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A New Vapor-Pressure Equation

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A new vapor-pressure equation which has only three adjustable parameters and has a simple form is established consistent with the renormalization-group theory of critical phenomena. The equation presented here is valid over the entire range from the triple point to the critical temperature for a chemically diverse set of compounds and does an excellent job representing data. The new equation also has a great advantage over all of the previous vapor-pressure equations in that it can be used to extrapolate extraordinarily from the usual range in which data are available both to the critical point and to the triple point. Furthermore, it reflects physical properties of the substance based upon the known physical behavior. Satisfactory results are presented for 44 simple, quantum, hydrobonding, nonpolar and polar substances, refrigerants, associating compounds, and others.

KEY WORDS: critical parameters; critical power law; vapor-liquid equilibrium; vapor pressure.

1. INTRODUCTION

Vapor-pressure equations represent the pressure–temperature behavior of fluids along their vapor–liquid saturation boundary. It is well-known that an accurate vapor-pressure equation is important in the field of chemical process design, in developing equations of state, in obtaining thermodynamic properties tables for pure substances, and in studying first-order and second-order vapor–liquid phase transitions. A generalized vapor-pressure equation is of great significance in fundamental theory and in engineering applications. For these reasons, a physical expression that describes the vapor pressure as a function of temperature along the entire vapor–liquid coexistence curve has been the objective of extensive studies based on both theoretical ideas and empirical approaches.

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2. SURVEY

The Clausius–Clapeyron equation, proposed in 1834, is one of the earliest fundamental contributions to physical chemistry. It is

$$\frac{dP}{dT}=\frac{\Delta H}{T\,\Delta V}=\frac{\Delta H}{RT^2/P\,\Delta Z} \tag{1}$$

$$-\frac{d\ln P}{d(1/T)}=\frac{\Delta H}{R\,\Delta Z} \tag{2}$$

The Clausius–Clapeyron equation gives the exact thermodynamic relation among the saturated vapor pressure P, the latent heat of vaporization ΔH, the temperature T, and the volume change ΔV or the compressibility-factor change ΔZ accompanying vaporization.

Most vapor-pressure estimation and correlation equations stem from an integration of Eq. (2). When this is done, an assumption must be made regarding the dependence of the quantity $\Delta H/\Delta Z$ on temperature. The simplest approach is to assume that the quantity $\Delta H/\Delta Z$ is constant and independent of temperature. Then the Clapeyron equation is obtained, *i.e.*, $\ln P = A + B/T$. It is a fairly good relation for approximating vapor pressures over small temperature intervals.

Antoine [1] proposed a three-parameter simple modification of the Clapeyron equation, which has been widely used in engineering practice. The applicable temperature range is not large and, in most instances, corresponds to a pressure interval of about 0.001 to 0.2 MPa. The Antoine equation is a useful approximate equation but does not represent vapor pressures to within experimental error.

Frost and Kalkwarf [2] maintained the assumption of the linear relationship for ΔH but calculated the ΔZ value in a more rigorous way from the Van der Waals equation of state. This choice, however, leads to a somewhat involved calculation and is responsible for the nonexplicit form of the resulting equation.

Riedel [3] applied two very rough approximations, namely, that ΔZ was equal to unity and that ΔH varies linearly with temperature. Furthermore, the inaccuracies introduced by these assumptions are reduced by a corrective term proportional to T_r^6, where $T_r = T/T_c$ is the reduced temperature and T_c the critical temperature.

Miller [4] applied Watson's empirical relation for ΔH and Haggenmaker's relation for ΔZ. Both these equations can be regarded as good approximations for these properties over a wide range of temperatures. However, after substitution of these two empirical relations into Eq. (2), the presence of the pressure in the ΔZ term prevents direct integration of the Eq. (2), and recourse to numerical methods is unavoidable.

Thek and Stiel [5] pointed out that the Riedel, Frost-Karkwarf, and Miller equations were inaccurate in the low-pressure range. Attempting to overcome the shortcomings of the previous proposals, they matched the combined effect of the ΔH and ΔZ dependence on temperature by expanding the ratio $\Delta H/\Delta Z$ as a power series in reduced temperature truncated after the fourth term. Furthermore, a corrective term was added, which in turn is a function of reduced temperature only. Their final equation is effective in calculating vapor pressures with satisfactory accuracy in both the low- and the high-pressure regions. However, an obvious drawback is the dependence of the vapor pressure on ΔH at the normal boiling temperature T_b, which appears as a proportionality factor in the series expansion.

Goodwin [6] included nonanalytic behavior at the critical point and presented vapor-pressure equations for oxygen and nitrogen, which could not be applied widely since only a few triple-point pressure of fluids are known.

Ambrose *et al.* [7] proposed that the Chebyshev polynomials may accurately describe vapor pressure of fluids from the triple point to the critical point, but this method contains several adjustable constants, even up to seven.

Wagner [8] developed a four-parameter equation with a stepwise procedure that optimizes selection of a functional form of an equation for each substance. The equation was initially derived to describe the vapor pressures of argon and nitrogen from the triple point to the critical temperature.

Thomas [9] proposed an equation based on the observation that the ratio of the value of $RTd \ln P/dT$ for any nonassociating compound to the value of the function for any other such compound at the same vapor pressure is constant over a range from a few millimeters of mercury to the critical pressure.

Xu [10] used a polynomial of the third degree relating the latent heat to the reduced temperature, and ΔZ was assumed constant. The inaccuracies are reduced by a corrective term proportional to T_r^4.

Vetere [11] proposed a four-parameter vapor-pressure equation. The equation incorporates an inflection-point condition and has a simple relation which describes the behavior with a minimal number of constants, a polynomial of the third degree by expressing the ratio $\Delta H/\Delta Z$ as a function of the reduced temperature only. However, ethanol and propanol are recognized exceptions.

Iglesias-Silva *et al.* [12] proposed a vapor-pressure equation from the asymptotic scaling-law behavior and extension of the Churchill–Usagi correlation technique from heat transfer and fluid mechanics. The equation and the determination of its coefficients seem to be complicated.

Unfortunately, the above vapor-pressure equations that are accurate often do not describe the entire vapor-pressure curve but do contain several adjustable parameters. The equations with a large number of coefficients represent the measured vapor pressures within experimental accuracy, but they show unfavorable behavior when extrapolated beyond the range of the measured values used when deriving the coefficients.

Based on the comprehensive analyses of the previous vapor-pressure equations, some problems have been considered:

Does there exist a more simple generalized physical form for the representation of the vapor pressures for a chemically diverse set of fluids?

Does the equation remain valid up to the critical point and conform to the exponent of the renormalization-group theory of critical phenomena? and

Does it possess good extrapolation from the usual range in which data are available to the triple point and to the critical point beyond the range of the measured values used when deriving the coefficients?

It is the purpose of this paper to make an effort to address the problems mentioned above.

3. DEVELOPMENT OF THE NEW VAPOR-PRESSURE EQUATION

For the reasons mentioned above, it seems that a new vapor-pressure equation should be developed that fulfills the following conditions.

(i) The experimental vapor-pressure values over the whole temperature range have a good reproducibility.

(ii) A simple physical form should be established.

(iii) The critical behavior in accordance with the renormalization-group theory of critical phenomena must be satisfied [13–16].

(iv) It should conform to the Riedel factor α_R and $d\alpha_R/dT$ values.

(v) As few coefficients as necessary should be considered so as not to impair the possibility of extrapolation.

Let us begin with the Riedel factor α_R, which describes the dependence of the saturated vapor pressure on temperature along the entire vapor–liquid coexistence curve:

$$\alpha_R = \frac{\partial \ln P_r}{\partial \ln T_r} \tag{3}$$

where the reduced vapor pressure $P_r = P/P_c$ with P_c being the critical pressure. It was introduced from the first-order phase transition equation, Eq. (2), the Clausius–Clapeyron equation, by Plank and Riedel [17]. What we want directly to do is to seek a functional form of α_R varying with temperature, since α_R presents the pressure as a function of temperature over the whole vapor–liquid phase transition. Taking these aspects into account, a preliminary expression is constructed for the reduced vapor pressure as a function of the reduced temperature T_r, namely,

$$\frac{\ln P_r}{\ln T_r} = f(T_r) \tag{4}$$

The following simple and reasonable form is proposed for the function f in Eq. (4):

$$f(T_r) = \sum_{i=1} A_i \tau^{n_i} \tag{5}$$

where $\tau = 1 - T_r$.

Considering the conditions stated above that the vapor-pressure equation ought to fulfill, we note that Eq. (4) is prescribed by the following physical conditions.

(i) The Riedel constant term and Riedel constant should be satisfied. Thus, the exponent of the first term should be zero, and the corresponding A_1 is the Riedel constant.

(ii) The critical exponent α conforming to the requirement of the renormalization-group theory of critical phenomena should be incorporated. It means that the exponent of the second term is identically equal to $2 - \alpha$.

After determining the first and second terms of Eq. (4), we discover that if only one more term is added, Eq. (4) can satisfy the calculation accuracy in the entire temperature range. By the least-squares regression for the experimental data of a chemically diverse set of substances listed in Table I, it is found that the exponent of the third term is 5.67. It is interesting that 5.67 is just equal to $3(2 - \alpha)$. Consequently, the new vapor-pressure equation is

$$\ln P_r = \ln T_r (A_1 + A_2 \tau^{n_1} + A_3 \tau^{n_2}) \tag{6}$$

with

$$n_1 = 2 - \alpha = 1.89, \qquad \alpha = 0.11, \qquad n_2 = 5.67 \tag{7}$$

Table I. Parameters for the New Vapor-Pressure Equation [Eq. (8)] from Full-Range Data and the Critical Constants

Compound	T_c (K)	P_c (MPa)	A_1	A_2	A_3	M[a]	Ref(s).
Argon	150.69	4.8653	5.78471374	6.24383974	12.3718357	57	8
Oxygen	154.581	5.043	5.91231393	6.54549694	12.5794134	179	18
Nitrogen	126.2	3.4002	5.9844923	6.76437425	14.681488	66	8
Chlorine	416.9	7.9719	6.2303934	7.47680282	16.8668022	61	19, 20
Carbon dioxide	304.136	7.3773	6.84599542	10.2023639	9.35969257	128	21, 22
Methane	190.551	4.5992	5.87304544	6.23280143	13.0721578	153	23
Ethane	305.33	4.8717	6.30717658	7.47042131	17.0958137	90	24–27
Propane	369.80	4.239	6.50580501	8.6776247	18.0116214	66	27–29
Butane	425.2	3.8	6.81692028	8.77671813	23.7680492	29	30, 31
Benzene	561.75	4.8758	6.82740545	9.34241485	24.1741504	116	32–37
Neon	44.448	2.664	5.64703512	5.33091354	12.2967739	68	27
Hydrogen	33.19	1.315	4.78105258	2.82220339	2.87949132	68	27
Helium	5.2014	0.2275	3.83707499	1.16239106	2.63104414	58	38
R11	471.15	4.487	6.83648252	8.45433425	22.0910034	27	39, 40
R12	385	4.14	6.70782089	8.77115631	18.4986419	71	40, 41
R22	369.3	4.988	6.88100147	9.47825336	20.3845615	104	41–43
R32	351.56	5.8282	7.24783849	9.44906806	21.9283714	29	44
R113	487.483	3.4099	7.03479385	9.96937179	22.8604393	25	45
R123	456.87	3.6655	7.17751407	10.4138793	23.9151554	112	46, 47
R134	392	4.64	7.24227094	9.9998064	82.8741302	65	48, 49
R142b	410.29	4.041	6.95436525	8.97622299	112.224586	78	49, 50
R134a	374.18	4.056	7.41535425	10.9633932	23.8982505	146	51–55
R152a	386.44	4.50	7.14697933	10.4557418	4.70639467	183	55 57
Water	647.14	22.064	7.60794067	10.1932439	21.1083545	53	58
Ammonia	405.5	11.35	7.11388492	9.51535415	19.5376377	83	27, 59
Nitromethane	588	6.31	7.96073532	6.91034173	51.2841186	23	60, 61
TFE	498.53	4.8	8.63110256	19.050188	14.7720022	84	62, 63
Methanol	512.64	8.0971	8.67447471	13.6874294	9.97769451	85	64–66
Ethanol	513.92	6.1484	8.78329658	17.797739	−0.5206533	47	65, 66
Acetic acid	592.71	5.786	8.38445949	9.78763198	29.3230476	39	67, 68
Ethyl fluoride	375.31	5.0277	6.9000082	9.12291336	16.228197	47	69
Pentafluorochloroacetone	410.65	2.8776	7.45677614	11.620016	26.5720901	20	70
Hexafluoroacetone	357.25	2.8412	7.51933526	12.1870098	24.4911994	14	70
Acetone	508.1	4.7	7.37726593	10.0870218	23.4207172	46	71
Diethyl ether	466.74	3.637	7.1713705	10.3994998	24.3123378	39	72
2-Methylbutane	460.95	3.39	6.92686796	9.26964282	22.4417114	35	73, 74
Pentan-1-ol	588.2	3.91	8.18587684	18.9232025	53.7686767	35	65, 66
Cyclohexane	553.64	4.0748	6.81255435	9.41438293	23.2468109	27	74, 75
Perfluorotoluene	534.5	2.71	8.1846466	12.7024135	32.9377937	27	76
Toluene	591.72	4.1056	7.12600946	9.81328392	24.3763809	29	33, 74
Ethylbenzene	617.12	3.6057	7.31366586	10.4335994	26.1998558	30	33, 74
o-Xylene	630.25	3.7336	7.37496614	10.3818836	25.9129962	31	33, 74
m-Xylene	616.97	3.5364	7.44022798	10.6410732	25.2128753	30	33, 74
p-Xylene	616.15	3.5113	7.44173097	10.3619289	26.6721134	30	33, 74
Overall						2833	

[a] The number of data points.

Substitution of the exponents values into Eq. (6) yields

$$\ln P_r = \ln T_r(A_1 + A_2\tau^{1.89} + A_3\tau^{5.67}) \tag{8}$$

Equation (8) contains only three adjustable parameters (A_1, A_2, A_3) that must be determined from the experimental data. A_1 is the Riedel constant. $\alpha = 0.11$ is the critical exponent derived from the renormalization-group theory of critical phenomena [13–16]. The exponent n_2 of the third term of Eq. (8) is 5.67. It is worth pointing out that the exponents n_1 and n_2 which are obtained for 44 diverse set of substances using only the experimental data without any constraints on derivatives are the same for all those substances. In this respect, Eq. (8) seems to possess a simple form in describing the vapor pressure as a function of temperature along the entire vapor–liquid phase transition curve.

4. DETERMINATION OF THE COEFFICIENTS

The new equation has been applied to the diverse set of substances listed in Table I including simple, nonpolar, polar, quantum, hydrobonding, and associating substances, which have been experimentally investigated in detail to obtain fairly reliable experimental data. The sources of these experimental data are listed in Table I. All data have been converted, whenever necessary, to the ITS-68 temperature scale, except where it is specially stated. The three parameters for each of these substances are determined by fitting the experimental data to the new vapor-pressure equation with nonweighted least-squares regression. The parameters of the new equation are also presented in Table I. Meanwhile, the critical temperature and the critical pressure used in fitting the coefficients of the new equation are also given in Table I.

We note that according to the modern understanding of critical phenomena, there is a theoretical value for not only the leading non-analytic critical exponent but also the corresponding amplitude [77–80], especially, certain ratios of amplitudes are universal constants [78]. As for the new vapor-pressure equation, the constraint that is consistent with the renormalization-group theory of critical phenomena is on only the exponent, and not the amplitude. On expanding our Eq. (8) in a power series in τ, the amplitude of the leading-order nonanalytic term from Table I is not consistent with the correct universal constant [79–80]. In practice, the parameters of the equation fitting from the experimental data rely partially on the accuracy and the range of the experimental data and the constraint of coefficients [81].

Table II. Deviations Between Experimental Values and Fits of Various Models to the Database

Compound	T_r range	Wagner equation, Eq. (9)		New equation, Eq. (8)	
		RRMS[a]	Max. dev.[b]	RRMS[a]	Max. dev.[b]
Argon	0.556–1	0.021	0.064	0.040	0.095
Oxygen	0.583–1	0.008	0.029	0.033	0.070
Nitrogen	0.500–1	0.021	0.056	0.047	0.120
Chlorine	0.413–1	0.073	0.173	0.075	0.160
Carbon dioxide	0.712–1	0.015	0.045	0.033	0.077
Methane	0.476–1	0.016	0.079	0.035	0.065
Ethane[c]	0.299–1	0.499	2.951	0.311	1.985
Propane[c]	0.256–1	3.179	14.95	2.537	13.22
Butane	0.65–0.9	0.123	0.289	0.139	0.349
Benzene	0.496–1	0.044	0.177	0.049	0.146
Neon	0.553–1	0.032	0.081	0.026	0.082
Hydrogen	0.422–1	0.063	0.363	0.099	0.450
Helium	0.433–1	0.135	0.420	0.122	0.469
R11	0.495–0.8	0.024	0.062	0.107	0.229
R12	0.467–1	0.085	0.331	0.168	0.639
R22	0.487–1	0.105	0.562	0.113	0.541
R32	0.544–1	0.254	0.615	0.254	0.623
R113	0.489–1	0.186	0.352	0.227	0.515
R123	0.675–1	0.106	0.531	0.111	0.523
R134	0.536–1	0.200	0.630	0.224	0.730
R134a	0.481–1	0.128	0.591	0.139	0.576
R142b	0.724–1	0.196	0.664	0.200	0.677
R152a	0.614–1	0.167	0.412	0.175	0.411
Water	0.422–1	0.026	0.059	0.036	0.117
Ammonia	0.482–1	0.098	0.259	0.105	0.286
Nitromethane	0.556–0.8	0.450	0.936	0.523	1.180
TFE	0.519–1	0.281	0.821	0.302	0.853
Methanol	0.561–1	0.096	0.418	0.214	0.799
Acetic acid	0.511–0.7	0.199	0.763	0.199	0.754
Ethyl fluoride	0.452–1	0.378	0.867	0.377	0.877
Ethanol	0.569–1	0.112	0.250	0.259	0.637
Pentafluorochloroacetone	0.565–1	0.311	0.704	0.319	0.756
Hexafluoroacetone	0.671–1	0.191	0.414	0.182	0.426
Acetone	0.510–1	0.089	0.268	0.118	0.436
Diethyl ether	0.536–1	0.099	0.230	0.128	0.363
2-Methylbutane	0.553–0.7	0.016	0.055	0.016	0.048
Pentan-1-ol	0.592–0.87	0.081	0.186	0.199	0.625
Cyclohexane	0.529–1	0.021	0.059	0.037	0.087
Perfluorotoluene	0.545–0.75	0.021	0.056	0.029	0.094
Toluene	0.521–1	0.040	0.112	0.054	0.123
Ethylbenzene	0.534–1	0.049	0.180	0.076	0.316
o-Xylene	0.534–1	0.027	0.071	0.045	0.121
m-Xylene	0.539–1	0.014	0.044	0.020	0.053
p-Xylene	0.538–1	0.026	0.063	0.043	0.074
Overall		0.11	0.32	0.13	0.39

[a] $\mathrm{RRMS} = \{[\sum_1^M |P_{\mathrm{expt}} - P_{\mathrm{calc}}|/P_{\mathrm{expt}}]^2/(M-N)\}^{0.5} \times 100$, where P_{expt} and P_{calc} are the experimental data and the corresponding calculated values, M is the number of data points, and N is the number of coefficients of each equation.

[b] The maximum percentage deviation of the experimental pressure from the calculated value.

[c] The relatively large deviations of ethane and propane come from the inaccurate experimental data near the triple point.

5. CALCULATION

A detailed comparison between the vapor-pressure values calculated from the new equation and the corresponding experimental data has been made. The root-mean-squares and the maximum deviations are presented in Table II for 44 substances ranging in reduced temperature from about 0.3 to 1 and involving 2833 data points used to develop the current equation. The equation here has an average overall relative root-mean-squares error of 0.13% and an overall maximum deviation of 0.39%, respectively. Except for propane, the root-mean-squares deviations of substances range from 0.02% for *m*-xylene to 0.37% for ethyl fluoride. However, the major contributions to the ethyl fluoride and the other slightly bigger deviations for several substances come from the inaccurate vapor-pressure data.

Considering the experimental uncertainties, the new equation is accurate for a chemically diverse set of compounds in the entire range from the triple point to the critical point. For example, for water, for which highly accurate experimental data are available, the critical temperature and the critical pressure tolerances given in the 1985 IAPS [58] are 0.015 and 0.145%, respectively.

6. EVALUATION

A simple form, a high accuracy, and a good extrapolation are the main requirements of a vapor-pressure equation. Many discussions and evaluations for other vapor-pressure equations were presented in the previous paragraphs. Among them, no equation with the exception of the Wagner equation is entirely satisfactory. Many investigators have evaluated the Wagner equation, such as Ambrose [82], Ambrose and Patel [83], Chase [84], McGarry [85], Reid et al. [86], Smith and Srivastava [87], etc. To put it briefly, the Wagner equation is of a useful form, which can present vapor pressures over a wide range with the best accuracy with a relatively small number of coefficients, and it may be used for interpolation between the usual range in which data are available and the critical point. Up to now, the Wagner equation was selected as the best equation. In addition to requiring a best fit of existing vapor-pressure data, the equation is constrained so as to generate a "reasonable shape" for the vapor-pressure curve from a reduced temperature of 0.5 up to the critical point. But the equation may not extrapolate well to reduced temperatures below 0.5 [86].

For this reason, the calculation and extrapolation results of our proposed equation have been compared with the corresponding values obtained from the Wagner equation, which has already been widely applied in engineering. The Wagner equation [8] reads

$$\ln P_r = (C_1\tau + C_2\tau^{1.5} + C_3\tau^3 + C_4\tau^6)/T_r \tag{9}$$

6.1. Comparison

The vapor-pressure equation presented here provides an accuracy comparable with that of the Wagner equation in representing all data listed in Table I. The calculated results used the Wagner equation with coefficients fitted from the experimental data just as the new equation, in the same temperature range as the new equation, are also listed in Table II. For 44 substances, except for ethane and propane, the new equation has an average overall relative root-mean-squares error of 0.13%; the Wagner equation, 0.11%. Meanwhile, the overall maximum deviations are 0.39 and 0.32%, respectively. While the accuracy of the new equation is slightly lower than that of the Wagner equation, considering the experimental uncertainties, the new equation is also valid over the entire range from the triple point to the critical point within experimental accuracy.

6.2. Extrapolation

It is desired to obtain lower values of the vapor pressure by extrapolation because the experimental data at lower pressures are rarely measured and not always accurate. If the substance has a high boiling temperature, its high-temperature experimental data are usually not known or it may be experimentally inaccessible because of decomposition. In consideration of these factors, extrapolation is an important feature for a vapor-pressure equation, and it is one of the cardinal principles to evaluate the superiority of the corresponding equation.

6.2.1. Extrapolation up to the Critical Point

The results of a comparison between the new equation and the Wagner equation extrapolating from the reduced temperature 0.75 to the critical point are presented in Table III for 40 substances listed in Table I involving 2656 data points, except that for four substances we cannot show extrapolation results for lack of experimental data in a wide enough temperature range. As shown in Table III, except for ethane and propane, the new equation has an average overall relative error of 0.14% (Wagner equation, up to 0.56%), an average overall root-mean-squares deviation of 0.18% (Wagner equation, 0.79%), and an overall maximum deviation of 0.47% (Wagner equation, 1.71%).

Table III. Comparison of the New Equation, Eq. (8), and the Wagner Equation, Eq. (9), on Extrapolation of T_r from 0.75 to 1

	Wagner equation			New equation		
Compound	RAAD[a]	RRMS[b]	Max. dev.[c]	RAAD[a]	RRMS[b]	Max. dev.[c]
Argon	0.089	0.122	0.237	0.048	0.064	0.133
Oxygen	0.016	0.021	0.045	0.039	0.054	0.119
Nitrogen	0.049	0.061	0.148	0.052	0.069	0.185
Chlorine	0.017	0.091	0.223	0.059	0.076	0.167
Carbon dioxide	0.629	0.937	1.944	0.062	0.090	0.198
Methane	0.031	0.043	0.101	0.031	0.041	0.095
Ethane[d]	0.580	0.738	2.574	0.143	0.311	1.976
Propane[d]	2.381	3.328	13.46	1.406	2.543	13.12
Butane	4.300	6.729	16.19	0.109	0.147	0.303
Benzene	0.028	0.045	0.155	0.033	0.050	0.160
Neon	0.047	0.103	0.366	0.021	0.026	0.080
Hydrogen	0.034	0.081	0.447	0.095	0.122	0.426
Helium	0.147	0.185	0.501	0.090	0.125	0.488
R11	0.017	0.025	0.058	0.119	0.175	0.517
R12	0.099	0.155	0.480	0.148	0.189	0.669
R22	0.063	0.107	0.581	0.092	0.128	0.498
R32	0.968	1.310	2.785	0.218	0.262	0.634
R113	0.209	0.303	0.919	0.198	0.243	0.548
R123	5.017	6.536	11.26	0.200	0.241	0.436
R134	2.291	2.651	4.264	0.241	0.289	0.623
R134a	0.290	0.383	0.883	0.083	0.139	0.591
R152a	0.258	0.344	0.847	0.149	0.178	0.412
Water	0.031	0.048	0.123	0.028	0.037	0.119
Ammonia	0.057	0.099	0.274	0.061	0.114	0.278
Nitromethane	0.589	1.111	3.875	0.457	0.534	1.121
TFE	0.278	0.334	0.864	0.332	0.400	0.813
Methanol	0.155	0.258	0.818	0.184	0.325	1.196
Ethyl fluoride	0.323	0.391	0.996	0.318	0.377	0.876
Ethanol	0.232	0.410	1.036	0.246	0.415	1.09
Pentafluoro-chloroacetone	0.285	0.358	0.790	0.383	0.434	0.864
Hexafluoroacetone	4.166	5.995	11.71	0.423	0.547	1.111
Acetone	0.080	0.174	0.661	0.068	0.119	0.446
Diethyl ether	0.139	0.237	0.633	0.084	0.129	0.378
Pentan-1-ol	0.064	0.099	0.363	0.242	0.369	1.088
Cyclohexane	0.378	0.669	1.411	0.057	0.089	0.271
Toluene	0.078	0.156	0.466	0.045	0.061	0.153
Ethylbenzene	0.036	0.064	0.174	0.050	0.085	0.334
o-Xylene	0.044	0.084	0.251	0.036	0.051	0.129
m-Xylene	0.027	0.046	0.123	0.016	0.023	0.061
p-Xylene	0.035	0.069	0.213	0.043	0.064	0.166
Overall	0.56	0.79	1.71	0.14	0.18	0.47

[a] RAAD $= [\sum_1^M |P_{\text{expt}} - P_{\text{calc}}|/P_{\text{expt}}]/M \times 100$, where P_{expt} and P_{calc} are the experimental data and the corresponding calculated values, and M is the number of data points.

[b] RRMS $= \{[\sum_1^M |P_{\text{expt}} - P_{\text{calc}}|/P_{\text{expt}}]^2/(M - N)\}^{0.5} \times 100$, where P_{expt} and P_{calc} are the experimental data and the corresponding calculated values, M is the number of data points, and N is the number of coefficients of each equation.

[c] The maximum percentage deviation of the experimental pressure from the calculated value.

[d] The relatively large deviations of ethane and propane come from the inaccurate experimental data near the triple point.

Table IV. Comparison of the New Equation, Eq. (8), and the Wagner Equation, Eq. (9), on Extrapolation from T_b to the Triple Temperature T_{triple}

Compound	Wagner equation			New equation		
	RAAD[a]	RRMS[b]	Max. dev.[c]	RAAD[a]	RRMS[b]	Max. dev.[c]
Argon	0.022	0.035	0.111	0.052	0.086	0.277
Nitrogen	0.056	0.153	0.706	0.174	0.524	2.467
Chlorine	0.357	0.853	4.521	0.212	0.454	2.375
Methane	0.025	0.058	0.225	0.131	0.313	1.150
Propane	4.901	13.32	53.95	2.314	6.815	36.13
Benzene	0.233	0.477	2.364	0.129	0.221	0.951
Neon	0.076	0.179	0.715	0.020	0.026	0.086
Hydrogen	0.599	2.535	17.21	0.191	0.749	5.152
R12	0.543	1.920	15.02	0.217	0.928	7.643
R22	0.575	1.780	8.171	0.325	0.890	4.132
R32	0.238	0.299	0.838	0.244	0.282	0.608
R113	0.883	1.791	5.762	0.794	1.645	5.745
R134a	0.370	1.425	12.57	0.146	0.373	2.486
R152a	0.157	0.189	0.525	0.145	0.179	0.558
Water	0.485	1.012	3.600	0.041	0.057	0.194
Ammonia	0.261	0.687	3.737	0.185	0.413	2.134
Methanol	0.387	0.603	1.726	2.111	3.383	8.966
Ethyl fluoride	2.651	8.537	43.04	0.321	0.381	0.885
Ethanol	1.035	2.281	8.637	1.984	4.357	16.27
Acetone	1.296	2.320	7.220	1.860	3.136	9.068
Diethyl ether	1.088	2.237	7.573	1.085	2.057	6.570
2-Methylbutane	0.554	1.039	3.150	0.150	0.260	0.774
Pentan-1-ol	1.319	2.887	11.25	1.332	2.746	10.44
Cyclohexane	1.426	2.598	7.060	0.508	0.887	2.284
Perfluorotoluene	0.698	1.023	2.302	0.949	1.410	3.227
Toluene	0.317	0.567	1.692	0.401	0.622	1.446
Ethylbenzene	1.475	2.593	7.245	0.490	0.836	2.403
o-Xylene	0.085	0.150	0.474	0.058	0.074	0.139
m-Xylene	0.289	0.497	1.390	0.117	0.186	0.438
p-Xylene	0.619	1.110	3.133	0.118	0.233	0.252
Overall	0.79	1.96	8.44	0.56	1.16	4.60

[a] RAAD = $[\sum_1^M |P_{expt} - P_{calc}|/P_{expt}]/M \times 100$, where P_{expt} and P_{calc} are the experimental data and the corresponding calculated values, and M is the number of data points.

[b] RRMS = $\{[\sum_1^M |P_{expt} - P_{calc}|/P_{expt}]^2/(M - N)\}^{0.5} \times 100$, where P_{expt} and P_{calc} are the experimental data and the corresponding calculated values, M is the number of data points, and N is the number of coefficients of each equation.

[c] The maximum percentage deviation of the experimental pressure from the calculated value.

It is remarkable that the new equation has an advantage over the Wagner equation in extrapolating up to the critical point; for the new equation the extrapolation results are excellent. For example, an average overall root-mean-squares deviation from extrapolating is only 0.05% higher than that from the calculated results given in Table II. Hence, we believe that the new equation can be extrapolated effectively from the usual range in which data are available to the critical point.

6.2.2. Extrapolation Below the Normal Boiling Point

The results of a comparison of the new equation with the Wagner equation when extrapolating from the normal boiling point to the triple point are presented in Table IV for 31 substances (including ethane) listed in Table I involving 1835 data points, except that for 13 substances we cannot show extrapolation results for lack of experimental data over a wide enough temperature range. As shown in Table IV, the new equation has an average overall relative error of 0.56% (Wagner equation, 0.79%), an average overall root-mean-squares deviation of 1.16% (Wagner equation, 1.96%), and an overall maximum deviation of 4.6% (Wagner equation, 8.4%). As examples, we also show the extrapolation results to the low-temperature region for ethane and R134a, given in Tables V and VI, respectively.

It is also obvious that the new equation has an advantage over the Wagner equation in extrapolating to lower values of the vapor pressure, for which the experimental data are usually not accurate. For example, if the

Table V. Comparison of the New Equation, Eq. (8), and the Wagner Equation, Eq. (9), for Ethane on Extrapolation from T_b to T_{triple}

Experimental data [24]		Extrapolation results, relative percentage deviation $(P_{expt} - P_{calc})/P_{expt} \times 100$	
Temperature (K)(ITS-48)	Pressure (kPa)	Wagner equation	New equation
91.34	0.155E-2	25.8	7.4
93.70	0.273E-2	25.3	7.2
96.24	0.499E-2	22.2	4.9
100.70	0.131E-1	18.2	2.6
105.60	0.331E-1	19.4	5.3
114.24	0.147	13.3	2.9
120.38	0.365	10.4	2.4
129.81	0.125E 1	6.0	0.85
135.77	0.245E 1	4.1	0.43
140.55	0.402E 1	3.2	0.36
144.14	0.571E 1	2.2	−0.03

Table VI. Comparison of the New Equation, Eq. (8), and the Wagner Equation, Eq. (9), for R134a on Extrapolation from T_b to T_{triple}

Experimental data [51, 52]		Extrapolation results, relative percentage deviation $(P_{expt} - P_{calc})/P_{expt} \times 100$	
Temperature (K)(ITS-90)	Pressure (kPa)	Wagner equation	New equation
180.010	1.152	12.6	2.5
190.010	2.834	8.4	2.4
200.010	6.335	4.8	1.5
210.010	12.932	2.6	0.84
214.435	17.301	1.9	0.58
216.869	20.179	1.6	0.47
218.289	22.033	1.4	0.41
220.010	24.435	1.3	0.47
223.588	30.219	0.90	0.26
226.340	35.365	0.69	0.18
228.866	40.691	0.54	0.13
230.010	43.274	0.56	0.19
231.025	45.749	0.41	0.08
232.798	50.269	0.33	0.05

experimental value of vapor pressure is 0.0015 MPa, and the calculated value is 0.0014 MPa, though the absolute deviation is very small, the relative error is up to 7%. From this example, it is clear why the extrapolated results in the low-temperature range display a relatively great deviation.

7. CONCLUSIONS

The vapor-pressure equation presented here, which possesses a simple physical form and is valid over the entire range from the triple point to the critical point, is constructed to conform to the renormalization-group theory of critical phenomena. The new equation, with only three adjustable parameters and two exponents, provides an accuracy comparable to that of the Wagner equation, which has four adjustable parameters and four exponents. The advantages of the new equation are its simple generalized form for a diverse set of substances and the representation of data with a high accuracy. Moreover, the new equation yields an excellent extrapolation from the usual range in which data are available both to the critical point and to the triple point.

Since the formulation is based upon the physical behavior as predicted by modern theory, the exponents and one of the adjustable parameters reflect the physical properties of the substances. The new equation has only two exponents: One is 1.89, based on the critical exponent α of 0.11; the other is 5.67. The parameter A_1 is the Riedel constant. These physical associations guarantee that the new equation can provide good predictive as well as correlative capabilities. The work here shows that the new equation can correlate accurately and extrapolate excellently the vapor-pressure behavior of simple, nonpolar, polar, quantum, hydrobonding, and associating compounds and others.

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