New Vapor Pressure Equations from Triple Point to Critical Point and a Predictive Procedure for Vapor Pressure

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The quadratic and the cubic equations, previously proposed by us, for the representation of vapor pressure from the triple point to the normal boiling point, have now been extended to the critical point by the addition of two more parameters to each of them. They have been compared with the equations proposed by Goodwin and Wagner. The extended quadratic equation employing only four parameters has been found to represent the vapor pressure of even such a complex substance as water quite adequately. Finally, a new predictive procedure has been proposed to predict the vapor pressure from normal boiling to critical point even when no vapor pressure data are present.

Introduction

Numerous procedures have been proposed for the representation of vapor pressure from the triple point to the critical point. Some of them have been recently reviewed by Wagner (*1*) and by Ambrose (*2*). While various organizations are still compiling Antoine constants, and use different Antoine equations for different regions of the liquid substances, the ESDU (*3*) uses one simple equation containing not more than 5 parameters to represent the vapor pressure for the entire liquid region. Experience has shown that such a procedure is not only expedient but is also the most accurate one. This paper is aimed at improving such procedures.

We begin this by defining certain symbols we encounter in our presentation.

T_t = triple point
T_b = normal boiling point
T_c = critical point
T_i = inversion point, the point where the deviations from a linear equation derived on the basis of the vapor pressure data at the normal boiling point and critical point changes sign as shown in Figure 1. In case the deviations do not change sign, but show an inflection, T_i will be referred to as the inflection point.
$T_x = T_t$ or T_b
$T_r = T/T_c$ (reduced temperature)
P_t = triple point pressure
P_b = 1 atm (101.325 kPa)
P_c = critical pressure
$P_x = P_t$ or P_b
P_i = pressure at the inversion point
$X = (T_x - T)/T$; $X_t = (T_t - T)/T$; $X_b = (T_b - T)/T$
$Y = (T_c - T)/T$; $Z = (T_c - T)/T_c$; $W = T_c/T$
$G = (T_x - T_c)/T_c$; $H = (T_c - T_x)/T_x$
σ = standard deviation
$(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}$ = relative deviation
σ_r = standard deviation based on relative deviations

We now introduce the following equations

The quadratic equation (3 parameters):

$$\ln (P/P_x) = AX + BX^2 \tag{1}$$

The cubic equation (4 parameters):

$$\ln (P/P_x) = AX + BX^2 + CX^3 \tag{2}$$

The new equation (4 parameters):

$$\ln (P/P_x) = AX + BX^2 + X(CZ^f + DZ^g) \tag{3}$$

The new equation (5 parameters):

$$\ln (P/P_x) = AX + BX^2 + CX^3 + X(DZ^f + EZ^g) \tag{4}$$

The new equation (4 parameters):

$$\ln (P/P_c) = AY + BY^2 + CZ^f + DZ^g \tag{5}$$

The new equation (5 parameters):

$$\ln (P/P_c) = AY + BY^2 + CY^3 + DZ^f + EZ^g \tag{6}$$

The Wagner equation (4 parameters):

$$\ln (P/P_c) = AY + W(BZ^f + CZ^g + DZ^h) \tag{7}$$

The Wagner equation (5 parameters):

$$\ln (P/P_c) = AY + W(BZ^f + CZ^g + DZ^h + EZ^i) \tag{8}$$

The Goodwin equation (4 parameters):

$$\ln (P/P_x) = A(X/G) + B(X/G)^2 + C(X/G)^3 + D(X/G)(Y/H)^f \tag{9}$$

The Goodwin equation (5 parameters):

$$\ln (P/P_x) = A(X/G) + B(X/G)^2 + C(X/G)^3 + D(X/G)^4 + E(X/G)(Y/H)^f \tag{10}$$

The A, B, C, D, and E of eq 1–10 are the coefficients to be determined; f, g, h, and i are the exponents either predetermined or to be determined through nonlinear regressions or through iteration.

The eq 1 and 2 were introduced by us previously (*4*) for representing vapor pressure from the triple point to the normal boiling point. T_x is the hidden parameter in these two equations. T_x is supplied and is not considered as an additional parameter in the eq 3, 4, 9, and 10. In 1 and 2, we may have any boiling point T_x between the triple point and the normal boiling point, and it may be determined through regression, either linear or nonlinear, as shown by us previously. The equations will be referred to as, for example, 1a, or 1b, depending upon whether the T_x is T_t or T_b. By adding two additional parameters to each of the eq 1 and 2, we obtain the eq 3 and 4. The same extensions will be used for the eq 2, 3, and 4. The eq 3 and 4 reduce to zero at $T = T_x$, but at $T = T_c$ they reduce to the eq 11 and 12, respectively:

$$\ln (P_c/P_x) = AG + BG^2 \tag{11}$$

$$\ln (P_c/P_x) = AG + BG^2 + CG^3 \tag{12}$$

The new eq 3 and 4 are related to the Goodwin equations (9) and (10) and to the Wagner equation (7). Our investigation reveals that at least two Goodwin terms and two Wagner terms are needed to make the vapor pressure equation a reliable one.

The new equations, eq 5 and 6, are also formulated on the basis of the quadratic and cubic equations but are constrained to go through the critical point. They are closely related to the Wagner equation (7). The extensions a and b also apply to the Goodwin equations (9) and (10). While constrained to produce

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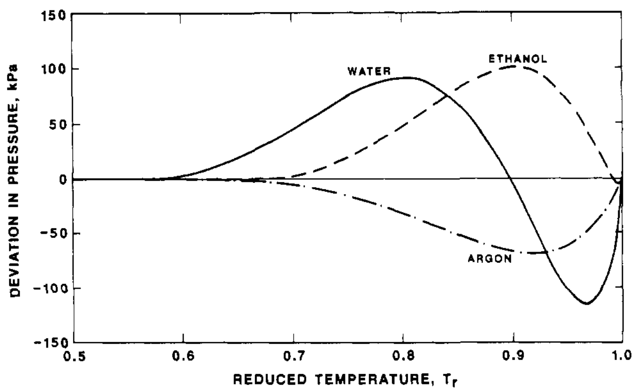

Figure 1. Plot of the pressure deviations vs. reduced temperature for water, ethanol, and argon. The pressure deviations are the differences between the observed pressure and the pressure calculated from the equation $\ln P = a - b/T$. The coefficients a and b were evaluated by using the pressure and temperature data points at the normal boiling point and the critical point.

the required pressures at T_x, the eq 5, 6, 7, and 8 are constrained to produce the selected critical pressure. It is much more important to produce better results in the low-pressure region than in the critical region. In this respect eq 3, 4, 9, and 10 are superior to the eq 5, 6, 7, and 8. The quadratic equation is most useful for the prediction of vapor pressure from the triple point to the normal boiling point as shown by us previously. The cubic equation plays an important role in the determination of the normal boiling point. Equations 3, 5, 7, and 9 contain only 4 parameters and appear to be quite adequate for the representation of vapor pressure of most compounds. The 5-parameter analogues of these equations namely, (4), (6), (8), and (10), are necessary only when much more accuracy in the representation of vapor pressure data is needed.

All the equations (3)–(10) satisfy the following criteria:

1. $d^2P/dT^2 = \infty$ at T_c.
2. $\Delta H/\Delta Z$ is minimum at $T_r = 0.85$–0.90.
3. $\Delta H/\Delta Z = (1/\beta)(1 - T_r)^\kappa$ *below the normal boiling point*.

d^2P/dT^2 should be indeterminate at the critical point (5)–(8). The criterion 2 was first pointed out by Waring (*9*), who noticed that $\Delta H/\Delta Z$ for water passes through a minimum at $T_r = 0.85$. ΔH is the enthalpy of vaporization and ΔZ is the change in the compression factor on evaporation; $\Delta Z = Z_V - Z_L = (V_V - V_L)P/RT$, V_V and V_L being the molar volumes of vapor and liquid, respectively. $\Delta H/\Delta Z$ is related to the vapor pressure by the equation

$$\Delta H/\Delta Z = RT^2 \, d \ln P/dT \tag{13}$$

which is derived from the Clapeyron equation. The third criterion follows from the Watson relation (*10*). The value of κ usually lies between 0.33 and 0.4 as shown by Gambill (*11*) but the value of 0.375 as recommended by Ambrose, Counsell, and Hicks (*12*) appears to be quite satisfctory. β is usually a constant for a given substance in the region between the triple point and the normal boiling point. In addition to the above criteria, we also have three additional criteria with respect to a function α, introduced by Plank and Riedel (*13*) and defined as

$$\alpha = (dP/dT)T/P \tag{14}$$

Although Plank and Riedel were concerned with the value of α at the critical temperature, we find its value to be useful at all temperatures from the triple point to the critical point. The behavior of α is particularly interesting in the critical region, since it goes to a minimum at $T_r = 0.97$–0.98. This behavior of the α-function may be seen from the plots of α vs. temperature made by Wagner (*1*) for both argon and nitrogen in the region close to the critical point. We have shown in Figure

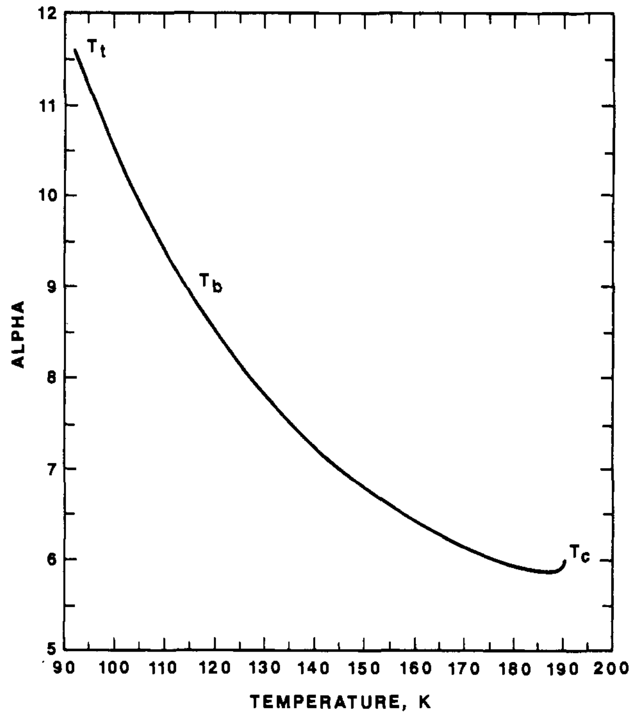

Figure 2. Plot of the α-function for methane vs. temperature from the triple point to the critical point.

2 a plot of the α-function for methane from the triple point to the critical point. This gives rise to the following criterion.

4. α = *minimum at* $T_r = 0.97$–0.98.

We have not found so far any exception to this new criterion. At the critical temperature, α becomes equal to $-A$ of the eq 5, 6, 7, and 8.

The mathematical expressions for α derived on the basis of eq 1–10 are given in Table XIII. The expressions for the α based on eq 3–10 lead to the following criterion.

5. $d\alpha/dT = \infty$ at T_c.

From eq 13 *and* 14 and the criterion 3, one can write for α the following expression

$$\alpha = (1/\beta RT)(1 - T_r)^\kappa \tag{15}$$

which satisfies the criterion 5, providing the value of κ is positive and less than unity. We may also express α alternatively as follows:

$$\alpha = a + bX \tag{16}$$

$$\alpha = a + bX + cX^2 \tag{17}$$

$$\alpha = \exp(a + bT + cT^2) \tag{18}$$

$$\alpha = \exp(a + bT_r + cT_r^2) \tag{19}$$

$$\alpha = a + bZ^f + cZ^g + dZ^h \tag{20}$$

The eq 16–19 do not satisfy the criterion 5 but may be used to express α as a function of temperature below the critical temperature. Equation 18 actually forms the basis of the Cox equation discussed by us previously (*4*). Equation 20 would satisfy the criterion 5 provided the value of f is positive and less than 1. In principle, we should be able to formulate a good vapor pressure equation on the basis of the α-function.

A sixth criterion may also be established with respect to the α-function. This has to do with the value of α at $T = T_x$. It can be easily verified that the constant A of the eq 1 and 2 is equal to $-\alpha$ at $T = T_x$. The most satisfactory value of α is that obtainable from the cubic equation (2) between the triple point and the normal boiling point. The sixth possible criterion, therefore, is that the value of α obtainable from any of the eq 3–10 at T_x be in agreement with the value obtainable from the

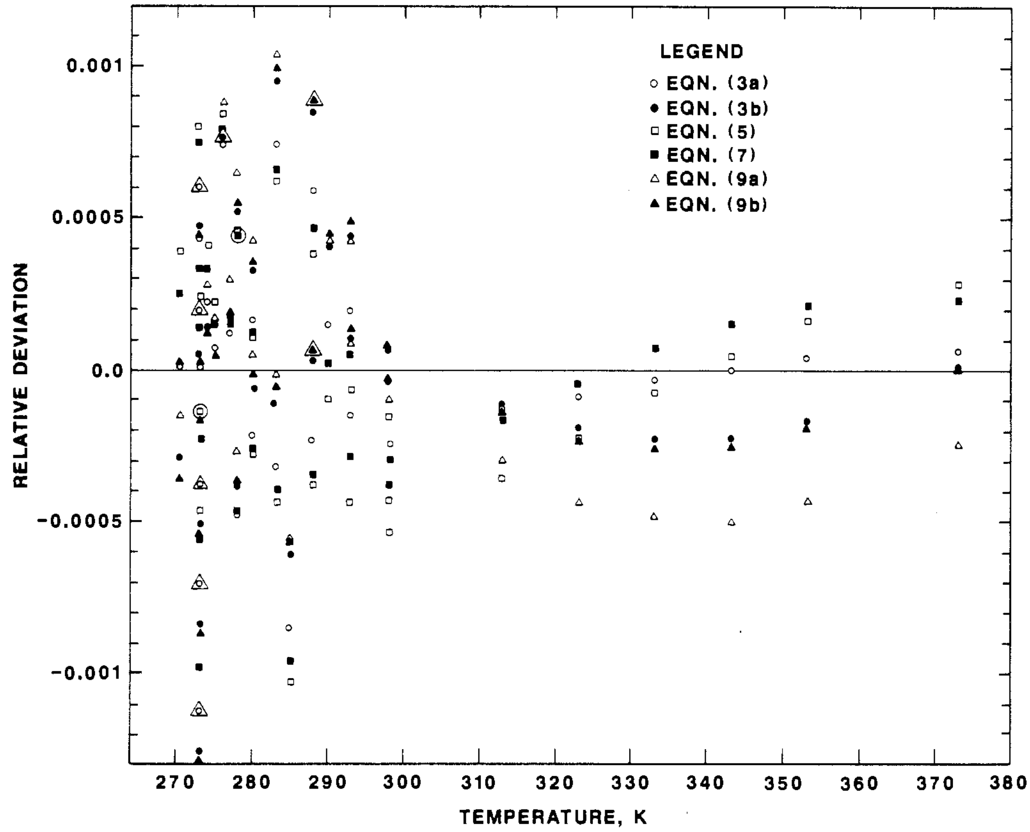

Figure 3. Plot of the relative deviations obtained on the basis of the 4-parameter eq 3a, 3b, 5, 7, 9a, and 9b for water below the normal boiling temperature.

cubic equation or for that matter from any other equation which can represent the vapor pressure data in the low-pressure region most accurately. If this criterion were not to be satisfied then either the vapor pressure equation or the vapor pressure is suspect. The tests conducted by us have indicated that the 4-parameter equations are, in general, defective in the low-pressure region. The disagreement may also be due to the vapor pressure data in the low-pressure region. For cases for which the triple point pressure is unavailable, it is better to estimate the triple point pressure as suggested by Ambrose and Davies (*14*) and use it in the regression in order to obtain a satisfactory value for α at T_t. The 5-parameter equations are most reliable at the triple point.

Results and Discussion

According to Scott and Osborn (*15*), the reliability of a vapor pressure equation depends upon its adequacy in the representation of the vapor pressure of such a complex substance as water. For this reason, we have selected water as the typical substance for testing the adequacy of the selected vapor pressure equations in this article. Using the vapor pressure data of water taken from the most reliable sources (*16–22*), we have found that all the equations, (3), (5), and (7), containing only 4 parameters are quite satisfactory. For the purpose of this paper, all the points are given equal weight except the critical point which is excluded. The critical point was taken from the NBS/NRS Steam Tables (*22*). The triple point pressure was taken from the work of Johnson, Guildner, and Jones (*21*) to be 0.61173 kPa at 273.16 K. The critical pressure was determined by us through iteration to be 22060 kPa. This value is slightly different from the value 22055 kPa recommended by the NBS/NRS Steam Tables (*22*). The 5-parameter eq 4, 6, 8, and 10 are possibly the best for the representation of the vapor pressure data for water. Although the Goodwin eq 9 is satisfactory for most substances, it is not adequate for water. Its 5-parameter analogue is, however, satisfactory for water. The results obtained on the basis of the eq 3–8 and 10a are compared in Table I. The constants A, B, C, and D and the exponents f, g, and h of the 4-parameter eq 3, 5, 7, and 9 are recorded in Table II. The constants A, B, C, D, and E and the exponents f, g, h, and i of the 5-parameter equations are recorded in Table III. The exponents f, g, h, and i of eq 8 are from Wagner and Polak (*23*). The ESDU (*3*) has chosen the values 1.5, 3.0, and 6.0 for f, g, and h of the 4-parameter Wagner equations. Recently, Wagner, Ewers, and Penterman (*24*) have suggested the values 1.5, 2.5, and 5.0, but the values 1.5, 2.25, and 4.25 found by us fit the vapor pressure data of water adequately. We have also recorded in Tables II and III the α values obtained on the basis of all these equations at T_t, T_b, and T_c. The value of β below the normal boiling point and the standard deviation, σ, is also recorded in Tables II and III. From a survey of the results presented in Table I, it can be seen that the most satisfactory of all the equations is the 5-parameter eq 4b. The eq 3b containing only 4 parameters is slightly less accurate than eq 4b. The Wagner equation (7) as well as the new equation (eq 5) do not fit the vapor pressure around the normal boiling point satisfactorily. Judging from the α value at the triple point, Wagner equation (7) and the new equation (5) are not satisfactory at the triple point. The best values for α_t and α_b may be obtained from the cubic equation. The constants of eq 1 and 2 are recorded in Table IV. They have been obtained by using the vapor pressure data of water in the range 270–373.15 K. The vapor pressure equations proposed by others for water (*15*, *25*, *26*, *27*) lack the simplicity of the equations considered in this article. Also the equation proposed by Scott and Osborn (*15*) is an analytic one and violates the criterion 1.

According to one of the referees of this article, the defect of any equation in the region below the normal boiling temperature is undetectable on the basis of the standard deviations calculated by using the absolute deviations. He recommended

Table I. Comparison of the Vapor Pressure Equations for Water

			(P(obsd) − P(calcd))/kPa									
ID.[a]	T/K	P/kPa[b]	(3a)	(3b)	(5)	(7)	(4a)	(4b)	(6)	(8)	(10a)	(3b)[c]
2	273.150	0.509	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	273.150	0.611	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001
2	273.150	0.611	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	273.160	0.611	0.000	−0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5	273.160	0.612	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
6	273.160	0.612	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	273.160	0.612	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	274.150	0.657	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	275.150	0.706	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	276.150	0.759	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
2	277.150	0.814	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	278.150	0.872	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	278.150	0.873	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	280.650	1.037	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	280.650	1.037	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	283.150	1.228	0.000	0.000	−0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	283.150	1.229	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
2	285.650	1.449	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001
1	288.150	1.705	0.000	0.000	−0.001	−0.001	0.000	0.000	0.000	0.000	0.000	0.000
2	288.150	1.707	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
2	290.650	2.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.000	−0.001
1	293.150	2.339	0.000	0.000	−0.001	−0.001	0.000	0.000	0.000	0.000	0.000	0.000
2	293.150	2.340	0.000	0.001	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001
1	298.150	3.169	0.000	0.000	−0.001	−0.001	0.000	0.000	0.000	0.000	0.000	0.000
3	298.150	3.169	−0.001	0.000	−0.002	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001
3	313.150	7.381	−0.001	−0.001	−0.003	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.002
3	323.150	12.345	−0.001	−0.003	−0.003	−0.001	−0.001	−0.001	−0.003	−0.003	−0.002	−0.004
3	333.150	19.933	−0.001	−0.005	−0.002	0.001	−0.002	−0.001	−0.004	−0.004	−0.001	−0.007
3	343.150	31.177	0.000	−0.007	0.001	0.005	−0.002	−0.002	−0.005	−0.006	−0.001	−0.010
3	353.150	47.375	0.002	−0.008	0.007	0.010	−0.001	−0.001	−0.005	−0.007	0.000	−0.011
3	373.150	101.325	0.007	0.000	0.028	0.024	0.001	0.000	0.000	−0.004	0.005	0.000
4	383.154	143.304	0.049	0.054	0.082	0.069	0.044	0.042	0.047	0.043	0.048	0.058
4	393.157	198.577	0.056	0.082	0.102	0.076	0.051	0.048	0.061	0.059	0.056	0.093
4	403.162	270.112	−0.002	0.056	0.056	0.014	−0.005	−0.008	0.016	0.016	−0.001	0.078
4	413.166	361.335	−0.028	0.074	0.039	−0.023	−0.027	−0.030	0.005	0.010	−0.027	0.109
4	432.170	475.913	−0.078	0.076	−0.008	−0.091	−0.072	−0.074	−0.027	−0.017	−0.078	0.130
4	433.175	618.062	−0.035	0.176	0.030	−0.073	−0.021	−0.021	0.033	0.050	−0.035	0.252
4	443.179	792.139	0.046	0.310	0.094	−0.024	0.069	0.071	0.125	0.149	0.043	0.411
4	453.184	1002.692	−0.117	0.186	−0.098	−0.220	−0.082	−0.078	−0.035	−0.005	−0.121	0.313
4	463.188	1255.285	−0.050	0.264	−0.075	−0.185	−0.004	0.002	0.020	0.053	−0.054	0.418
4	473.193	1555.055	−0.133	0.152	−0.215	−0.294	−0.078	−0.072	−0.094	−0.063	−0.135	0.330
4	483.197	1907.950	−0.151	0.055	−0.299	−0.322	−0.091	−0.087	−0.163	−0.140	−0.145	0.251
4	493.201	2319.978	−0.234	−0.163	−0.452	−0.394	−0.174	−0.174	−0.317	−0.308	−0.214	0.041
4	503.204	2797.756	−0.144	−0.264	−0.425	−0.267	−0.093	−0.100	−0.311	−0.326	−0.103	−0.067
4	513.208	3347.940	−0.074	−0.429	−0.399	−0.130	−0.042	−0.056	−0.330	−0.375	−0.006	−0.259
4	523.211	3977.675	0.145	−0.467	−0.194	0.186	0.148	0.127	−0.190	−0.269	0.244	−0.350
4	533.214	4694.245	0.307	−0.554	−0.004	0.465	0.270	0.247	−0.081	−0.193	0.433	−0.517
4	543.217	5505.322	0.257	−0.799	0.028	0.543	0.173	0.154	−0.138	−0.276	0.396	−0.876
4	548.218	5949.044	0.380	−0.739	0.213	0.726	0.270	0.258	0.002	−0.142	0.515	−0.886
4	553.219	6419.526	0.455	−0.696	0.362	0.854	0.319	0.316	0.111	−0.036	0.577	−0.923
4	563.221	7445.148	0.355	−0.747	−0.447	0.829	0.169	0.196	0.133	0.000	0.416	-1.156
4	573.223	8592.046	0.453	−0.425	0.756	0.931	0.227	0.294	0.420	0.331	0.395	-1.046
4	583.224	9869.683	0.234	−0.246	0.740	0.617	−0.013	0.097	0.437	0.427	−0.005	-1.099
4	593.225	11289.429	−0.117	−0.074	0.532	0.058	−0.353	−0.216	0.333	0.432	−0.577	-1.159
4	598.226	12056.459	−0.357	−0.038	0.323	−0.327	−0.574	−0.437	0.204	0.363	−0.928	-1.232
4	603.226	12864.222	−0.034	0.543	0.639	−0.168	−0.221	−0.100	0.618	0.838	−0.701	−0.747
4	613.227	14607.721	−0.074	0.862	0.456	−0.550	−0.167	−0.141	0.673	0.995	−0.818	−0.561
4	623.227	16536.747	−0.241	0.650	−0.022	−0.948	−0.208	−0.370	0.446	0.798	−0.764	−0.765
4	628.227	17577.152	−0.667	0.006	−0.633	-1.374	−0.568	−0.843	−0.067	0.254	−0.914	-1.320
4	633.227	18673.894	−0.038	0.324	−0.158	−0.616	0.120	−0.238	0.458	0.706	0.098	−0.833
4	635.227	19128.843	0.033	0.271	−0.127	−0.449	0.209	−0.158	0.489	0.696	0.337	−0.791
4	637.227	19594.026	0.442	0.580	0.265	0.084	0.631	0.283	0.862	1.022	0.905	−0.367
4	639.227	20068.835	0.161	0.253	−0.003	−0.045	0.357	0.068	0.555	0.662	0.752	−0.558
4	641.227	20554.486	−0.114	0.032	−0.224	−0.143	0.080	−0.089	0.266	0.320	0.533	−0.617
4	643.227	21052.397	0.341	0.721	0.337	0.505	0.521	0.568	0.723	0.727	0.895	0.263
4	644.227	21305.608	0.192	0.802	0.267	0.452	0.259	0.569	0.582	0.567	0.598	0.453
4	645.227	21561.453	−0.663	0.296	−0.490	−0.315	−0.514	−0.088	−0.259	−0.287	−0.519	0.067
4	646.227	21821.656	−0.835	0.664	−0.540	−0.419	−0.712	0.009	−0.415	−0.442	-1.150	0.566
7	647.126	22060.000	−0.429	1.905	0.000	0.000	−0.338	0.777	0.000	0.000	-1.564	1.940

[a] ID. 1, Besley and Bottomley (*16*); 2, Douslin (*17*); 3, Stimson (*18*); 4, Osborne, Stimson, Fiock and Ginnings (*19*); 5, Prytz (*20*); 6, Johnson, Guildner, and Jones (*21*); 7, NBS/NRS Steam Tables for critical temperature (*22*). [b] For the sake of this table the observed pressures were shown rounded to three places after the decimal for the first 30 observations. [c] This refers to the deviations obtained on the basis of eq 3b with the points above the normal boiling point and below the critical point not participating in the regression. In place of all these points, an additional point with T = 580.000 K and pressure equal to 9442.527 kPa calculated from eq 21 was used.

Table II. Constants of the 4-Parameter Equations for Water

	equation					
const	3a	3b	5	7	9a	9b
A	-17.678684	-11.868212	-7.862038	-7.869123	8.809532	4.464503
B	0.828603	1.999582	-0.203124	2.003247	2.753596	1.083562
C	-3.314618	-4.451665	1.917098	-1.813041	-1.069863	-0.164437
D	-4.312329	-8.025567	-5.136087	-2.405901	2.649319	1.171406
f	1.50	1.55	1.50	1.50	1.32	1.22
g	3.29	3.95	6.00	2.25		
h				4.25		
σ	0.225	0.338	0.266	0.372	1.208	1.624
σ_r[a]	0.00030	0.00034	0.00034	0.00032	0.00036	0.00037
σ_r[b]	0.00045	0.00050	0.00049	0.00046	0.00053	0.00051
α_t	19.846	19.829	19.859	19.854	19.829	19.825
α_b	13.316	13.312	13.315	13.316	13.312	13.312
α_c	7.867	7.820	7.862	7.969	8.113	8.360
β	0.018	0.018	0.018	0.018	0.018	0.018

[a] Standard deviation based on relative deviations from the triple point to the critical point. [b] Standard deviation based on relative deviations below the normal boiling temperature.

Table III. Constants of the 5-Parameter Equations for Water

	equation					
const	4a	4b	6	8	10a	10b
A	-17.650073	-11.880951	-7.867226	-7.864939	8.385026	4.585420
B	0.921524	1.817797	-0.235995	1.902006	3.652543	1.097441
C	0.075143	-0.358975	0.031495	-2.379234	-1.333139	-0.279857
D	-3.332385	-4.129636	1.947708	-9.493641	-0.211373	-0.019689
E	-4.501325	-6.009070	-7.650007	9.356228	3.081890	1.051922
f	1.50	1.50	1.50	1.50	1.45	1.37
g	3.32	3.50	6.50	2.50		
h				6.50		
i				7.50		
σ	0.222	0.196	0.272	0.340	0.393	0.485
σ_r[a]	0.00030	0.00030	0.00031	0.00031	0.00030	0.00030
σ_r[b]	0.00046	0.00046	0.00047	0.00047	0.00046	0.00046
α_t	19.843	19.844	19.840	19.839	19.843	19.843
α_b	13.315	13.315	13.314	13.314	13.315	13.315
α_c	7.867	7.820	7.862	7.869	7.922	7.984
β	0.018	0.018	0.018	0.018	0.018	0.018

[a] Standard deviation based on relative deviations from the triple point to the critical point. [b] Standard deviation based on relative deviations below the normal boiling temperature.

Table IV. Constants of the Eq 1 and 2 for Water

	equation			
const	1a	1b	2a	3a
A	-19.896537	-13.363884	-19.847177	-13.314231
B	-3.066515	-1.643660	-2.516920	-1.969654
C	273.168660	373.119095	273.160517	373.149768
D			1.441277	0.565395
σ	0.023	0.023	0.001	0.001
σ_r	0.00076	0.00076	0.00038	0.00038
α_t	19.897	19.897	19.847	19.847
α_b	13.364	13.364	13.314	13.314
β	0.018	0.018	0.018	0.018

the calculation of the standard deviations based on the relative deviations given by $(P_{exptl} - P_{calcd})/P_{exptl}$. We have, therefore, calculated such standard deviations based on the relative deviations and recorded them in the Tables II–XIII, using the symbol σ_r. These standard deviations do not, however, affect our earlier conclusions but they help highlight the defects of the vapor pressure equations below the normal boiling temperature while they mask the large absolute deviations at higher temperatures. In any case we agree with the referee that the standard deviations based on relative deviations are more meaningful than the standard deviations based on absolute deviations. The relative deviations obtained on the basis of the 4-parameter equations are shown graphically in Figures 3 and 4.

The above equations have been tested for a wide variety of substances and the same conclusions are drawn as with water.

Table V. Constants of the Eq 3a for Various Substances

const	methane	benzene	nitrogen	argon	oxygen
A	-10.182850	-13.349312	-10.208219	-8.572984	-14.937528
B	2.304823	0.781938	2.015495	2.290292	1.812160
C	-2.201223	-3.122045	-2.392160	-2.352673	-2.087957
D	-5.375955	-6.637640	-5.540867	-5.856691	-4.522111
f	1.50	1.50	1.50	1.50	1.50
g	3.35	3.35	3.35	3.35	3.35
T_c	190.555	562.161	126.200	150.690	154.581
T_t	90.680	353.242	63.148	83.804	54.361
σ	0.284	0.290	0.189	0.371	0.164
σ_r	0.00020	0.00022	0.00028	0.00029	0.00011
α_t	11.636	15.137	11.595	9.654	17.086
α_b	9.196	10.873	9.121	9.220	9.438
α_c	5.995	7.009	6.116	5.898	6.079
β	0.089	0.022	0.127	0.110	0.110

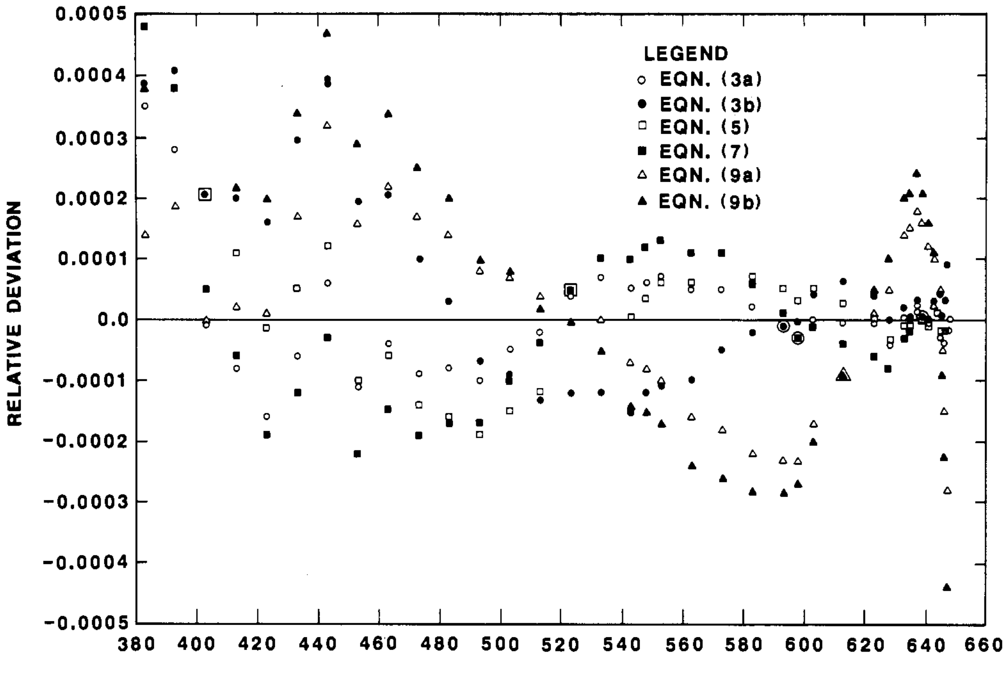

Figure 4. Plot of the relative deviations obtained on the basis of the 4-parameter eq 3a, 3b, 5, 7, 9a, and 9b for water above the normal boiling temperature.

Table VI. Constants of the Eq 3b for Various Substances

const	methane	benzene	nitrogen	argon	oxygen
A	−8.170039	−9.732746	−8.196031	−8.210497	−8.432226
B	2.518205	1.891007	2.272766	2.356966	2.274787
C	−3.056869	−4.334186	−3.155023	−2.850425	−2.890493
D	−7.893296	−10.219543	−8.357627	−8.052901	−8.372496
f	1.55	1.55	1.55	1.55	1.55
g	3.95	3.95	3.95	3.95	3.95
T_c	190.555	562.161	126.200	150.690	154.581
T_b	111.632	353.242	77.348	87.290	90.188
σ	0.264	0.301	0.250	0.423	0.253
σ_r	0.00017	0.00022	0.00022	0.00026	0.00020
α_t	11.640	15.144	11.621	9.662	16.925
α_b	9.192	10.872	9.117	9.219	9.439
α_c	6.008	6.999	6.102	5.905	6.025
β	0.089	0.022	0.126	0.110	0.111

The results on the basis of eq 3 and 4 for a few typical compounds are shown in Tables V–VIII. The compounds include nitrogen, argon, oxygen, methane, and benzene. The vapor pressure data for these compounds are from reliable sources (*1*, *15*, *24*, *28–34*). Judging from the standard deviations recorded in Tables V–VIII, we find these equations to be extremely satisfactory for these compounds. We have also found it possible to fix the values of the exponents f and g for eq 3a, 3b, 4a, and 4b for practically all the substances tested in this article. Since the triple points and the low-pressure data are usually not available, we select eq 3b and 4b.

Predictive Procedures

1. Zeroth-Order Approximation. We have already shown (*4*) how the quadratic equation can be used for the prediction of vapor pressure from the triple point to the normal boiling point. A simple equation such as eq 21 can now be used to obtain the vapor pressure from the normal boiling point to the critical point as shown below. Equation 21 is referred to as the Clapeyron equation and is also discussed by Reid, Prausnitz, and Sherwood (*35*).

$$\ln P = a - b/T \tag{21}$$

where $b = \Delta H/\Delta ZR$. On the basis of eq 13 and 14 α is given by the following expression:

$$\alpha = \Delta H/\Delta ZRT \tag{22}$$

Equation 21 may, therefore, be written as follows:

$$\ln P = a - \alpha \tag{23}$$

It follows from eq 23 that when the pressure is expressed as P/P_t, or P/P_b, or P/P_c, the following conditions are obeyed

Table VII. Constants of the Eq 4a for Various Substances

const	methane	benzene	nitrogen	argon	oxygen
A	−10.277025	−13.391401	−10.198031	−8.883885	−15.104085
B	1.875931	0.571577	2.058812	0.873589	1.275208
C	−0.477635	−0.252950	0.045962	1.614501	−0.432193
D	−2.265333	−3.165810	−2.391777	−2.233650	−2.096072
E	−4.453736	−6.111294	−5.634290	−1.922376	−4.085843
f	1.50	1.50	1.50	1.50	1.50
g	3.35	3.35	3.35	3.35	3.35
T_c	190.555	562.161	126.200	150.651	154.581
T_t	90.680	278.68	63.148	83.804	54.361
σ	0.097	0.255	0.192	0.375	0.203
σ_r	0.00013	0.00021	0.00028	0.00024	0.00009
α_t	11.648	15.142	11.594	9.671	17.155
α_b	9.193	10.873	9.121	9.220	9.433
α_c	6.014	7.020	6.115	5.903	6.085
β	0.089	0.022	0.127	0.109	0.109

Table VIII. Constants of the Eq 4 for Various Substances

const	methane	benzene	nitrogen	argon	oxygen
A	-8.250120	-9.801688	-8.263900	-8.4456922	-8.479508
B	2.139985	1.499906	1.914219	1.229753	1.929615
C	-0.442781	-0.549661	-0.471124	-1.348862	-0.558801
D	-2.641107	-3.807586	-2.744418	-2.383031	-2.695696
E	-5.231639	-6.674194	-5.374371	-2.536030	-4.847068
f	1.50	1.50	1.50	1.50	1.50
g	3.50	3.50	3.50	3.50	3.50
T_c	190.555	562.161	126.200	150.690	154.810
T_b	111.632	353.242	77.348	87.290	90.188
σ	0.094	0.268	0.187	0.389	0.124
σ_r	0.00013	0.00021	0.00021	0.00024	0.00008
α_t	11.647	15.152	11.624	9.668	17.241
α_b	9.193	10.873	9.119	9.219	9.430
α_c	6.005	7.003	6.103	5.907	6.055
β	0.089	0.022	0.126	0.109	0.109

respectively: (1) $a = \alpha_t$ at T_t; (2) $a = \alpha_b$ at T_b; (3) $a = \alpha_c$ at T_c.

If we constrain eq 21 to go through the normal boiling point and the critical point, and express the pressures in atmospheres, the constants a and b of the eq 21 will be given by the following expressions:

$$a = (\ln P_c)T_c/(T_c - T_b)$$

$$b = aT_b$$

Equation 21 may now be simplified as follows

$$\ln P = -aX_b \tag{24}$$

$$\ln (P/P_c) = -aYT_b/T_c \tag{25}$$

which may be written alternatively as follows:

$$\ln P = -\alpha_b X_b \tag{26}$$

$$\ln (P/P_c) = -\alpha_c Y \tag{27}$$

Figure 1 illustrates the type of deviations one obtains by the use of eq 26 for water, argon, and ethanol. Around $T_r = 0.90$ the deviations change their sign for water and several classes of substances such as hydrocarbons, esters, ketones, etc. These compounds have an inversion point, T_i. Approximately around the same T_r compounds such as alcohols, amines, etc., have a maximum positive deviation. In such cases this point is referred to as the inflection point. Compounds such as argon and halogenated hydrocarbons, on the other hand, have maximum negative deviation close to this T_r. These deviations, on a relative basis, are, in general, so small for most of these compounds that one may use eq 26 itself for the calculation of the vapor pressure between the normal boiling temperature and the critical temperature. We shall refer to this procedure as the zeroth-order approximation. The α values which we obtain on the basis of the eq 26 differ slightly from those which we obtain from the eq 1–10. We may resort to this procedure when no vapor pressure data are available above the normal boiling temperature.

2. First-Order Approximation. We shall now describe the first-order approximation to the vapor pressure. It consists in using all the available vapor pressure data up to the normal boiling point and then just two additional data points above the normal boiling temperature. These two additional points are (1) the T_c and P_c, and (2) T_i and P_i. For testing the above hypotheses and also for testing which of the ten equations considered in this paper would be most appropriate for predictive purposes, we use water as our example. The T_i for water is close to 580 K ($T_r = 0.90$) as can be seen from the Figure 1. The value of $a = 12.715$ and of $b = -4744.597$ for water. The pressure at T_i calculated from eq 13 is 9442.527 kPa. The constants as well as the standard deviations, σ's, and nonweighted standard deviations of all the equations are shown in Tables IX and X. The nonweighted standard deviation is the standard deviation obtained on the basis of deviations of all the points used and unused in the regressions. These equations fit the low-pressure data with sufficient accuracy and then predict the vapor pressure above the normal boiling point quite satisfactorily. The fit is excellent with the eq 3b. The results obtained on the basis of eq 3b based on the predictive procedure are also shown in Table I. They compare favorably with the deviations obtained on the basis of the regular procedures. The results obtained on the basis of the 5-parameter equations are not satisfactory, presumably due to overfitting as pointed by one of the referees. The question now is as to how we can obtain the four values namely, T_c, P_c, T_i, and P_i for substances for which they are not known. Fortunately, several empirical procedures (*36–44*) are now available for the prediction of both T_c and P_c. Equations 11, 12, and 26 may also be used for the estimation of the critical pressure. Several deviation plots for the isomeric hexanes were drawn by Kay (*45*). McMicking and Kay (*46*) listed the calculated deviations for heptanes and octanes. From these we see that T_i occurs normally around a T_r of 0.88. The T_i is slightly above the temperature at which $\Delta H/\Delta Z$ goes to a minimum. According to McGarry (*47*), the temperature at which the minimum in $\Delta H/\Delta Z$ occurs is a function of the normal boiling point: the higher the normal boiling point, the higher this temperature would be. Similarly, T_i also may be considered to be a function of the normal boiling point. For the purpose of the first-order approximation, we shall assume that T_i occurs around $T_r = 0.90$. We shall also assume that the exponents f and g are optimized at 1.55 and 3.95 for eq 3b. The only unknown now is P_i. In order to calculate P_i from eq 26, we shall introduce a factor called the flex factor

Table IX. Constants of the Predictive 4-Parameter Equations for Water

	equation					
const	3a	3b	5	7	9a	9b
A	-17.625665	-11.876514	-7.900076	-7.886539	8.798717	4.477823
B	0.919542	1.979964	-0.248706	2.076640	2.773195	1.066982
C	-3.441608	-4.415632	2.068462	-1.913650	-1.078937	-0.161704
D	-4.196342	-8.026502	-3.228613	-2.332365	2.653968	1.157570
f	1.50	1.55	1.50	1.50	1.32	1.22
g	3.29	3.95	6.00	2.25		
h				4.25		
$\sigma_r{}^a$	0.00068	0.00049	0.00048	0.00044	0.00067	0.00050
$\sigma_r{}^b$	0.00065	0.00021	0.00096	0.00053	0.00033	0.00038
α_t	19.828	19.833	19.860	19.849	19.817	19.831
α_b	13.322	13.311	13.322	13.320	13.312	13.311
α_c	7.888	7.815	7.900	7.887	8.113	8.344
β	0.018	0.018	0.018	0.018	0.018	0.018

[a] Standard deviation based on relative deviations below the normal boiling temperature. [b] Standard deviation based on relative deviations for all observations above the normal boiling temperature.

Table X. Constants of the Predictive 5-Parameter Equations for Water

const	equation 4a	4b	6	8	10a	10b
A	−17.550273	−11.867620	−7.897848	−7.906216	8.525269	4.550555
B	1.356613	1.817299	−0.263622	2.056907	3.499316	1.148475
C	0.530766	−0.435004	0.021672	−2.635651	−1.413453	−0.291466
D	−3.214357	−4.246483	2.065603	−6.781610	−0.118149	−0.024374
E	−5.303798	−5.679914	−5.281576	5.938759	2.928770	1.087985
f	1.50	1.50	1.50	1.50	1.45	1.37
g	3.32	3.50	6.50	2.50		
h				6.50		
i				7.50		
σ_r[a]	0.00068	0.00045	0.00045	0.00045	0.00068	0.00045
σ_r[b]	0.00061	0.00036	0.00081	0.00097	0.00036	0.00036
α_t	19.820	19.848	19.847	19.847	19.819	19.848
α_b	13.312	13.318	13.320	13.320	13.313	13.318
α_c	7.845	7.865	7.898	7.906	7.896	8.002
β	0.018	0.018	0.018	0.018	0.018	0.018

[a] Standard deviation based on relative deviations below the normal boiling temperature. [b] Standard deviation based on relative deviations for all observations above the normal boiling temperature.

Table XI. Constants of the Eq 26 and 27 and the Flex Factors for Various Substances

compound	α_b	α_c	T_b	T_c	χ	ref
water	12.715	7.332	373.150	647.126	1.000	(*16–22*)
methane	9.212	5.397	111.632	190.555	0.974	(*28*)
ethane	9.791	5.918	184.554	305.33	0.984	(*59, 62, 63*)
propane	9.954	6.219	231.054	369.85	0.989	(*59, 64, 65, 73*)
butane	10.094	6.473	272.66	425.14	0.992	(*59–61*)
ethylene	9.768	5.864	169.415	282.2	0.986	(*55, 56*)
acetylene	10.558	6.454	188.472	308.32	0.998	(*68, 69*)
cyclohexane	10.239	6.545	353.881	553.64	0.996	(*34, 58, 66*)
benzene	10.436	6.557	353.242	562.161	0.997	(*30–34*)
methanol	12.837	8.457	337.696	512.640	1.014	(*52, 53*)
ethanol	12.986	8.880	351.440	513.920	1.044	(*52, 53*)
1-propanol	12.679	8.747	370.300	536.775	1.067	(*52, 54*)
2-propanol	12.800	8.950	355.390	508.296	1.070	(*52, 54*)
1-butanol	12.342	8.568	390.882	563.051	1.070	(*52, 54*)
2-butanol	12.212	8.490	372.660	536.015	1.070	(*52, 54*)
2-methyl-1-propanol	12.309	8.562	381.04	547.778	1.075	(*52, 54*)
2-methyl-2-propanol	12.322	8.653	355.49	506.205	1.075	(*52, 54*)
1-pentanol	12.138	8.485	411.15	588.15	1.050	(*52, 53*)
1-octanol	11.836	8.495	468.35	652.5	1.009	(*52, 53, 76*)
chlorine	10.242	5.876	239.184	416.90	0.990	(*74*)
ethyl fluoride	10.477	6.573	235.45	375.31	1.000	(*75*)
acetone	10.899	7.062	329.217	508.10	0.998	(*70*)
acetic acid	11.888	7.843	391.035	592.71	0.998	(*72*)
ethyl acetate	11.025	7.380	350.26	523.30	1.005	(*71*)
diethyl ether	10.501	6.920	307.581	466.74	1.002	(*51*)
1-propylamine	10.853	6.996	320.369	497.0	1.015	(*3, 77*)
2-propylamine	10.755	6.951	304.907	471.8	1.015	(*3, 77*)
nitrogen	9.076	5.563	77.348	126.20	0.979	(*1*)
oxygen	9.380	5.473	90.188	154.581	0.977	(*24, 29*)
argon	9.202	5.330	87.290	150.69	0.976	(*1*)
carbon monoxide	9.184	5.644	81.638	132.85	0.983	(*49, 50*)
carbonyl sulfide	10.054	5.916	222.9	378.8	0.987	(*57, 67*)

and denote it by the symbol χ. The flex factor, χ for a substance is defined as

$$\chi = P_{l(\mathrm{exptl})}/P_{l(\mathrm{calcd})} \quad \text{at } T_r = 0.90 \tag{28}$$

where $P_{l(\mathrm{calcd})}$ is obtained from eq 26. The flex factor may be considered as a measure of the complexity of a molecule at $T_r = 0.90$. It may also be related to the van der Waals constant a. We assume that the pressure is normal when it is given by the eq 26. This is the case when $\chi = 1$. When $\chi < 1$, we assume that the pressure is lessened because of attraction by the mass of molecules in the bulk gas. When $\chi > 1$ the pressure is enhanced on account of repulsion. The flex factor may alternatively be looked upon as the power of a molecule to attract other molecules towards itself. Thus it may find great use in the study of mixtures. The flex factor may be related to Pitzer's acentric factor (*48*) as well as to Stiel's polarity factor (*35*) in concept, but they represent different functions. These factors, in general, represent different functions at different T_r. The flex factors of some molecules are recorded in Table XI together with the constants of eq 26 and 27. Given the flex factor, one can calculate P_l and use the first-order approximation to the vapor pressure. Fortunately, for a large number of substances, the flex factor is equal to unity and we encounter relatively little problem in the prediction of vapor pressure. For substances for which the flex factor is not equal to unity, it is necessary to estimate it. For example, if we know the flex factor for 1-pentanol, we can assume the same factor to be valid for all of its isomers. Thus we can, in general, use the first-order approximation to the vapor pressure. Test of this procedure for a large number of substances has revealed that the procedure is, indeed, quite satisfactory. Similar results are obtained with eq 3a with the exponents f and g having the values 1.5 and 3.35. We have recorded the results obtained with eq 3b in Table XII for a number of substances. The vapor pressure data for these compounds are taken from reliable sources (*49–77*). We have used graphical interpola-

Table XII. First-Order Approximation: Constants of the Eq 3b for Various Substances

compound	A	B	C	D	σ_r[a]	σ_r[b]
water	−11.908 768	1.906 813	−4.317 389	−7.886 524	0.000 52	0.000 58
methane	−8.196 404	2.452 845	−2.960 683	−7.816 273	0.000 22	0.000 24
ethane	−9.462 159	0.798 532	−1.411 911	−5.957 056	0.003 75	0.004 84
propane	−8.952 340	2.655 006	−5.505 578	−6.363 559	0.006 55	0.005 81
butane	−9.007 002	3.049 617	−5.873 902	−9.651 789	0.002 70	0.003 29
ethylene	−8.994 073	1.935 515	−3.057 512	−8.477 172	0.000 76	0.000 47
acetylene	−10.045 373	1.319 277	−2.905 940	−9.799 399	0.000 40	0.002 37
cyclohexane	−9.527 448	1.971 018	−4.453 953	−10.164 153	0.000 64	0.000 59
benzene	−9.717 584	1.932 356	−4.395 194	−10.296 149	0.000 15	0.000 30
methanol	−12.727 971	0.320 894	−2.658 842	−3.394 946	0.000 30	0.002 00
ethanol	−13.271 159	−0.902 147	−3.951 898	5.190 496	0.000 13	0.001 31
1-propanol	−13.125 612	−1.439 823	−5.975 239	8.733 184	0.000 09	0.002 26
2-propanol	−13.250 821	−1.498 131	−6.672 664	10.615 046	0.000 09	0.002 69
1-butanol	−12.655 908	−1.025 719	−7.705 747	3.495 925	0.000 05	0.004 20
2-butanol	−12.305 436	−0.308 134	−9.709 805	0.323 374	0.000 08	0.011 48
2-methyl-1-propanol	−12.699 812	−1.282 989	−7.798 184	4.569 191	0.000 19	0.003 05
2-methyl-2-propanol	−12.503 713	−0.610 480	−10.007 340	4.309 713	0.000 07	0.002 27
1-pentanol	−11.651 089	1.616 401	−12.177 628	−5.842 219	0.000 27	0.001 42
1-octanol	−10.042 394	−6.370 723	−18.616 030	−27.682 396	0.002 86	0.002 01
chlorine	−9.477 864	1.792 787	−3.038 638	−7.384 808	0.000 70	0.004 07
ethyl fluoride	−10.073 233	1.085 470	−2.616 926	−5.011 352	0.003 59	0.006 33
acetone	−10.302 747	1.692 518	−4.028 711	−9.096 402	0.000 20	0.002 09
acetic acid	−10.982 406	2.660 199	−4.182 332	−14.367 847	0.000 52	0.000 37
ethyl acetate	−10.443 097	1.761 144	−5.286 084	−10.159 110	0.000 21	0.001 76
diethyl ether	−9.942 502	1.636 966	−4.477 357	−8.845 618	0.000 35	0.002 35
1-propylamine	−10.482 203	1.042 553	−4.467 469	−10.932 741	0.000 05	0.001 23
2-propylamine	−10.243 682	1.449 188	−5.396 020	−9.480 064	0.001 31	0.002 49
nitrogen	−8.166 938	2.347 970	−3.279 657	−8.405 931	0.000 45	0.000 34
oxygen	−8.405 606	2.340 113	−2.985 541	−8.470 138	0.000 18	0.000 26
argon	−8.029 280	2.787 231	−3.924 632	−5.492 141	0.000 24	0.003 92
carbon monoxide	−8.332 804	2.208 147	−3.399 466	−8.377 530	0.001 13	0.000 57
carbonyl sulfide	−9.122 383	2.260 928	−3.959 088	−7.995 762	0.002 19	0.005 60

[a] Relative standard deviation for weighted observations below the normal boiling temperatures. [b] Relative standard deviation for all observations above the normal boiling temperature.

Table XIII. Mathematical Expressions for the α-Function Based on Eq 1–10[a]

eq	α
(1)	$-(T_x/T)[A + 2BX]$
(2)	$-(T_x/T)[A + 2BX + 3CX^2]$
(3)	$-(T_x/T)[A + 2BX + CZ^f + DZ^g] - (X/T_c)[fCZ^{f'} + gDZ^{g'}]$
(4)	$-(T_x/T)[A + 2BX + 3CX^2 + DZ^f + EZ^g] - (X/T_c)[fDZ^{f'} + gEZ^{g'}]$
(5)	$-W[A + 2BY] - (1/T_c)[fCZ^{f'} + gDZ^{g'}]$
(6)	$-W[A + 2BY + 3CY^2] - (1/T_c)[fDZ^{f'} + gEZ^{g'}]$
(7)	$-W[A + BZ^f + CZ^g + DZ^h] - [fBZ^{f'} + gCZ^{g'} + hDZ^{h'}]$
(8)	$-W[A + BZ^f + CZ^g + DZ^h + EZ^i] - [fBZ^{f'} + gCZ^{g'} + hDZ^{h'} + iEZ^{i'}]$
(9)	$-(T_x/TG)[A + 2BX + 3CX^2 + D(Y/H)^f] - (T_cX/TGH)[fD(Y/H)^{f'}]$
(10)	$-(T_x/TG)[A + 2BX + 3CX^2 + 4DX^3 + E(Y/H)^f] - (T_cX/TGH)[fE(Y/H)^{f'}]$

[a] In the above expressions we have $f' = f - 1$; $g' = g - 1$; $h' = h - 1$; $i' = i - 1$. From α one can derive the following: $dP/dT = \alpha P/T$; $\Delta H/\Delta Z = (RT^2/P)(dP/dT) = RT\alpha$.

tions to obtain the flex factors of some of the above molecules.

3. Second-Order Approximation. A third procedure, which may be referred to as the second-order approximation to the vapor pressure, consists in using one actual experimental data point closest to T_l. The results obtained by using this procedure are extremely satisfactory for a number of compounds and are essentially similar to those already shown in Table XII. The advantage in this procedure is that it eliminates the need to determine vapor pressures in the entire range from the normal boiling point to the critical point.

4. The Group-Additivity Procedures. Other predictive procedures involve prediction of the constants of the vapor pressure equations. Several group additivity procedures have been described by us previously (*4*) for the estimation of the constants of the quadratic equation with respect to alkanes. Similar group additivity procedures may also be used for the estimation of the constants of some of the vapor pressure equations considered in this paper. For example, for the calculation of the value α_c of the alkanes we have the following group additivity equation

$$\alpha_c = an^{2/3} + a_1n_1 + a_2n_2 + a_3n_3 + a_4n_4 \qquad (29)$$

where n is the number of carbon atoms, n_1 is the number of primary carbon atoms, n_2 is the number of secondary carbon atoms, n_3 is the number of tertiary carbon atoms, and n_4 is the number of quaternary carbon atoms in the alkane molecule. The constants have the following values: $a = 0.22278$; $a_1 = 3.04664$; $a_2 = 0.15871$; $a_3 = -2.85149$; $a_4 = -5.97162$. These constants are obtained on the basis of the Wagner constant A reported by ESDU (*3*) for 80 alkanes in the range C_1–C_{18}. Such group additivity procedures will be considered elsewhere after we apply the vapor pressure equations to various classes of compounds.

Conclusion

In conclusion, we wish to remark, that it is no longer desirable to make extensive compilations of the Antoine or other type of constants based on low-pressure data. The predictive procedures shown in this paper produce a good fit for the low-pressure data and also provide vapor pressures above the normal boiling point up to the critical point. We find the first-order approximation using the flex factors to be quite simple to use and is very accurate in the prediction of vapor pressure above the normal boiling temperature. We also wish to make the general observation that none of the 4-parameter equations may be accurate at all the three points, namely, T_t, T_b, and T_c. For a better representation of the vapor pressure data from the triple point to the critical point one should resort to the 5-parameter equations such as eq 4a or eq 4b. This may be necessary only when accurate vapor pressures are available.

Goodwin (*49*, *50*) has also emphasized the cubic behavior of the residuals of eq 21.

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