

An Accurate Vapor Pressure Equation with Good Extrapolation Characteristics

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A new vapor pressure equation that has only three adjustable parameters and a simple form is presented in this paper. The equation is valid over the entire range from the triple point to the critical temperature for a chemically diverse set of compounds. It can represent the experimental data with an accuracy comparable to the Wagner vapor pressure equation. The advantage of the new equation is that it can be used to extrapolate well from a small amount of data in the usual range to the entire vapor–liquid coexistence region both up to the critical temperature and down to the triple point. Satisfactory results are presented for more than 40 substances in tables, and it has been shown that the new vapor pressure equation is generally valid in a wide range.

KEY WORDS: equation of state; thermodynamic properties; vapor–liquid equilibria; vapor pressure.

1. INTRODUCTION

As a function of temperature along the vapor–liquid coexistence boundary, the generalized vapor pressure equation is of great importance in statistical thermodynamic theory and engineering applications, such as for obtaining thermodynamic properties tables for pure substances, developing equations of state, studying vapor–liquid phase transitions, designing chemical processes, and so on. A good vapor pressure equation should

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have both excellent agreement with experimental data and good extrapolation behavior. Up to now, many vapor pressure equations [1] have been developed, but none of these equations is entirely satisfactory. Specifically, some equations cannot extrapolate well up to the critical point or down to the triple point. In addition, almost all of the current vapor pressure equations have an excessive number of parameters.

The purpose of this work is to develop a new vapor pressure equation which can represent the experimental data within the uncertainty of measurements and has fewer parameters with good extrapolation behavior.

2. NEW VAPOR PRESSURE EQUATION

Before the Wagner vapor pressure equation was presented, most of the previous vapor pressure equations were not satisfactory, as they did not provide both a simple form and high accuracy. Moreover, these equations did not show favorable behaviors extrapolating beyond the range of the measured values. The Wagner equation [2] was developed by an elaborate statistical method in 1973. It has four parameters,

$$\ln P_r = (a_1\tau + a_2\tau^{1.5} + a_3\tau^3 + a_4\tau^6)/T_r \quad (1)$$

where $\tau = 1 - T_r$, $T_r = T/T_c$, $P_r = P_v/P_c$, T_c is the critical temperature, P_v is the saturated pressure, P_c is the critical saturated pressure, and a_1 – a_4 are the independent parameters that are determined from the experimental data. At present, it has been shown that the Wagner equation can represent experimental data satisfactorily with high accuracy for almost all substances in the entire range from the triple point to the critical point. In order to provide better agreement with experimental data and meet practical needs, the Wagner equation has some variant forms, which have different exponential values or parameter numbers. The Wagner equation has made a great contribution to research on vapor pressure equations.

Taking into consideration that the Wagner equation has no physical meaning and its form is somewhat complex, H. W. Xiang of our research group provided a new vapor pressure equation that has a physical meaning and a simple form. The Xiang equation [3, 4] is described by

$$\ln P_r = \ln T_r (A_0 + A_1\tau^{1.89} + A_2\tau^{5.67}) \quad (2)$$

where A_0 , A_1 , and A_2 are the parameters that are determined from experimental data. The Xiang equation has some advantages over previous equations. First, the number of parameters of the Xiang equation is reduced, second the accuracy of the Xiang equation can be close to that of the Wagner equation, and finally the extrapolation behavior along

the vapor–liquid coexistence boundary to the critical temperature is better than that of the Wagner equation.

Prior to this work, we intended to only make a comparison between the Wagner equation and the Xiang equation. We observed that the accuracy of the Wagner equation is rather superior to that of the Xiang equation, but that the Xiang equation has fewer parameters and the accuracy difference between the two equations is not very significant. Furthermore, the calculated results indicated that both equations can extrapolate the experimental data along the vapor–liquid coexistence boundary to the critical point satisfactorily, and further analyses showed that the extrapolated values of the Xiang equation have better accuracy than those of the Wagner equation. We think that the reason for the better performance lies in the second term value of $\tau^{1.89}$ in the Xiang equation, which can describe the characteristics of fluids near the critical point exactly. In Ref. 2, Wagner indicated that if the exponent were 1.88, the result would be more accurate. However, this observation ultimately was not applied in the Wagner equation.

But the calculated results also indicated that both equations cannot extrapolate the experimental data along the vapor–liquid coexistence boundary to the triple point satisfactorily. After detailed analyses, we think that both the Wagner equation and the Xiang equation have no term that can exactly describe the characteristics of the region near the triple point. In addition, neither equation can extrapolate the vapor pressure data satisfactorily, if the parameters of the equation were fitted over a small range of experimental data.

On the basis of the above analyses, we considered that a new vapor pressure equation should conform to the following assumptions and rules:

1. The term $\tau^{1.89}$ should be used in the new equation, because it can describe the characteristics of the saturated vapor pressure near the critical point more exactly. In addition, it has been shown in our analysis that the exponent of 1.89 can be adjusted in a certain range and the final results would not be greatly influenced.
2. The definition of the reduced temperature should be modified. Regardless of the Wagner equation or the Xiang equation, a conclusion could be drawn that the saturated vapor pressure is zero only when the saturated temperature is 0 K on the absolute temperature scale. The authors consider that the conclusion may be unreasonable and should be changed. Namely, the temperature at which a substance cannot exist in the vapor phase probably is not the absolute zero of temperature. Hence, in this paper, the authors assume that there is a temperature designated as the “pressure

zero temperature" T_p such that if the actual temperature is below the "pressure zero temperature" the substance cannot exist in the vapor phase, and the saturated vapor pressure is zero. On the basis of this assumption, a new form of reduced temperature is adopted in the new vapor pressure equation.

After extensive analyses and comparisons, a new vapor pressure equation has been developed. The exact form is

$$\ln P_r = \ln T_{rp} [a_0(1 - \tau)^{3.76} + a_1(1 - \tau)^{-0.56} + a_2\tau^{1.89}] \quad (3)$$

where

$$P_r = P / P_c \quad (4)$$

$$T_{rp} = (T - T_p) / (T_c - T_p) \quad (5)$$

$$\tau = 1 - T_{rp} = 1 - (T - T_p) / (T_c - T_p) \quad (6)$$

$$a_2 = -a_0 / 0.56 \quad (7)$$

and a_0 , a_1 , and T_p are three adjustable parameters. The parameters a_0 and a_1 are fitted from experimental data using a Powell optimization method. The experimental points received weights proportional to $P^{-0.05}$ to reflect the uncertainties of pressures. The parametric determination of T_p consisted of repeating the nonlinear fit procedure for various fixed values of T_p to achieve a minimum sum-of-squares error.

3. COMPARISONS OF THE NEW VAPOR PRESSURE EQUATION WITH OTHER EQUATIONS

In order to evaluate the new equation, the agreement with experimental data and the extrapolation behavior down to the triple point and up to the critical point were compared with those of the Wagner equation and the Xiang equation. Forty-one substances that have reliable and accurate vapor pressure experimental data in the published literature were used.

3.1. Agreement with Experimental Data

The agreement with experimental data of high accuracy is the basic requirement of the vapor pressure equation. The Wagner equation is generally regarded as the best equation to represent vapor pressures over wide ranges within the experimental uncertainties. Hence, the new vapor equation is mainly compared with the Wagner equation.

The critical temperature, the critical pressure, and the fitted parameters of the new equation for some substances are given in Table I. The relative root-mean-square errors and the maximum relative deviations between the calculated results and experimental data for 41 substances are listed in Table II. The Wagner equation has an average overall relative root-mean-square error of 0.048% and an average maximum relative deviation of 0.170%; the average overall relative root-mean-square error and the average overall maximum relative deviation of the Xiang equation are 0.055 and 0.183%, respectively; the average overall relative root-mean-square error of the new equation is 0.073% and the average maximum relative deviation is 0.237%. It can be seen in Table II that the accuracy of the new equation is only slightly lower than those of the Wagner equation and the Xiang equation. Considering the experimental uncertainties, the new equation is valid over the entire range from the triple point to the critical point within experimental uncertainty.

3.2. Extrapolation Behavior

In general, the experimental vapor pressure data at low temperature are rarely measured or have poor accuracy because of the experimental instruments and limited conditions. Similarly, it is difficult to measure the vapor pressure at high temperature with high accuracy. Therefore, a vapor pressure equation with good extrapolation behavior is desired.

3.2.1. Extrapolation to the Triple Point

In this section, comparisons between the new equation and the other two equations (the Wagner equation and the Xiang equation) extrapolating to the triple point are discussed. For lack of experimental data in a sufficiently wide temperature range, 22 substances listed in Table I were compared, and comparisons for other substances are not feasible. The comparisons between the new equation and the other two equations extrapolating from a reduced temperature T_r of 0.75 to the triple point are listed in Table III. The parameters of equations were determined using only the experimental data between $0.75T_r$ and T_c , and comparisons were

Table I. Parameters for the New Vapor Pressure Equation, Eq. (3), and the Critical Constants of Some Substances

Substance	T_c (K)	P_c (kPa)	T_p	a_1	a_2	Refs.
Argon	150.69	4862.249	8.1	0.568985	4.848377	[2]
Nitrogen	126.2	3396.217	8.4	0.571350	4.944445	[2]
Oxygen	154.581	5036.215	9.2	0.571556	4.923652	[5]
Neon	44.4	2654.478	1.5	0.615294	4.815779	[6]
Krypton	209.4	5583.678	16.1	0.759724	4.713273	[6]
Xenon	289.7	5896.698	20.6	0.704943	4.768329	[6]
Fluorine	144	5320.182	20.6	0.837477	4.501828	[6]
Chlorine	417.15	7703.492	34.2	0.549854	5.007963	[6]
CO	132.91	3487.009	10.4	0.542743	4.900927	[6]
CO ₂	304.136	7371.615	45.0	0.655202	5.122690	[7]
Methane	190.551	4594.22	9.5	0.563330	4.943051	[8]
Ethane	305.33	4865.493	28.4	0.643200	5.025642	[9]
Propane	369.8	4234.489	68.8	0.758713	4.561986	[10]
Water	647.14	21898.54	52.6	0.456054	6.261918	[11]
Methanol	512.64	7653.214	33.7	-0.038372	7.373024	[12]
Ethanol	513.92	5407.129	33.7	-1.037412	7.626054	[12]
1-Propanol	536.78	4300.519	51.4	-1.552352	7.015606	[12]
2-Propanol	508.3	3629.449	38.9	-2.340792	7.304414	[12]
1-Butanol	563.05	3252.957	65.4	-2.098292	6.378581	[12]
2-Butanol	563.05	2511.428	44.9	-4.902910	5.080543	[12]
1-Decanol	687.7	2044.846	151.6	0.125474	5.673620	[12]
Benzene	561.75	4854.844	62.8	0.557235	5.369335	[13]
<i>n</i> -Butane	425.2	3738.285	37.4	0.461563	5.505814	[14]
Heptane	540.13	2707.524	69.9	0.573955	5.802538	[15]
HCFC123	456.9	3658.167	40.4	0.498006	5.897286	[16, 17, 18]
HCFC123a	461.7	3722.746	48.5	0.565158	5.714652	[17]
HFC124	395.43	3472.614	43.1	0.307241	5.663688	[19]
HCFC22	369.3	5383.923	42.3	0.911296	5.546823	[20]
HFC125	339.33	3595.507	40.7	0.510162	5.698258	[19]
HFC134a	374.25	4038.651	45.6	0.561046	5.784966	[21, 22]
HFC143a	345.861	3762.604	68.9	0.859650	4.865113	[23]
HFC152a	386.411	4476.77	39.8	0.540505	5.729963	[24]
HFC227ea	375.95	2974.866	51.5	0.612004	5.751540	[25]
HFC245fa	427.2	3536.605	56.3	0.352759	5.851797	[26]
HFC32	351.26	5086.539	2.7	-0.626415	6.422063	[19]
HFC338mccq	431.95	2669.179	59.8	0.419406	5.908076	[27]
Nitromethane	588	5723.822	53.4	0.397849	5.991130	[28, 29]
Hexafluoroacetone	357.1	2796.782	61.1	0.711075	5.474784	[30]
Pentafluorochloroacetone	410.65	2837.394	54.9	0.567703	5.756642	[30]
2,2,2-Trifluoroethanol	499.29	4851.105	109.4	0.597748	5.988512	[31]
Dimethyl ether	400.378	5295.612	11.4	0.294913	5.999835	[32]

Table II. Deviations between Experimental Data and Calculated Values of the New Equation, Eq. (3), Wagner Equation, Eq. (1), and Xiang Equation, Eq. (2)

Substance	<i>T</i> range (K)	Average deviation (%)			Maximum deviation (%)		
		Wagner	Xiang	New	Wagner	Xiang	New
Argon	83–150	0.015	0.035	0.027	0.063	0.093	0.077
Nitrogen	63–126	0.015	0.038	0.030	0.054	0.116	0.117
Oxygen	90–154	0.006	0.028	0.021	0.018	0.071	0.142
Neon	22–44	0.027	0.028	0.022	0.057	0.070	0.040
Krypton	115–160	0.006	0.008	0.006	0.028	0.033	0.029
Xenon	161–224	0.009	0.010	0.009	0.034	0.035	0.034
Fluorine	95–142	0.120	0.174	0.129	0.212	0.315	0.262
Chlorine	183–416	0.145	0.142	0.162	0.490	0.469	0.614
CO	68–129	0.153	0.153	0.158	0.533	0.536	0.546
CO ₂	216–304	0.008	0.021	0.043	0.016	0.041	0.090
Methane	90–190	0.008	0.023	0.070	0.045	0.075	0.141
Ethane	214–305	0.055	0.063	0.078	0.368	0.363	0.331
Propane	311–367	0.015	0.017	0.018	0.032	0.037	0.036
Water	273–646	0.022	0.024	0.334	0.061	0.064	0.861
Methanol	288–337	0.011	0.012	0.011	0.044	0.042	0.042
Ethanol	292–366	0.006	0.009	0.007	0.024	0.022	0.022
1-Propanol	333–377	0.005	0.006	0.006	0.016	0.014	0.015
2-Propanol	325–362	0.012	0.012	0.012	0.071	0.071	0.071
1-Butanol	351–398	0.003	0.003	0.003	0.007	0.007	0.008
2-Butanol	340–380	0.026	0.030	0.030	0.165	0.173	0.174
1-Decanol	400–528	0.015	0.040	0.048	0.047	0.099	0.117
Benzene	278–560	0.027	0.032	0.060	0.155	0.151	0.447
<i>n</i> -Butane	278–358	0.023	0.023	0.023	0.043	0.062	0.059
Heptane	335–503	0.023	0.027	0.023	0.097	0.102	0.096
HCFC123	273–453	0.247	0.244	0.291	1.115	1.165	1.203
HCFC123a	303–458	0.285	0.298	0.326	0.889	0.796	0.926
HFC124	221–286	0.009	0.010	0.009	0.042	0.046	0.043
HCFC22	217–248	0.011	0.011	0.011	0.056	0.057	0.057
HFC125	218–284	0.012	0.012	0.012	0.056	0.056	0.057
HFC134a	214–373	0.015	0.023	0.062	0.071	0.075	0.420
HFC143a	263–345	0.049	0.058	0.057	0.216	0.213	0.213
HFC152a	219–354	0.015	0.019	0.017	0.053	0.067	0.065
HFC227ea	233–375	0.058	0.066	0.076	0.250	0.251	0.295
HFC245fa	264–351	0.031	0.037	0.035	0.088	0.090	0.085
HFC32	235–266	0.021	0.024	0.024	0.131	0.151	0.149
HFC338mccq	259–351	0.021	0.022	0.022	0.068	0.071	0.073
Nitromethane	328–409	0.004	0.004	0.005	0.014	0.017	0.018
Hexafluoroacetone	239–356	0.124	0.137	0.177	0.397	0.427	0.383
Pentafluorochloroacetone	232–409	0.246	0.234	0.278	0.700	0.725	0.615
2,2,2-Trifluoroethanol	353–499	0.023	0.039	0.101	0.051	0.082	0.195
Dimethyl ether	233–399	0.040	0.050	0.170	0.097	0.145	0.549
Overall		0.048	0.055	0.073	0.170	0.183	0.237

Table III. Comparisons of the New Equation, Eq. (3), Wagner Equation, Eq. (1), and Xiang Equation, Eq. (2), on Extrapolation of T_r from 0.75 to the Triple Point Temperature T_{tr}

Substance	Average deviation (%)			Maximum deviation (%)		
	Wagner	Xiang	New	Wagner	Xiang	New
Argon	0.580	2.454	0.568	3.135	13.915	2.776
Nitrogen	0.603	2.699	0.778	8.142	38.209	8.046
Oxygen	0.168	0.752	0.523	1.667	7.477	3.788
Neon	2.162	3.727	0.224	17.338	30.697	1.638
Fluorine	1.178	0.730	0.358	11.129	7.357	1.585
Chlorine	9.692	215.226	3.361	66.796	3214.56	22.566
CO	78.231	58.614	3.831	717.668	502.457	19.749
Methane	1.982	0.373	2.501	18.136	3.925	18.251
Water	33.518	0.775	13.384	279.552	3.010	62.988
Benzene	4.932	6.519	2.393	41.649	55.390	14.882
<i>n</i> -Butane	8.993	–	0.395	35.258	–	0.998
Heptane	0.429	0.805	0.062	2.502	4.960	0.225
HCFC123	0.301	0.298	0.502	1.093	1.765	6.762
HCFC123a	2.763	1.246	1.222	29.202	8.545	7.820
HFC125	4.920	0.026	0.074	28.404	0.064	0.385
HFC134a	1.664	2.000	1.278	11.797	14.038	7.525
HFC152a	0.324	1.316	0.390	2.432	8.463	1.758
HFC227ea	0.122	0.205	0.610	1.416	2.394	4.652
HFC245fa	7.920	0.240	0.120	68.627	2.057	0.470
Hexafluoroacetone	0.807	0.447	0.187	4.097	1.646	0.731
Pentafluorochloroacetone	14.577	17.930	0.774	88.515	113.625	2.119
Dimethyl ether	1.993	1.337	0.672	17.455	10.982	6.825
Overall	8.085	14.442	1.555	66.182	183.88	8.934

made for all the experimental data. As shown in Table III, the new equation extrapolates the experimental data with an average overall root-mean-square deviation of 1.555%, compared to 8.085% for the Wagner equation and 14.442% for the Xiang equation, and an average overall maximum deviation of 8.934% compared to 66.182% for the Wagner equation and 183.88% for the Xiang equation. It is obvious that the new vapor pressure equation has an advantage over the Wagner equation and the Xiang equation in extrapolating to the triple point. Taking into consideration that experimental data at low temperatures are difficult to obtain and the measurement accuracy is limited, the new equation has a practical value in engineering applications.

In order to evaluate the extrapolation behavior of the new equation, further comparisons have been done with the vapor pressure data of N_2 ,

O₂, and Ar, which have a high accuracy in the full vapor–liquid temperature range. For those data, the uncertainties of temperature are within ± 5 mK, and the uncertainties of pressure are within $(2.0\text{--}1.3)\times 10^{-4}P_v$ for the pressure range from 0.1 to 0.3 MPa and $10^{-4}P_v$ above 0.3 MPa.

The extrapolation of T_r from 0.7, 0.75, 0.8, and 0.9 to the triple point temperature for N₂, O₂, and Ar were all compared, and the final results are shown in Table IV. It is obvious that when the equations extrapolate from different reduced temperatures to the triple point, the Wagner equation has a large deviation between the experimental data and the calculated results, and the Xiang equation is better, but the Xiang equation is obviously not as good as the new equation. The new equation gives an average overall root-mean-square deviation of 0.875% compared to 12.883% for the Xiang equation, and an average overall maximum deviation of 6.648% compared to 38.291% for the Xiang equation. In addition, Figs. 1, 2, and 3 give further illustrations of the extrapolation performance for the three vapor equations with the experimental data of argon. As shown in Fig. 1, the best extrapolation for the Wagner equation is T_r from 0.7 to the triple point temperature. The extrapolation will become worse when T_r increases; particularly, it cannot be considered at T_r from 0.9 to the triple point temperature. The extrapolation behavior of the Xiang equation is better than, but similar to, that of the Wagner equation as shown in Fig. 2. On the other hand, the maximum percentage deviation of the new equation is less than 10% and better than that of the other two equations.

According to Ref. 33, the slope of the vapor pressure vs. temperature curve has direct impact on the enthalpy of vaporization. Hence, the temperature behavior of the first derivative of the pressure (dP/dT) from the new vapor equation was checked with the experimental data of argon. The details are given in Fig. 4. As shown in Fig. 4, the new equation does not lead to negative enthalpies of vaporization at low temperature when the extrapolation of T_r is from 0.7, 0.8, and 0.9 to the triple point temperature. However, as shown in Fig. 5, the curve corresponding to the Xiang equation does not have the proper shape on the extrapolation of T_r from 0.9 to the triple point temperature. Moreover, the Wagner equation leads to negative enthalpies of vaporization at low temperature in the same case. The result agrees with the conclusion from Ref. 33 that indiscriminate use of the Wagner equation can lead to substantial extrapolation errors and erroneous enthalpies of vaporization especially at low temperatures. This may be the reason why the Wagner and Xiang equations cannot extrapolate well at low temperatures. In addition, according to Ref. 33, a negative value for the enthalpy of vaporization is caused by a negative slope, i.e., the vapor pressure–temperature dependence might have local

Table IV. Comparisons of the New Equation, Eq. (3), Wagner Equation, Eq. (1), and Xiang Equation, Eq. (2), on Extrapolation of T_r from 0.7, 0.75, 0.8, and 0.9 to the Triple Point Temperature T_{tr} for N_2 , O_2 , and Ar

Substance	Fit range T	Average deviation (%)			Maximum deviation (%)		
		Wagner	Xiang	New	Wagner	Xiang	New
N_2	$T_{tr}-0.7$	0.198	1.390	0.442	2.703	19.699	4.620
	$T_{tr}-0.75$	0.675	3.110	0.713	8.999	44.145	7.351
	$T_{tr}-0.8$	2.233	1.241	2.514	24.315	10.560	22.823
	$T_{tr}-0.9$	22.202	50.698	1.655	99.952	100.0	17.622
O_2	$T_{tr}-0.7$	0.069	0.311	0.092	0.703	3.361	0.679
	$T_{tr}-0.75$	0.140	0.852	0.466	1.389	8.435	3.373
	$T_{tr}-0.8$	0.697	1.381	0.910	6.089	13.135	6.201
	$T_{tr}-0.9$	488.534	44.059	0.387	13380	100.0	2.389
Ar	$T_{tr}-0.7$	0.073	1.508	0.400	0.423	8.646	1.963
	$T_{tr}-0.75$	0.371	2.441	0.733	1.990	13.842	3.560
	$T_{tr}-0.8$	9.342	6.704	1.686	51.953	37.667	7.923
	$T_{tr}-0.9$	4.51E5	40.899	0.503	5.545E6	100.000	1.276
	Overall	–	12.883	0.875	–	38.291	6.648

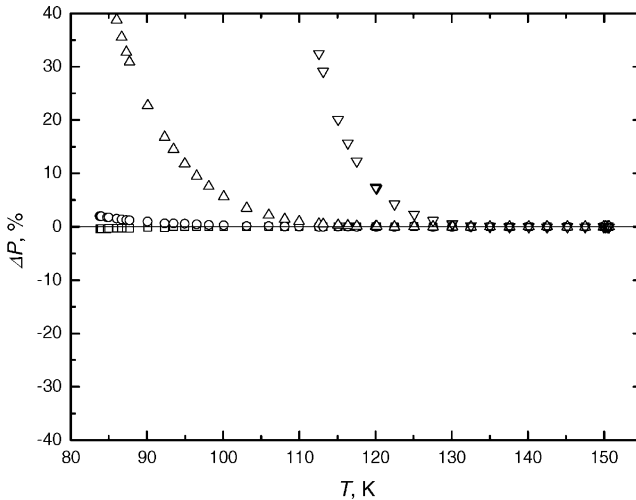


Fig. 1. Deviations of the Wagner equation from experimental data for argon [2]: (□) extrapolation of T_r from 0.7 to T_{tr} ; (O) extrapolation of T_r from 0.75 to T_{tr} ; (Δ) extrapolation of T_r from 0.8 to T_{tr} ; (▽) extrapolation of T_r from 0.9 to T_{tr} .

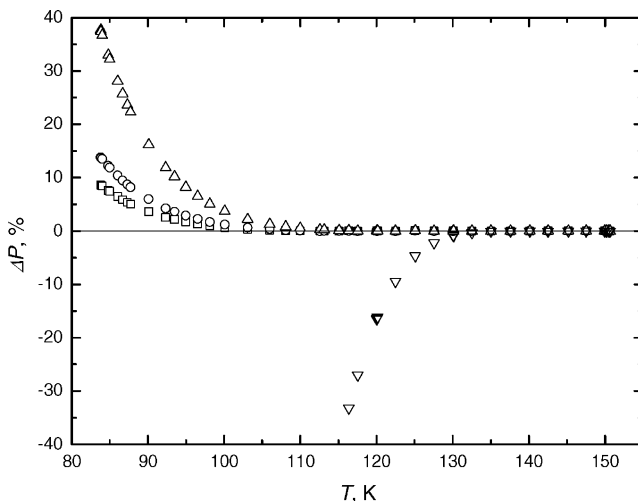


Fig. 2. Deviations of the Xiang equation from experimental data for argon [2]: (\square) extrapolation of T_r from 0.7 to T_{tr} ; (\circ) extrapolation of T_r from 0.75 to T_{tr} ; (Δ) extrapolation of T_r from 0.8 to T_{tr} ; (∇) extrapolation of T_r from 0.9 to T_{tr} .

minima and/or maxima. This is also indicated in Fig. 6. The shape of the curve of the Xiang equation is also not proper.

Furthermore, the dP/dT values of all the substances listed in Table III were computed using the new equation, and no negative enthalpies of vaporization were found. But this is not true for the Wagner and Xiang equations. This analysis shows that the particular results for extrapolating experimental data using the Wagner and Xiang equations are not accidental, but result from the nature of the equations.

3.2.2. Extrapolation to the Critical Point

In this section, comparisons between the new equation and the other two equations (the Wagner equation and the Xiang equation) extrapolating up to the critical point are made. For lack of experimental data in a sufficiently wide temperature range, only the 25 substances listed in Table I were compared, and other substances have not been studied. The comparisons between the new equation and the Wagner equation and the Xiang equation extrapolating from a reduced temperature of 0.75 to the critical point are listed in Table V. The critical temperature T_c was from experimental data, and the critical pressure P_c was determined in the extrapolation. As shown in Table V, the new equation extrapolates the

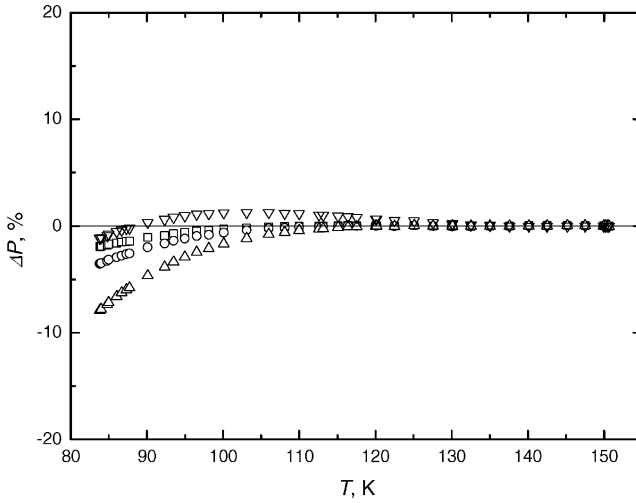


Fig. 3. Deviations of the new equation from experimental data for argon [2]: (\square) extrapolation of T_r from 0.7 to T_{tr} ; (\circ) extrapolation of T_r from 0.75 to T_{tr} ; (Δ) extrapolation of T_r from 0.8 to T_{tr} ; (∇) extrapolation of T_r from 0.9 to T_{tr} .

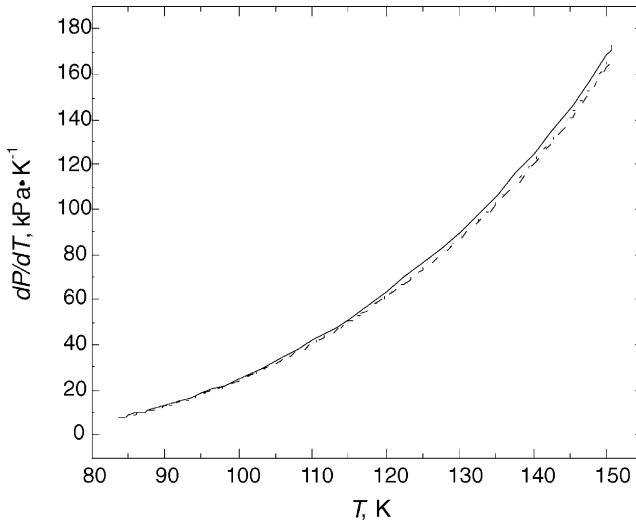


Fig. 4. Temperature behavior of the first derivative of the pressure from the vapor pressure equation of this work on extrapolation of T_r from 0.7, 0.8, and 0.9 to triple point: solid line, 0.7; dashed line, 0.8; dotted line, 0.9.

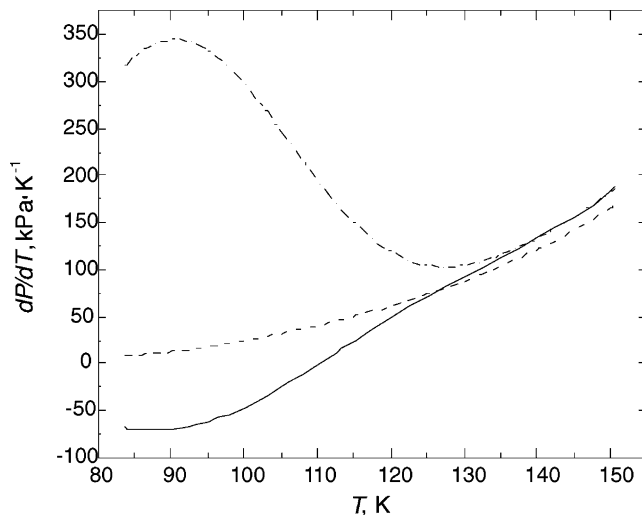


Fig. 5. Temperature behavior of the first derivative of the pressure from equations on extrapolation of T_r from 0.9 to triple point: solid line, Wagner equation; dashed-dotted line, Xiang equation; short-dashed line, this work.

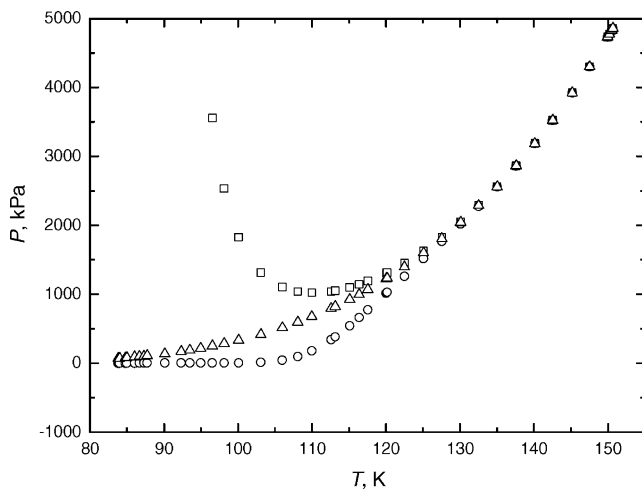


Fig. 6. Pressure–temperature behavior of argon extrapolated T_r from 0.9 to T_{tr} : (□) Wagner equation; (O) Xiang equation; (Δ) this work.

Table V. Comparisons of the New Equation, Eq. (3), Wagner Equation, Eq. (1), and Xiang Equation, Eq. (2), on Extrapolation of T_r from 0.75 to 1.0

Substance	Average deviation (%)			Maximum deviation (%)		
	Wagner	Xiang	New	Wagner	Xiang	New
Argon	1.488	0.386	1.109	7.148	1.338	4.188
Nitrogen	1.156	0.128	0.210	5.990	0.319	0.864
Oxygen	0.320	0.041	0.317	1.539	0.173	1.137
Neon	0.225	0.145	0.157	1.522	0.425	0.815
Krypton	0.048	0.016	0.011	0.349	0.094	0.043
Xenon	0.009	0.011	0.009	0.033	0.058	0.046
Fluorine	3.515	1.616	0.732	16.875	7.286	2.521
Chlorine	5.680	1.014	2.491	34.163	3.499	10.973
CO	4.598	0.208	0.203	32.166	0.542	0.546
Methane	1.361	0.103	0.289	3.322	0.205	0.703
Water	0.645	0.138	2.142	4.279	0.651	12.405
Benzene	0.373	0.125	0.524	3.333	0.656	4.272
<i>n</i> -butane	0.048	17.451	0.119	0.124	64.003	0.522
Heptane	0.237	0.051	0.096	2.827	0.247	0.833
HCFC123	682.826	4.747	4.400	6580.4	12.289	11.790
HCFC123a	34.243	54.188	2.241	99.800	238.104	4.134
HFC124	0.010	0.012	0.011	0.040	0.052	0.044
HFC125	0.110	0.026	0.028	0.893	0.147	0.158
HFC134a	2.172	0.134	0.177	19.421	0.762	2.182
HFC152a	2.016	0.089	0.249	12.056	0.351	1.457
HFC227ea	1.703	2.391	1.758	13.262	8.882	7.172
HFC245fa	0.074	0.154	0.165	0.258	0.971	1.085
HFC338mccq	0.045	0.022	0.028	0.356	0.070	0.115
Pentafluorochloroacetone	356.744	0.589	1.167	2954.72	0.959	3.922
Dimethyl ether	0.756	1.114	0.943	6.148	4.462	2.411
Overall	44.016	3.396	0.783	392.041	13.862	2.974

experimental data with an average overall root-mean-square deviation of 0.783% (the Wagner equation, 44.016%; the Xiang equation, 3.396%) and an average overall maximum deviation of 2.974% (the Wagner equation, 392.041%; the Xiang equation, 13.862%). It is obvious that the new vapor pressure equation is better than the Wagner equation and the Xiang equation in extrapolating from a reduced temperature of 0.75 to the critical point.

In order to evaluate the extrapolation behavior of the new equation to the critical temperature, further comparisons have been done with N_2 , O_2 , and Ar, which have vapor pressure data with high accuracy over the

Table VI. Comparisons of the New Equation, Eq. (3), Wagner Equation, Eq. (1), and Xiang Equation, Eq. (2), on Extrapolation of T_r from 0.7, 0.75, 0.8, and 0.9 to 1.0 for N_2 , O_2 , and Ar

Substance	Fit range T_r	Average deviation (%)			Maximum deviation (%)		
		Wagner	Xiang	New	Wagner	Xiang	New
N_2	0.7–1.0	0.275	0.251	0.404	1.558	0.663	1.576
	0.75–1.0	0.584	0.088	0.084	3.162	0.255	0.361
	0.8–1.0	0.121	0.071	0.124	0.652	0.339	0.491
	0.9–1.0	0.035	0.074	0.033	0.141	0.356	0.118
O_2	0.7–1.0	12.569	0.102	1.450	50.347	0.235	5.233
	0.75–1.0	0.320	0.041	0.317	1.539	0.173	1.137
	0.8–1.0	0.051	0.056	0.039	0.297	0.280	0.158
	0.9–1.0	0.007	0.061	0.019	0.024	0.303	0.184
Ar	0.7–1.0	3.178	0.652	1.535	14.364	2.138	5.670
	0.75–1.0	1.488	0.386	1.109	7.148	1.338	4.188
	0.8–1.0	0.602	0.111	0.353	3.023	0.470	1.388
	0.9–1.0	0.026	0.069	0.026	0.081	0.304	0.097
	Overall	1.605	0.164	0.458	6.861	0.571	1.717

full vapor–liquid temperature range. The extrapolations of T_r from 0.7, 0.75, 0.8, and 0.9–1.0 (the critical temperature) for N_2 , O_2 , and Ar were all compared, and the final results are shown in Table VI. The new equation gives an average overall root-mean-square deviation of 0.458% (the Wagner equation, 1.605%; the Xiang equation, 0.164%) and an average overall maximum deviation of 1.717% (the Wagner equation, 6.861%; the Xiang equation, 0.571%). It has been shown that when the equations extrapolate from different reduced temperatures to the critical point, the behavior of the Wagner equation is less reliable compared to the new equation, but the Xiang equation is a little better than the new equation. The main reason is that the Xiang equation has an advantage over the other equations in extrapolating from a reduced temperature of 0.7 to the critical point.

Further analysis indicates that, if the Wagner and Xiang equations extrapolate T_r from 0.6 to 1.0, the results cannot be considered at all. At the same time, the dP/dT values of O_2 were computed using the Wagner, Xiang, and new equations, and the curve shape of the equations except the new equation are clearly not proper. The curve of the Xiang equation is shown in Fig. 7. However, as shown in Fig. 8, the new equation can work well on extrapolation of T_r from 0.6, 0.7, and 0.8 to the critical point.

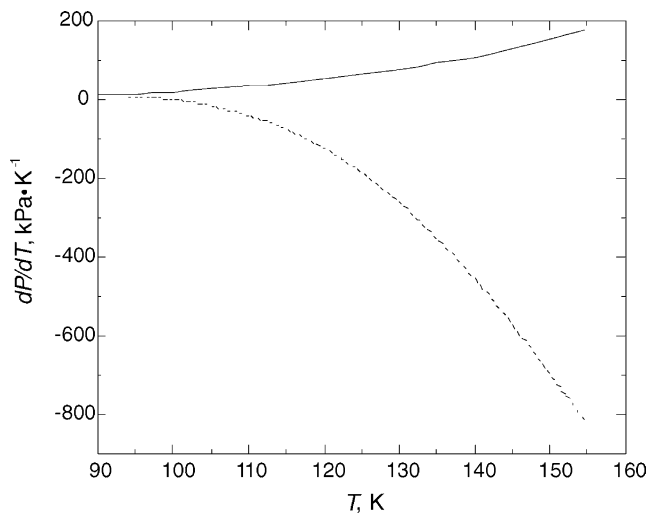


Fig. 7. Temperature behavior of the first derivative of the pressure from equations on extrapolation of T_r from 0.6 to critical point: solid line, this work; short-dashed line, Xiang equation.

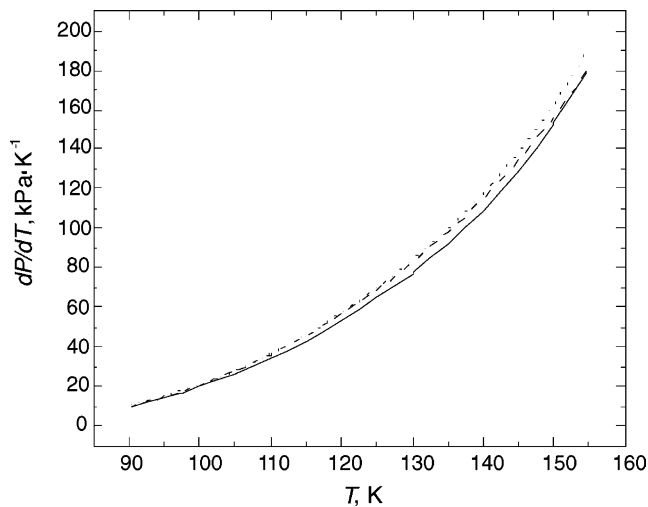


Fig. 8. Temperature behavior of the first derivative of the pressure from the vapor equation of this work on extrapolation of T_r from 0.6, 0.7, and 0.8 to critical point: solid line, 0.6; dashed line, 0.7; dotted line, 0.8.

4. CONCLUSION

On the basis of the assumption of “pressure zero temperature” T_p and using the corresponding-states principle, a new vapor pressure equation has been developed in this work for many substances with different chemical structures. This vapor pressure equation is valid over the entire range from the triple point to the critical temperature for a wide variety of fluids. The new equation, which has a relatively simple form and only three adjustable parameters, can provide an accuracy comparable with that of the well known Wagner equation. In addition, the extrapolation behavior of the new equation to the critical point or to the triple point is clearly better than that of the previous equations.

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LIST OF SYMBOLS

P	pressure
P_c	pressure of critical point
P_r	reduced pressure
P_v	saturated vapor pressure
T	absolute temperature
T_c	temperature at critical point
T_r	reduced temperature
T_p	vapor temperature corresponding to pressure of zero
T_{rp}	reduced temperature of new vapor equation
T_{tr}	temperature at the triple point

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