

# Nonanalytic Vapor Pressure Equation With Data for Nitrogen and Oxygen

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The specific heat of a two phase liquid-vapor system at constant volume apparently increases without limit at temperatures approaching the critical point, suggesting (via a thermodynamic relation) that the vapor pressure derivative  $d^2P/dT^2$  may behave similarly. This nonanalytic behavior at the critical point is used in the present vapor pressure formula to gain simplicity and accuracy, as seen by use of data for nitrogen and oxygen.

Key words: Critical point; equation; formula; liquid; nitrogen; nonanalytic; oxygen; vapor pressure.

## List of Symbols

$A, B, C$	constant coefficients.
$a, b, c, d, e$	constant coefficients.
$\Delta$	$100 \cdot (P/P_{\text{calc}} - 1)$ .
$\epsilon$	a nonintegral exponent, $1 < \epsilon < 2$ .
$F(x)$	any function of $T$ , nonanalytic at $T_c$ .
$P$	pressure, 1 atm = 0.101325 MN/m <sup>2</sup> .
$P_c$	critical-point pressure.
$P_t$	triple-point pressure.
$T$	temperature, K.
$T_c$	critical-point temperature.
$T_t$	triple-point temperature.
$x(T) \equiv (1 - T_t/T)/(1 - T_t/T_c)$ .	
$y(P) \equiv \log (P/P_t)/\log (P_c/P_t)$ .	

## 1. Introduction

An accurate vapor pressure equation is essential for computing thermodynamic properties of fluids, but a satisfactory function remains undiscovered [1].<sup>1</sup> To achieve accuracy for thermal property computations, many authors resort to polynomial representations of experimental vapor pressure data. This has the serious disadvantage that derivatives,  $dP/dT$  etc., may not be reliable.

A new approach to this problem resides in the proposal that  $d^2P/dT^2$  be infinite at the critical point, as given by a term  $P \sim -(T_c - T)^2 \cdot \log (T_c - T)$  where subscript  $c$  refers to the critical point [2]. Other work on critical phenomena [3] suggests that this pole also might be described by use of a nonintegral exponent  $\epsilon$  in a term  $(T_c - T)^\epsilon$ ,  $1 < \epsilon < 2$ .

Our particular need was for a reduced equation sufficiently simple to permit examination of existing data on fluorine. I have therefore used data only on the similar substances nitrogen and oxygen in the present work. Application of this equation to new data on fluorine will be reported independently [4].

## 2. Data and Method

I have examined nitrogen and oxygen for deviations from the basic vapor pressure equation,

$$\log (P) = a - b/T, \quad (1)$$

as have many previous workers. To normalize the variables, I eliminate the constants of (1) by use of triple-point and critical-point properties in the definitions.

$$x(T) \equiv (1 - T_t/T)/(1 - T_t/T_c),$$

$$y(P) \equiv \log (P/P_t)/\log (P_c/P_t),$$

where subscript  $t$  refers to the triple point. These variables range from zero to unity. Equation (1) now reads simply  $y = x$ , and we may conveniently examine plots of the deviations  $(y - x)$  as a function of  $x$ . For each substance the plot is qualitatively a simple cubic, with roots  $x_1 = 0$ ,  $0 < x_2 < 1$ ,  $x_3 = 1$ .

## 3. The Vapor Pressure Equation

Qualitative behavior of the above deviations is

$$(y - x) = A \cdot x \cdot (B - x) \cdot (1 - x). \quad (2)$$

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<sup>1</sup>Figures in brackets indicate the literature references at the end of this paper.

Precise oxygen vapor pressures [5] still cannot be represented accurately by (2). Addition of a nonanalytic term,  $F(x)$ , however, yields an accurate equation for nitrogen and oxygen,

$$y = x + A \cdot x \cdot (B - x) \cdot (1 - x) + C \cdot F(x). \quad (3)$$

Equation (3) is converted to a working equation by multiplying the terms in brackets and collecting powers of  $x$ ,

$$\log (P/P_t) = a \cdot x + b \cdot x^2 + c \cdot x^3 + d \cdot F(x). \quad (3a)$$

This equation is used throughout the following work. It is constrained to a given triple-point pressure,  $P_t$ . As vapor pressures in the mm Hg range have very low relative accuracy, figure 1a, this constraint is desirable and useful. If  $P_t$  is unknown and is to be estimated from the equation, we have the following option with no constraints,

$$\log (P) = a + b \cdot x + c \cdot x^2 + d \cdot x^3 + e \cdot F(x). \quad (3b)$$

Excellent representation of vapor pressure data for nitrogen and oxygen is obtained with either of the nonanalytic forms

$$F_1(x) = -(1-x)^2 \cdot \log (1-x), \quad (4a)$$

$$F_2(x) = x \cdot (1-x)^\epsilon \quad (4b)$$

where exponent  $\epsilon$  is nonintegral,  $1 < \epsilon < 2$ . In the following we shall see that (4b) is better for oxygen as  $T$  approaches  $T_c$ . For nitrogen, data of the precision necessary to choose between (4a) and (4b) are not available, and hence I do not plot the nitrogen deviations in this report. Nitrogen results are given only to indicate that (3) is not unique for oxygen.

As a guide for comparing results given below, the most accurate vapor pressure equation currently available for oxygen probably is that of Hust and Stewart [9],

$$\log (P) = \sum_{i=0}^7 A_i \cdot T^i, \quad (5)$$

with eight coefficients. We note absence of a term  $1/T$ . This is no oversight, as these authors intensively investigated many well-known forms [1].

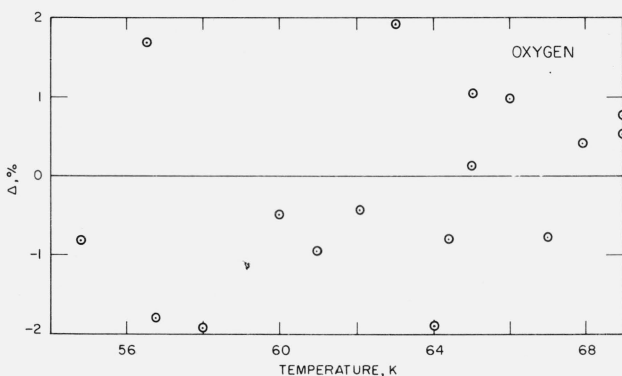


FIGURE 1a. Low temperature deviations for oxygen with (3a) and  $F_1(x)$ .

## 4. Some Results for Nitrogen and Oxygen

The nitrogen data used here are those selected by Strobridge [6], namely from [7] and [8]. The oxygen data are the same as selected by Hust [9], namely from [5]. Fixed-point constants used for the present work are in table 1. Results for eq (3a) are in table 2. Each column gives the form of  $F(x)$ , the derived critical-point pressure  $P_c$ , the relative critical-point slope,  $[d \ln(P)/d \ln(T)]_c$ , exponent  $\epsilon$  and the coefficients, the number of datum pairs,  $NP$ , and the root mean square of individual, relative deviations, RMS.

Hoge [5] gives about 218 data for oxygen. For table 2, some imprecise low-temperature data were eliminated to yield an rms deviation of 0.06 percent. For all 218 data the rms relative deviation is 0.34 percent, about the same as found by Hust and Stewart only by use of the eight-constant power series and by weighting the data and deviations according to their uncertainties. Our deviation was obtained with no weighting, and with fewer arbitrary coefficients.

Approaching the critical point, these oxygen data are extremely precise, enabling us to see that  $F_2(x)$  gives a much better representation at  $T > 141$  K than does the logarithmic form,  $F_1(x)$ . This is evident upon comparing deviations via  $F_1(x)$  in figure 1 with the corresponding deviations via  $F_2(x)$  in figure 2. On these plots  $\Delta \equiv 100 \cdot (P/P_{\text{calc}} - 1)$ .

TABLE 1. Fixed-point constants used

	Nitrogen	Oxygen
$T_t$ .....K...	63.14[10]	54.353[5]
$P_t$ .....atm...	<sup>a</sup> 0.1233	0.00150[5]
$P_t$ .....MN/m <sup>2</sup> ...	.0124934	.0001519875
$T_c$ .....K...	<sup>a</sup> 126.25	154.77[5]

<sup>a</sup> Adjusted to minimize deviations.

TABLE 2. Some results for equation (3a)

	Nitrogen	Oxygen	Oxygen
$F(x)$ .....	( <sup>a</sup> )	( <sup>a</sup> )	( <sup>b</sup> )
$P_c$ .....atm...	33.524	50.105	50.139
$P_c$ .....MN/m <sup>2</sup> ...	3.396819	5.076889	5.080334
$(d \ln(P)/d \ln(T))_c$ ...	5.8775	5.9203	6.0117
$\epsilon$ .....			1.633
$a$ .....	5.2149143	7.5955889	5.9479153
$b$ .....	0.5126235	5.1202773	8.2487892
$c$ .....	-.1221435	-2.2994456	-3.7796060
$d$ .....	.6158760	3.2246189	4.8725595
$NP$ .....	89	188	188
RMS.....%	0.051	0.060	0.059

<sup>a</sup>  $F(x) \equiv -(1-x)^2 \cdot \log (1-x)$ .

<sup>b</sup>  $F(x) \equiv (1-x)^\epsilon \cdot x$ .

Table 3 compares results from (5) with results from (3a) using the nonanalytic form (4b). The last two columns give percent deviations of first and second derivatives via (5) from values obtained via (3a). These are plotted in figure 3. It is interesting to see that the

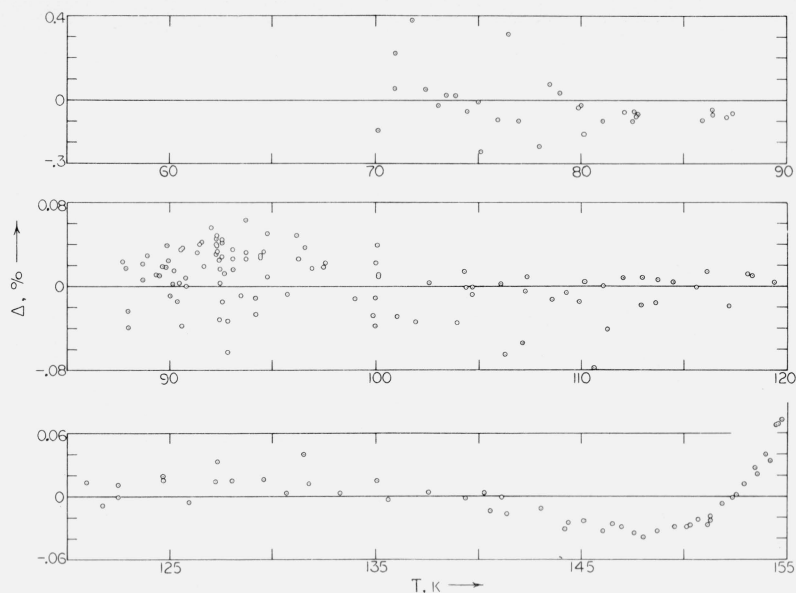


FIGURE 1. Deviations for oxygen with (3a) and  $F_1(x)$ .

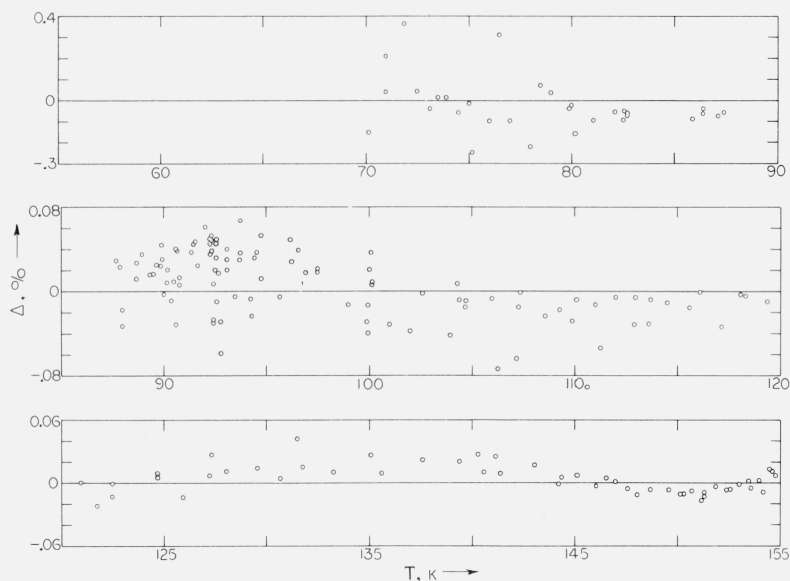


FIGURE 2. Deviations for oxygen with (3a) and  $F_2(x)$ .

number of inversions on these plots corresponds exactly to the number of terms used in the power series (5).

We also may compare the curvature  $d^2P/dT^2$  calculated by (3a) with results derived from our specific heat measurements on the two-phase, liquid vapor system for oxygen [11]. In the thermodynamic relation [2],

$$\overline{C}_v/T = -d^2G/dT^2 + (d^2P/dT^2) \cdot v, \quad (6)$$

$\overline{C}_v$  is heat capacity of the two phase system at constant volume,  $G$  is the Gibbs free energy per mol, and  $v$  is the overall, average molal volume. Data for  $\overline{C}_v(T)$  at

two or more different densities must be interpolated onto isotherms. Equation (6) then gives  $d^2P/dT^2$  as the slope of plots of  $\overline{C}_v/T$  versus  $v$ . Results have relatively large uncertainties, exceeding those expected from the vapor pressure equation. Table 4 gives this comparison of  $d^2P/dT^2$  from (3a) with results from specific heat data via (6).

As a preliminary measure of the generality of (3), table 5 gives the constants obtained when using  $F_1(x)$ . These values were derived from results such as those in table 2. Fluorine results are quite preliminary. Constants for all three substances have the same signs and about the same magnitudes.

TABLE 3. Comparison of oxygen vapor pressure equations

Goodwin				Hust-Stewart			Percent	Percent
<i>T</i> , K	<i>P</i> , ATM	<i>dP/dT</i>	<i>d</i> <sup>2</sup> <i>P/dT</i> <sup>2</sup>	<i>P</i> , ATM	<i>dP/dT</i>	<i>d</i> <sup>2</sup> <i>P/dT</i> <sup>2</sup>	<i>dP/dT</i>	<i>d</i> <sup>2</sup> <i>P/dT</i> <sup>2</sup>
54.353	0.0015	0.00046	0.00012	0.0015	0.00046	0.00012	−0.197	−0.514
60.000	.0072	.00182	.00040	.0072	.00181	.00039	−.448	−.478
65.000	.0230	.00491	.00089	.0229	.00489	.00088	−.373	−.206
70.000	.0616	.01120	.00169	.0614	.01118	.00169	−.198	.042
75.000	.1433	.02241	.00285	.1430	.02240	.00286	−.038	.168
80.000	.2970	.04034	.00438	.2967	.04037	.00439	.058	.168
85.000	.5608	.06674	.00623	.5608	.06680	.00624	.085	.084
90.180	.9997	.10464	.00845	1.0000	.10470	.00844	.062	−.035
95.000	1.6108	.15074	.01072	1.6113	.15077	.01070	.017	−.125
100.000	2.5088	.21056	.01323	2.5092	.21049	.01321	−.030	−.160
105.000	3.7379	.28328	.01587	3.7377	.28311	.01586	−.059	−.112
110.000	5.3640	.36946	.01861	5.3629	.36925	.01862	−.057	.013
115.000	7.4557	.46958	.02145	7.4537	.46946	.02148	−.025	.172
120.000	10.0838	.58410	.02438	10.0818	.58425	.02445	.026	.281
125.000	13.3217	.71364	.02746	13.3214	.71415	.02753	.072	.239
130.000	17.2466	.85906	.03075	17.2494	.85976	.03075	.081	−.017
135.000	21.9410	1.02171	.03438	21.9467	1.02206	.03424	.034	−.395
140.000	27.4959	1.20376	.03857	27.5013	1.20319	.03836	−.048	−.529
145.000	34.0172	1.40910	.04382	34.0178	1.40801	.04391	−.077	.207
150.000	41.6391	1.64619	.05178	41.6383	1.64736	.05255	.071	1.487
151.000	43.3115	1.69914	.05421	43.3123	1.70106	.05489	.113	1.255
152.000	45.0383	1.75483	.05734	45.0413	1.75723	.05751	.137	0.294
153.000	46.8224	1.81427	.06189	46.8277	1.81617	.06044	.105	−2.346
154.000	48.6688	1.87999	.07097	48.6746	1.87824	.06374	−.093	−10.180
154.100	48.8572	1.88716	.07263	48.8628	1.88463	.06410	−.134	−11.744
154.200	49.0463	1.89452	.07462	49.0516	1.89105	.06445	−.183	−13.625
154.300	49.2361	1.90210	.07711	49.2410	1.89752	.06481	−.241	−15.944
154.400	49.4267	1.90997	.08038	49.4311	1.90402	.06518	−.312	−18.911
154.500	49.6181	1.91822	.08505	49.6218	1.91055	.06555	−.400	−22.927
154.600	49.8104	1.92708	.09278	49.8132	1.91713	.06592	−.516	−28.950
154.700	50.0036	1.93710	.11141	50.0052	1.92374	.06630	−.690	−40.487

TABLE 4. Comparisons of *d*<sup>2</sup>*P/dT*<sup>2</sup> for oxygen

$\overline{C}_v/T = -d^2G/dT^2 + (d^2P/dT^2) \cdot v$			
<i>T</i> , K	<i>d</i> <sup>2</sup> <i>P/dT</i> <sup>2</sup> , atm/K <sup>2</sup>		Expt'l. $\overline{C}_v$
	V.P. eq (3a)		
60.00	0.0004		0.0007 ± 100%
65.00	.0009		.0012
70.00	.0017		.0020
75.00	.0029		.0031
80.00	.0044		.0046
85.00		.0062	.0064
90.18		.0085	.0084
95.00		.0107	.0106
100.00		.0132	.0130
105.00		.0159	.0155
110.00		.0186	.0182
115.00		.0215	.0211
120.00		.0244	.0240
125.00		.0275	.0271 ± 2%

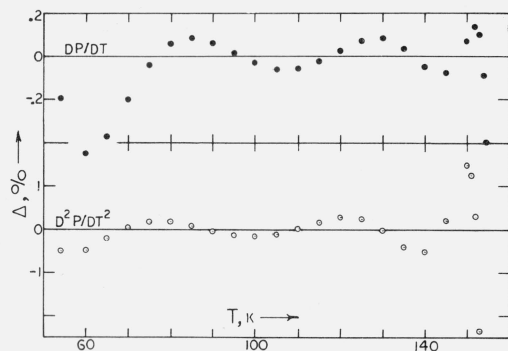


FIGURE 3. Comparison of derivatives from (5) for oxygen with values from (3a) using (4b).

TABLE 5. Constants for (3) with logarithmic  $F(x)$ 

	Nitrogen	Oxygen	Fluorine
A.....	-0.0218	-0.2208	-0.1109
B.....	3.1969	1.2267	1.2507
C.....	0.1099	0.3096	0.1913

The oxygen data used here may have a uniquely high precision near the critical point. As (3a) gives an excellent representation of these data, this is good evidence that the vapor pressure formula indeed should be nonanalytic at the critical point, as was suggested by Yang and Yang in 1964.

## 5. Comments

The following comments have been received, of interest in the rapidly developing theory of critical states. Griffiths and Rushbrooke have proven that if  $d^2P/dT^2$  diverges as  $|T-T_c|^{-\theta}$ , then  $\theta < \alpha' + \beta$  [3b], which brings up the lower limit on  $\epsilon$  found in the present report for oxygen vapor pressure data.

The scaling laws limit the value of  $\epsilon$  even further, namely to close to 2. These laws are postulates, not proofs [12]. Recently, a nonanalytic scaling law vapor pressure equation has been used for  $\text{CO}_2$  near the critical point [13].

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