A Generalized Equation of State for the Thermodynamic Properties of Polar Fluids

The generalized relationships of Lee and Kesler for the thermodynamic properties of nonpolar fluids have been combined with an accurate equation of state for water which is utilized as the reference substance for polar fluids for reduced temperatures from 0.4 to 2.5 and reduced pressures to 10. The input data required are the critical temperature, critical pressure, acentric factor, and a polarity factor Y obtained from experimental pressure-volume-temperature data. Comparisons between calculated and experimental thermodynamic properties indicate that highly accurate results are obtained by the method of this study for most polar fluids. A modified procedure is presented for the compressibility factors of substances with large acentric factors such as alcohols. Tabulated values of the polar fluid correction terms are presented for the compressibility factor, fugacity coefficient, and enthalpy, entropy, and heat capacity departures for the complete range investigated.

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SCOPE

Accurate generalized procedures for the calculation of thermodynamic properties of fluids and mixtures are required for the design of chemical processes. Suitable analytical procedures are available for nonpolar fluids. For polar fluids, the available equations of state are limited to specific fluids and ranges of conditions, or the procedures have not been presented in analytical form to enable the calculation of derived thermodynamic properties. In this study, a generalized equation of state has been developed for the accurate calculation of the compressibility factor and derived thermodynamic properties of polar fluids for wide ranges of temperature and pressure.

CONCLUSIONS AND SIGNIFICANCE

The relationships of this study enable the accurate calculation of compressibility factors and derived thermodynamic properties of polar fluids in the gaseous and liquid regions for wide ranges of temperature and pressure. Large errors in these properties result for polar fluids at elevated pressures by the use of previously available equations of state for nonpolar fluids.

It is shown that the compressibility factor of a polar fluid can be expressed as a linear relationship in the third and fourth parameters ω and Y and the compressibility factors of a simple fluid ($\omega = 0$), nonpolar reference fluid ($\omega = 0.4$), and water ($\omega = 0.344$, $Y = 1.0$) at constant T_R and P_R. Similar linear relationships are also presented for derived thermodynamic properties, including fugacity coefficients and enthalpy, entropy, and heat capacity departures. These linear relationships are applicable for all the fluids tested in this study, including alcohols, in the gaseous region, and in the liquid region for polar substances with parameters ω and Y less than the values for water. The results of this study can be extended for substances with larger parameters in the liquid region by the inclusion of quadratic terms in ω. The relationships of this study can also be utilized for the calculation of the thermodynamic properties of polar mixtures at elevated temperatures and pressures by the use of effective parameters T_{CM}, P_{CM}, ω_M, and Y_M.

PREVIOUS GENERALIZED RELATIONSHIPS FOR POLAR FLUIDS

Accurate generalized relationships for polar fluids should include four characteristic constants for each substance to account for size and polarity effects (Stipp et al., 1973). Hirschfelder et al. (1958) presented analytical relationships for the reduced density for nonpolar and polar fluids in the gaseous and liquid regions in terms of the reduced temperature and reduced pressure, with the critical compressibility factor and Riedel parameter as third and fourth parameters. Large errors resulted with this approach for water at elevated pressures, and its accuracy for certain regions has been questioned (Johnson, 1981).

For dilute polar gases, Eubank and Smith (1962) extended the correlation of Pitzer et al. (1955) for nonpolar fluids by the inclusion of a fourth parameter involving a reduced dipole group. For polar fluids, Stipp et al. (1973) have expressed the compressibility factor as:

$$Z = Z^{*(0)} + \omega Z^{*(1)} + \chi Z^{*(2)} + \omega\chi Z^{*(3)} + \chi^2 Z^{*(4)} \quad (1)$$

where $Z^{*(0)} \ldots Z^{*(4)}$ are functions of reduced temperature, T_R, and reduced pressure, P_R, and ω is the acentric factor,

$$\omega = -\log P_{RS|T_R=0.7} - 1.00 \quad (2)$$

The polarity factor χ is defined in terms of the acentric factor as

$$\chi = \log P_{RS|T_R=0.6} + 1.70\omega + 1.552 \quad (3)$$

Values of the polar fluid correction terms were established for the gaseous and liquid regions for reduced temperatures from 0.8 to 1.15 and reduced pressures from 0.2 to 6.0 by the use of experimental pressure-volume-temperature (PVT) data for 10 polar fluids.

For the reduced saturated liquid volume of polar fluids, Halm and Stiel (1970) developed the relationship

$$v^* = \frac{P_C v_S}{RT_C} = v^{*(0)} + \omega v^{*(1)} + \chi v^{*(2)} + \omega^2 v^{*(3)} + \chi^2 v^{*(4)} + \omega\chi v^{*(5)} \quad (4)$$

where $v^{*(0)}, \ldots v^{*(5)}$ are tabulated functions of reduced temperature for T_R from 0.56 to 1.0. A linear relationship was also developed for the compressibility factor of saturated vapors for polar fluids with positive values of χ. Kalback and Starling (1976) presented analytical relationships for the compressibility factor of nonpolar and polar gases and saturated liquids. The compressibility factor was expressed as a power series in reduced density, with the coefficients of the series as functions of ω and χ. Good results were obtained for a number of substances including several polar fluids.

For nonpolar fluids, Starling (1973) developed a generalized, modified Benedict-Webb-Rubin equation of state with ω as the third parameter. Nishiumi (1980) extended this relationship to polar fluids by the inclusion of two additional terms involving three constants which were determined from vapor pressure values and from second virial coefficient data or dipole moments. Good results were obtained by this approach for the thermodynamic properties of polar fluids, except for T_R between 1 and 1.3 and P_R between 1 and 3. The approach was not applicable for alcohols. Nishiumi and Robinson (1981) modified the procedure for the compressibility factor to include only a fourth parameter for polar fluids, ψ_E, obtained from second virial coefficients. The correction for the compressibility factor of polar fluids was found to involve a linear term in ψ_E and a nonlinear term in $\omega\psi_E$. Tables of values of the correction terms were presented for T_R from 0.4 to 4.0 and P_R to 40.0. Comparable results were obtained by this approach as with the original six-parameter equation, but large errors resulted for the compressibility factor for several polar fluids including water in the liquid region.

Gmehling et al. (1979) utilized a perturbed-hard chain model which included the formation of chemical dimers to develop an equation of state for polar fluids with four adjustable molecular parameters. Perturbation theory was also used to develop equations of state for polar fluids by Yokoyama et al. (1983) and by Miyano (1983). In the latter study, the dimensionless parameters of the equation of state were related to ω and χ. Mathias (1983) proposed a modified Redlich-Kwong equation of state for polar fluids which utilizes the critical temperature, critical pressure, acentric factor, and a polarity parameter determined from experimental vapor pressure data.

DEVELOPMENT OF THE GENERALIZED EQUATION OF STATE FOR POLAR FLUIDS

The approach utilized in this study for polar fluids is an extension of the procedure of Lee and Kesler (1975). For nonpolar fluids the Lee-Kesler generalized equation of state enables the accurate calculation of the compressibility factor and derived thermodynamic properties for reduced temperatures from 0.3 to 4 and reduced pressures from 0.01 to 10. The Lee-Kesler generalized equation of state is expressed in the form of a modified Benedict-Webb-Rubin equation as

$$Z = 1 + \frac{B}{V_R} + \frac{C}{V_R^2} + \frac{D}{V_R^5} + \frac{c_4}{T_R^3 V_R^2}\left(\beta + \frac{\gamma}{V_R^2}\right)\exp\left(\frac{-\gamma}{V_R^2}\right) \quad (5)$$

where

$$B = b_1 - b_2/T_R - b_3/T_R^2 - b_4/T_R^3 \quad (6)$$

$$C = c_1 - c_2/T_R + c_3/T_R^3 \quad (7)$$

$$D = d_1 + d_2/T_R \quad (8)$$

and $V_R = P_C v/RT_C$.

The constants of this equation are presented for a simple fluid with $\omega = 0$ and a reference fluid with $\omega^{(r)} = 0.3978$. These constants were determined by the use of experimental PVT, enthalpy, and second virial coefficient data for argon, krypton, and hydrocarbons.

TABLE 1. CONSTANTS OF EQS. 13 AND 15

i	A_{i1}	A_{i2}	A_{i3}	A_{i4}	A_{i5}	A_{i6}	A_{i7}
1	29.492937	−5.1985860	6.8335354	−0.1564104	−6.3972405	−3.9661401	−0.69048554
2	−132.13917	7.7779182	−26.149751	−0.72546108	26.409282	15.453061	2.7407416
3	274.64632	−33.301902	65.326396	−9.2734289	−47.740374	−29.142470	−5.1028070
4	−360.93828	−16.254622	−26.181978	4.3125840	56.323130	29.568796	3.9636085
5	342.18431	−177.31074	0	0	0	0	0
6	−244.50042	127.48742	0	0	0	0	0
7	155.18535	137.46153	0	0	0	0	0
8	5.9728487	155.97836	0	0	0	0	0
9	−410.30848	337.31180	−137.46618	6.7874983	136.87317	79.847970	13.041253
10	−416.05860	−209.88866	−733.96848	10.401717	645.81880	399.17570	71.531353

$a_1 = 1{,}857.065$; $a_2 = 3{,}229.12$; $a_3 = -419.465$; $a_4 = 36.6649$; $a_5 = -20.5516$; $a_6 = 4.85233$.

TABLE 2. AVERAGE % ERRORS FOR POLAR FLUIDS

Substance	Range		No. of Points	Average % Error Z		Sources*
	T_R	P_R		This Study	Normal Fluids	
		Superheated Vapor and Saturated Vapor				
Ammonia	0.54–1.43	0.00–9.86	35	1.15	5.33	1, 2
Acetone	1.00–1.06	2.08–7.84	29	1.08	15.38	3
Methyl Fluoride	1.01–1.33	0.37–2.70	55	1.92	5.71	4, 5
Methyl Chloride	0.78–1.20	0.12–4.70	62	1.00	2.44	6
Hydrogen Chloride	0.49–1.07	0.00–2.51	65	1.97	6.22	7, 8, 9
Ethylene Oxide	0.67–1.02	0.01–0.86	28	1.77	1.97	10
CH_2F_2 (R-32)	0.85–1.35	0.15–3.15	27	1.79	3.70	11
		Compressed Liquid and Saturated Liquid				
Ammonia	0.54–0.94	0.00–9.86	50	1.22	18.10	1, 2, 12, 13
Acetone	0.58–0.99	0.02–10.78	55	1.22	14.92	3, 8
Methyl Chloride	0.74–0.99	0.16–4.73	46	0.83	5.61	6
Hydrogen Chloride	0.49–1.0	0.00–1.02	92	1.39	19.18	7, 8, 9, 14
R-32	0.67–0.98	0.02–3.45	39	1.61	15.10	11
Ethylene Oxide	0.67–0.98	0.02–0.9	11	1.27	10.99	10

* 1. Din (1962)
2. Haar and Gallagher (1978)
3. Keller and Stiel (1977)
4. David et al. (1952)
5. Michels et al. (1952)
6. Hsu and McKetta (1964)
7. DaPonte and Stavely (1981)
8. International Critical Tables (1928)
9. Thomas (1962)
10. Walters and Smith (1952)
11. Malbrunot et al. (1968)
12. Kumagai and Toruimi (1971)
13. Zander and Thomas (1979)
14. Franck et al. (1962)

The compressibility factor of a nonpolar fluid with an intermediate acentric factor is calculated as

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}}(Z^{(r)} - Z^{(0)}) \tag{9}$$

where $Z^{(0)}$ and $Z^{(r)}$ are the compressibility factors of the simple and reference fluids, respectively, at a specified reduced temperature and pressure. Relationships are also presented for derived thermodynamic properties as functions of T_R and V_R, including the reduced enthalpy departure $(H - H^0)/RT_C$, reduced entropy departure $(S - S^0)/R$, fugacity coefficient f/P, and the reduced heat capacity departures $(C_V - C_V^0)/R$ and $(C_P - C_P^0)/R$. The derived thermodynamic properties can be calculated from the values of $V_R^{(0)}$ and $V_R^{(r)}$ at T_R and P_R by the use of relationships of the form of Eq. 8. Tabulated functions were also presented for the fugacity coefficient and the reduced enthalpy, entropy, and constant-pressure heat capacity departures for the complete ranges of reduced temperature and reduced pressure.

TABLE 3. VALUES OF T_C, P_C, ω, AND Y FOR POLAR FLUIDS

Substance	T_C K	P_C MPa	ω	Y
Ammonia	405.6	11.30	0.252	0.739
Acetone	508.2	4.70	0.305	0.652
Ethylene Oxide	469.0	7.19	0.202	0.565
Hydrogen Chloride	324.6	8.31	0.126	0.565
Methyl Fluoride	317.8	5.88	0.191	0.739
Methyl Chloride	416.25	6.68	0.152	0.304
CH_2F_2 (R-32)	351.56	5.83	0.278	0.696
Water	647.29	22.088	0.344	1.00
Ethanol	514.0	6.13	0.641	0.213
Methanol	512.58	8.10	0.559	0.652
iso-Propanol	508.4	4.76	0.663	0.0521
n-Propanol	536.7	5.17	0.626	−0.0521

In this study the following linear approximation to Eq. 1 has been utilized for the compressibility factor of a polar fluid at a particular reduced temperature and pressure:

$$Z = Z^{(0)} + \omega Z^{(1)} + YZ^{(2)} \tag{10}$$

where $Z^{(0)}$, $Z^{(1)}$, and $Z^{(2)}$ are functions of T_R and P_R. This linear relationship has been found to be satisfactory for polar fluids with acentric and polarity factors less than the values for water $(0 < \omega < 0.344, 0 < \chi < 0.023)$. Many polar fluids have parameters in this range, including ammonia, halocarbons, oxides, and ketones. The fourth parameter, Y, of Eq. 10 is determined from PVT data for the fluid.

The functions $Z^{(0)}$ and $Z^{(1)}$ are obtained by the use of the Lee-Kesler equation of state. From Eq. 9,

$$Z^{(1)} = \frac{(Z^{(r)} - Z^{(0)})}{\omega^{(r)}} \tag{11}$$

The value of the fourth parameter Y is taken as 1.0 for water, and the polar fluid correction term at each T_R and P_R is calculated from Eqs. 10 and 11 as

$$Z^{(2)} = Z^{(w)} - (Z^{(0)} + 0.344Z^{(1)}) \tag{12}$$

In order to represent the compressibility factor of water, $Z^{(w)}$, for a wide range of temperatures and pressures it has been found that a more accurate relationship is required than the modified Benedict-Webb-Rubin form. Goin et al. (1977) determined constants of the modified Benedict-Webb-Rubin equation of state for water and found that thermodynamic properties could be predicted with good accuracy only to pressures of about 17 MPa (P_R < 0.78). Similar deviations result for other polar substances from the use of the Benedict-Webb-Rubin equation of state (Gomez-Nieto and Thodos, 1976). Therefore the accurate equation of state

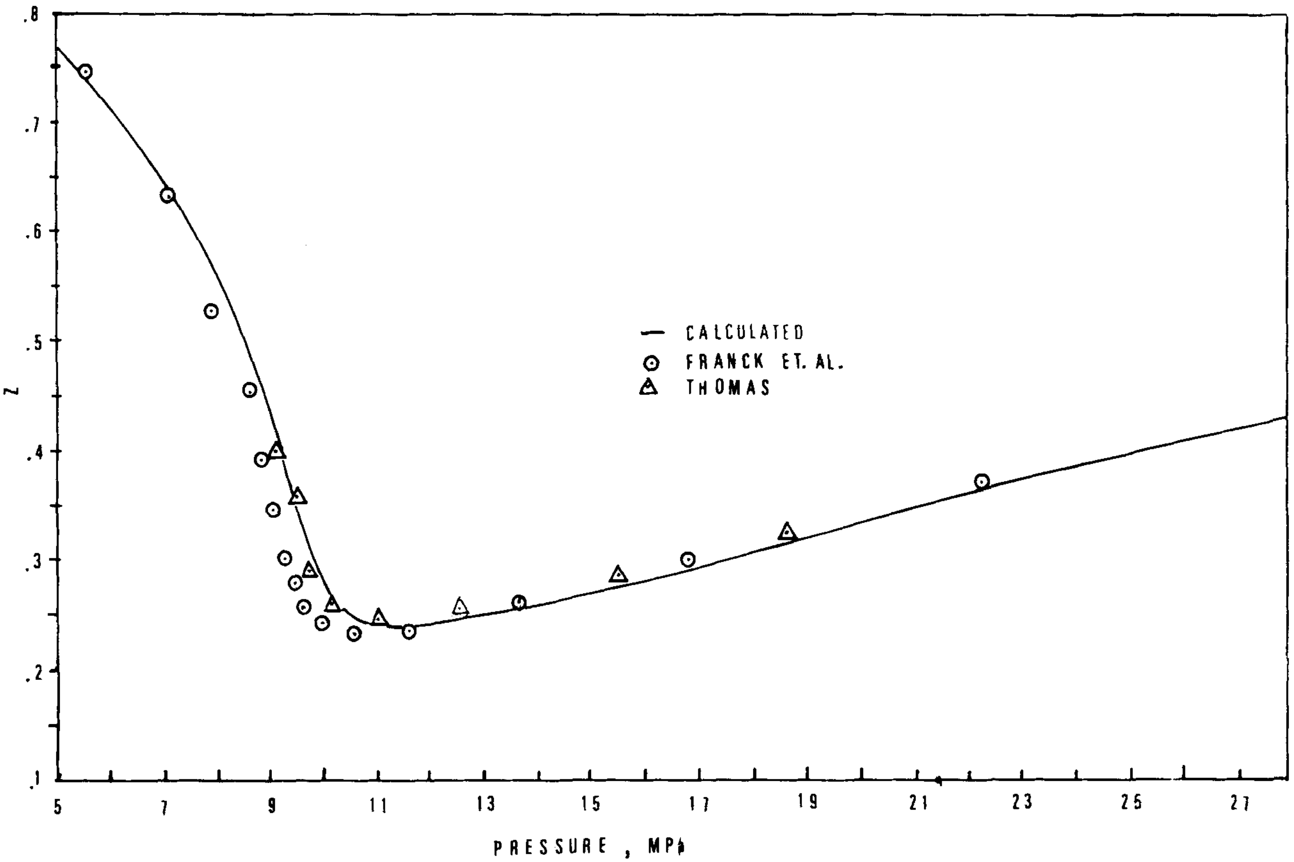

Figure 1. Compressibility factor of hydrogen chloride at 333.15 K.

for water presented by Keenan et al. (1969) has been utilized. This equation enables the calculation of the thermodynamic properties of this substance for reduced temperatures from 0.4 to 2.5 and reduced pressures to 10.0. A similar equation of state has been utilized to represent the thermodynamic properties of ammonia (Haar and Gallagher, 1978).

The value of $Z^{(w)}$ is obtained from the equation of state as

$$Z^{(w)} = \left[1 + \rho_w Q + \rho_w^2 \left(\frac{\partial Q}{\partial \rho_w}\right)_\tau\right] \tag{13}$$

where $Z^{(w)} = P/0.46151\rho_w T$, ρ_w is the density of water, and

$$Q = (\tau - 1.544912) \sum_{j=1}^{7} \left\{(\tau - \tau_{aj})^{j-2} \times \left[\sum_{i=1}^{8} A_{ij}(\rho_w - \rho_{aj})^{i-1} + e^{-4.8\rho_w}(A_{9j} + A_{10j}\rho_w)\right]\right\} \tag{14}$$

In Eq. 14, $\tau = 1{,}000/T$, $\tau_{aj} = 1.544912$ and $\rho_{aj} = 0.634$ ($j = 1$), $\tau_{aj} = 2.5$ and $\rho_{aj} = 1.0$ ($j > 1$). The constants A_{ij} are presented in Table 1.

The Helmholtz free energy for this equation can be represented as

$$A_w = A_w^0 + RT[\ln \rho_w + \rho_w Q] \tag{15}$$

where

$$A_w^0 = \left[\sum_{i=1}^{6} a_i/\tau^{i-1} + 46. \ln T - (1{,}011.249 \ln T)/\tau\right] 18.0153 \tag{16}$$

The coefficients a_1 to a_6 are included in Table 1. The enthalpy and entropy departures of water at specified values of T and P are determined from the value of ρ_w calculated from Eqs. 13 and 14 and the relationships

$$\frac{H_w - H_w^0}{RT} = \left[\rho_w \tau \left(\frac{\partial Q}{\partial \tau}\right)_{\rho_w} + \rho_w Q + \rho_w^2 \left(\frac{\partial Q}{\partial \rho_w}\right)_\tau\right] \tag{17}$$

$$\frac{S_w - S_w^0}{R} = \ln Z^{(w)} - \rho_w Q + \rho_w \tau \left(\frac{\partial Q}{\partial \tau}\right)_{\rho_w} \tag{18}$$

where

$$H_w^0 = \frac{d(A_w^0 \tau)}{d\tau} + RT \tag{19}$$

$$S_w^0 = -R \ln \left(\frac{P}{0.46151T}\right) - \frac{dA_w^0}{dT} \tag{20}$$

The fugacity coefficient of water is obtained as

$$\ln \left(\frac{f}{P}\right)_w = \frac{H_w - H_w^0}{RT} - \frac{S_w - S_w^0}{R} \tag{21}$$

The heat capacity departure of water can be calculated as

$$\left(\frac{C_v - C_v^0}{R}\right)_w = -\rho_w \tau^2 \left(\frac{\partial^2 Q}{\partial \tau^2}\right)_{\rho_w} \tag{22}$$

and

$$\frac{(C_p - C_p^0)_w}{R} = \frac{(C_v - C_v^0)_w}{R} - 1 + \frac{T}{\rho_w^2} \left(\frac{\partial P}{\partial T}\right)_{\rho_w}^2 \Big/ \left(\frac{\partial P}{\partial \rho_w}\right)_T \tag{23}$$

where $C_p^0 = dH_w^0/dT$, and the derivatives of Eq. 23 result from Eq. 13.

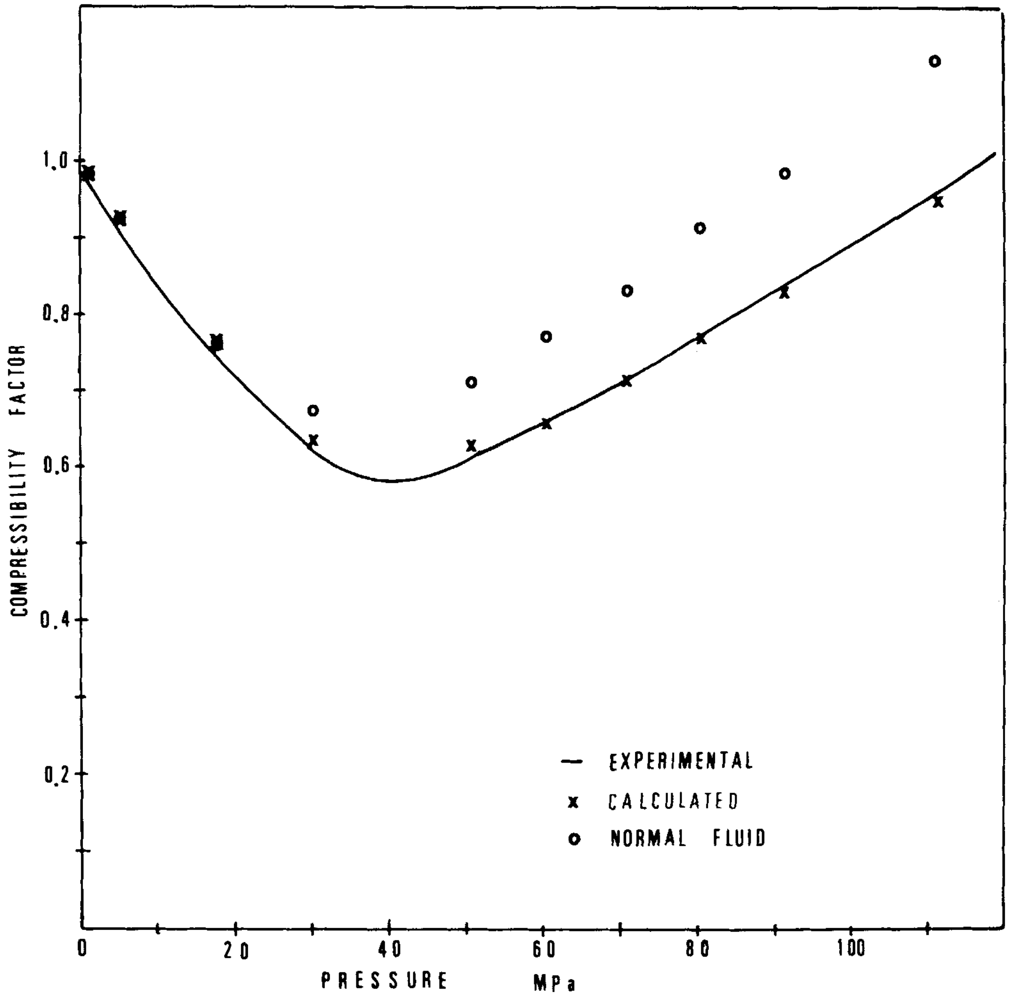

Figure 2. Compressibility factor of ammonia vapor at 520 K.

APPLICATION OF THE EQUATION OF STATE

In order to apply the equation of state for a polar fluid at a particular T_R and P_R, values of $Z^{(0)}$ and $Z^{(r)}$ are initially determined by the solution of the Lee-Kesler relationships for $V_R^{(0)}$ and $V_R^{(r)}$. The value of $Z^{(w)}$ is then obtained by the solution of Eq. 13 for ρ_w with $T = 647.29T_R$, $P = 22.088P_R$. The compressibility factor of the substance results from Eqs. 10–12. The derived properties are calculated in a similar manner from the values of $V_R^{(0)}$, $V_R^{(r)}$, and ρ_w. For example, the enthalpy departure of the fluid is obtained as

$$\Delta H^* = \Delta H^{*(0)} + \omega \Delta H^{*(1)} + Y \Delta H^{*(2)} \tag{24}$$

where $\Delta H^* = (H - H^0/RT_C)$ and

$$\Delta H^{*(1)} = \frac{\Delta H^{*(r)} - \Delta H^{*(0)}}{\omega^{(r)}} \tag{25}$$

$$\Delta H^{*(2)} = \frac{H_w - H_w^0}{R647.29} - \Delta H^{*(0)} - 0.344\Delta H^{*(1)} \tag{26}$$

The values of $\Delta H^{*(0)}$ and $\Delta H^{*(r)}$ are calculated as functions of T_R and $V_R^{(0)}$, and T_R and $V_R^{(r)}$, respectively, by the relationship of Lee and Kesler (1975). The value of $H_w - H_w^0$ is determined from T and ρ_w by Eq. 17.

In order to solve for $V_R^{(0)}$ and $V_R^{(r)}$ from Eq. 5, a procedure based on the approach of Plocker and Knapp (1976) has been utilized. For the liquid region, initial estimates of the roots are obtained from the equation of Chen and Su (1975) for the compressibility factor as a function of T_R and P_R. In the gaseous region for T_R and P_R less than 1.0, the initial value is $Z = 1.0$ (ideal gas). For the solution of Eqs. 13 and 14 for ρ_w, the false position method (Carnahan et al., 1969) has been found to be effective for the vapor and liquid phases. Good initial estimates of the roots are required for this method. For the liquid region, the initial values of ρ_w are determined from the relationships of Yen and Woods (1966). Ideal gas behavior is assumed initially for the gas at low pressures. For the gas at high pressures, approximate roots are obtained from the steam tables of Keenan et al. (1969). Because of the limitations of the ranges of Eqs. 13 and 14, the equation of state of this study is suitable for reduced temperatures from 0.4 to 2.5 and reduced pressures to 10.

For the saturated liquid, the reduced volume is expressed as

$$V_{RS} = V_{RS}^{(0)}(T_R) + \omega V_{RS}^{(1)}(T_R) + Y V_{RS}^{(2)}(T_R) \tag{27}$$

where

$$V_{RS}^{(1)} = \frac{(V_{RS}^{(r)} - V_{RS}^{(0)})}{\omega^{(r)}} \tag{28}$$

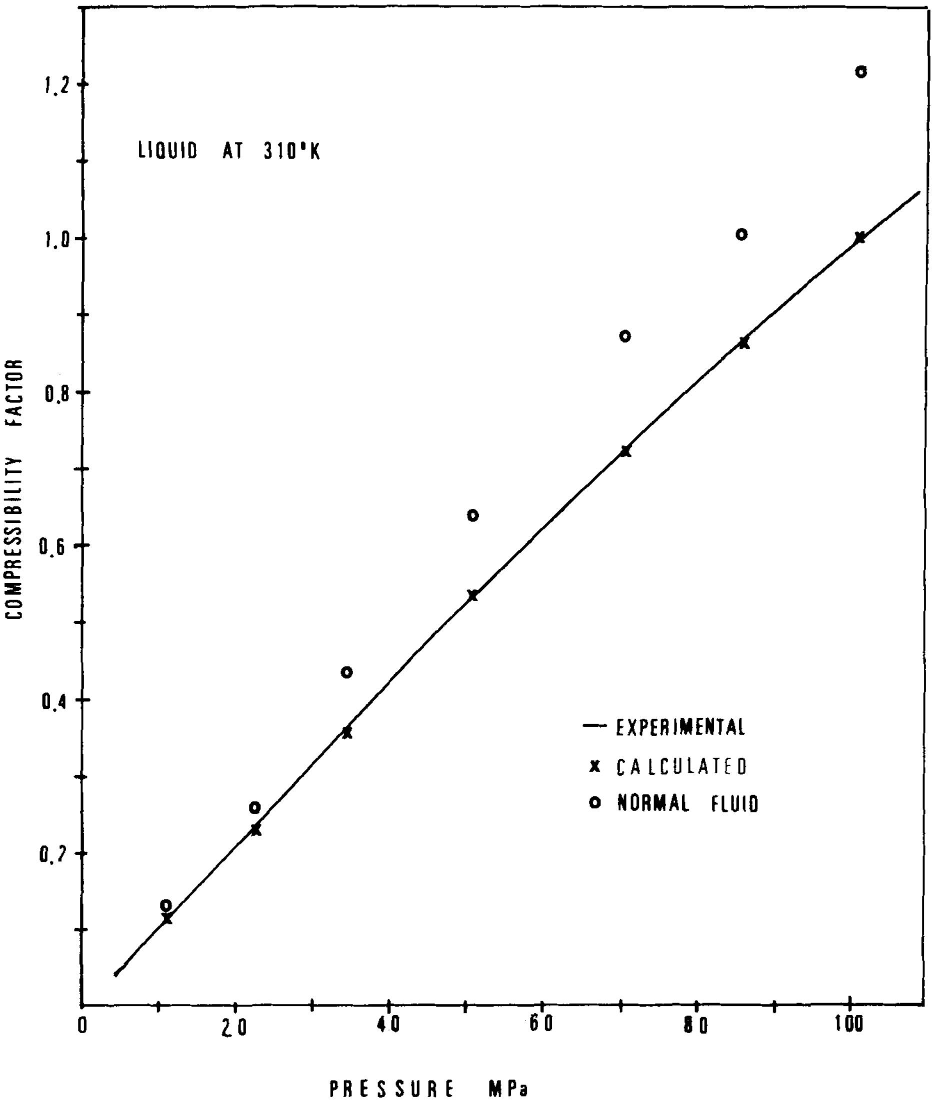

Figure 3. Compressibility factor of ammonia liquid at 310 K.

The values of $V_{RS}^{(0)}$ and $V_{RS}^{(r)}$ in Eq. 27 are determined by the application of Eq. 5 at T_R and the reduced vapor pressures of the simple fluid and reference fluid respectively. The value of $V_{RS}^{(2)}$ is then calculated from the solution of Eqs. 13 and 14 for ρ_{wS} at $T = 647.29T_R$ and the vapor pressure of water at T as follows:

$$V_{RS}^{(2)} = \frac{0.0739}{\rho_{wS}} - (V_{RS}^{(0)} + 0.344V_{RS}^{(1)}) \tag{29}$$

The vapor pressures of the reference fluids are determined from the analytical relationships of Lee and Kesler (1975) and of Keenan et al. (1969). The compressibility factors of the saturated vapor are calculated in a similar manner with Eqs. 10–12 and the values of $Z^{(0)}$, $Z^{(r)}$, and $Z^{(w)}$ for the reference gases at saturation conditions. The derived properties for the saturated liquid and vapor are obtained with the values of $V_{RS}^{(0)}$, $V_{RS}^{(r)}$, and ρ_{wS} for the saturated reference fluids.

TABLE 4. COMPARISONS OF DERIVED THERMODYNAMIC PROPERTIES OF AMMONIA

Data from Din (1962) and Haar and Gallagher (1978)

State	Range		No. of Points	Avg. Dev. H (J/g)		Avg. % Error f/P		Avg. % Error C_V	
	T_R	P_R		This Study	Normal	This Study	Normal	This Study	Normal
Liquid	0.76–0.94	0.35–9.87	14	6.2	13.6	0.8	9.3	7.3	22.2
Sat. Liq.	0.54–0.99	0.00–0.91	9	9.4	17.2	1.4	1.5	6.0	24.9
Vapor	0.74–1.43	0.01–9.87	26	5.9	15.3	0.9	3.2	3.3	9.8
Sat. Vap.	0.54–0.99	0.00–0.91	9	9.5	35.6	1.7	1.7	4.2	20.6

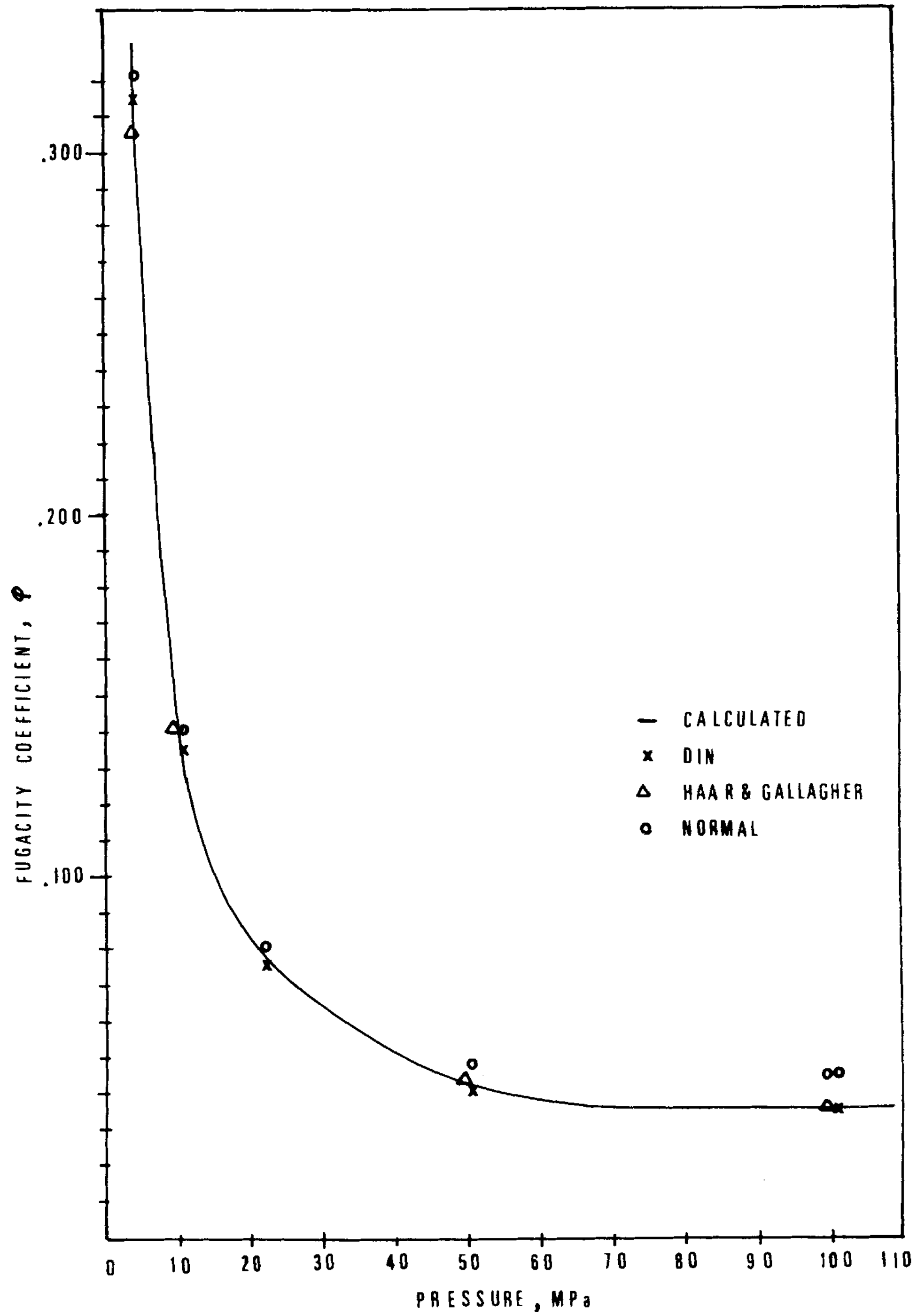

Figure 4. Fugacity coefficient of ammonia liquid at 310 K.

RESULTS OF COMPARISONS WITH EXPERIMENTAL DATA

For polar fluids with acentric and polarity factors less than the values for water, the parameter Y is approximately equal to $\chi/0.023$. The value of Y is conveniently determined from the saturated liquid density of the fluid at $T_R = 0.8$ through Eq. 27, as follows:

$$V_{RS}|_{T_R=0.8} = 0.1326 - 0.0547\omega - 0.0222Y \qquad (30)$$

Values of Y can also be determined from any available PVT data for the dense gas or liquid. Equations 1 and 10 can also be equated at any reduced temperature and pressure to obtain a relationship for Y in terms of ω and χ. For example, at $T_R = 1.05$ and $P_R = 6.0$,

$$Y = 0.22\omega + 70.05\chi - 95.7\omega\chi + 96.8\chi^2 \qquad (31)$$

In Table 2 results of comparisons between the calculated and experimental values of the compressibility factor for the vapor and liquid regions are presented for a number of polar fluids, including ammonia, acetone, methyl chloride, HCl, methyl fluoride, R-32(CH_2F_2), and ethylene oxide. The reduced temperature and pressure ranges, number of points, and data sources for each sub-

TABLE 5. VALUES OF $Z^{(2)}$

T_R	P_R 0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
0.40	-0.0002	-0.0010	-0.0021	-0.0042	-0.0085	-0.0130	-0.0176	-0.0223	-0.0272	-0.0348	-0.0480	-0.0767	-0.1402	-0.2079	-0.3113
0.45	-0.0002	-0.0012	-0.0024	-0.0049	-0.0098	-0.0149	-0.0200	-0.0252	-0.0305	-0.0385	-0.0523	-0.0812	-0.1435	-0.2111	-0.3203
0.50	-0.0003	-0.0013	-0.0026	-0.0052	-0.0105	-0.0158	-0.0212	-0.0266	-0.0321	-0.0404	-0.0546	-0.0839	-0.1461	-0.2127	-0.3202
0.55	-0.0139	-0.0013	-0.0027	-0.0054	-0.0108	-0.0163	-0.0218	-0.0274	-0.0330	-0.0416	-0.0560	-0.0856	-0.1474	-0.2126	-0.3159
0.60	-0.0065	-0.0014	-0.0027	-0.0055	-0.0110	-0.0166	-0.0222	-0.0279	-0.0336	-0.0422	-0.0568	-0.0865	-0.1481	-0.2121	-0.3117
0.65	-0.0029	-0.0277	-0.0028	-0.0055	-0.0111	-0.0168	-0.0224	-0.0282	-0.0339	-0.0426	-0.0572	-0.0870	-0.1482	-0.2112	-0.3077
0.70	-0.0012	-0.0114	-0.0446	-0.0056	-0.0112	-0.0169	-0.0226	-0.0283	-0.0341	-0.0428	-0.0574	-0.0872	-0.1479	-0.2098	-0.3037
0.75	-0.0004	-0.0044	-0.0163	-0.0056	-0.0112	-0.0169	-0.0226	-0.0283	-0.0341	-0.0428	-0.0575	-0.0872	-0.1475	-0.2084	-0.2999
0.80	0.0000	-0.0012	-0.0054	-0.0299	-0.0112	-0.0169	-0.0226	-0.0284	-0.0341	-0.0429	-0.0576	-0.0872	-0.1471	-0.2072	-0.2966
0.85	0.0001	0.0002	-0.0009	-0.0085	-0.0111	-0.0168	-0.0226	-0.0283	-0.0341	-0.0429	-0.0576	-0.0872	-0.1469	-0.2063	-0.2939
0.90	0.0002	0.0008	0.0010	-0.0008	-0.0191	-0.0167	-0.0224	-0.0282	-0.0341	-0.0429	-0.0576	-0.0873	-0.1468	-0.2057	-0.2919
0.93	0.0002	0.0010	0.0015	0.0013	-0.0066	-0.0430	-0.0223	-0.0282	-0.0341	-0.0429	-0.0577	-0.0873	-0.1468	-0.2055	-0.2910
0.95	0.0002	0.0010	0.0017	0.0021	-0.0023	-0.0184	-0.0221	-0.0281	-0.0341	-0.0430	-0.0577	-0.0874	-0.1467	-0.2053	-0.2905
0.97	0.0002	0.0011	0.0019	0.0026	0.0005	-0.0080	-0.0396	-0.0281	-0.0342	-0.0431	-0.0578	-0.0874	-0.1466	-0.2052	-0.2901
0.98	0.0002	0.0011	0.0019	0.0028	0.0014	-0.0049	-0.0210	-0.0283	-0.0345	-0.0433	-0.0580	-0.0874	-0.1466	-0.2051	-0.2896
0.99	0.0002	0.0011	0.0019	0.0029	0.0022	-0.0025	-0.0128	-0.0288	-0.0350	-0.0437	-0.0582	-0.0875	-0.1465	-0.2050	-0.2893
1.00	0.0002	0.0011	0.0019	0.0030	0.0028	-0.0008	-0.0077	-0.0266	-0.0363	-0.0444	-0.0586	-0.0876	-0.1465	-0.2049	-0.2890
1.01	0.0002	0.0011	0.0019	0.0031	0.0033	0.0006	-0.0045	-0.0104	-0.0398	-0.0454	-0.0590	-0.0876	-0.1463	-0.2046	-0.2889
1.02	0.0002	0.0011	0.0019	0.0032	0.0036	0.0017	-0.0021	-0.0061	-0.0509	-0.0473	-0.0596	-0.0878	-0.1462	-0.2044	-0.2887
1.05	0.0002	0.0010	0.0019	0.0032	0.0042	0.0035	0.0017	-0.0003	-0.0041	-0.0582	-0.0634	-0.0885	-0.1458	-0.2039	-0.2881
1.10	0.0002	0.0009	0.0017	0.0030	0.0043	0.0044	0.0036	0.0023	0.0001	-0.0138	-0.0678	-0.0911	-0.1451	-0.2027	-0.2871
1.15	0.0002	0.0008	0.0015	0.0026	0.0039	0.0041	0.0035	0.0023	0.0002	-0.0064	-0.0422	-0.0925	-0.1443	-0.2011	-0.2857
1.20	0.0001	0.0007	0.0012	0.0022	0.0032	0.0034	0.0028	0.0015	-0.0005	-0.0057	-0.0268	-0.0860	-0.1433	-0.1991	-0.2839
1.30	0.0001	0.0004	0.0007	0.0012	0.0017	0.0015	0.0006	-0.0007	-0.0028	-0.0072	-0.0196	-0.0637	-0.1372	-0.1943	-0.2790
1.40	0.0000	0.0001	0.0003	0.0004	0.0002	-0.0005	-0.0016	-0.0032	-0.0054	-0.0096	-0.0198	-0.0525	-0.1249	-0.1868	-0.2733
1.60	-0.0001	-0.0003	-0.0005	-0.0011	-0.0025	-0.0042	-0.0061	-0.0084	-0.0109	-0.0153	-0.0245	-0.0485	-0.1057	-0.1644	-0.2571
1.80	-0.0001	-0.0005	-0.0011	-0.0022	-0.0045	-0.0070	-0.0097	-0.0126	-0.0158	-0.0208	-0.0301	-0.0516	-0.0985	-0.1467	-0.2328
2.00	-0.0001	-0.0007	-0.0014	-0.0028	-0.0057	-0.0088	-0.0120	-0.0154	-0.0189	-0.0244	-0.0342	-0.0549	-0.0959	-0.1360	-0.2093
2.20	-0.0001	-0.0008	-0.0015	-0.0030	-0.0061	-0.0094	-0.0129	-0.0165	-0.0202	-0.0260	-0.0358	-0.0557	-0.0931	-0.1280	-0.1899
2.40	-0.0001	-0.0007	-0.0015	-0.0030	-0.0061	-0.0094	-0.0128	-0.0164	-0.0200	-0.0256	-0.0351	-0.0539	-0.0882	-0.1191	-0.1728

TABLE 6. VALUES OF $\left(\frac{H^0 - H}{RT_c}\right)^{(2)}$

T_R	P_R 0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
0.40	-0.763	-0.764	-0.765	-0.766	-0.769	-0.771	-0.774	-0.777	-0.780	-0.783	-0.788	-0.796	-0.801	-0.801	-0.801
0.45	-0.656	-0.657	-0.657	-0.658	-0.660	-0.662	-0.663	-0.665	-0.667	-0.670	-0.673	-0.678	-0.686	-0.690	-0.695
0.50	-0.534	-0.535	-0.535	-0.536	-0.537	-0.538	-0.539	-0.540	-0.541	-0.543	-0.545	-0.549	-0.554	-0.556	-0.554
0.55	0.057	-0.410	-0.410	-0.410	-0.411	-0.412	-0.413	-0.413	-0.414	-0.415	-0.417	-0.420	-0.423	-0.424	-0.420
0.60	0.033	-0.290	-0.290	-0.290	-0.291	-0.292	-0.292	-0.293	-0.293	-0.294	-0.295	-0.297	-0.299	-0.299	-0.292
0.65	0.019	0.136	-0.181	-0.181	-0.181	-0.182	-0.182	-0.183	-0.183	-0.183	-0.184	-0.185	-0.186	-0.184	-0.175
0.70	0.010	0.072	0.224	-0.086	-0.086	-0.086	-0.086	-0.086	-0.086	-0.087	-0.087	-0.088	-0.087	-0.084	-0.074
0.75	0.006	0.038	0.108	-0.004	-0.004	-0.004	-0.004	-0.004	-0.004	-0.004	-0.004	-0.005	-0.004	-0.001	0.010
0.80	0.003	0.020	0.054	0.198	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.068	0.078
0.85	0.002	0.010	0.027	0.088	0.122	0.122	0.123	0.122	0.122	0.122	0.122	0.121	0.122	0.124	0.132
0.90	0.001	0.004	0.012	0.039	0.178	0.165	0.166	0.167	0.167	0.166	0.166	0.166	0.166	0.167	0.173
0.93	0.000	0.002	0.007	0.023	0.098	0.351	0.187	0.188	0.188	0.188	0.187	0.186	0.187	0.188	0.193
0.95	0.000	0.001	0.004	0.015	0.065	0.196	0.201	0.202	0.202	0.201	0.198	0.197	0.198	0.199	0.204
0.97	0.000	0.000	0.002	0.009	0.042	0.120	0.375	0.218	0.216	0.212	0.208	0.206	0.207	0.209	0.214
0.98	0.000	0.000	0.001	0.006	0.033	0.094	0.241	0.232	0.226	0.219	0.214	0.210	0.211	0.214	0.219
0.99	0.000	-0.001	0.000	0.004	0.026	0.074	0.174	0.257	0.242	0.229	0.219	0.214	0.215	0.218	0.223
1.00	0.000	-0.001	-0.001	0.002	0.019	0.057	0.130	0.340	0.268	0.241	0.225	0.217	0.218	0.222	0.226
1.01	0.000	-0.001	-0.002	0.000	0.013	0.043	0.097	0.190	0.321	0.257	0.232	0.220	0.221	0.224	0.229
1.02	0.000	-0.001	-0.002	-0.002	0.008	0.032	0.073	0.134	0.432	0.280	0.239	0.222	0.223	0.227	0.231
1.05	0.000	-0.002	-0.004	-0.006	-0.004	0.007	0.025	0.048	0.075	0.351	0.268	0.228	0.225	0.231	0.237
1.10	-0.001	-0.003	-0.006	-0.010	-0.015	-0.016	-0.014	-0.011	-0.007	0.025	0.246	0.233	0.222	0.231	0.243
1.15	-0.001	-0.004	-0.007	-0.013	-0.022	-0.028	-0.033	-0.036	-0.038	-0.037	0.055	0.208	0.210	0.222	0.239
1.20	-0.001	-0.004	-0.008	-0.015	-0.026	-0.035	-0.043	-0.049	-0.054	-0.058	-0.032	0.131	0.189	0.205	0.229
1.30	-0.001	-0.004	-0.009	-0.017	-0.031	-0.043	-0.053	-0.062	-0.070	-0.079	-0.082	-0.018	0.117	0.159	0.193
1.40	-0.001	-0.005	-0.009	-0.018	-0.033	-0.047	-0.059	-0.070	-0.079	-0.091	-0.104	-0.088	0.022	0.097	0.150
1.60	-0.001	-0.004	-0.009	-0.017	-0.033	-0.047	-0.061	-0.074	-0.086	-0.102	-0.124	-0.146	-0.114	-0.040	0.066
1.80	-0.001	-0.003	-0.007	-0.013	-0.026	-0.039	-0.051	-0.063	-0.074	-0.090	-0.113	-0.144	-0.149	-0.104	0.011
2.00	0.000	-0.002	-0.004	-0.008	-0.016	-0.024	-0.032	-0.040	-0.047	-0.058	-0.074	-0.096	-0.101	-0.067	0.037
2.20	0.000	0.000	-0.001	-0.002	-0.004	-0.006	-0.009	-0.011	-0.013	-0.015	-0.019	-0.019	0.003	0.049	0.155
2.40	0.000	0.001	0.002	0.004	0.008	0.012	0.016	0.020	0.024	0.031	0.043	0.071	0.139	0.215	0.344

TABLE 7. VALUES OF $\left(\frac{S^0 - S}{R}\right)^{(2)}$

T_R	P_R														
	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
0.40	-1.399	-1.401	-1.404	-1.409	-1.421	-1.431	-1.443	-1.454	-1.464	-1.479	-1.503	-1.545	-1.611	-1.671	-1.773
0.45	-1.149	-1.150	-1.153	-1.157	-1.166	-1.175	-1.184	-1.193	-1.201	-1.215	-1.235	-1.274	-1.347	-1.416	-1.521
0.50	-0.892	-0.894	-0.896	-0.900	-0.907	-0.915	-0.922	-0.929	-0.938	-0.949	-0.967	-1.002	-1.070	-1.134	-1.222
0.55	0.091	-0.655	-0.657	-0.661	-0.668	-0.675	-0.681	-0.688	-0.695	-0.705	-0.722	-0.756	-0.820	-0.882	-0.967
0.60	0.049	-0.447	-0.448	-0.451	-0.458	-0.465	-0.471	-0.478	-0.484	-0.494	-0.509	-0.541	-0.604	-0.663	-0.745
0.65	0.026	0.190	-0.274	-0.277	-0.283	-0.289	-0.295	-0.301	-0.307	-0.316	-0.332	-0.362	-0.422	-0.479	-0.558
0.70	0.014	0.095	0.296	-0.135	-0.141	-0.147	-0.152	-0.158	-0.164	-0.173	-0.188	-0.217	-0.275	-0.330	-0.407
0.75	0.007	0.048	0.135	-0.022	-0.028	-0.033	-0.039	-0.045	-0.050	-0.059	-0.073	-0.102	-0.160	-0.215	-0.291
0.80	0.004	0.024	0.065	0.236	0.061	0.056	0.050	0.045	0.039	0.031	0.016	-0.013	-0.071	-0.126	-0.203
0.85	0.002	0.012	0.032	0.102	0.130	0.126	0.120	0.113	0.108	0.100	0.085	0.056	-0.002	-0.059	-0.137
0.90	0.001	0.006	0.015	0.046	0.195	0.174	0.170	0.165	0.160	0.150	0.136	0.107	0.048	-0.009	-0.089
0.93	0.001	0.003	0.009	0.027	0.108	0.372	0.192	0.188	0.183	0.174	0.158	0.129	0.071	0.014	-0.067
0.95	0.000	0.002	0.006	0.019	0.073	0.206	0.207	0.203	0.197	0.188	0.170	0.141	0.083	0.027	-0.055
0.97	0.000	0.001	0.004	0.013	0.049	0.128	0.385	0.219	0.212	0.200	0.181	0.150	0.093	0.037	-0.045
0.98	0.000	0.001	0.003	0.010	0.040	0.101	0.248	0.234	0.223	0.207	0.187	0.154	0.097	0.041	-0.042
0.99	0.000	0.001	0.002	0.008	0.032	0.080	0.180	0.259	0.238	0.216	0.192	0.158	0.101	0.045	-0.038
1.00	0.000	0.000	0.001	0.006	0.025	0.064	0.135	0.342	0.265	0.229	0.198	0.161	0.104	0.049	-0.035
1.01	0.000	0.000	0.001	0.004	0.019	0.050	0.103	0.193	0.318	0.245	0.204	0.163	0.106	0.051	-0.031
1.02	0.000	0.000	0.000	0.002	0.014	0.039	0.079	0.138	0.427	0.267	0.212	0.166	0.108	0.053	-0.029
1.05	0.000	-0.001	-0.002	-0.002	0.003	0.014	0.032	0.055	0.080	0.336	0.240	0.172	0.111	0.058	-0.022
1.10	0.000	-0.002	-0.003	-0.006	-0.008	-0.007	-0.004	0.000	0.004	0.031	0.220	0.176	0.107	0.058	-0.018
1.15	0.000	-0.002	-0.004	-0.008	-0.014	-0.018	-0.020	-0.022	-0.024	-0.023	0.050	0.154	0.096	0.049	-0.021
1.20	-0.001	-0.003	-0.005	-0.010	-0.017	-0.024	-0.029	-0.033	-0.037	-0.042	-0.024	0.089	0.079	0.036	-0.030
1.30	-0.001	-0.003	-0.006	-0.011	-0.021	-0.030	-0.037	-0.044	-0.050	-0.058	-0.065	-0.031	0.022	-0.001	-0.059
1.40	-0.001	-0.003	-0.006	-0.012	-0.023	-0.033	-0.042	-0.050	-0.058	-0.068	-0.081	-0.083	-0.049	-0.047	-0.091
1.60	-0.001	-0.003	-0.006	-0.012	-0.023	-0.033	-0.043	-0.053	-0.062	-0.075	-0.094	-0.122	-0.140	-0.139	-0.147
1.80	0.000	-0.002	-0.005	-0.009	-0.019	-0.028	-0.037	-0.046	-0.055	-0.068	-0.088	-0.121	-0.161	-0.177	-0.180
2.00	0.000	-0.002	-0.003	-0.007	-0.013	-0.020	-0.027	-0.034	-0.041	-0.051	-0.068	-0.097	-0.136	-0.158	-0.166
2.20	0.000	-0.001	-0.002	-0.004	-0.008	-0.012	-0.016	-0.020	-0.025	-0.031	-0.041	-0.060	-0.087	-0.103	-0.110
2.40	0.000	0.000	-0.001	-0.001	-0.003	-0.004	-0.006	-0.007	-0.009	-0.011	-0.014	-0.020	-0.028	-0.031	-0.029

stance are included along with the corresponding average percent errors for the normal fluid relationship, Eq. 9 (or Eq. 27 with $Y = 0$ for saturated liquids). For these calculations the values of ω were determined from the reduced vapor pressures of the fluid at $T_R = 0.7$, and optimum values of Y were obtained from the experimental PVT data. The values of the critical constants, ω, and Y utilized are presented in Table 3. It can be seen from Table 2 that in general good results are obtained by the method of this study for the substances considered, with the use of a single value of Y for the gaseous and liquid regions. For methyl fluoride accurate data for the critical constants and saturated liquid density are not available.

In Figure 1 experimental values of the compressibility factor of HCl at 333.15 K are compared with the calculated values. It can be seen that large errors result for part of the pressure range for the data of Franck et al. (1962), but the values calculated with Eq. 10 are in closer agreement with the experimental values of Thomas (1962). Larger deviations result for the normal fluid relationship for most of the pressure range.

Extensive tables of the thermodynamic properties of ammonia in the gaseous and liquid regions have been determined by Din (1962) by the analysis of available data, and by Haar and Gallagher (1978) by the use of an equation of state similar to Eqs. 13 and 14. In Figures 2 and 3 experimental values of the compressibility factor of ammonia for the vapor at 520 K and the compressed liquid at 310 K for pressures to 110 MPa are compared with values calculated from Eq. 10. Errors of as much as 20% result with the normal fluid relationship. Larger deviations result for the values presented by Din (1962) for the saturated vapor at high reduced temperatures, but the calculated values are in closer agreement with the experimental data of Berthoud (1918) and the values determined by Haar and Gallagher (1978).

In Table 4 values of the enthalpy, fugacity, and constant-volume heat capacity resulting from the studies of Din and of Haar and Gallagher for ammonia are compared with the values calculated by the method of the study and with the normal fluid relationship for the vapor, liquid, saturated vapor, and saturated liquid regions. It can be seen that considerable improvement is obtained with the relationships of this study. For 58 points (Haar and Gallagher, 1978), the average error of C_V is 4.8% for the method of this study and 16.8% with the normal fluid relationships. In Figure 4 a comparison is presented for the fugacity coefficient of ammonia liquid at 310 K with values calculated from the relationship of this study. Errors of as much as 24% result with the normal fluid relationship, while the maximum error with the approach of this study is 3.46%.

Equations 13–16 result in negligible errors for the thermodynamic properties of water compared to the values in the steam tables of Keenan et al. For water, errors of over 30% result at elevated pressures from the use of the normal fluid relationships for the compressibility factor.

In Tables 5–9 values of the polar fluid correction terms $Z^{(2)}$, $[(H^0 - H)/RT_c]^{(2)}$, $[(S^0 - S)/R]^{(2)}$, $[\log(f/P)]^{(2)}$, and $[(C_p - C_p^0/R)]^{(2)}$ determined from the relationships of this study are presented for T_R from 0.4 to 2.5 and P_R from 0.01 to 10.0. For $T_R = 1.0$ and some reduced temperatures at $P_R = 10.0$ the analytical procedures could not be utilized and the tabulated values were obtained graphically. Tables 5–9 can be used with the tables for

TABLE 8. VALUES OF $[\mathrm{LOG}\,(f/P)]^{(2)}$

	P_R														
T_R	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
0.40	0.221	0.221	0.221	0.220	0.218	0.216	0.214	0.212	0.211	0.208	0.203	0.193	0.170	0.144	0.100
0.45	0.134	0.134	0.134	0.132	0.131	0.128	0.126	0.124	0.122	0.119	0.113	0.101	0.077	-0.051	0.010
0.50	0.077	0.076	0.076	0.074	0.072	0.070	0.068	0.065	0.063	0.060	0.054	0.042	0.017	-0.009	-0.050
0.55	-0.006	0.039	0.038	0.037	0.035	0.032	0.030	0.028	0.025	0.022	0.016	0.003	-0.022	-0.048	-0.088
0.60	-0.003	0.016	0.015	0.014	0.012	0.009	0.007	0.004	0.002	-0.002	-0.008	-0.020	-0.046	-0.072	-0.112
0.65	-0.001	-0.008	0.002	0.001	-0.002	-0.004	-0.006	-0.009	-0.011	-0.015	-0.021	-0.034	-0.059	-0.085	-0.125
0.70	0.000	-0.003	-0.011	-0.006	-0.008	-0.010	-0.013	-0.015	-0.018	-0.021	-0.028	-0.040	-0.065	-0.091	-0.131
0.75	0.000	-0.001	-0.004	-0.007	-0.010	-0.012	-0.015	-0.017	-0.019	-0.023	-0.029	-0.042	-0.067	-0.093	-0.132
0.80	0.000	0.000	-0.001	-0.005	-0.009	-0.011	-0.014	-0.016	-0.018	-0.022	-0.028	-0.041	-0.066	-0.092	-0.130
0.85	0.000	0.000	0.000	-0.001	-0.006	-0.008	-0.010	-0.013	-0.015	-0.019	-0.025	-0.038	-0.063	-0.089	-0.127
0.90	0.000	0.000	0.001	0.001	-0.001	-0.004	-0.006	-0.009	-0.011	-0.015	-0.021	-0.034	-0.059	-0.084	-0.122
0.93	0.000	0.000	0.001	0.001	0.001	-0.002	-0.004	-0.006	-0.008	-0.012	-0.018	-0.031	-0.056	-0.082	-0.119
0.95	0.000	0.000	0.001	0.002	0.002	0.000	-0.002	-0.004	-0.007	-0.010	-0.016	-0.029	-0.054	-0.080	-0.117
0.97	0.000	0.000	0.001	0.002	0.002	0.002	0.000	-0.002	-0.005	-0.008	-0.015	-0.027	-0.052	-0.078	-0.115
0.98	0.000	0.000	0.001	0.002	0.002	0.002	0.001	-0.001	-0.004	-0.007	-0.014	-0.026	-0.051	-0.077	-0.115
0.99	0.000	0.000	0.001	0.002	0.003	0.003	0.002	0.000	-0.003	-0.006	-0.013	-0.025	-0.050	-0.076	-0.114
1.00	0.000	0.000	0.001	0.002	0.003	0.003	0.002	0.000	-0.001	-0.005	-0.012	-0.024	-0.049	-0.075	-0.113
1.01	0.000	0.000	0.001	0.002	0.003	0.003	0.003	0.002	0.000	-0.004	-0.011	-0.024	-0.049	-0.074	-0.112
1.02	0.000	0.000	0.001	0.002	0.003	0.003	0.003	0.003	0.001	-0.003	-0.010	-0.023	-0.048	-0.073	-0.111
1.05	0.000	0.000	0.001	0.002	0.003	0.003	0.004	0.004	0.004	0.001	-0.007	-0.020	-0.045	-0.071	-0.111
1.10	0.000	0.000	0.001	0.001	0.003	0.003	0.004	0.004	0.004	0.004	-0.001	-0.015	-0.041	-0.066	-0.104
1.15	0.000	0.000	0.001	0.001	0.002	0.003	0.003	0.004	0.004	0.004	0.001	-0.012	-0.037	-0.062	-0.100
1.20	0.000	0.000	0.001	0.001	0.002	0.002	0.003	0.003	0.003	0.003	0.001	-0.009	-0.034	-0.059	-0.096
1.30	0.000	0.000	0.000	0.001	0.001	0.001	0.002	0.002	0.001	0.001	-0.001	-0.007	-0.030	-0.054	-0.090
1.40	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	-0.001	-0.003	-0.009	-0.028	-0.051	-0.086
1.60	0.000	0.000	0.000	-0.000	-0.001	-0.002	-0.002	-0.003	-0.004	-0.005	-0.007	-0.013	-0.030	-0.050	-0.082
1.80	0.000	0.000	0.000	-0.001	-0.002	-0.003	-0.004	-0.005	-0.006	-0.008	-0.011	-0.018	-0.034	-0.052	-0.081
2.00	0.000	0.000	-0.001	-0.001	-0.002	-0.004	-0.005	-0.006	-0.008	-0.010	-0.013	-0.021	-0.037	-0.054	-0.080
2.20	0.000	0.000	-0.001	-0.001	-0.003	-0.004	-0.005	-0.007	-0.008	-0.010	-0.014	-0.022	-0.037	-0.054	-0.079
2.40	0.000	0.000	-0.001	-0.001	-0.003	-0.004	-0.005	-0.007	-0.008	-0.010	-0.014	-0.022	-0.037	-0.052	-0.075

$Z^{(0)}$, $Z^{(1)}$, and the other normal fluid functions presented by Lee and Kesler (1975) for hand calculations of the thermodynamic properties of a polar fluid. At the critical point Eq. 10 becomes

$$Z_C = 0.2901 - 0.0879\omega - 0.0266Y \qquad (32)$$

MODIFIED PROCEDURE FOR ALCOHOLS

Because of the use of a linear relationship in Eq. 10, a modified procedure is required for substances with large values of ω and χ such as alcohols. For these substances a constant value of Y results from PVT data for the gaseous region by use of Eq. 10. For the saturated liquid region, the values of Y obtained from experimental density data with Eqs. 27 to 29 decrease considerably with decreasing reduced temperatures. However, it has been found that for these substances a constant value of Y, which is consistent with the value for the gaseous region, can be obtained by the use of a nonlinear relationship for the density of normal fluids, as indicated by Eq. 4. In place of Eq. 27 the saturated liquid volume is calculated as

$$V_{RS} = v^{*(0)} + \omega v^{*(1)} + \omega^2 v^{*(3)} + Y v^{*(2)'} \qquad (33)$$

where $v^{*(0)}$, $v^{*(1)}$, and $V^{*(3)}$ are the coefficients of Eq. 4. The values of these functions determined by Halm and Stiel (1970) were related to $1 - T_R$ by least-squares procedures. The values of $v^{*(2)'}$ were obtained from the corresponding saturated liquid densities for water by the application of Eq. 33 with $\omega = 0.344$ and $Y = 1$. The coefficients of Eq. 33 determined in this manner are presented in Table 10 for T_R from 0.56 to 1.0.

For substances with large values of ω and χ, a single saturated liquid volume point can be used to determine the effective value of Y from Eq. 33. For methanol, ethanol, n-propanol, and isopropanol, the values of T_C, P_C, ω, and the effective values of Y are included in Table 3. These parameters are used for the gaseous region, saturated liquid volumes with Eq. 33, and the compressed liquid region for $T_R > 0.85$. In Table 11, the results of comparisons between experimental compressibility factors for the alcohols and the corresponding values calculated by the modified procedures are presented for the applicable regions. It can be seen that generally good results are obtained with values of Y consistent with Eq. 33. Largest errors with the normal fluid relationships result for methanol.

For the compressed liquid region for $T_R < 0.85$, similar variations in Y with decreasing reduced temperature are obtained with Eq. 10 for substances with large values of ω. This behavior indicates that a term in ω^2 is also required in Eq. 10 for this region for substances with large values of ω and χ.

DISCUSSION

The results of this study indicate that the compressibility factor and derived thermodynamic properties of many polar fluids at

TABLE 9. VALUES OF $\left(\frac{C_p - C_p^0}{R}\right)^{(2)}$

T_R	P_R														
	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
0.40	-2.204	-2.198	-2.191	-2.186	-2.186	-2.171	-2.180	-2.181	-2.178	-2.180	-2.181	-2.113	-1.753	-1.401	-1.040
0.45	-2.297	-2.301	-2.306	-2.316	-2.335	-2.353	-2.371	-2.388	-2.402	-2.423	-2.454	-2.500	-2.555	-2.606	-2.785
0.50	-2.516	-2.518	-2.521	-2.525	-2.534	-2.542	-2.550	-2.558	-2.564	-2.574	-2.589	-2.615	-2.653	-2.684	-2.767
0.55	0.601	-2.477	-2.478	-2.481	-2.487	-2.492	-2.497	-2.502	-2.507	-2.513	-2.524	-2.542	-2.569	-2.589	-2.610
0.60	0.372	-2.301	-2.302	-2.305	-2.310	-2.314	-2.318	-2.323	-2.327	-2.334	-2.344	-2.362	-2.394	-2.421	-2.452
0.65	0.216	1.774	-2.048	-2.051	-2.055	-2.058	-2.062	-2.066	-2.071	-2.076	-2.084	-2.100	-2.130	-2.157	-2.194
0.70	0.123	0.908	3.495	-1.771	-1.774	-1.778	-1.780	-1.783	-1.786	-1.790	-1.795	-1.804	-1.821	-1.837	-1.861
0.75	0.070	0.485	1.510	-1.499	-1.503	-1.505	-1.508	-1.510	-1.512	-1.514	-1.515	-1.517	-1.517	-1.517	-1.518
0.80	0.040	0.265	0.751	3.390	-1.241	-1.245	-1.250	-1.253	-1.255	-1.258	-1.258	-1.257	-1.245	-1.231	-1.210
0.85	0.023	0.147	0.395	1.397	-0.972	-0.988	-0.996	-0.996	-1.000	-1.006	-1.009	-1.008	-1.000	-0.983	-0.950
0.90	0.013	0.084	0.215	0.673	3.661	-0.725	-0.749	-0.757	-0.763	-0.754	-0.754	-0.756	-0.763	-0.758	-0.729
0.93	0.010	0.061	0.152	0.450	1.941	12.532	-0.678	-0.685	-0.671	-0.650	-0.612	-0.599	-0.619	-0.627	-0.608
0.95	0.008	0.050	0.122	0.348	1.358	5.020	-0.770	-0.758	-0.706	-0.627	-0.538	-0.496	-0.520	-0.541	-0.531
0.97	0.007	0.041	0.098	0.272	0.978	2.867	22.812	-1.119	-0.918	-0.690	-0.502	-0.400	-0.418	-0.452	-0.456
0.98	0.006	0.037	0.088	0.241	0.838	2.278	8.637	-1.708	-1.221	-0.787	-0.500	-0.349	-0.352	-0.398	-0.418
0.99	0.006	0.034	0.080	0.214	0.720	1.845	5.287	-3.471	-1.852	-0.994	-0.529	-0.310	-0.310	-0.362	-0.348
1.00	0.005	0.031	0.073	0.190	0.630	1.500	3.900		-3.500	-1.380	-0.590	-0.254	-0.247	-0.305	-0.298
1.01	0.005	0.028	0.065	0.170	0.540	1.263	2.795	7.132	-8.471	-1.905	-0.659	-0.233	-0.196	-0.261	-0.250
1.02	0.005	0.026	0.059	0.152	0.469	1.058	2.176	4.422	-3.306	-2.815	-0.786	-0.219	-0.158	-0.227	-0.209
1.05	0.004	0.020	0.045	0.110	0.314	0.650	1.168	1.882	2.997	3.674	-1.163	-0.174	-0.027	-0.094	-0.100
1.10	0.003	0.014	0.030	0.068	0.173	0.320	0.508	0.719	0.919	2.443	3.323	0.051	0.162	0.106	0.001
1.15	0.002	0.010	0.021	0.045	0.104	0.177	0.259	0.342	0.417	0.627	2.833	1.041	0.318	0.267	0.155
1.20	0.001	0.007	0.015	0.031	0.068	0.110	0.153	0.194	0.230	0.300	0.980	1.808	0.499	0.380	0.278
1.30	0.001	0.003	0.007	0.015	0.034	0.055	0.077	0.098	0.118	0.150	0.274	1.014	0.904	0.543	0.413
1.40	0.000	0.001	0.002	0.004	0.014	0.027	0.042	0.059	0.077	0.106	0.173	0.491	0.921	0.692	0.436
1.60	-0.001	-0.004	-0.007	-0.013	-0.020	-0.023	-0.022	-0.019	-0.014	-0.003	0.026	0.126	0.416	0.563	0.386
1.80	-0.001	-0.006	-0.012	-0.024	-0.044	-0.062	-0.077	-0.090	-0.102	-0.116	-0.132	-0.135	-0.052	0.058	0.103
2.00	-0.001	-0.007	-0.015	-0.029	-0.057	-0.084	-0.110	-0.135	-0.159	-0.193	-0.245	-0.326	-0.403	-0.408	-0.370
2.20	-0.001	-0.007	-0.015	-0.030	-0.061	-0.091	-0.122	-0.153	-0.183	-0.229	-0.301	-0.431	-0.620	-0.729	-0.792
2.40	-0.001	-0.007	-0.014	-0.029	-0.058	-0.089	-0.120	-0.152	-0.184	-0.232	-0.312	-0.464	-0.717	-0.899	-1.066

TABLE 10. COEFFICIENTS OF EQ. 32 FOR SATURATED LIQUID VOLUMES

T_R	$V^{*(0)}$	$V^{*(1)}$	$V^{*(3)}$	$V^{*(2)}$
0.56	0.1102	−0.081	0.069	−0.014
0.58	0.1115	−0.080	0.067	−0.015
0.60	0.1128	−0.079	0.064	−0.015
0.62	0.1143	−0.079	0.062	−0.016
0.64	0.1158	−0.078	0.060	−0.016
0.66	0.1175	−0.078	0.058	−0.017
0.68	0.1193	−0.078	0.057	−0.017
0.70	0.1212	−0.078	0.056	−0.018
0.72	0.1233	−0.079	0.056	−0.018
0.74	0.1255	−0.079	0.055	−0.019
0.76	0.1280	−0.080	0.055	−0.019
0.78	0.1307	−0.081	0.056	−0.020
0.80	0.1336	−0.083	0.056	−0.020
0.82	0.1368	−0.085	0.058	−0.021
0.84	0.1404	−0.087	0.059	−0.021
0.86	0.1445	−0.090	0.061	−0.022
0.88	0.1491	−0.093	0.064	−0.022
0.90	0.1545	−0.096	0.067	−0.023
0.92	0.1610	−0.100	0.070	−0.023
0.94	0.1691	−0.104	0.073	−0.024
0.96	0.1799	−0.108	0.077	−0.025
0.98	0.1971	−0.113	0.080	−0.026
1.00	0.291	−0.114	0.069	−0.027

elevated pressures can be calculated by the extension of the normal fluid relationships with only linear terms in the fourth parameter Y established from the properties of water. The use of a linear approximation to the more complete relationship for the compressibility factor, such as Eq. 1, represents a considerable simplification and enables comparable accuracy to be obtained as for nonpolar fluids. The relationships of this study can be extended for substances with larger acentric factors by the inclusion of additional terms in ω^2 for the liquid region.

The tabulated functions enable the rapid estimation of the thermodynamic properties of polar fluids. The analytical relationships can also be used for repetitive computer calculations. The results of this study are also useful to establish the ranges of applicability of simpler analytical relationships for the compressibility factor of polar fluids.

The relationships of this study can also be extended to the thermodynamic properties of polar mixtures. Appropriate pseudocritical combining rules are required for the mixture parameters T_{CM}, P_{CM}, ω_M, and Y_M.

NOTATION

a_i = constants of Eq. 16
A_{ij} = constants of Eq. 14
A_w = Helmholtz free energy of water
b_1, b_2, b_3, b_4 = constants in Eq. 6
c_1, c_2, c_3, c_4 = constants in Eqs. 5 and 7

TABLE 11. AVERAGE % ERRORS FOR ALCOHOLS

Substance	Range T_R	Range P_R	No. of Points	Average % Error Z This Study	Average % Error Z Normal	Sources*
			Saturated Liquid (Eq. 33)			
Methanol	0.53–0.99		26	1.14	10.08	1, 2
Ethanol	0.53–0.96		29	0.71	2.88	1, 2
n-Propanol	0.55–0.99		29	0.18	7.14	1, 2, 3
iso-Propanol	0.59–0.99		17	0.44	7.26	1, 3
			Liquid ($T_R > 0.85$)			
Methanol	0.88–0.96	0.37–8.65	57	1.53	18.98	4, 5, 6
Ethanol	0.92–0.99	1.35–11.25	30	1.03	5.14	7
iso-Propanol	0.93–0.97	1.45–9.84	13	1.87	0.87	8
			Gas and Saturated Vapor			
Methanol	0.53–1.18	0.00–8.10	78	2.60	11.04	2, 4, 6
Ethanol	0.53–1.21	0.00–11.25	68	0.89	5.89	2, 7
n-Propanol	0.52–1.06	0.00–1.87	37	1.30	1.23	9
iso-Propanol	1.01–1.13	1.74–9.84	18	1.32	1.97	8

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* 1. Hales and Ellender (1976)
2. Young (1910)
3. Ambrose and Townsend (1963)
4. Finkelstein and Stiel (1970)
5. Machado and Streett (1983)
6. Zubarev and Bagdonas (1967)
7. Lo and Stiel (1969)
8. Tseng and Stiel (1971)
9. Martin et al. (1963)

d_1, d_2 = constants in Eq. 8
B, C, D = constants in Eq. 5
C_p = constant pressure heat capacity, J/gmol·K
C_v = constant volume heat capacity, J/gmol·K
f = fugacity, MPa
H = enthalpy, J/gmol
ΔH^* = reduced enthalpy departure
P = pressure, MPa
P_c = critical pressure, MPa
P_R = reduced pressure P/P_C
Q = function defined in Eq. 14
R = gas constant, 8.3143MPa·cm^3/gmol·K or J/gmol·K
S = entropy, J/gmol·K
T = temperature, K
T_c = critical temperature, K
T_R = reduced temperature, T/T_c
v = molar volume, cm^3/gmol
$v^{*(0)}, v^{*(5)}$ = functions of Eq. 4
$v^{*(2)\prime}$ = polar correction term for Eq. 33
V_R = reduced volume, $P_C v/RT_C$
Y = fourth parameter, defined in Eq. 10
Z = compressibility factor
Z_C = critical compressibility factor
$Z^{*(0)}, Z^{*(4)}$ = functions of Eq. 1
$Z^{(w)}$ = compressibility factor of water

Greek Letters

β = constant of Eq. 5
γ = constant of Eq. 5
ρ_w = density of water, g/cm^3
ρ_{aj} = constants of Eq. 14
= 1,000/T
τ_{aj} = constants of Eq. 14
χ = fourth parameter defined in Eq. 3
ψ_E = fourth parameter for polar fluids
ω = acentric factor, $-\log P_{RS}|_{T_R=0.7} - 1.0$

Subscripts and Superscripts

(r) = reference fluid function
S = saturated state
w = water
o = ideal gas
(0) = simple fluid function
(1) = nonpolar fluid correction function
(2) = polar fluid correction function

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