5026	0.14929	−0.20118
Ammonia	11.339	405.40	0.48224	0.59157	−7.5292	0.12442	−0.17763
Decafluorobutane	2.3290	386.33	0.48922	0.70163	−8.3155	0.19332	−0.22834
Sulfur dioxide	7.8753	430.64	0.45908	0.61102	−8.4646	0.18010	−0.20910
R14	3.7758	227.51	0.43488	0.63777	−8.6804	0.13538	−0.21164
R21	5.1842	451.48	0.44299	0.62464	−8.6894	0.16972	−0.21619
Dodecafluoropentane	2.0368	420.56	0.47556	0.72024	−9.5447	0.25787	−0.26209
Fluorine	5.2394	144.41	0.37034	0.58886	−9.9961	0.11636	−0.21752
Oxygen	5.0428	154.58	0.35167	0.58344	−10.448	0.099423	−0.21719
Water	22.064	647.10	0.42213	0.57661	−10.493	0.17027	−0.21182
Ethene	5.0417	282.35	0.36830	0.59989	−10.630	0.15800	−0.23559
R23	4.8317	299.29	0.39433	0.63862	−11.330	0.19858	−0.24971
Nitrogen trifluorine	4.4607	234.00	0.36325	0.61597	−11.341	0.16569	−0.24485
Carbonyl sulfide	6.3688	378.77	0.35457	0.58875	−11.501	0.18143	−0.24543
R32	5.7826	351.25	0.38816	0.63060	−11.699	0.18934	−0.24681
R11	4.4076	471.11	0.34531	0.63013	−13.426	0.23386	−0.27834
R123	3.6619	456.83	0.36337	0.65883	−13.678	0.27356	−0.29266
Octane	2.4978	569.32	0.38005	0.70043	−14.043	0.28811	−0.30650
R128	2.6402	345.02	0.36360	0.68506	−14.084	0.26658	−0.30098
Decane	2.1014	617.70	0.39420	0.72409	−14.219	0.29892	−0.31388
Hexane	3.0429	507.82	0.35018	0.67319	−14.684	0.25972	−0.30004
Ethane	4.8718	305.33	0.29592	0.60444	−15.276	0.19374	−0.27790
Nonane	2.2820	594.55	0.36952	0.71299	−15.451	0.31293	−0.32426
Butane	3.7960	425.12	0.31732	0.64137	−15.556	0.24412	−0.29737
R13	3.8790	302.00	0.30464	0.63467	−16.283	0.26662	−0.30692
R22	4.9900	369.30	0.31338	0.62914	−16.392	0.28638	−0.30661
Heptane	2.7311	540.13	0.33797	0.68785	−16.560	0.31158	−0.32684
R12	4.1362	385.12	0.30146	0.63201	−16.652	0.27073	−0.30845
Pentane	3.3710	469.70	0.30545	0.65831	−17.604	0.28844	−0.32215
Propene	4.6646	365.57	0.27355	0.61677	−18.390	0.26199	−0.31214
Toluene	4.1264	591.75	0.30080	0.64850	−18.467	0.32516	−0.33021
R124	3.6243	395.42	0.30348	0.66053	−18.725	0.33581	−0.33695
Propane	4.2477	369.82	0.23114	0.62479	−23.941	0.30664	−0.34584
2-Methylbutane	3.3757	460.35	0.24471	0.65379	−24.425	0.36052	−0.36660
2-Methylpentane	3.0426	497.70	0.24410	0.66980	−26.070	0.39047	−0.38198

Parameters a_1 and b_0 used in equation (32).

4. Results

In order to check equation (32), we analyzed the t dependence of the vapor-pressure of 53 pure substances. We used the data reported in the NIST program [33]. The critical point data, the triple point data, and the normal boiling temperature came from the same source, and, together with the substances considered, are given in the first six columns of table 1. The substances are ordered in decreasing value of the reduced triple point pressure (sixth column). For each substance, the corresponding parameters a_1 and b_0 of equation (32) were calculated from equa-

TABLE 2
Absolute relative deviations for the vapor-pressure

	R1 (equation (2))		R2 (equation (10))		Equation (32)	
Substance	Δ_{max} (%)	$\overline{\Delta}$ (%)	Δ_{max} (%)	$\overline{\Delta}$ (%)	Δ_{max} (%)	$\overline{\Delta}$ (%)
Cyclopropane	2.49	1.03	1.87	1.11	1.30	0.71
Propyne	4.24	2.51	0.99	0.47	1.47	0.80
R114	0.51	0.24	0.32	0.16	0.82	0.41
Neon	1.44	0.62	0.34	0.16	1.09	0.59
Argon	0.63	0.27	0.31	0.13	0.98	0.49
Xenon	0.68	0.35	0.35	0.14	0.90	0.44
Krypton	0.88	0.46	0.47	0.21	0.81	0.38
2,2-Dimethylpropane	0.31	0.14	0.17	0.08	0.90	0.42
R116	1.10	0.40	0.13	0.06	0.88	0.41
R41	2.86	1.44	0.20	0.09	1.02	0.50
Carbon monoxide	0.40	0.11	0.40	0.17	0.89	0.39
Nitrogen	0.61	0.28	0.36	0.16	0.98	0.42
Hydrogen sulfide	0.73	0.34	0.91	0.44	0.81	0.33
Methane	1.92	0.71	0.49	0.20	1.04	0.46
Cyclohexane	2.02	0.24	0.71	0.33	0.81	0.34
Benzene	3.04	0.39	1.01	0.58	0.49	0.18
R125	1.06	0.35	0.59	0.21	1.14	0.51
R115	5.34	1.44	0.85	0.40	0.72	0.29
R113	1.16	0.28	1.05	0.43	0.84	0.31
Ammonia	5.78	1.67	0.38	0.18	1.61	0.79
Decafluorobutane	6.82	0.64	1.78	0.58	0.86	0.34
Sulfur dioxide	1.25	0.33	0.93	0.50	1.13	0.47
R14	3.77	1.31	2.01	0.81	0.77	0.28
R21	2.97	0.26	0.80	0.36	1.17	0.58
Dodecafluoropentane	26.79	3.63	2.85	0.87	1.05	0.49
Fluorine	4.68	0.48	1.60	0.71	0.90	0.34
Oxygen	5.49	0.65	2.35	0.99	0.77	0.36
Water	17.24	4.28	1.06	0.53	1.54	0.70
Ethene	11.19	1.00	2.69	1.16	0.80	0.33
R23	5.81	1.92	2.54	0.98	0.87	0.32
Nitrogen trifluorine	4.35	0.69	3.11	1.05	1.11	0.49
Carbonyl sulfide	14.52	1.31	3.57	1.58	1.53	0.43
R32	14.09	3.47	2.67	1.04	0.88	0.31
R11	15.98	1.39	4.65	1.68	0.98	0.44
R123	21.10	1.79	5.37	1.90	0.74	0.34
Octane	15.84	1.34	5.20	1.76	1.04	0.60
R128	12.01	1.15	4.87	1.70	0.88	0.48
Decane	14.18	1.33	4.99	1.77	2.19	0.91
Hexane	3.59	1.28	4.74	1.69	0.77	0.46
Ethane	13.24	1.38	5.73	2.01	2.03	0.64
Nonane	18.52	1.77	6.29	2.30	1.60	0.66
Butane	10.56	1.50	6.22	2.24	1.38	0.48
R13	37.19	3.08	7.28	2.58	2.09	0.63
R22	27.56	2.24	7.12	2.48	1.92	0.68
Heptane	22.59	1.91	7.33	2.49	0.85	0.39
R12	34.56	2.74	8.38	2.96	3.22	0.92
Pentane	18.73	1.93	8.19	2.86	1.63	0.52
Propene	36.74	3.26	6.01	2.23	0.71	0.33
Toluene	40.32	3.36	10.35	3.78	3.36	0.99
R124	44.41	3.67	8.34	2.91	0.84	0.32
Propane	65.10	4.88	11.17	3.95	3.72	1.18
2-Methylbutane	92.01	6.16	16.53	5.60	7.40	2.02
2-Methylpentane	93.36	6.44	16.68	5.73	5.30	1.42
Overall		1.62		1.35		0.55

tions (28) and (35), respectively. The values obtained are reported in the last two columns of table 1. Figure 1a shows (solid lines) equation (32) for water, R12, and 2-methylpentane, and figure 1b shows a plot of relative deviations of data and calculated values of function ϕ for the same substances.

In order to analyze the reliability of the theoretical equations, we took $N = 99$ data for each substance between $t_0 = 0$ (triple point) and $t_{100} = 1$ (critical point) with $\Delta t \equiv t_i - t_{i-1} = 0.01$ $(i = 1, \ldots, N)$, and calculated the maximum absolute relative deviation (MARD)

$$\Delta_{\max}\ (\%) = \mathrm{Max}\left[\left|1 - \frac{P_{\mathrm{r},i}^{(\mathrm{calc})}}{P_{\mathrm{r},i}^{(\mathrm{exp})}}\right| \times 100\right] \quad (i = 1, \ldots, N), \tag{36}$$

and the average absolute relative deviation (AARD)

$$\overline{\Delta}\ (\%) = \frac{1}{N}\sum_{i=1}^{N}\left[\left|1 - \frac{P_{\mathrm{r},i}^{(\mathrm{calc})}}{P_{\mathrm{r},i}^{(\mathrm{exp})}}\right| \times 100\right], \tag{37}$$

where $P_{\mathrm{r},i}^{(\mathrm{calc})} = P_{\mathrm{r}}(t_i)$ is the value calculated from equation (32) and $P_{\mathrm{r},i}^{(\mathrm{exp})}$ denotes the corresponding experimental value. The MARDs, $\Delta_{\max}$, and the AARDs, $\overline{\Delta}$, are listed in table 2 for the three methods considered: R1 [based on the Riedel equation (2) with constants A', B', C', and D' evaluated from equations (5), (7), (8), and (9) with $K_1 = 0.0838$ and $K_2 = 3.758$], R2 [based on the Riedel equation (10) with constants A'', B'', C'', and D'' evaluated from equations (11) to (14) and (7)], and the method based on the use of equation (32).

As can be seen, the overall AARD is reduced from 1.62% when the R1 method is used to 1.35% and 0.55%, respectively, when the predictive R2 and the new equations are used. We note that the overall AARD of the R2 method is equal to the 1.35% obtained by Shaver *et al.* [4] for 47 substances using a vapor-pressure equation that also needs the triple data as an input, while our proposed equation provides a significantly lower AARD. Table 2 also shows that, in general, both the R2 method and the new equation appreciably reduce the MARDs with respect to those obtained from the R1 method. Obviously, this is due to the fact that equations (10) and (32) pass through the triple point while equation (2) does not.

Besides these overall results, one notes from table 2 that the MARDs and the AARDs show a tendency to increase as the triple point pressure decreases for the two methods based on the Riedel equation, R1 and R2. This tendency is less apparent for the new equation for which the two deviations are very similar for the substances considered.

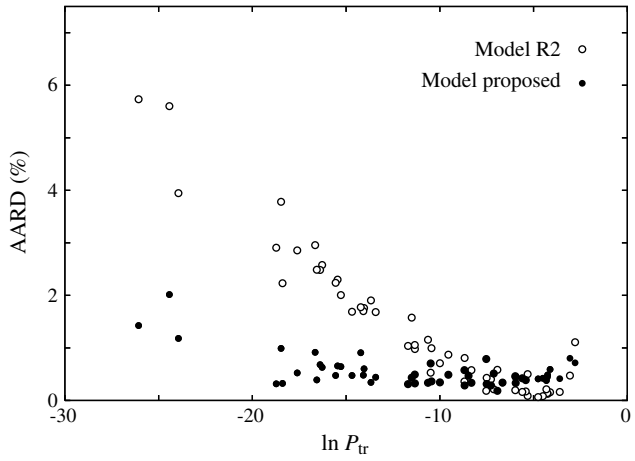

FIGURE 2. Plot of the average absolute relative deviation (AARD) *versus* the logarithm of the reduced triple point pressure. Hollow and filled circles show, respectively, the behavior of the AARD for the R2 equation and the model here proposed.

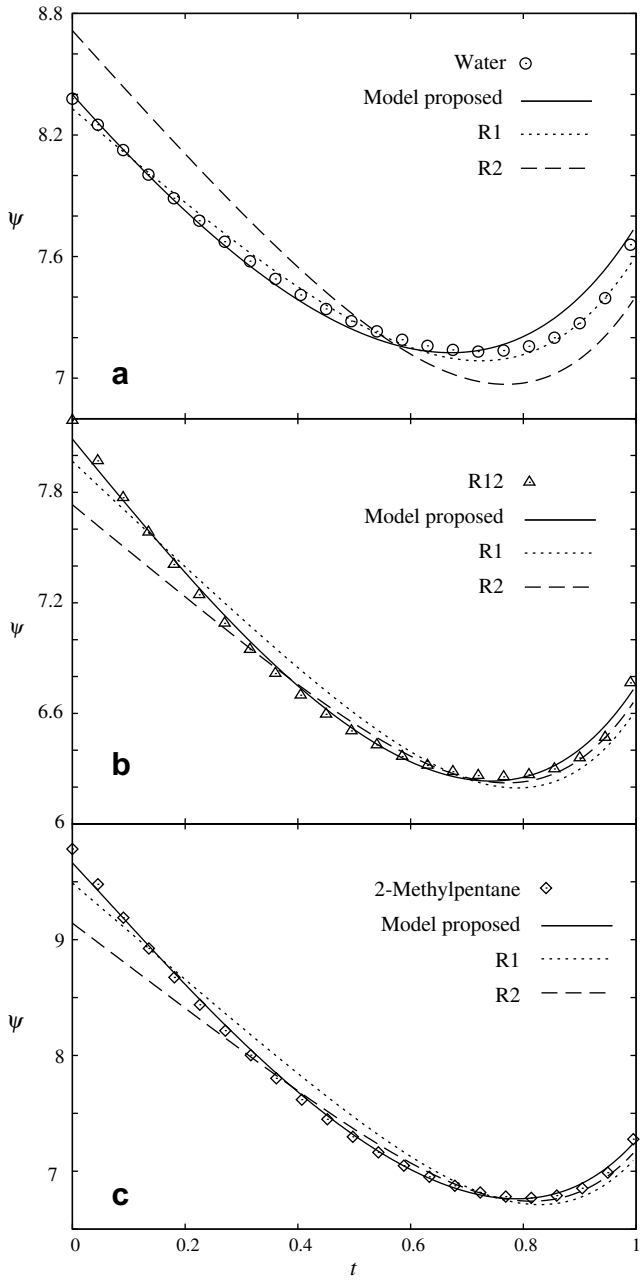

FIGURE 3. Plot of the function ψ (equation (38)) *versus* reduced temperature t. The points represent values from NIST data for the substances (a) water, (b) refrigerant R12, and (c) 2-methylpentane. Solid, dashed, and dotted lines show, respectively, the results of the model proposed equation (32), R1 model, and R2 model.

These tendencies are shown in figure 2, where we represent the AARDs of both the R2 equation and the model here proposed, equation (32), *versus* the natural logarithm of the triple point pressure for the substances studied. One observes that the AARDs of equation (32) are smaller than those of the R2 model for very low and intermediate triple point pressures.

Certainly, the proposed equation (32) requires the triple point pressure as input data, and this pressure is not always available with the required accuracy. In such cases equation (32) suggests the use of the triple point as an adjustable parameter. Of course under these circumstances equation (32) would lose its fully predictive character to become another equation for correlating empirical vapor-pressure data.

Finally, we have also compared the Waring curves [45–47] for the R1, R2, and proposed models with those obtained from NIST data. These curves are obtained by calculating the parameter ψ, defined as

$$\psi \equiv -\frac{\mathrm{d}\log P_{\mathrm{r}}}{\mathrm{d}(1/T_{\mathrm{r}})} = \frac{\Delta H}{RT_{\mathrm{c}}\Delta Z}, \tag{38}$$

where ΔH and ΔZ are the enthalpy of vaporization and the difference between the compressibility factor of the vapor and liquid phases. We have found that the behavior of ψ calculated from the proposed model is better than the calculated form R1 and R2 equations, specially near the triple point. In figure 3, we show the behavior of ψ *versus* the reduced temperature t for the three fluids considered in figure 1. Points represent the data from NIST whereas the solid, dotted, and dashed lines correspond to the calculations made from equation (32), R1 and R2 models, respectively.

5. Conclusions

A simple and fully predictive equation, equation (32), has been proposed for estimating the vapor-pressure of pure substances along the whole coexistence curve, from the triple point to the critical point. The equation is based on the use of a dimensionless temperature t defined in terms of both the triple point temperature and the critical temperature, and consists of the familiar Clausius–Clapeyron equation form times a corrective function of t given as the product of two polynomial terms constructed by imposing that the vapor-pressure equation passes through the triple point and the normal boiling point. The proposed equation then has only one unknown parameter which is obtained from an additional condition: there must be an inflection point at the critical temperature. Therefore, this equation needs as input data the pressure and temperature at the triple point, the pressure and temperature at the critical point, and the normal boiling temperature.

Vapor-pressure data for 53 pure substances taken from the NIST program were used to evaluate the new equation. The Riedel equation was also used for comparison because it is the most widely recognized vapor-pressure equation with a predictive character. Two versions of the Riedel equation were considered: the original Riedel equation that requires only T_{b}, T_{c}, and P_{c} as input data, and a version that, like the equation proposed here, also requires T_{t} and P_{t} as input parameters. In this sense, the superiority of the original Riedel equation must be emphasized. However, while that equation contains two *universal* empirical parameters, the newly proposed equation and the second version of the Riedel equation do not contain any empirical parameter. We note that other vapor-pressure equations that use the triple point data as input [3–6,8,14,15] also require several empirical parameters, and thus cannot *a priori* be considered as predictive.

We find that, for the set of the 53 substances considered here, the proposed equation predicted the temperature dependence of the vapor-pressure along the whole coexistence curve with a fair degree of accuracy. This accuracy was clearly better than that obtained with either version of the Riedel equation for substances with a small reduced triple point pressure, although it was slightly worse for substances with a large reduced triple point pressure (P_{tr} greater than $\sim 2.5 \times 10^{-4}$). In addition, the use of the new equation and of the second version of the Riedel equation reduces appreciably the maximum relative deviation with respect to the original Riedel equation.

The application of the new equation and of the second version of the Riedel equation requires knowing of the triple point temperature and pressure. The triple point temperature is accurately known for the vast majority of pure substances, but the triple point pressure is not always available or is often inaccurate because of the experimental difficulties in measuring the usually very low vapor pressures close to the triple point. Hence the triple point based equations should only be used if the triple point pressure is known with sufficient accuracy. This fact limits the applicability of this kind of equation. However, in the cases where P_{tr} is not available, $\ln P_{\mathrm{tr}}$ can be considered as an unknown parameter which can be evaluated by finding, if possible, an additional condition for the vapor-pressure equation [*e.g.*, of an empirical character, like equation (8) in the Riedel method] or by considering it to be an adjustable parameter (in this case, one must use a fitting procedure weighting adequately the experimental data in order to reflect the uncertainties of pressures [13]).

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