A new accurate method for prediction of the vapor pressures of pure substances over the entire region[1]

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ABSTRACT

A new method is presented to predict vapor pressures of pure substances over the entire vapor-pressure curve. The method uses a nonlinear analysis to solve the three substance-dependent parameters of the Xiang-Tan vapor-pressure equation with the Clausius-Clapeyron relation. Experimental data are not needed for vapor pressure, enthalpy of vaporization, and saturated liquid and vapor densities. The method has been used to predict the vapor pressures of a chemically diverse set of pure substances that have accurate data available over the entire range. The predicted pressures show excellent agreement with experimental data with high accuracy.

(**Keywords: boiling point; critical parameters; critical point; pure; thermodynamic properties; triple point; vapor-liquid equilibrium; vapor pressure**)

1. INTRODUCTION

Accurate vapor pressures are important in practical applications, in developing equations of state and in obtaining thermodynamic properties tables for substances [1]. Vapor-pressure equations represent the pressure-temperature behavior of substances along the vapor-liquid saturation curve. Vapor-pressure data in the medium-pressure range, about 1 to 150kPa, are often abundant and much more reliable than in the low-pressure range. Measurements are less complicated and high quality data can be easily obtained near the normal boiling temperature, with an error below 0.01% [2]. However, experimental vapor pressures below 1 kPa are generally scarce and usually not very reliable; vapor-pressure data in the low-pressure range are rarely consistent at their upper temperature limit with values obtained by different techniques at higher temperatures. Experimental difficulties in determining the vapor pressure at low pressures include the effect of contamination of samples by lower boiling compounds and incomplete degassing which can cause important systematic errors [2,3]. Differences of tens of percent between data from different literature sources are quite common [2]. If the substance has a high-boiling-point temperature, its high-temperature experimental data are usually not known or it may experimentally be inaccessible because of decomposition [4]. For these reasons, prediction from a minimum amount of experimental information is therefore important.

Many equations have been proposed for predicting vapor-pressure behavior especially extending into the low-temperature region. These generalized vapor-pressure equations usually require knowledge of the critical and boiling point temperatures and one or more physical properties to determine the constants [5-10]. The main disadvantage of these equations is that they generally fail to adequately describe the critical and low-temperature regions [2].

The simplest approach is to extrapolate from vapor pressures measured in the medium pressure range using an equation with an optimum number of parameters to obtain the low-

and high-temperature vapor pressures. The input data must be reliable and available over a sufficiently wide temperature interval to allow meaningful extrapolation. The form of the correlation equation used can also largely affect the results as shown by Scott and Osborn [11] and by Ruzicka and Majer [2] for some relationships. A more sophisticated procedure is to simultaneously fit the data and subject the resulting parameters to several semiempirical constraints. This approach improves the ability of the correlation equation to extrapolate to higher and lower pressures and has been used to describe the vapor pressure curve between the triple point and the critical point [4, 12, 13].

The method for extrapolating vapor pressures incorporating thermal data from the Clausius-Clapeyron equation was first described by King and Al-Najjar [14] and further developed by Ambrose and Davies [15], by Ruzicka and Majer [16], and by Weber [3]. The simultaneous analysis of vapor pressures and related thermal data necessitates compiling and evaluating of experimental data for several different properties, calorimetric enthalpies of vaporization, liquid and ideal gas heat capacities and saturated densities which are relatively seldom measured. Very recently, a similar improved method by Tillner-Roth also needed at least saturated densities as input data [17]. Therefore, these methods can be applied for only limiting fluids.

Ruzima and Majer [2] concluded that it is very dangerous to use flexible equations with more than three parameters in extrapolations when the experimental data are scarce and/or of low quality. The three-parameter form with the normal boiling point has been shown to be very dependable [2]. Simple functions such as the three-parameter Antoine equation [18] and the Cox equation [19] can accurately describe vapor pressures over only the low-temperature range. Recently, Xiang and Tan [20] proposed a simple three-parameter vapor-pressure equation that describes vapor pressures accurately over the entire vapor-pressure curve.

In this work, a more detailed extrapolation test of the Xiang-Tan vapor-pressure equation will be presented based on accurate and abundant experimental data in the medium-pressure range. A new method is then developed to predict the vapor pressure from a very limited amount of experimental information.

2. Predictions using the Xiang-Tan vapor-pressure equation

The Xiang-Tan vapor-pressure equation has only three parameters, a simple physical form, and is valid over the entire range from the triple point to the critical point and reproduces experimental data within the experimental uncertainties. The advantages of this equation are its simple universality for a diverse set of substances and its highly accurate representation of experimental data. It can be used to accurately correlate and extrapolate the vapor-pressure behavior of simple, nonpolar, polar, quantum, hydrobonding, and associating compounds. The equation is [20],

$$\ln p_r = (a_0 + a_1 \tau^{1.89} + a_2 \tau^{5.67}) \ln T_r \qquad (1)$$

where the reduced vapor pressure $p_r = p / p_c$ with p and p_c being the vapor pressure and the critical pressure, respectively. The reduced temperature $T_r = T / T_c$ with T and T_c being the temperature and the critical temperature respectively, and $\tau = 1 - T_r$. a_0, a_1, and a_2 are the three substance-dependent parameters that can be determined from experimental data. a_0 is the Riedel constant. The exponent 1.89 in the second term of equation (1) was derived from the critical exponent α =0.11 from the renormalization-group theory of critical phenomena. The exponent 5.67 in the third term is equal to 3 times 1.89.

To test the accuracy of Eq.(1), it is necessary to establish a reliable database of substances which data are available over the entire range. Accurate experimental vapor-pressure data covering the entire range are available for argon, nitrogen, benzene, 1,1,1,2-tetrafluoroethane, and water. The data source and substance-dependent parameters are given in Table 1. The parameters in the Xiang-Tan vapor-pressure equation are determined for each substance using a least-squares fit with all of the data over the entire region. The

critical pressures are adjusted within the experimental uncertainties reported in the literature to improve the correlations when determining the substance-dependent parameters for these substances. All data were converted, whenever necessary, to the ITS-90 temperature scale. The calculated normal-boiling temperature for each substance is also listed in Table I. Calculated comparison for parameters determined using all data in the entire range and extrapolated results up to the critical point and down to the triple point is presented in Table II for parameters determined using only data in the medium-pressure range. The deviations show that the Xiang-Tan parameters can accurately describe and simply extrapolate the entire vapor-pressure curve within the experimental accuracy for these substances. From the result, we can see that the equation can excellently predict the vapor pressures down to the triple point and up to the critical point if 0.2 reduced-temperature-range data are accurately available in the vicinity of the normal boiling point. It should be indicated that the near-triple point pressures have a estimated uncertainties of 1% by Tillner-Roth [17] from his predicted method. Extrapolation result from 0.1 reduced-temperature-range near the normal boiling point are specially shown in Fig.1. The maximum deviation is not exceed 0.5% which the experimental accuracy can not reach. These results show that the Xiang-Tan equation can dependably extrapolate from the normal-boiling-point range to the critical point and to the triple point. Of course, the highly accurate data are needed in a relatively large range at the vicinity of the normal boiling point. If no such data are available, the following prediction method can be used to supplement the Xiang-Tan equation.

3. Predictions using the Xiang-Tan equation with the Clausius-Clapeyron relationship

The Clausius-Clapeyron relation

$$dp / dT = \Delta H / T\Delta V \qquad (2)$$

gives the exact thermodynamic relationship 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. It can be transformed into

$$T_r^2 d \ln p_r / dT_r = \Delta H / RT_c \Delta Z \qquad (3)$$

where R is the universal gas constant. If the quantity $\Delta H / \Delta Z$ is known as a function of temperature, the vapor pressure can be obtained from the integration of equation (3). However, it is difficult to obtain the exact or very accurate expression for $\Delta H / \Delta Z$ as a function of temperature over the entire range from the triple point to the critical point.

The vapor pressure can be accurately predicted when the three substance-dependent parameters of the Xiang-Tan equation are determined that has already been shown to accurately describe the vapor pressure and has the least numbers of parameters. The first parameter, a_0, is the Riedel factor which can, in principle, be determined from the thermodynamic properties at the critical point. This parameter listed in Table I is used in the following discussion. Since much information is generally available at the normal-boiling-point temperature for at almost substances, this information can be applied to Eq.(1) to determine another parameter:

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$$\ln p_{br} = (a_0 + a_1 t_b^{1.89} + a_2 t_b^{5.67}) \ln T_{br} \qquad (4)$$

with $p_{br} = p_b / p_c$, $p_b = 101.325$ kPa. In principle, equation (4) can be solved once the normal boiling-point temperature T_b is known. The solution accuracy depends on the accuracy of T_b. Generally, T_b can be estimated with an accuracy of 0.010K or better.

One other condition is needed near the triple point or low-temperature region to determine the another Xiang-Tan parameter. $\Delta H / \Delta Z$ can be accurately represented to an accuracy of 0.05% or better for a chemically diverse set of substances with the following correlation from the triple point to the normal boiling point,

$$\Delta H / \Delta Z = c_0 \exp(c_1 \mathrm{c}^{1/2}) \tag{5}$$

where $\mathrm{c} = 1/T_r - 1$. The three temperature points are needed for determining the two parameters of equation (5) and the remaining Xiang-Tan parameter of Eq.(1). Indicating these three temperature points by the subscripts t, m, and b, the Clausius-Clapeyron relation can be written as,

$$(T_r^2 d \ln p_r / dT_r)_t = c_0 \exp(c_1 \mathrm{c}_t^{1/2}) \tag{6}$$

$$(T_r^2 d \ln p_r / dT_r)_m = c_0 \exp(c_1 \mathrm{c}_m^{1/2}) \tag{7}$$

$$(T_r^2 d \ln p_r / dT_r)_b = c_0 \exp(c_1 \mathrm{c}_b^{1/2}) \tag{8}$$

The ratios of equation (6) to Eq.(7) and to Eq.(8) are

$$(T_r^2 d \ln p_r / dT_r)_t / (T_r^2 d \ln p_r / dT_r)_m = \exp\left[\ c_1(\mathrm{c}_t^{1/2} - \mathrm{c}_m^{1/2})\ \right] \tag{9}$$

$$(T_r^2 d \ln p_r / dT_r)_t / (T_r^2 d \ln p_r / dT_r)_b = \exp\left[\ c_1(\mathrm{c}_t^{1/2} - \mathrm{c}_b^{1/2})\ \right] \tag{10}$$

Equations (9) and (10) can be used to obtain a condition for determining a Xiang-Tan parameter after eliminating c_1. However, since the Xiang-Tan equation for vapor pressure and Eq.(5) for $\Delta H / \Delta Z$ are approximate, we can therefore not expect that just three temperature points can give the best solution for determining the third parameter in the Xiang-Tan equation. As an alternative, many points from near the triple point to the normal-boiling point can be used with a least squares solution. The determined parameters would

then be dependable within the accuracies of the vapor-pressure equation and the $\Delta H / \Delta Z$ equation.

Ambrose et al. [4,13] suggested that the parameters of a vapor-pressure equation should be restricted to those sets which yield little differences in g at $T_r = 0.5$ and $T_r = 0.6$, where $g = T_r^2 d \ln p_r / dT_r t^{-0.375}$ which is obtained from the Watson correlation for ΔH [34] and $\Delta Z = 1$. The ratio $g(T_r = 0.5)/g(T_r = 0.6)$=1 can be used to approximately determine the initial parameters of the Xiang-Tan equation which can then be used to determine the initial value of c_1 of Eq.(5).

The calculated results from the regression analysis given in Table III and also in Fig. 2 show that the method can reliably predict the vapor pressure especially down to the triple point with high accuracy. The slightly great deviation occurs near the triple point. In Fig. 2, for R134a, it should be indicated that near the triple point the pressure has uncertainties of 1% as stimated by Tillner-Roth [17] from his predicted results.

4. Conclusions

A new thermodynamically consistent method has been proposed to predict vapor pressures of pure substances over the entire vapor-pressure curve. The method includes nonlinear analysis of the three substance-dependent parameters of the Xiang-Tan vapor-pressure equation with the Clausius-Clapeyron relationship. Experimental data are not needed for the vapor pressure, enthalpy of vaporization, or saturated liquid and vapor densities. The normal-boiling point may be combined in the regression analysis when the normal boiling point temperature is accurately available. This method has been tested to predict the vapor pressures of a chemically diverse of set of pure substances argon, nitrogen, benzene, 1,1,1,2-tetrafluoroethane, and water which have accurate data available over the entire range. The predictions show excellent agreement with experimental data. The determined parameters are presented along with the critical constants, the normal boiling-point temperatures which are beneficial for calculating other thermodynamic properties such as the entropy of the

saturated vapor, the entropy and enthalpy of vaporization, and the liquid phase heat capacities and for checking the reliability of experimental vapor-pressure data or the inconsistency between the enthalpies of vaporization and the vapor pressures and the virial coefficients at low-temperature region.

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Table I. Characteristic constants and data sources and points, the Xiang-Tan substance-dependent parameters obtained from the experimental data over the entire range and the calculated normal boiling temperature T_b.

Substance	T_c (K)	p_c (kPa)	a_0	a_1	a_2	Refs.	Data points	T_b
Argon	150.687	4863	5.788230	6.217258	12.76841	21	24	87.304
Nitrogen	126.212	3400.2	5.984684	6.764163	14.57305	22	67	77.357
Benzene	561.71	4875.8	6.826234	9.351254	24.19658	24-29	158	353.224
R134a	374.18	4056	7.414954	10.95162	24.19478	17,30-32	146	247.089
Water	647.1	22046	7.603329	10.21109	21.08574	33	53	373.133

Table II. Calculated and extrapolated comparison of the Xiang-Tan vapor-pressure equation with the experimental data over the entire region

Substance	Calculated deviation[a]		Extrapolation deviation[b]		Extrapolation deviation[c]	
	RMS	Max.dev.%	RMS	Max. dev %	RMS	Max. dev.%
Argon	0.032	0.060	0.046	0.109	0.048	0.114
Nitrogen	0.049	0.121	0.077	0.195	0.093	0.431
Benzene	0.047	0.162	0.052	0.201	0.094	0.347
R134a	0.249	1.22	0.50	2.5	1.0	5.0
Water	0.028	0.056	0.046	0.115	0.12	0.43

[a] $RMS = 100\left(\Sigma_1^n\left(1 - p_{cald} / p_{\exp t}\right)^2 / (n-3)\right)^{1/2}$ is the root-mean-squares deviation.

[b] The parameters are determined from the experimental data in the temperature range $-0.1 + T_{br}$ to $0.1 + T_{br}$. The deviations are compared over the entire region.

[c] The parameters are determined from the experimental data in the temperature range $-0.05 + T_{br}$ to $0.05 + T_{br}$. The deviations are compared over the entire region.

Table III. The Xiang-Tan substance-dependent parameters obtained from the regression analysis with Clausius-Clapeyron relation and the deviations from the experimental data.

Substance	T_c (K)	p_c (kPa)	a_0	a_1	a_2	ARD [a] %	RMS[a] %	Max.dev. %
Argon	150.687	4863	5.793631	6.155555	13.78217	0.039	0.055	0.112
Nitrogen	126.212	3400.2	5.985936	6.754552	14.899639	0.052	0.071	0.212
Benzene	561.71	4875.8	6.826008	9.350790	24.30099	0.060	0.081	0.287
R134a	374.18	4056	7.414530	10.93404	24.47372	0.162	0.317	1.57
Water	647.1	22046	7.603327	10.22128	20.95664	0.046	0.060	0.172

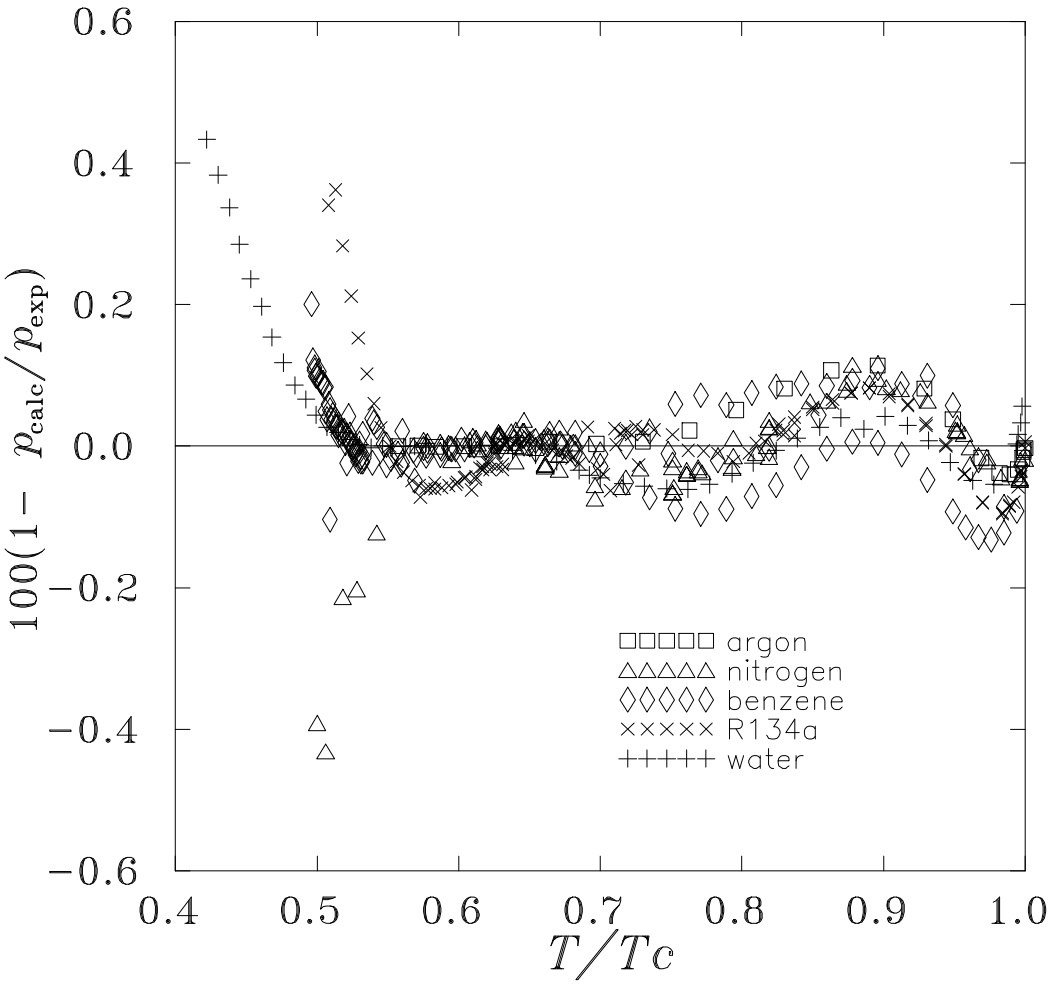
a $ARD = 100\Sigma_1^n \left|1 - p_{cald} / p_{\exp t}\right| / n$ is the average relative deviation.

$RMS = 100\left(\Sigma_1^n \left(1 - p_{cald} / p_{\exp t}\right)^2 / (n-3)\right)^{1/2}$ is the root-mean-squares deviation.

Figure captions

Fig. 1. The extrapolation comparison of Eq.(1) with the experimental data, the parameters are obtained from the experimental data only in the range between $-0.05 + T_{br}$ and $0.05 + T_{br}$, T_{br} the normal boiling temperature.

Fig. 2. The calculated comparison with the experimental data, the parameters are obtained from the nonlinear regression analysis with Eqs.(1) and (5).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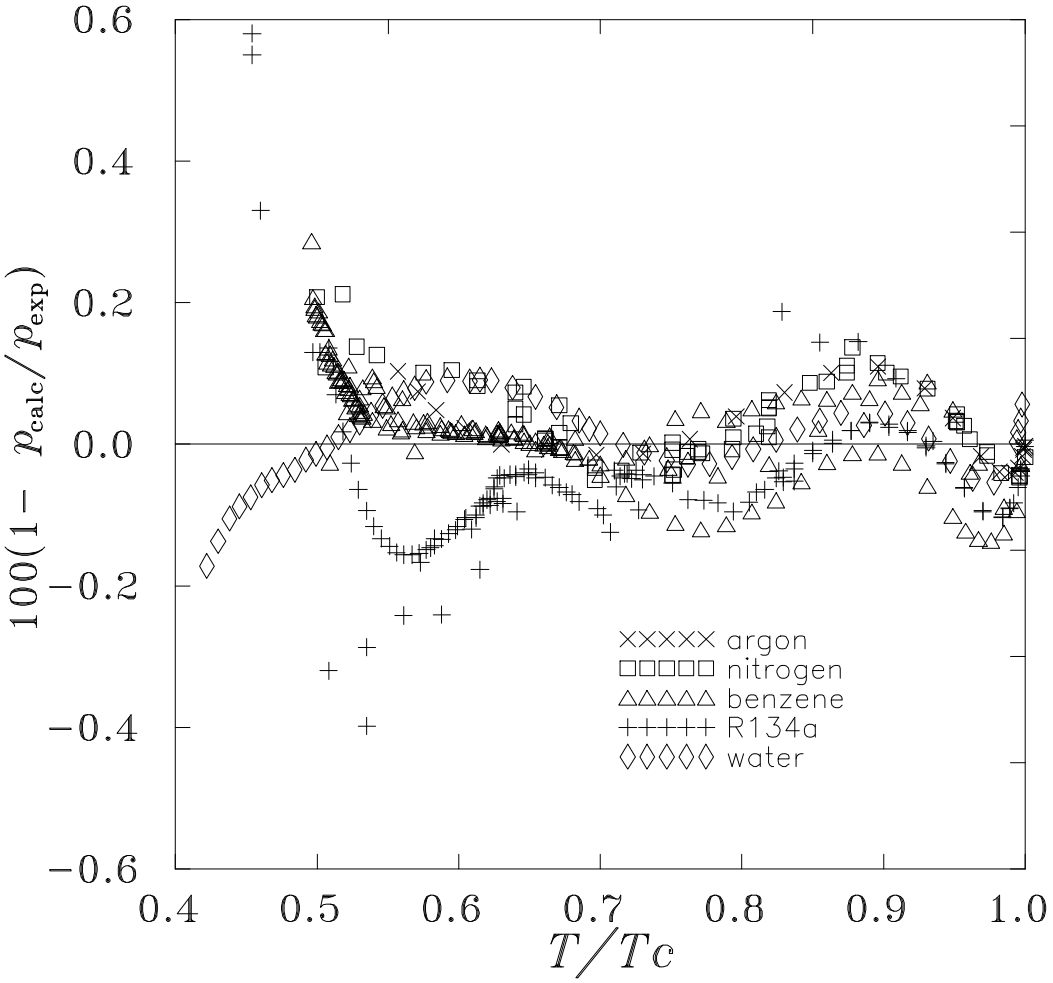
$100(1-\ p_{\mathrm{calc}}/p_{\mathrm{exp}})$
T/Tc
argon
nitrogen
benzene
R134a
water

Fig.1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T/Tc
argon
nitrogen
benzene
R134a
water

Fig.2