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NOMENCLATURE

K = vapor-liquid equilibrium ratio, y/x
x = mole fraction of a component in liquid phase
y = mole fraction of a component in vapor phase

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Extended Benedict-Webb-Rubin Equation of State

Application to Eight Fluorine Compounds

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The Benedict-Webb-Rubin equation of state (BWR) is extended by the introduction of three additional coefficients. The extended equation predicts the P-V-T behavior of pure fluids in a wide temperature and density range. It fits the critical point exactly and has the first two derivatives of pressure with respect to volume vanish at this point. The critical isometric and the vapor pressure curve have a common tangent at the critical point. Furthermore, the extended equation predicts the residual (excess) caloric properties more precisely than the original one. A program in FORTRAN IV has been developed to determine the coefficients for the equation. It allows the variation of the critical constants within an arbitrary given range to get closer results. The coefficients of the equation for CCl_2F_2, $CClF_3$, CF_4, CHF_3, $C_2Cl_2F_4$, C_2ClF_5, SF_6, and C_4F_8 are determined. The deviation between measured and calculated values of pressure and density is generally within the error limits of the experiments.

THE BENEDICT-WEBB-RUBIN equation of state (BWR equation) was originally developed in 1940 to correlate and predict the thermodynamic properties of light hydrocarbons and their mixtures (*3*). Since this time, many efforts have been extended towards investigation of the applicability of the BWR equation to other compounds. Successful results have been achieved by "normal" as well as polar [e.g., sulfur dioxide (*19*)] and quantum [e.g., helium-4 (*23*)] compounds. Cooper and Goldfrank (*10*) compiled the constants of the BWR equation of state for 38 compounds. As the BWR technique gained widespread use, more and more shortcomings were reported. Most of the difficulties have been observed in predicting pressure-volume-temperature (P-V-T) characteristics of fluids within the critical region and at a density more than 1.5 times the critical. Moreover, the representation of the caloric properties like enthalpy and heat capacity in many cases is not satisfactory (*32*).

To eliminate some of these difficulties, attempts (*4*) have been made to extend the BWR equation through additional coefficients. However, the literature does not give clear procedure for evaluating the new coefficients. This presentation discusses this aspect of the problem.

The present work involved the following steps. Extend the BWR equation by three additional coefficients. Establish the coefficients for eight fluorine compounds regarding the conditions at the critical point and by regression analysis of the available P-V-T data. Test the accuracy of pressure prediction. Test the effect of variation of the critical data on the prediction of the P-V-T data. Derive expressions for the thermodynamic properties: enthalpy, entropy, fugacity, isometric heat capacity, isobaric heat capacity, Joule-Thomson coefficients, and sound velocity. Demonstrate the superiority of the extended BWR equation to the original equation by predicting the thermodynamic properties of tetrafluoromethane.

EXTENSION OF THE BWR EQUATION OF STATE

The original BWR equation (*3*) expresses the pressure, P, as a function of the molal density, d, and the absolute temperature, T. It is commonly written as:

$$P = RTd + \left(B_0RT - A_0 - \frac{C_0}{T^2}\right)d^2 + (bRT - a)d^3 + \frac{c}{T^2}(1 + \gamma d^2)e^{-\gamma d^2} d^3 + a\alpha d^6 \qquad (1)$$

R is the universal gas constant. A_0, B_0, C_0, a, b, c, α, and γ are specific constants evaluated by a least-squares technique outlined by Brough, Schlinger, and Sage (*6*), minimizing the sum of squares of deviations in the calculated pressure values. Details of the method are outlined elsewhere (*6*). Although the least-squares technique was used, the minimization of maximum and average-absolute deviations was taken into consideration.

However, as has been discussed by Lin and Naphtali (*22*), it is not possible to determine a unique set of constants for this equation that will correlate accurately liquid-vapor phase behavior, as well as a gas phase *P-V-T* behavior, over a wide range of temperature and pressure. Several solutions to this problem have been proposed in these references: One or more of the coefficients are varied for use in the different regions of the *P-V-T* surface (*42*); various modifications in the functional representation are utilized; individual sets of constants are developed, one based on gas-phase *P-V-T* data and another on data in the liquid region (*38*).

According to Equation 1, the isometrics are represented analytically as

$$P = A(d) + B(d)\cdot T + \frac{C(d)}{T^2} \tag{2}$$

Equation 2 enables a rather fair representation of the isometrics in a wide temperature and pressure range. However, the derived thermodynamic properties, such as enthalpy and heat capacity, are considerably less accurate. To calculate the enthalpy and heat capacity, one must build the derivatives $(\partial P/\partial T)_d$ and $(\partial^2 P/\partial T^2)_d$, respectively. These differentiations cause additional errors. Bloomer and Rao (*4*) suggested the following extension.

$$P = A(d) + B(d)\cdot T + \frac{C(d)}{T^2} + \frac{D(d)}{T^4} \tag{3}$$

whereas Rabinovich (*37*) made use of an extended form of the Martin-Hou expression (*26*) to correlate the compressibility data for hydrogen

$$P = A(d) + B(d)\cdot T + C(d)\cdot e^{-k_1 T} + D(d)\cdot e^{-k_2 T} \tag{4}$$

Equations 3 and 4 are suggested to give better results than Equation 2. However, some additional difficulties arise by the determination of the exponents k_1 and k_2 in Equation 4. The author (*33*) combined Equation 1 with Equation 3 to correlate the compressibility data of trifluoromethane. The modified or extended BWR equation can be written as:

$$\begin{aligned} P_r = {} & T_r d_r/Z_c + \left(A_1 + A_2 T_r + \frac{A_3}{T_r^2} + \frac{A_4}{T_r^4}\right) d_r^2 + \\ & \left(A_5 + A_6 T_r + \frac{A_7}{T_r^2}\right) d_r^3 + \\ & \left(A_8 + \frac{A_9}{T_r^2}\right) \frac{e^{-\beta d_r^2}}{T_r^2} (1 + \beta d_r^2) d_r^3 + A_{10} d_r^6 \end{aligned} \tag{5}$$

where T_r, P_r, and d_r are the reduced temperature, pressure, and density, respectively. Z_c is the critical compressibility factor, $P_c V_c/RT_c$. A_1 through A_{10} and β are specific constants.

To achieve thermodynamical consistence at the critical point, the following conditions will be applied:

1. $T_r = P_r = d_r = 1$
2. $(\partial P_r/\partial d_r)_{T_r = 1} = 0$
3. $(\partial^2 P_r/\partial d_r^2)_{T_r = 1} = 0$
4. $(\partial P_r/\partial T_r)_{d_r = 1} = (dP_r/dT_r)_{\text{satd}} = \alpha_c$

The introduction of the first condition causes the critical isotherm to pass through the critical point—i.e., the equation of state will be satisfied at this point. By use of the foregoing second and third conditions, two properties of the critical isotherm in a pressure *vs.* volume graph are accomplished, namely, that at the critical point the slope is zero and an inflection occurs. The justification of the fact that the vapor-pressure curve at the critical point is identical with the slope of the critical-density isometric is achieved through the fourth condition. This equality is already proved from a thermodynamic point of view (*26*) and also mathematically (*36*). The slope, dP_r/dT_r, at the critical point is identical with the slope of the reduced vapor-pressure curve in a $\ln P_r$ *vs.* $1/T_r$ graph $[d\ln P_r/d(1/T)]$ and is denoted as the critical parameter, α_c.

Applying the above four conditions in Equation 5, one can eliminate four coefficients.

$$A_{10} = \tfrac{1}{6}[3 - 1/Z_c + (A_8 + A_9)e^{-\beta}\beta^2(5 - 2\beta)] \tag{6}$$

$$A_5 = \tfrac{1}{3}[5/Z_c - 12 - (A_8 + A_9)\, e^{-\beta}(3 + 3\beta + 4\beta^2 - 4\beta^3)] - (A_6 + A_7) \tag{7}$$

$$A_2 = \alpha_c - 1/Z_c + 2A_3 + 4A_4 - A_6 + 2A_7 + 2(A_8 + 2A_9)e^{-\beta}(1 + \beta) \tag{8}$$

$$A_1 = \tfrac{1}{2}[9 - 5/Z_c + (A_8 + A_9)\, e^{-\beta}\beta^2(1 - 2\beta)] - (A_2 + A_3 + A_4) \tag{9}$$

Substituting Equations 6 to 9 into Equation 5 gives

$$\begin{aligned} P_r = {} & T_r d_r/Z_c + \tfrac{1}{2}(9 - 5/Z_c)d_r^2 + \tfrac{1}{3}(5/Z_c - 12)d_r^3 + \\ & \tfrac{1}{6}(3 - 1/Z_c)d_r^6 + (\alpha_c - 1/Z_c)(T_r - 1)d_r^2 + \left(2T_r - 3 + \frac{1}{T_r^2}\right) d_r^2 A_3 + \\ & \left(4T_r - 5 + \frac{1}{T_r^4}\right) d_r^2 A_4 + (T_r - 1)(d_r - 1)d_r^2 A_6 + \\ & \left[\left(\frac{1}{T_r^2} - 1\right) d_r + 2(T_r - 1)\right] d_r^2 A_7 + \\ & \left[\frac{e^{-\beta}}{2}\beta^2(1 - 2\beta) - \frac{e^{-\beta}}{3}(3 + 3\beta + 4\beta^2 - 4\beta^3)d_r + \frac{e^{-\beta}}{6}\beta^2(5 - 2\beta)d_r^4 + 2e^{-\beta}(1 + \beta)(T_r - 1) + \frac{e^{-\beta d_r^2}}{T_r^2}(1 + \beta d_r^2)d_r\right] d_r^2 A_8 + \\ & \left[\frac{e^{-\beta}}{2}\beta^2(1 - 2\beta) - \frac{e^{-\beta}}{3}(3 + 3\beta + 4\beta^2 - 4\beta^3)d_r + \frac{e^{-\beta}}{6}\beta^2(5 - 2\beta)d_r^4 + 4e^{-\beta}(1 + \beta)(T_r - 1) + \frac{e^{-\beta d_r^2}}{T_r^4}(1 + \beta d_r^2)d_r\right] d_r^2 A_9 \end{aligned} \tag{10}$$

Rearranging Equation 10 and dividing by $T_r d_r$, one obtains:

$$\begin{aligned} & \frac{P_r}{T_r d_r} - 1/Z_c + \tfrac{1}{2}(5/Z_c - 9)\frac{d_r}{T_r} + \tfrac{1}{3}(12 - 5/Z_c)\frac{d_r^2}{T_r} + \tfrac{1}{6}(1/Z_c - 3)\frac{d_r^5}{T_r} + (\alpha_c - 1/Z_c)(T_r - 1)\frac{d_r}{T_r} = \\ & A_3\left(2T_r - 3 + \frac{1}{T_r^2}\right)\frac{d_r}{T_r} + A_4\left(4T_r - 5 + \frac{1}{T_r^4}\right)\frac{d_r}{T_r} + A_6(T_r - 1)(d_r - 1)\frac{d_r}{T_r} + A_7\left[\left(\frac{1}{T_r^2} - 1\right)d_r + 2(T_r - 1)\right]\frac{d_r}{T_r} + \\ & A_8\left[\frac{e^{-\beta}}{2}\beta^2(1 - 2\beta) - \frac{e^{-\beta}}{3}(3 + 3\beta + 4\beta^2 - 4\beta^3)d_r\ \frac{e^{-\beta}}{6}\beta^2(5 - 2\beta)d_r^4 + 2e^{-\beta}(1 + \beta)(T_r - 1) + \frac{e^{-\beta d_r^2}}{T_r^2}(1 + \beta d_r^2)d_r\right]\frac{d_r}{T_r} + \\ & A_9\left[\frac{e^{-\beta}}{2}\beta^2(1 - 2\beta) - \frac{e^{-\beta}}{3}(3 + 3\beta + 4\beta^2 - 4\beta^3)d_r + \frac{e^{-\beta}}{6}\beta^2(5 - 2\beta)d_r^4 + 4e^{-\beta}(1 + \beta)(T_r - 1) + \frac{e^{-\beta d_r^2}}{T_r^4}(1 + \beta d_r^2)d_r\right]\frac{d_r}{T_r} \end{aligned} \tag{11}$$

The division by $T_r d_r$ in Equation 11 is done to give the experimental P-V-T data at low temperatures and small densities more weight in the determination of the remaining coefficients by the least-squares technique, as explained below.

Equation 11 contains only seven coefficients: A_3, A_4, A_6, A_7, A_8, A_9, and β. The problem of evaluating these coefficients is now a mathematical manipulation of the coefficients such that there is a minimum deviation between experimental and calculated pressures:

Absolute percentage deviation Δ_i =

$$100 \cdot (Pi_{\text{exptl}} - Pi_{\text{calcd}}) / Pi_{\text{exptl}} \qquad (12)$$

The subscript, i, refers to the ith measurements for a particular system under consideration. The minimum error corresponds to the condition for which either the sum of the squares of the absolute percentage deviations or the average absolute percentage deviations is a minimum.

A method based on the least squares technique similar to that proposed by Brough *et al.* (*6*) is used in the present work to evaluate the coefficients. The method consists of determining the six coefficients, A_3, A_4, A_6, A_7, A_8, and A_9, for assumed values of β. A six-by-six matrix is established for each assumed β, which is then solved by computer methods for matrix solution. The sum of the squares of the absolute percentage deviation (S.S.A.P.D.), the average absolute deviation (A.A.P.D.), and the standard deviation are then calculated for each set of coefficients. These errors are defined as follows:

$$\text{A.A.P.D.} = 1/n \sum |\Delta_i| \qquad (13)$$

$$\text{S.S.A.P.D.} = \sum \Delta_i^2 \qquad (14)$$

$$\text{Standard Dev.} = \left(\frac{\sum \Delta_i^2}{n-1} \right)^{1/2} \qquad (15)$$

where n is the total number of P-V-T data considered, and Δ_i is defined as in Equation 12.

The optimum β is then taken as the one leading to the minimum value of errors (S.S.A.P.D. or A.A.P.D.). The calculations were carried out using an IBM 360 Model 40 digital computer. The program is written in FORTRAN IV language, with double precision floating point variables (*34*). To solve the set of the six linear simultaneous equations, a program of double precision matrix inversion (*18*) was used. International units (° K, bar, kg/m^3) are used throughout the calculations.

The optimization method proposed by Boas (*5*) using the Fibonacci numbers is applied. This is an efficient sequential search routine to follow for the case of one variable and where the assumption of unmodality prevails. The iteration procedure is terminated if the relative variation in deviation falls below a given value

$$\left| \frac{\text{Dev}_J - \text{Dev}_{J-1}}{(\text{Dev}_J + \text{Dev}_{J+1})/2} \right| \leq 0.0005 \qquad (16)$$

Dev_J and Dev_{J+1} are the deviations by iteration step J and $J + 1$, respectively. The variation range for β is taken as $0.3 \leq \beta \leq 1.0$. This range has been considered adequate for all compounds investigated.

DETERMINATION OF THE RIEDEL PARAMETER

Straub (*40*) evaluated the Riedel parameter, α_c, for different compounds. The following relationship between α_c and the critical compressibility factor, Z_c, was found:

$$\alpha_c = 10.1548 - \frac{3.2551\, Z_c}{1 - 2.81\, Z_c} + \frac{0.3305\, Z_c^2}{(1 - 2.81\, Z_c)^2} \qquad (17)$$

Equation 17 is supposed to give the α_c values for compounds with $0.22 \leq Z_c \leq 0.33$, with an average deviation of 0.5%. Further investigation showed that Equation 17 gives excellent results for hydrocarbons and ammonia. For other compounds, such as perfluorocyclobutane (C_4F_8), Equation 17 gives too low values. The program developed to calculate the coefficients of the equation of state (*34*) allows ±20% variation in α_c values with respect to that obtained from Equation 17. However, any other given values can be assumed. The optimum value of α_c is obtained in a similar manner as β (minimizing the errors).

OPTIMIZATION PROCEDURE

The critical data (T_c, P_c, and especially d_c) cannot be determined experimentally with a very high degree of accuracy, and it is quite possible that the values first chosen are somewhat in error. It is likely that an improvement can be obtained by adjusting these data. The program used was developed such that it allows the adjustment of T_c, P_c, and d_c in the same manner as β and α_c. The order of successive variation of the parameters β, α_c, d_c, P_c, and T_c is described later. After each minimization loop, the variation limits of a parameter will be cut down as follows: assume x_1 and x_2 are the given limits of the parameter x, and x_M is the optimal value found for x. Then if $|x_M - x_1| > |x_M - x_2|$, the new value for x_1 is $(x_1 + x_M)/2$; otherwise, the new value of x_2 is $(x_2 + x_M)/2$.

The procedure for optimum evaluation of the coefficients in the equation of state can be summarized as follows:

1. Select the best values of T_c, P_c, and d_c.
2. Calculate $Z_c = P_c/RT_c d_c$ and α_c from Equation 17.
3. Set the variation limits of T_c, P_c, d_c, α_c, and β; otherwise, the following values are assumed: $\beta_1 = 0.3$, $\beta_2 = 1.0$, $\alpha_{c1} = 0.8\ \alpha_c$, and $\alpha_{c2} = 1.2\ \alpha_c$. Decide the error to be minimized (A.A.P.D. or S.S.A.P.D.).

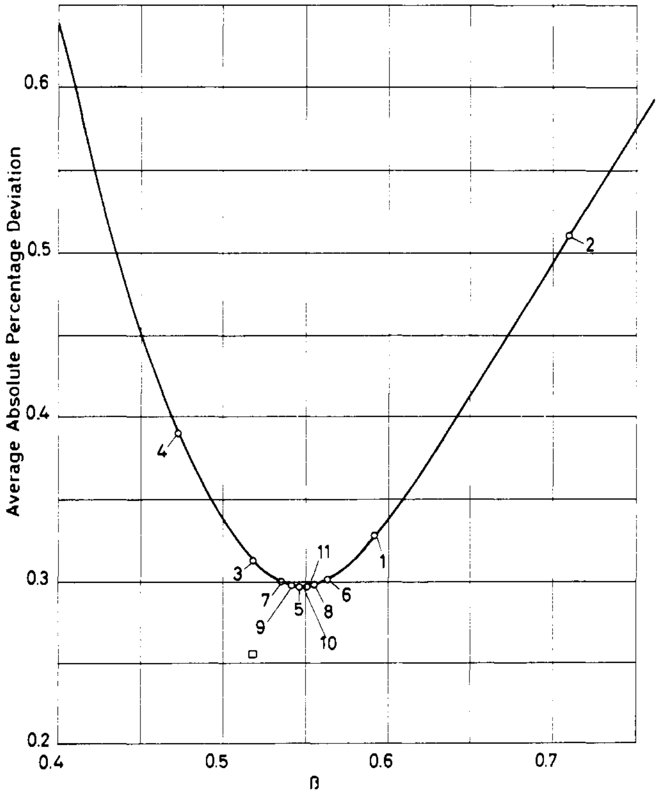

Figure 1. Effect of β on the average absolute percentage deviation in pressure for monochlorotrifluoromethane. The numbers indicate the order of variation of β according to the Fibonacci search technique

Optimum value found after variation of the other parameters

4. T_c, P_c, d_c, and α_c are set as constants; β varies according to the Fibonacci search technique until a minimum deviation is attained.

5. Keep β constant and vary α_c to get a new minimum.

6. Step 4 and 5 may be alternately repeated to adjust β and α_c.

The following three steps deal with the variation of the critical data (T_c, P_c, d_c) and possible adjustment of α_c and β. These steps are bypassed if variation of the critical data is not required.

7. Vary d_c, P_c, and T_c successively in the same manner as β and α_c.

8. Step 4 and 5 are repeated.

9. Step 7 and 8 may be repeated.

10. The best values found for T_c, P_c, d_c, α_c, and β are approximated as follows:

T_c, d_c	2 decimal points
P_c, α_c	3 decimal points
β	4 decimal points

The coefficients of the equation of state will be finally evaluated for these approximated parameters.

To demonstrate the applicability of the developed equation of state and the efficiency of the optimization method used, the coefficients for some fluorine compounds are evaluated. For monochlorotrifluoromethane, the different steps are written down in some detail. The initial critical values assumed are:

$T_c = 302.00°\,K$ $P_c = 39.000$ bar $d_c = 580.00$ kg/m^3
Molecular weight $M = 104.468$
Critical compressibility factor $Z_c = 0.27976$
Riedel parameter from Equation 17 = 6.502

The minimization of A.A.P.D. is assumed to be desired. The following variation limits for the different parameters are assumed

$$301.80 \leqq T_c \leqq 302.35$$
$$38.00 \leqq P_c \leqq 39.15$$
$$566.00 \leqq d_c \leqq 582.00$$
$$5.85 \leqq \alpha_c \leqq 7.80$$
$$0.4 \leqq \beta \leqq 0.9$$

The limit of variation for T_c, P_c, and d_c are within the boundaries of the data as reported by different authors. For the evaluation, 433 *P-V-T* points for monochlorotrifluoromethane in the gaseous and liquid phases are used. They contain experimental data published by Albright and Martin (*1*) and Michels *et al.* (*31*), as well as values given by Riedel (*39*). The data cover the temperature range of 194° to 423° K, the pressure range 1 to 472 bar, and the density range 4.5 to 1052 kg/m^3. Figure 1 shows computer variation of β (step 1) and the corresponding resultant average deviations. Figure 2 is a plot of the minimum deviation found after every variation loop for the different parameters. Therefore, the average error in pressure has been reduced from 0.296 to 0.256%—

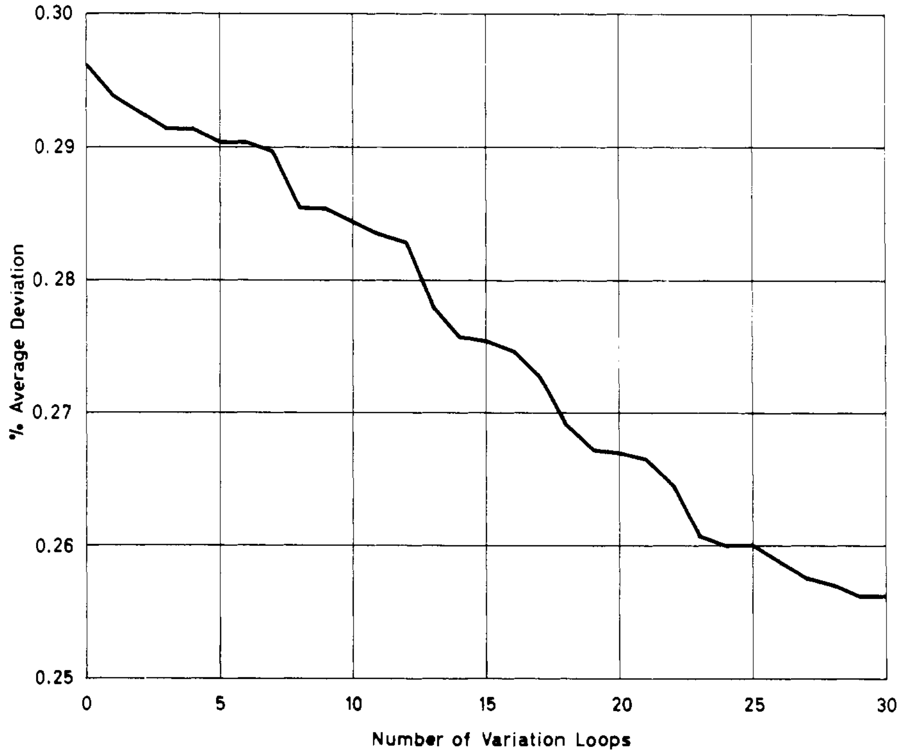

Figure 2. Minimization of the average absolute percentage deviation (A.A.P.D.) for monochlorotrifluormethane by successive variation of the different parameters

Initial values: $T_c = 302°$ K, $P_c = 39$ bar, $d_c = 580$ kg/m^3, $\alpha_c = 6.502$, and $\beta = 0.5500$

Values in variation loops:

0–5	5–10	10–15	15–20	20–25	25–30
$\alpha_c = 6.529$	$d_c = 579.666$	$d_c = 578.183$	$d_c = 577.040$	$d_c = 576.440$	$d_c = 575.5$
$\beta = 0.5549$	$P_c = 39.022$	$P_c = 39.057$	$P_c = 39.097$	$P_c = 39.136$	$P_c = 39.15$
$\alpha_c = 6.545$	$T_c = 302.090$	$T_c = 302.181$	$T_c = 302.256$	$T_c = 302.331$	$T_c = 302.35$
$\beta = 0.5421$	$\beta = 0.5393$	$\beta = 0.5323$	$\beta = 0.5248$	$\beta = 0.5202$	$\beta = 0.5180$
$\alpha_c = 6.568$	$\alpha_c = 6.588$	$\alpha_c = 6.601$	$\alpha_c = 6.623$	$\alpha_c = 6.623$	$\alpha_c = 6.619$

Table I. Comparison Between Initial and Final Values for the Different Parameters Used in the Evaluation of the Constants for the Equation of State for Monochlorotrifluoromethane

Property	Initial	Final	Variation
T_c, °K	302.0	302.35	+0.35° K
P_c, bar	39.0	39.150	+0.38%
d_c, kg/m^3	580.0	575.50	−0.78%
α_c	6.502	6.618	+1.78%
β	0.5500	0.5180	−5.82%
A.A.P.D.	0.2962	0.2562	−13.51%
S.S.A.P.D.	70.849	56.506	−20.24%
Standard dev.	0.4042	0.3625	−10.31%

Table II. Coefficients for the Equation of State

Property	CCl_2F_2(R12)	$CClF_3$ (R13)	CF_4 (R14)	CHF_3 (R23)	$C_2Cl_2F_4$ (R114)	C_2ClF_5 (R115)	C_4F_8 (RC318)	SF_6 (R846)
M	120.925	104.468	88.011	70.019	170.936	154.479	200.044	146.066
T_c, °K	385.19	302.35	227.49	299.09	418.84	353.16	388.48	318.73
P_c, bar	41.429	39.150	37.727	48.353	32.657	31.558	27.998	37.793
d_c, kg/m^3	557.38	575.50	625.58	525.06	585.18	610.74	620.00	729.05
α_c	6.915	6.619	6.693	7.185	7.264	8.056	7.392	6.651
$1/Z_c$	3.5631289	3.5372515	3.5635399	3.8565342	3.6505096	3.6785329	3.5754730	3.4998179
A_1	10.957906	−0.53167130	−4.7518336	−1.8712373	2.0671936	−16.960070	−2.2117031	2.7175825
A_2	−5.9572301	0.13870908	2.1147699	0.61364539	−0.17129480	8.8882696	0.95867686	−1.1209876
A_3	−12.597972	−4.8467287	−1.3167177	−3.6345455	−8.8318215	5.7438564	−2.3490314	−7.9533437
A_4	3.2562151	0.88857843	−0.43057317	−0.36725953	2.3346446	−2.2897160	−0.86387645	2.0935047
A_5	−15.376646	−3.0154836	−0.75528170	−2.5941695	−5.3725425	−18.203728	−3.1528736	0.238431307
A_6	8.5136186	2.1971127	1.2049568	2.3128894	2.7626667	9.0687202	2.7440341	0.350845138
A_7	2.3894590	−0.080495584	−2.2852734	1.4529941	−0.73615221	2.4347747	0.0094372746	−1.1128842
A_8	9.0057757	2.4786042	2.4777399	−0.52366991	5.9098432	13.852765	0.23368882	1.4530336
A_9	−2.7450471	0.29621599	1.2250846	1.9355716	−0.57045316	−5.2155403	2.1363810	0.896589421
A_{10}	0.37783090	0.20348817	0.23133410	0.085968052	0.38433008	0.58554745	0.18066005	0.174569983
β	0.4010	0.5180	0.4485	0.7936	0.4656	0.4220	0.5636	0.5348
Abs. av. dev., %	0.53	0.26	0.13	0.21	0.78	0.43	0.41	0.39
Av. sq. dev., %	0.7498	0.1305	0.0302	0.0792	1.1746	0.3368	0.3516	0.2913
Standard dev.	0.8668	0.3625	0.1735	0.2808	1.0925	0.5813	0.5939	0.5415
Temp. range, °K	303–473	283–423	273–623	222–392	298–480	213–447	256–623	288–523
Max. press., bar	136	472	399	139	109	70	400	186
Max. density, kg/m^3	987	1052	1100	998	935	885	1400	1539
Source of *P-V-T* data	(*7*), (*13*), (*20*), (*31*)	(*14*), (*31*), (*39*)	(*11*)	(*16*)	(*24*), (*29*)	(*27*), (*30*)	(*2*), (*12*), (*25*)	(*9*), (*28*), (*35*)
Number of *P-V-T* points used	429	433	306	80	64	201	213	186

i.e., a relative reduction of 13.5%. This may be considered a significant improvement. A comparison between the initial values (after step 1) and the final approximated values for the different parameters, as well as the deviations, is presented in Table I. The corresponding set of coefficients is given in Table II. The average percentage deviation between experimental values and the predicted pressures was 0.256%. The largest deviations were observed along the largest isometric measured by Albright and Martin ($d \approx 712$ kg/m^3). The maximum error in pressure was 1.44%. This is probably within the error limits of the experiments, especially since the deviation by the neighboring isometrics measured by Michels *et al.* (*31*)($d = 684$, $d = 730$) amounts to only 0.22%.

APPLICATION OF THE EQUATION OF STATE FOR EIGHT FLUORINE COMPOUNDS

In the foregoing part of this paper the constants for the equation of state for monochlorotrifluoromethane (refrigerant 13 = R 13) are evaluated. For the other seven fluorine compounds, dichlorodifluoromethane (R 12), tetrafluoromethane (R 14), trifluoromethane (R 23), dichlorotetrafluoroethane (R 114), monochloropentafluoroethane (R 115), octafluorocyclobutane (RC 318), and sulfurhexafluoride (R 846), the constants are determined in the same manner. All published P-V-T data were used with equal weights. The variation of the critical data results in a reduction in the error of the same magnitude as men-

Table III. Derived Thermodynamic Functions

Pressure

$$P_r = T_r d_r/Z_c + \left(A_1 + A_2T_r + \frac{A_3}{T_r^2} + \frac{A_4}{T_r^4}\right)d_r^2 + \left(A_5 + A_6T_r + \frac{A_7}{T_r^2}\right)d_r^3 + \left(A_8 + \frac{A_9}{T_r^2}\right)\frac{e^{-\beta d_r^2}}{T_r^2}(1 + \beta d_r^2)d_r^3 + A_{10}d_r^6 \qquad (18)$$

Enthalpy

$$\frac{H}{RT_c} = \frac{1}{RT_c}\int C_v^\circ dT +$$

$$Z_c\left[\left(A_1 + 3\frac{A_3}{T_r^2} + 5\frac{A_4}{T_r^4}\right)d_r + \left(A_5 + 3\frac{A_7}{T_r^2}\right)\frac{d_r^2}{2} + \frac{1}{\beta T_r^2}\left(3A_8 + 5\frac{A_9}{T_r^2}\right)\left\{1 - e^{-\beta d_r^2}\left(1 + \frac{\beta d_r^2}{2}\right)\right\} + A_{10}\frac{d_r^5}{5} + \frac{P_r}{d_r}\right] + K \qquad (19)$$

Entropy

$$\frac{S}{R} = \frac{1}{R}\int\frac{C_v^\circ}{T}dT - \ln d_r -$$

$$Z_c\left[\left(A_2 - 2\frac{A_3}{T_r^3} - 4\frac{A_4}{T_r^5}\right)d_r + \left(A_6 - 2\frac{A_7}{T_r^3}\right)\frac{d_r^2}{2} - \frac{2}{\beta T_r^3}\left(A_8 + 2\frac{A_9}{T_r^2}\right)\left\{1 - e^{-\beta d_r^2}\left(1 + \frac{\beta d_r^2}{2}\right)\right\}\right] + K_1 \qquad (20)$$

Fugacity

$$\ln(f/p) = \frac{Z_c}{T_r}\left[\left(A_1 + A_2T_r + \frac{A_3}{T_r^2} + \frac{A_4}{T_r^4}\right)d_r + \left(A_5 + A_6T_r + \frac{A_7}{T_r^2}\right)\frac{d_r^2}{2} + \frac{1}{\beta T_r^2}\left(A_8 + \frac{A_9}{T_r^2}\right)\left\{1 - e^{-\beta d_r^2}\left(1 + \frac{\beta d_r^2}{2}\right)\right\} + \right.$$

$$\left. A_{10}\frac{d_r^5}{5}\right] - \ln Z + Z - 1 \qquad (21)$$

Isometric heat capacity

$$\frac{C_v}{R} = \frac{C_v^\circ}{R} - \frac{Z_c}{T_r^3}\left[\left(6A_3 + 20\frac{A_4}{T_r^2}\right)d_r + 3A_7d_r^2 + 1/\beta\left(6A_8 + 20\frac{A_9}{T_r^2}\right)\left\{1 - e^{-\beta d_r^2}\left(1 + \frac{\beta d_r^2}{2}\right)\right\}\right] \qquad (22)$$

Isobaric heat capacity

$$\frac{C_p}{R} = \frac{C_v}{R} +$$

$$(Z_cT_r)\frac{\left[1/Z_c + \left(A_2 - 2\frac{A_3}{T_r^3} - 4\frac{A_4}{T_r^5}\right)d_r + \left(A_6 - 2\frac{A_7}{T_r^3}\right)d_r^2 - 2\left(A_8 + 2\frac{A_9}{T_r^2}\right)\frac{e^{-\beta d_r^2}}{T_r^3}(1 + \beta d_r^2)\right]^2}{\frac{T_r}{Z_c} + 2\left(A_1 + A_2T_r + \frac{A_3}{T_r^2} + \frac{A_4}{T_r^4}\right)d_r + 3\left(A_5 + A_6T_r + \frac{A_7}{T_r^2}\right)d_r^2 + \left(A_8 + \frac{A_9}{T_r^2}\right)\frac{e^{-\beta d_r^2}}{T_r^2}(3 + 3\beta d_r^2 - 2\beta^2d_r^4)d_r^2 + 6A_{10}d_r^5} \qquad (23)$$

Joule-Thomson coefficient

$$\frac{\mu_{JT}}{T_c/P_c} = \left(\frac{R}{C_p}\right)\frac{Z_c}{d_r}\cdot$$

$$\left[\frac{\frac{T_r}{Z_c} + \left(A_2T_r - 2\frac{A_3}{T_r^2} - 4\frac{A_4}{T_r^4}\right)d_r + \left(A_6T_r - 2\frac{A_7}{T_r^2}\right)d_r^2 - 2\left(A_8 + \frac{A_9}{T_r^2}\right)\frac{e^{-\beta d_r^2}}{T_r^2}(1 + \beta d_r^2)d_r^2}{\frac{T_r}{Z_c} + 2\left(A_1 + A_2T_r + \frac{A_3}{T_r^2} + \frac{A_4}{T_r^4}\right)d_r + 3\left(A_5 + A_6T_r + \frac{A_7}{T_r^2}\right)d_r^2 + \left(A_8 + \frac{A_9}{T_r^2}\right)\frac{e^{-\beta d_r^2}}{T_r^2}(3 + 3\beta d_r^2 - 2\beta^2d_r^4)d_r^2 + 6A_{10}d_r^5} - 1\right] \qquad (24)$$

Sound velocity

$$W/(10^5P_c/d_c)^{1/2} =$$

$$\left\{\frac{C_p}{C_v}\left[\frac{T_r}{Z_c} + 2\left(A_1 + A_2T_r + \frac{A_3}{T_r^2} + \frac{A_4}{T_r^4}\right)d_r + 3\left(A_5 + A_6T_r + \frac{A_7}{T_r^2}\right)d_r^2 + \left(A_8 + \frac{A_9}{T_r^2}\right)\frac{e^{-\beta d_r^2}}{T_r^2}(3 + 3\beta d_r^2 - 2\beta^2d_r^4)d_r^2 + 6A_{10}d_r^5\right]\right\}^{1/2} \qquad (25)$$

tioned for monochlorotrifluoromethane. A comprehensive presentation of the optimal values found is given in Table II. Tables with these values have been made of comparisons of the pressures predicted from the equation of state with the experimentally measured pressures reported in the literature.

The precision of experimental data was important in the evaluation of the constants. Data taken in the region of the critical point or in the liquid phase are more inconsistent than those in the vapor phase. This reflects the inherent experimental difficulties in this region. The accuracy of the predicted pressures depends on several things, such as the primary data given, the number of points used, the weight put on the points, the range of temperature and pressure used, the criterion on which the fit is obtained, etc. Possibly the average deviation reported in Table II would be substantially improved if only reliable P-V-T data were considered.

DERIVATION OF THERMODYNAMIC FUNCTIONS

The equation of state developed permits all the usual differentiations and integrations required for calculation of the residual (excess) thermodynamic properties. Table III shows the derived expressions for some thermodynamic functions.

COMPARISON OF THE CALCULATED THERMODYNAMIC PROPERTIES OF REAL GASEOUS TETRAFLUOROMETHANE WITH LITERATURE DATA

The thermodynamic properties of compressed gaseous tetrafluoromethane were determined in tabular form by Harrison and Douslin (*5*). They declared these tabulated values as standards, in the sense that they reflect faithfully all of the trends that appear in the experimental data from which they are derived. Because the computations are based directly on unsmoothed experimental compressibility values (*11*) measured at even temperatures and densities, the introduction of spurious trends from arbitrary smoothing of the basic data was prevented. A combination of analytical and graphical correlational methods was adopted to ensure full utilization of the inherent accuracy and precision of the experimental results.

The thermodynamic functions calculated are the excess molal enthalpy $H - H^\circ$, the excess molal entropy $S - S^\circ$, and the excess molal Gibbs energy $G - G^\circ$. The superscript degree mark in H°, S°, or G° is for the ideal gas at 1 atm (1.01325 bar). In the present work, the values for $(H - H^\circ)$ and $(S - S^\circ)$ for gaseous tetrafluoromethane are calculated from Equations 19 and 20. The excess molal Gibbs energy values are obtained from $(G - G^\circ) = (H - H^\circ) - T(S - S^\circ)$. A comparison of the calculated P, $-(H - H^\circ)$, $-(S - S^\circ)$, and $(G - G^\circ)$ with those given by Harrison and Douslin, and the corresponding values calculated with the original BWR equation in the temperature range 0° to 350° C with an interval of 50° C is presented in Tables IV to VII. The average absolute deviations in P, $-(H - H^\circ)$, $-(S - S^\circ)$, and $(G - G^\circ)$ are 0.13, 2.27, 0.23, and 0.07%, respectively, whereas the corresponding deviations obtained by use of the original BWR equation are 0.55, 11.18, 1.14, and 0.22%, respectively. This agreement is considered to be very good for pressures, entropies, and Gibbs energies.

For enthalpies, however, the deviation is as much as 4.2%. This relatively large deviation is not serious, and the results can be considered as substantial improvement with respect to the values predicted by the original BWR equation, where some individual points were off by as much as 28%. Furthermore, the deviation in the enthalpy values presented in Table V shows different signs. This means that the equation of state shows no systematic errors. However, at low densities, remarkable deviations are found. This is probably caused by an inaccurate representation of the second virial coefficient, *B(T)*, or its first derivative with respect to temperature.

For calculation of the thermodynamic functions at low densities, Harrison and Douslin integrated the following expressions:

$$\text{For entropy } RT\cdot[dB(T)/dT] + R\cdot B(T) \tag{26}$$

$$\text{For Gibbs energy } -RT\cdot B(T) \tag{27}$$

$$\text{For enthalpy } RT^2\cdot[dB(T)/dT] \tag{28}$$

From Equation 26 to 28, it is obvious that the enthalpy depends on $[dB(T)/dT]$ more than the other two functions. For tetrafluoromethane, values for $B(T)$ were determined (*11*) by extrapolating P-V-T data under pressures of 15 atm and higher to zero pressure. Values for $[dB(T)/dT]$

Table IV. Percentage Deviation in $P = 100\,(P_{\text{calcd}} - P_{\text{Douslin}})/P_{\text{Douslin}}$

Moles per Liter	0° C		50° C		100° C		150° C		200° C		250° C		300° C		350° C	
	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR
0.75	0.06	−0.65	0.05	0.00	−0.03	0.14	−0.09	0.12	−0.16	0.01	−0.20	−0.11	−0.24	−0.23	−0.27	−0.34
1.0	0.09	−0.83	0.07	0.02	−0.02	0.21	−0.12	0.16	−0.18	0.03	−0.23	−0.11	−0.26	−0.25	−0.30	−0.39
1.5	0.10	−1.14	0.10	0.07	−0.02	0.31	−0.12	0.26	−0.19	0.11	−0.25	−0.08	−0.29	−0.27	−0.31	−0.43
2.0	0.08	−1.38	0.11	0.13	0.01	0.45	−0.09	0.38	−0.17	0.20	−0.22	−0.01	−0.25	−0.22	−0.27	−0.41
2.5	0.02	−1.52	0.10	0.21	0.03	0.57	−0.04	0.51	−0.12	0.30	−0.16	0.08	−0.19	−0.14	−0.20	−0.33
3.0	−0.06	−1.53	0.07	0.31	0.06	0.68	0.00	0.61	−0.05	0.40	−0.10	0.17	−0.10	−0.03	−0.11	−0.23
3.5	−0.17	−1.42	0.04	0.44	0.08	0.79	0.06	0.71	0.01	0.49	−0.02	0.26	−0.02	0.08	−0.02	−0.09
4.0	−0.28	−1.15	0.01	0.60	0.11	0.88	0.10	0.77	0.07	0.56	0.04	0.34	0.06	0.19	0.07	0.06
4.5	−0.37	−0.74	0.00	0.77	0.12	0.94	0.16	0.82	0.13	0.61	0.09	0.41	0.13	0.31	0.15	0.20
5.0	−0.44	−0.21	−0.03	0.92	0.14	0.98	0.16	0.80	0.15	0.62	0.13	0.46	0.17	0.41	0.19	0.34
5.5	−0.48	0.39	−0.03	1.05	0.14	0.96	0.18	0.78	0.17	0.61	0.12	0.47	0.17	0.48	0.19	0.46
6.0	−0.44	1.02	−0.02	1.15	0.13	0.89	0.19	0.72	0.12	0.54	0.08	0.46	0.15	0.53	0.19	0.60
6.5	−0.36	1.58	0.01	1.17	0.12	0.77	0.16	0.60	0.06	0.46	−0.00	0.42	0.07	0.57		
7.0	−0.24	1.99	0.01	1.07	0.09	0.59	0.10	0.43	−0.00	0.36	−0.10	0.38				
7.5	−0.08	2.18	0.06	0.90	0.05	0.35	0.01	0.24	−0.16	0.19						
8.0	0.07	2.08	0.05	0.58	0.00	0.09	−0.11	0.03	−0.34	0.03						
8.5	0.18	1.68	0.07	0.23	−0.06	−0.19	−0.31	−0.24								
9.0	0.21	1.00	0.10	−0.14	−0.17	−0.47	−0.45	−0.40								
9.5	0.15	0.16	0.08	−0.50	−0.25	−0.65										
10.0	0.08	−0.59	0.07	−0.73	−0.39	−0.77										
10.5	−0.08	−1.12	0.06	−0.75												
11.0	−0.29	−1.21	0.11	−0.41												

were calculated from the differentiated equation of the Lennard-Jones $[n,m]$ potential with $n = 500$, $m = 6$ fitted to $B(T)$ values. To these calculated derivatives were added small graphically determined temperature derivatives of the differences between "observed" and calculated values for the second virial coefficient according to the [500, 6] potential.

Another reason for the difference in the enthalpy may arise from the different definition in the absolute temperature scale used. Harrison *et al.* used the thermodynamic temperature scale, whereas in this work, the most recent definition, 0° C = 273.15° K, was used. This causes a small, but significant, error. A further advantage of the extended equation is the accurate representation of the volumetric behavior in the critical region (*8*): T_c = 227.5° K, P_c = 36.96 atm, d_c = 7.11 moles per liter, whereas the corresponding values predicted by the original BWR equation are considerably in error (T_c = 231.15° K, P_c = 43.27 atm, d_c = 9.1 moles per liter).

REPRESENTATION OF THE VAPOR PRESSURE

The equation of state can be applied to predict the saturation vapor pressure by matching pressure and fugacity on both liquid and vapor regions. For C_4F_8, Equations 18 and 21 together with the specific constants in Table II are used to calculate the vapor pressure from the triple point (−40.2°C) to the critical point (+115.33° C). The results obtained, using the original and modified equation of state as well as the experimental data (*2, 12, 15, 21, 25, 41*), are shown in Figure 3. Significant improvement with respect to the original equation is detected, especially at low temperatures. The calculated vapor pressure using the original equation is about 52% in error, whereas the

Table V. Percentage Deviation in $-(H - H°) = 100\,[-(H - H°)_{\text{calcd}} + (H - H°)_{\text{Harrison}}]/-(H - H°)_{\text{Harrison}}$

Moles per Liter	0° C		50° C		100° C		150° C		200° C		250° C		300° C		350° C	
	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR
0.75	0.67	22.72	−2.60	9.98	−3.97	0.54	−4.35	−6.68	−4.15	−12.41	−3.75	−17.33	−2.83	−21.49	−1.88	−25.60
1.0	0.67	22.29	−2.53	9.76	−3.88	0.50	−4.25	−6.58	−4.15	−12.31	−3.74	−17.19	−3.14	−21.62	−2.16	−25.79
1.5	0.83	21.59	−2.27	9.43	−3.57	0.54	−3.99	−6.33	−4.08	−12.06	−3.77	−16.93	−3.34	−21.54	−2.83	−26.25
2.0	0.94	20.80	−1.97	9.13	−3.31	0.51	−3.79	−6.14	−3.94	−11.74	−3.88	−16.74	−3.59	−21.48	−3.27	−26.55
2.5	1.07	20.00	−1.68	8.80	−3.01	0.52	−3.59	−5.95	−3.79	−11.40	−3.84	−16.40	−3.69	−21.31	−3.66	−26.82
3.0	1.15	19.13	−1.39	8.45	−2.73	0.50	−3.38	−5.75	−3.68	−11.09	−3.77	−16.04	−3.83	−21.16	−3.91	−27.01
3.5	1.23	18.24	−1.11	8.08	−2.44	0.49	−3.17	−5.55	−3.53	−10.74	−3.72	−15.68	−3.85	−20.92	−4.09	−27.18
4.0	1.27	17.29	−0.87	7.67	−2.18	0.45	−2.94	−5.33	−3.40	−10.40	−3.59	−15.26	−3.80	−20.63	−4.20	−27.36
4.5	1.29	16.33	−0.66	7.24	−1.92	0.42	−2.78	−5.16	−3.25	−10.04	−3.46	−14.82	−3.71	−20.32	−4.22	−27.53
5.0	1.27	15.35	−0.47	6.81	−1.70	0.38	−2.57	−4.91	−3.09	−9.64	−3.28	−14.34	−3.54	−19.96	−4.09	−27.70
5.5	1.24	14.40	−0.30	6.40	−1.51	0.34	−2.39	−4.68	−2.94	−9.25	−3.04	−13.79	−3.28	−19.57	−3.78	−27.88
6.0	1.18	13.49	−0.19	5.98	−1.35	0.31	−2.25	−4.45	−2.74	−8.78	−2.78	−13.23	−2.98	−19.15	−3.49	−28.29
6.5	1.09	12.62	−0.13	5.59	−1.23	0.31	−2.11	−4.17	−2.56	−8.30	−2.48	−12.64	−2.47	−18.69		
7.0	0.99	11.83	−0.06	5.27	−1.13	0.34	−1.97	−3.85	−2.42	−7.84	−2.22	−12.09				
7.5	0.87	11.13	−0.03	4.99	−1.04	0.42	−1.85	−3.52	−2.18	−7.28						
8.0	0.75	10.53	−0.01	4.80	−0.98	0.53	−1.75	−3.17	−1.97	−6.72						
8.5	0.65	10.06	−0.01	4.66	−0.96	0.66	−1.58	−2.72								
9.0	0.58	9.71	−0.04	4.56	−0.93	0.83	−1.56	−2.42								
9.5	0.55	9.47	−0.07	4.50	−0.96	0.94										
10.0	0.54	9.30	−0.09	4.46	−0.97	1.04										
10.5	0.57	9.15	−0.12	4.38												
11.0	0.65	9.00	−0.17	4.18												

Table VI. Percentage Deviation in $-(S - S°) = 100\,[-(S - S°)_{\text{calcd}} + (S - S°)_{\text{Harrison}}]/(S - S°)_{\text{Harrisan}}$

Moles per Liter	0° C		50° C		100° C		150° C		200° C		250° C		300° C		350° C	
	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR
0.75	0.11	1.76	−0.14	0.65	−0.21	0.11	−0.22	−0.17	−0.21	−0.33	−0.20	−0.43	−0.19	−0.48	−0.18	−0.52
1.0	0.13	2.07	−0.16	0.78	−0.24	0.14	−0.25	−0.20	−0.24	−0.39	−0.23	−0.50	−0.22	−0.57	−0.20	−0.61
1.5	0.18	2.60	−0.18	0.99	−0.28	0.18	−0.30	−0.24	−0.29	−0.48	−0.27	−0.62	−0.25	−0.71	−0.24	−0.76
2.0	0.22	3.02	−0.19	1.16	−0.31	0.23	−0.32	−0.26	−0.31	−0.54	−0.30	−0.71	−0.27	−0.81	−0.26	−0.87
2.5	0.26	3.35	−0.19	1.30	−0.32	0.27	−0.34	−0.27	−0.33	−0.59	−0.31	−0.77	−0.28	−0.88	−0.26	−0.96
3.0	0.29	3.61	−0.17	1.41	−0.31	0.31	−0.34	−0.28	−0.33	−0.62	−0.31	−0.82	−0.28	−0.93	−0.26	−1.01
3.5	0.31	3.81	−0.15	1.50	−0.30	0.34	−0.34	−0.28	−0.33	−0.64	−0.31	−0.84	−0.27	−0.96	−0.25	−1.04
4.0	0.32	3.94	−0.13	1.56	−0.28	0.36	−0.33	−0.28	−0.32	−0.65	−0.30	−0.85	−0.26	−0.97	−0.24	−1.06
4.5	0.33	4.03	−0.10	1.61	−0.26	0.38	−0.31	−0.28	−0.31	−0.65	−0.28	−0.85	−0.25	−0.97	−0.23	−1.05
5.0	0.34	4.06	−0.07	1.63	−0.24	0.39	−0.30	−0.28	−0.30	−0.64	−0.27	−0.84	−0.23	−0.95	−0.21	−1.03
5.5	0.34	4.06	−0.04	1.63	−0.22	0.39	−0.29	−0.27	−0.29	−0.63	−0.26	−0.82	−0.21	−0.92	−0.19	−1.00
6.0	0.34	4.03	−0.02	1.61	−0.20	0.38	−0.27	−0.27	−0.28	−0.62	−0.25	−0.80	−0.20	−0.89	−0.17	0.96
6.5	0.33	3.97	−0.00	1.58	−0.19	0.37	−0.27	−0.26	−0.28	−0.60	−0.24	−0.77	−0.18	−0.84		
7.0	0.32	3.89	0.01	1.53	−0.18	0.35	−0.26	−0.26	−0.28	−0.58	−0.24	−0.73				
7.5	0.30	3.78	0.02	1.48	−0.17	0.33	−0.26	−0.25	−0.29	−0.56						
8.0	0.28	3.67	0.03	1.42	−0.18	0.31	−0.27	−0.25	−0.30	−0.54						
8.5	0.26	3.55	0.03	1.36	−0.18	0.29	−0.29	−0.24								
9.0	0.24	3.44	0.03	1.30	−0.20	0.27	−0.31	−0.24								
9.5	0.22	3.34	0.02	1.25	−0.22	0.25										
10.0	0.22	3.25	0.01	1.20	−0.25	0.24										
10.5	0.22	3.18	0.00	1.17												
11.0	0.23	3.12	−0.01	1.15												

Table VII. Percentage Deviation in $G - G^\circ = 100\,[(G - G^\circ)_{\text{calcd}} - (G - G^\circ)_{\text{Harrison}}]/(G - G^\circ)_{\text{Harrison}}$

Moles per Liter	0° C		50° C		100° C		150° C		200° C		250° C		300° C		350° C	
	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR	EBWR	BWR
0.75	0.05	−0.47	0.03	0.00	−0.02	0.09	−0.07	0.06	−0.12	−0.01	−0.14	−0.09	−0.16	−0.16	−0.18	−0.22
1.0	0.06	−0.54	0.04	0.01	−0.02	0.12	−0.08	0.08	−0.12	0.00	−0.16	−0.09	−0.18	−0.17	−0.20	−0.25
1.5	0.06	−0.67	0.05	0.02	−0.02	0.16	−0.08	0.12	−0.13	0.02	−0.17	−0.08	−0.19	−0.18	−0.21	−0.27
2.0	0.06	−0.76	0.06	0.04	−0.01	0.20	−0.08	0.16	−0.13	0.05	−0.17	−0.07	−0.19	−0.18	−0.21	−0.28
2.5	0.05	−0.82	0.06	0.07	−0.01	0.24	−0.07	0.20	−0.12	0.08	−0.16	−0.04	−0.18	−0.16	−0.20	−0.27
3.0	0.03	−0.84	0.05	0.09	−0.00	0.28	−0.06	0.24	−0.11	0.12	−0.14	−0.02	−0.16	−0.14	−0.18	−0.25
3.5	0.01	−0.84	0.05	0.12	0.01	0.32	−0.04	0.27	−0.09	0.15	−0.13	0.01	−0.14	−0.11	−0.15	−0.22
4.0	−0.02	−0.80	0.04	0.16	0.01	0.35	−0.03	0.29	−0.07	0.17	−0.11	0.04	−0.12	−0.08	−0.13	−0.18
4.5	−0.04	−0.73	0.04	0.21	0.02	0.37	−0.02	0.32	−0.06	0.19	−0.09	0.06	−0.10	−0.05	−0.11	−0.15
5.0	−0.05	−0.64	0.03	0.24	0.02	0.39	−0.01	0.33	−0.05	0.20	−0.08	0.08	−0.09	−0.02	−0.10	−0.11
5.5	−0.06	−0.54	0.03	0.28	0.03	0.40	−0.00	0.33	−0.04	0.21	−0.08	0.09	−0.08	0.01	−0.09	−0.07
6.0	−0.06	−0.43	0.03	0.31	0.03	0.40	0.00	0.33	−0.05	0.21	−0.08	0.10	−0.08	0.03	−0.08	−0.03
6.5	−0.05	−0.33	0.04	0.33	0.03	0.38	0.00	0.31	−0.06	0.19	−0.10	0.10	−0.09	0.05		
7.0	−0.04	−0.26	0.04	0.32	0.02	0.35	−0.01	0.28	−0.07	0.18	−0.12	0.09				
7.5	−0.02	−0.21	0.04	0.30	0.02	0.31	−0.03	0.25	−0.10	0.15						
8.0	0.01	−0.20	0.04	0.25	0.01	0.26	−0.05	0.20	−0.14	0.12						
8.5	0.02	−0.24	0.05	0.19	−0.01	0.20	−0.10	0.14								
9.0	0.02	−0.32	0.05	0.13	−0.03	0.14	−0.13	0.10								
9.5	0.02	−0.42	0.05	0.06	−0.05	0.09										
10.0	0.01	−0.52	0.05	0.00	−0.08	0.05										
10.5	−0.01	−0.61	0.05	−0.02												
11.0	−0.05	−0.63	0.05	0.03												

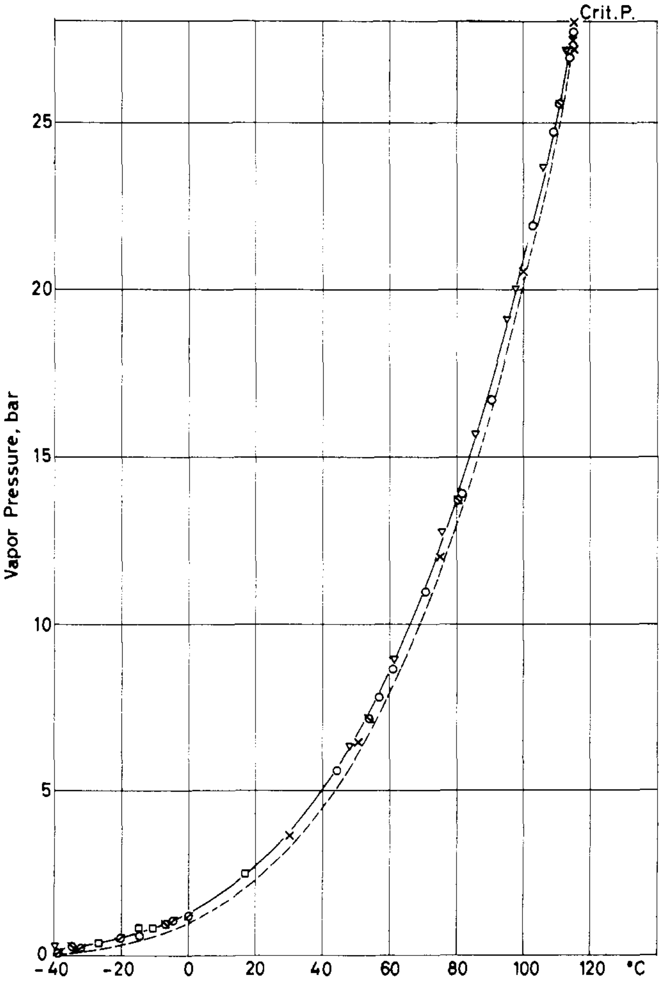

Figure 3. Vapor pressure for octafluorocyclobutane (C_4F_8)

Experimental

∇ Bambach (2)

X Douslin *et al.* (12)

Ø Furukawa *et al.* (14)

⦰ Kletskii *et al.* (21)

O Martin (25)

☐ Whipple (41)

------Calc. BWR

——Calc. EBWR

corresponding error using the modified equation amounts to 5.4%. As stated, the coefficients of both equations are determined from gas phase P-V-T data.

CONCLUSIONS

The improved representation of the residual caloric properties, as well as P-V-T data and the accurate representation of the volumetric behavior in the critical region, justify the extension of the original BWR equation. Obviously, more terms may be put into the equation to get better agreement with the data, but complexity is the penalty. The extended equation presented is not substantially more complicated than the original one, especially since computer calculations are usually made.

The present equation of state is not only developed to calculate the thermodynamic properties of the above-mentioned eight fluorine compounds, but also for many other fluids, such as hydrocarbons, and polar substances like ammonia and hydrogen chloride. For these compounds, the constants for the equation will be published later.

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NOMENCLATURE

A, B, C, D = functions of density

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$ = constants of the BWR equation of state

$A_1, A_2, A_3, A_4, A_5, A_6, A_7, A_8, A_9, A_{10}, \beta$ = constants of the extended BWR equation of state, reduced units

$B(T)$ = second virial coefficient, cm³/gram mole

C_v° = ideal gas state heat capacity at constant volume, J/(gram mole)(° K)

C_p = constant pressure heat capacity, J/(gram mole)(° K)

C_v = constant volume heat capacity, J/(gram mole)(° K)

d = density, d_c = critical density, kg/m^3
e = natural logarithm base, 2.7182818. . .
f = fugacity, bar
G = Gibbs energy, J/gram mole
H = enthalpy, J/gram mole
K, K_1 = integration constants to be determined at arbitrary reference conditions
M = molecular weight
R = universal gas constant 0.083143 (bar)(m^3/kg mole)/(° K) = 8.3143 J/(gram mole)(° K)
S = entropy J/(gram mole)(° K)
T = absolute temperature ° K = t° C + 273.15
V = molal volume, (m^3)/(kg mole)
W = sound velocity, m/s
Z = compressibility factor = PV/RT
α_c = critical parameter $[(T/P)\cdot(dP/dT)]_c$
μ_{JT} = Joule-Thomson coefficient, ° K/bar
c = subscript indicating critical state
r = subscript indicating reduced parameters, e.g., $T_r = T/T_c$, $P_r = P/P_c$, $d_r = d/d_c$
° = superscript indicating standard state

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