International Journal of Thermophysics, Vol. 8, No. 3, 1987

Toward an Analytic Equation of State for Fluorine

K. M. de Reuck[1]

Received July 1, 1986

There are more than 1000 good experimental measurements of fluid fluorine, which cover the range from the triple point to 300 K for pressures up to 23 MPa. The development of an equation of state to fit these data is described. The form of equation used is that of a reduced Helmholtz energy function which includes an equation to represent the behavior of the ideal gas. The coefficients in the equation are determined by a least-squares method where the terms used are selected statistically from a given bank, thus reducing intercorrelation. Two banks of terms were chosen and various fits made using $P\rho T$ data alone, and multiproperty fits with both banks. The serious consequence of using $P\rho T$ data alone is demonstrated, and the difference in quality between the two banks is described. The problems of inconsistency between the single-phase and the saturated density data are discussed. New equations are given which represent the ideal-gas properties.

KEY WORDS: equation of state; fluorine; ideal-gas properties; multiproperty fitting.

1. INTRODUCTION

A large program of experimental measurement of thermodynamic properties of fluorine was carried out at the NBS, Boulder, more than 10 years ago. At that time extensive tables of the properties were published by Prydz and Straty [1], who used a network of isotherm and isochore polynomials together with a truncated virial equation to represent the $P\rho T$ data. An equation of state to represent all these data to within their experimental accuracy has not so far been developed.

---

[1] Imperial College Thermophysical Properties Data Centre, Department of Chemical Engineering and Chemical Technology, Imperial College of Science and Technology, London SW7 2BY, United Kingdom.

0195-928X/87/0500-0375$05.00/0

Fluorine is the only member of the halogen group for which there is an adequate set of measurements, and because of the hazardous nature of these substances, additional measurements are not likely to be made. A good equation of state for fluorine is therefore needed in order both to improve the prediction of other members of the group and to simplify computer calculations for design processes.

The work presented here describes a number of multiproperty fits of the data to different forms of analytic equations of state.

2. SELECTED DATA

Since the measurements made at the NBS, Boulder, are so extensive, and are of known high accuracy, it is these data which have mainly been considered here for the purpose of fitting an equation of state.

2.1. Critical Point

There is only one reported attempt to measure the value of the critical temperature, which was by Cady and Hildebrand [2] in 1930. Their report states that they "made no extended efforts to obtain reproducible results" and concluded that "an approximate value of the critical temperature is, therefore, 144 K." There are no experimental measurements of either the critical pressure or density.

There are two values of the critical temperature and density reported in the literature, which were both estimated from the single-phase $P\rho T$ data of Prydz and Straty [1]. Goodwin [3] estimated the critical constants by fitting the temperature as a function of the saturated densities, for temperatures above 120 K. The densities were found by extrapolating a preliminary equation of state to intersect with the vapor pressure curve. Later, Prydz and Straty repeated the method, but this time the individual pseudo-isochores were extrapolated to the vapor pressure curve. It is this last set of values,

$$T_c = 144.31 \pm 0.05 \text{ K}$$

$$\rho_c = 0.01510 \pm 0.000004 \text{ mol} \cdot \text{cm}^{-3}$$

which has been chosen for use here. The value for P_c is that calculated from the vapor pressure curve of Prydz and Straty using the chosen value for T_c and is

$$P_c = 5.215 \text{ Pa}$$

2.2. Two-Phase Data

More than 120 measurements of the vapor pressure were made by Straty and Prydz [4] using their $P\rho T$ pressure measuring system together with the gasometer pressure gauges. Other measurements in the literature show considerable systematic deviations from these data.

The saturated vapor density has not been measured but there are several published sets of measurements of saturated liquid densities, which deviate systematically from one another and, in some cases, by large amounts.

Prydz and Straty [1] obtained data for both saturated densities by fitting the first few points of each experimental pseudo-isochore to a low-order polynomial and then extrapolating these to intersect with their vapor pressure curve. These extrapolated values were finally fitted to separate equations as functions of temperature. The saturated vapor pressure and density values chosen for use here were taken, at 2 K intervals, from their Table 15 in Ref. 1.

2.3. Single-Phase Data

The major set, of more than 1000 experimental $P\rho T$ measurements by Prydz and Straty [1], covers the range from 54 K, near the triple point, to 300 K, approximately $2T_c$, for pressures up to 23 MPa. A gas expansion method was used similar to that used previously by Goodwin [5] for hydrogen and Weber [6] for oxygen.

More than 100 measurements of the heat capacity at constant volume were made by Prydz and Goodwin [7] using a calorimeter and cryostat which had already been used for similar measurements on oxygen [8]. The measurements were made in the compressed gaseous and liquid region along 11 pseudo-isochores for temperatures from 80 to 300 K and for pressures up to 23 MPa.

Straty and Younglove [9] made 14 measurements of the speed of sound in the liquid along two isotherms, before a destructive reaction in the cell terminated the experiment. They estimated the uncertainty in the measurements to be less than ±0.05%.

3. FORM OF THE EQUATION OF STATE

The form of equation chosen is in terms of a reduced Helmholtz function written as

$$\frac{A}{RT} = \alpha(\omega, \tau) + \ln(\omega/\omega_0) + \alpha^{\mathrm{id}}(\tau) \tag{1}$$

where the function $\alpha(\omega, \tau)$ represents the difference between the reduced Helmholtz energy of the real and that of the ideal gas at the point (ω, τ). If the entropy and enthalpy are taken to be zero at an arbitrary reference point (P_0, T_0) in the ideal gas, then the density-dependent part of the ideal gas is represented by $\ln(\omega/\omega_0)$ and the temperature-dependent part by the function $\alpha^{\mathrm{d}}(\tau)$. The dimensionless variables used are $\omega = \rho/\rho_{\mathrm{c}}$ and $\tau = T_{\mathrm{c}}/T$. The ideal-gas properties are discussed in Section 4.

3.1. Choice of the "Bank" of Terms

Prydz and Straty [1] reported that an attempt was made to fit the single-phase $P\rho T$ data to an equation of state which had been used for other cryogenic fluids, but they were unable to obtain a representation of the data to within its precision, in particular in the critical region. Instead, they fitted a low-density equation, in terms of the second and third virial coefficient for densities up to 0.0060 $\mathrm{mol \cdot cm^{-3}}$, and for higher densities, 70 isotherm polynomials were used.

The method of fitting which has been chosen for use here is that described by de Reuck and Armstrong [10]. Briefly, this is a search procedure, based on a weighted linear least-squares method, which selects from an initial set of terms only those which are statistically important. The method was initially developed by Wagner [11] for determining vapor pressure equations.

An early fit was made using a bank of 50 terms similar to that used successfully for propylene [12]. This did not result in a satisfactory equation, so the bank was extended to 63 terms. This led to an improvement in the representation of the $P\rho T$ data, but the deviations of the C_{v} data were considerably outside their precision, and negative pressures were calculated at low temperatures when applying the Maxwell criterion for saturation properties.

Several changes were therefore made to the bank, which was enlarged to a total of 112 terms, of which the last 12 were designed to be useful in the critical region. The new functional form of the real part of the reduced Helmholtz energy is therefore

$$\alpha(\omega, \tau) = \sum_{i=1}^{\mathrm{I1}} \sum_{j=1}^{\mathrm{J1}} n_{ij} \omega^{\alpha_i} \tau^{(\beta_j - 1)/2} + e^{-\omega^2} \sum_{i=\mathrm{I1}}^{\mathrm{I2}} \sum_{j=\mathrm{J1}}^{\mathrm{J2}} n_{ij} \omega^{\gamma_i} \tau^{(\delta_j - 1)} + \sum_{i=\mathrm{I2}}^{\mathrm{I3}} \sum_{j=\mathrm{J2}}^{\mathrm{J3}} n_{ij} e^{-\varepsilon_i \omega^2/2} \omega^{\varepsilon_i} \tau^{(\eta_j - 1)} \tag{2}$$

where the α_i, β_j, γ_i, δ_j, ε_i, and η_j could be selected at the start of any fitting process.

Since it is common to find that for an analytic equation of state, in the near-critical region, the isotherms have pressures which are too low for gas densities and too high for liquid densities, the third set of terms was designed to compensate for this. Along an isotherm these terms make no contribution to the pressure at the critical density and also tend to zero at both low and high densities. The temperature exponents of these terms were made large so that the derivatives needed for C_v, i.e., $(\partial^2\alpha/\partial\tau^2)_\omega$, would also be large near the critical point, as described by Schmidt and Wagner [13]. The two banks of terms selected are as follows.

Bank A	Bank B
$\alpha_i = i$ for $i = 1, 2, 3, \ldots, 9$	$\alpha_i = i$ for $i = 1, 2, 3, \ldots, 10$
$\beta_j = j$ for $j = 1, 2, 3, \ldots, 5$	$\beta_j = j$ for $j = 1, 3, 5, \ldots, 11$
$\gamma_i = i$ for $i = 1, 2, 3, \ldots, 11$	$\gamma_i = i$ for $i = 1, 3, 5, \ldots, 15$
$\delta_j = j$ for $j = 2, 3, 4, \ldots, 6$	$\delta_j = j$ for $j = 2, 3, 4, \ldots, 6$
$\varepsilon_i = i$ for $i = 16, 26, 36, 46$	$\varepsilon_i = i$ for $i = 16, 26, 36, 46$
$\eta_j = j$ for $j = 10, 15, 20$	$\eta_j = j$ for $j = 10, 15, 20$

3.2. Functions to be Minimized

At this stage it was decided to fit only those properties which are linear in terms of the coefficients, that is, 1017 $P\rho T$ data points, 111 $C_v\rho T$ points, and 47 $P_\sigma\rho^l\rho^g T_\sigma$ points from the coexistence curve. The following sums of weighted squares to be minimized are

$$S_1^2 = \sum_{m=1}^{M1} W1_m\{(Z_m - 1)/\omega_m - [\partial\alpha(\omega_m, \tau_m)/\partial\omega]_\tau\}^2 \tag{3}$$

$$S_2^2 = \sum_{m=1}^{M2} W2_m \left\{\frac{(C_{v,m} - C^{\mathrm{id}}_{v,m})}{R\tau_m^2} + [\partial^2\alpha(\omega_m, \tau_m)/\partial\tau^2]_\omega\right\}^2 \tag{4}$$

$$S_3^2 = \sum_{m=1}^{M3} W3_m \left\{\frac{P_{\sigma,m}}{RT_{\sigma,m}}\left(\frac{\rho^l_m - \rho^g_m}{\rho^l_m\rho^g_m}\right) - \ln\left(\frac{\rho^l_m}{\rho^g_m}\right) - [\alpha(\omega^l_m, \tau_m) - \alpha(\omega^g_m, \tau_m)]\right\}^2 \tag{5}$$

The weights W1, W2, and W3, which are in inverse proportion to the variances, were calculated for each point, from the experimental uncertainties in the measured properties, using the equation for the effective variance given by McCarty [14]. As derivatives of the surface with respect to temperature and density are needed to calculate the effective variances, the weights were recalculated before each fit, using an equation from a previous fit with the same bank of terms.

However, the fitting process is particularly sensitive to the weights which are used, and it is only the experimenter who can make accurate estimates of the errors of each parameter for each point. The correlator has to make a judgment from the information provided.

For weights W1 and W2 the errors for the temperature over the range are given; for W1 the errors for the pressure are tabulated, and for W2 the errors for C_v at each point are given. But for both W1 and W2 it is difficult to estimate the error in the density. As the saturation curve values used are smoothed data, W3 was given the same value for each point, and this value was kept smaller than that of W1 or W2.

4. IDEAL-GAS PROPERTIES

Tables of the thermodynamic properties of the ideal gas have been published in JANAF [15] in 1960, by Prydz and Straty [1] in 1973, and by Glushko et al. [16] in 1978. Prydz and Straty recalculated the properties because new measurements of the dissociation energy had been published in 1969 by Dibeler et al. [17] which superceded the values used in the JANAF tables. The tables by Glushko et al. have all been recalculated using the most recent critically selected values for all the required constants, and so their choice of constants has been used here.

4.1. Isobaric Heat Capacity

The tables of Glushko et al. list only values of the ideal-gas properties at 100 K intervals, starting at 100 K, but for the calculation of tables for the real fluid and for use in computer packages, it is necessary to have an equation which represents the ideal-gas heat capacity over the temperature range 50 to 300 K. Therefore values of C_p^{id}/R, at 5 K intervals, were calculated from the equations given by Prydz and Straty [1] but using the values from Glushko et al. for the relevant molecular constants, together with the values for the gas constant and the constant relating wave-number and energy, taken from the CODATA Recommended Key Values for Thermodynamics [18].

These 90 data points, from 50 to 500 K, were then fitted to an equation using Wagner's [11] selection method as described by de Reuck and Armstrong [10]. The equation selected was

$$\frac{C_p^{id}}{R} = f_1 + f_2/T^2 + f_3 T^3 + f_4 T^5 + f_5 \frac{u^2 e^u}{(e^u - 1)^2} \tag{6}$$

where $u = f_6/T$. The coefficients f_i are listed in Table I.

Table I. Numerical Values of the Coefficients f_i in Eq. (6)

i	f_i
1	3.50107509
2	-1.44978015
3	$2.55399748 \times 10^{-10}$
4	$-3.55716062 \times 10^{-16}$
5	1.00686930
6	1.2861326×10^{3}

The standard deviation of the data points from Eq. (6) is 2×10^{-5}. The difference between the values for C_p^{id} given by Glushko et al. and those calculated from Eq. (6) are all positive, but the maximum difference at 300 K is only $0.003\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. However, the differences continue to increase with rising temperature. The maximum difference between the values of Prydz and Straty and those calculated from Eq. (6) is only $\pm 0.0005\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

From the form of the equation it is clear that it should not be extrapolated far outside the temperature range of the fitted data, since as $T \to 0$ the value of $C_p^{id}/R \to \infty$, and for temperatures above about 1000 K the value of C_p^{id}/R will continue to rise indefinitely.

4.2. Entropy and Enthalpy

Since the entropy and enthalpy do not have absolute values it is necessary to choose a zero reference state of (P_0, T_0) from which the differences in entropy and enthalpy can be calculated by the appropriate integration of Eq. (6).

The resulting equations are, for entropy,

$$\frac{S^{id}(P, T) - S^{id}(P_0, T_0)}{R} = \left\{ f_1 \ln T - \frac{f_2}{2T^2} + \frac{f_3 T^3}{3} + \frac{f_4 T^5}{5} + f_5 \left[\frac{ue^u}{e^u - 1} - \ln(e^u - 1) \right] \right\}_{T_0}^{T} \tag{7}$$

and, for enthalpy,

$$\frac{H^{id}(T) - H^{id}(T_0)}{R} = \left[f_1 T - \frac{f_2}{T} + \frac{f_3 T^4}{4} + \frac{f_4 T^6}{6} + \frac{f_5 f_6}{(e^u - 1)} \right]_{T_0}^{T} \tag{8}$$

For the temperature range 100 to 300 K the differences between the entropy given by Glushko et al. and that calculated from Eq. (7) are all negative with a maximum of $-0.006\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 100 K; and those of Prydz and Straty are all positive with a maximum of $0.01\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 300 K. The differences for the enthalpy are $\pm 0.3\ \mathrm{J \cdot mol^{-1}}$ for Glushko et al. and $\pm 0.02\ \mathrm{J \cdot mol^{-1}}$ for Prydz and Straty.

5. COMPARISONS

A measure of the quality of a fit of N data points to a surface represented by M coefficients is given by

$$\bar{\chi} = \left[\sum_{n=1}^{N} W_{n,x}(X_{n,\mathrm{exp}} - X_{n,\mathrm{calc}})^2/(N - M - 1) \right]^{1/2}$$

where X represents all of the properties being fitted, and W their weights. For a good fit $\bar{\chi}$ should be of the order of unity.

The quality of fit of a set of N data points for a single property, X, can be represented by the "relative deviation," defined as

$$\mathrm{RD} = \left[\frac{1}{N} \sum_{n=1}^{N} \left(\frac{(X_{n,\mathrm{exp}} - X_{n,\mathrm{calc}})}{X_{n,\mathrm{exp}}} 100 \right)^2 \right]^{1/2}$$

These two parameters, $\bar{\chi}$ and RD, are used to describe the different fits.

5.1. Equations Resulting from Different "Banks"

A number of fits were made using identical sets of input data to both banks of terms. The pattern of results was similar for both A and B, but in all cases the $\bar{\chi}$ value for A was always smaller than for B for the same data set.

For both A and B, when $P\rho T$ data alone were fitted, $\bar{\chi}$ was less than 1, which suggests that either the data were overfitted or the estimated errors were too large. However, the deviations of the experimental C_v values from those calculated from these fits were very large, particularly in the dense liquid, where they increased to -100%, and in the near-critical region, where they were $+22\%$. A similar, although smaller, effect was found by Weber [19] when comparing experimental C_v measurements for ethylene with an early form of equation of state.

When the experimental C_v data were included in the fit the $\bar{\chi}$ value for both A and B increased to between 1 and 2, but the deviations for the C_v data now lay within the experimental errors for the majority of the points.

The terms selected by both A and B, when the C_v data were added, included the same three terms from those which had been designed for the critical region.

For both A and B the maximum density exponent selected for the polynomial terms was 8, and that for the exponential terms was 9.

Since A always gave a lower value for $\bar{\chi}$ than did B, all further discussion refers only to bank A.

5.2. Saturation Curve

Saturation properties were first added to the fit, called fit (3), with a very low weight of 1×10^{-3}. This resulted in almost no change in the fit to the $P\rho T$ or C_v data, but all the vapor pressure deviations were positive, although small, with a maximum value of 0.018 MPa at 144 K. The critical point calculated from this fit, that is, the point on the surface where $(\partial P/\partial \rho)_T$ and $(\partial^2 P/\partial \rho^2)_T$ were both zero, was given by $T_c = 145.500$ K, $P_c = 5.460$ MPa, and $\rho_c = 0.01493$ mol · cm^{-3}. The saturated liquid and vapor density deviations were all quite small except very close to the critical point.

Another fit, called fit (5), was made with the weights on the saturation properties increased by a factor of 10^4, when two more terms were selected and the overall fit improved. However, the vapor pressure deviations were now all negative and very much larger, particularly at the higher temperatures, where they were of the order of 0.3 MPa. Also the saturated vapor density deviations were all negative and increased steadily to -30% just below the critical point. The calculated value of the critical point from this fit was $T_c = 144.391$ K, $P_c = 5.225$ MPa, and $\rho_c = 0.01520$ mol · cm^{-3}.

A comparison of these two fits is shown in Table II, and superficially, fit (5) is superior to fit (3). However, the very large deviations of fit (5) from the saturation data, particularly the vapor pressures, which are experimental measurements of a high accuracy, make fit (3) the more reliable of the two. There is some inconsistency between the relatively good fit of the saturation data for fit (3), with its rather high critical temperature, and the very poor fit of the saturation data for fit (5), with the apparently good critical temperature. This inconsistency must be resolved before a satisfactory equation can be finalized.

The remaining comparisons are made with the equation resulting from fit (3). The terms selected by this fit for use in Eq. (2) are listed in Table III.

5.3. Isochoric Heat Capacity

A comparison of the experimental C_v values with those calculated using the equation from fit (3) shows deviations of less than $\pm 1.5\%$ for all

Table II. Comparisons of Fit (3) with Fit (5)[a]

Region	Fit (3), 18 coefficients, $\bar{\chi} = 1.397$		Fit (5), 20 coefficients, $\bar{\chi} = 1.340$	
	RD of P	RD of ρ	RD of P	RD of ρ
Gas 1	0.239	0.252	0.145	0.162
Gas 2	0.170	0.080	0.144	0.064
Liq. 1	3.920	0.079	2.252	0.053
Liq. 2	7.822	0.038	7.784	0.025
Crit.	0.188	1.209	0.123	0.562
All	3.161	0.421	2.668	0.212

[a] Gas 1, $\rho/\rho_c < 1$; Gas 2, $\rho/\rho_c > 1$ and $T/T_c < 1$; Liq. 2, $P/P_c < 1$; Liq. 1, $P/P_c > 1$ and $T/T_c < 1$; Crit., $1.5 > \rho/\rho_c > 0.66$ and $1.25 > T/T_c > 0.8$.

except 8 of the 112 data points. Two of the larger deviations are very close to the critical point, where the maximum is +5.37%. The RD of all the fitted points is 1.07.

5.4. Speed of Sound in the Liquid

Deviations between the experimental values of the speed of sound and those calculated using the equation from fit (3) are shown in Fig. 1. A different trend is shown by those calculated by Straty and Younglove [9]. When the experimental pressure was used for calculation the RD was 0.87, but this increased to 0.93 when the density values derived by Straty and Younglove were used.

Table III. Terms Selected by Fit (3) for Eq. (2)

α	β	γ	δ	ε	η
1	2	1	2	16	10
1	3	1	3	16	15
2	3	1	4	16	20
3	1	1	5		
5	4	1	6		
7	3	2	4		
		2	5		
		4	2		
		6	4		

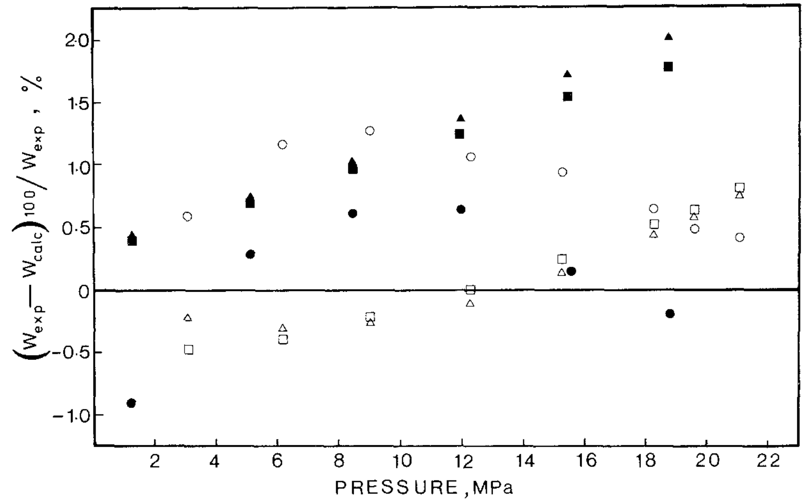

Fig. 1. Comparisons of experimental results for the speed of sound in the liquid with prediction. Open symbols, 130 K; filled symbols, 110 K. (□) Values calculated from fit (3) using experimental pressures [9]; (△) values calculated from fit (3) using densities derived by Straty and Younglove [9]; (○) values calculated by Straty and Younglove [9].

6. CONCLUSIONS

A satisfactory fit to all the experimental data for fluorine can be made using the method of fitting together with the set of terms in "bank" A. However, there are some inconsistencies between the measured single-phase and vapor pressure data and the derived critical point and saturated densities.

An accurate measurement of the critical temperature would be very helpful in resolving these.

Another approach is to calculate saturated densities from the extrapolation of equations of state fitted to limited regions of the surface, rather than extrapolating individual isotherms or isochores. Small differences from the saturated vapor densities of Prydz and Straty [1] were found when extrapolating the virial equation of de Reuck [20] to the same vapor pressure curve.

Alternatively, the experimental vapor pressure data can be fitted nonlinearly, as described by Ahrendts and Baehr [21].

It is important to note the confirmation of Weber's [19] results which showed the necessity for multiproperty fitting of an equation of state if it is to be used to calculate derived properties.

ACKNOWEDGMENT

This work was supported by the Department of Trade and Industry of the United Kingdom.

REFERENCES

1. R. Prydz and G. C. Straty, NBS Technical Note 392, Sept. (1973).
2. G. H. Cady and J. H. Hildebrand, *J. Am. Chem. Soc.* **52**:3839 (1930).
3. R. D. Goodwin, *J. Res. Natl. Bur. Stds.* **74A2**:221 (1970).
4. G. C. Straty and R. Prydz, *Adv. Cryogen. Eng.* **15**:36 (1970).
5. R. D. Goodwin, *J. Res. Natl. Bur. Stds.* **65C**:231 (1961).
6. L. A. Weber, *J. Res. Natl. Bur. Stds.* **74A**:93 (1970).
7. R. Prydz and R. D. Goodwin, *J. Res. Natl. Bur. Stds.* **74A**:661 (1970).
8. R. D. Goodwin and L. A. Weber, *J. Res. Natl. Bur. Stds.* **73A**:15 (1969).
9. G. C. Straty and B. A. Younglove, *J. Chem. Phys.* **58**:2191 (1973).
10. K. M. de Reuck and B. Armstrong, *Cryogenics* **19**:505 (1979).
11. W. Wagner, Fortschr.-Ber. VDI-Z, Reihe 3, No. 39 (1974) (German) [Shortened English translation: Report PC/T15, IUPAC TTPC, London (1977)].
12. S. Angus, B. Armstrong, and K. M. de Reuck, *International Thermodynamic Tables of the Fluid State—7. Propylene* (Pergamon, Oxford, 1980).
13. R. Schmidt and W. Wagner, *Fluid Phase Equil.* **19**:175 (1985).
14. R. D. McCarty, *Experimental Thermodynamics, Vol. II,* B. Le Neindre and B. Vodar, eds. (Butterworths, London, 1968), Chap. 10, p. 513.
15. *JANAF Interim Thermochemical Tables* (Dow Chemical Company, Midland, Mich. 1960).
16. V. P. Glushko et al., *Thermodynamic Properties of Individual Substances* (Nauka, Moscow, 1978) (Russian).
17. V. H. Dibeler, J. A. Walker, and K. E. McCulloh, *J. Chem. Phys.* **10**:4230 (1969).
18. CODATA Recommended Key Values for Thermodynamics 1977, Bull. No. 28 (1978).
19. L. A. Weber, *J. Chem. Eng. Data* **27**:203 (1982).
20. K. M. de Reuck, *High Temp. High Press.* **17**:201 (1985).
21. J. Ahrendts and H. Baehr, *Int. Chem. Eng.* **21**:572 (1981).