International Journal of Thermophysics, Vol. 25, No. 2, March 2004 (© 2004)

A Fundamental Equation for Calculation of the Thermodynamic Properties of Ethanol[1]

H. E. Dillon[2] and S. G. Penoncello[3,4]

A formulation for the thermodynamic properties of ethanol (C_2H_5OH) in the liquid, vapor, and saturation states is presented. The formulation is valid for single-phase and saturation states from 250 to 650 K at pressures up to 280 MPa. The formulation includes a fundamental equation and ancillary functions for the estimation of saturation properties. The experimental data used to determine the fundamental equation include pressure-density-temperature, ideal gas heat capacity, speed of sound, and vapor pressure. Saturation values computed from the ancillary functions were used to ensure thermodynamic consistency at the vapor-liquid phase boundary. Comparisons between experimental data and values computed using the fundamental equation are given to verify the uncertainties in the calculated properties. The formulation presented may be used to compute densities to within ±0.2%, heat capacities to within ±3%, and speed of sound to within ±1%. Saturation values of the vapor pressure and saturation densities are represented to within ±0.5%, except near the critical point.

KEY WORDS: ethanol; ethyl alcohol; equation of state; fundamental equation; thermodynamic properties.

1. INTRODUCTION

Ethanol (C_2H_5OH) is used in many industrial applications. In recent years, ethanol has received significant consideration as a renewable bio-fuel that

---

[1] Paper presented at the Fifteenth Symposium on Thermophysical Properties, June 22–27, 2003, Boulder, Colorado, U.S.A.

[2] Center for Applied Thermodynamic Studies, University of Idaho, Moscow, Idaho 83844-1011, U.S.A.

[3] Department of Mechanical Engineering, Center for Applied Thermodynamic Studies, College of Engineering, University of Idaho, Moscow, Idaho 83844-1011, U.S.A.

[4] To whom correspondence should be addressed. E-mail: stevep@uidaho.edu

can help reduce dependence on fossil fuels. The design of engineering systems utilizing ethanol requires an accurate knowledge of the thermodynamic properties of the fluid. This paper presents a formulation for ethanol that includes a fundamental equation for the calculation of thermodynamic properties, and supporting ancillary functions.

The formulation presented for ethanol is valid in the single-phase regions from 250 to 650 K at pressures to 280 MPa. Ancillary functions for the vapor pressure, saturated liquid density, and saturated vapor density are provided as estimating functions for iterative computer programs which are used to calculate the thermodynamic properties of ethanol with various pairs of independent variables. Saturation properties can be computed by invoking the Maxwell criterion or by simultaneous solution of the vapor pressure equation with the fundamental equation. The method of simultaneous solution produces values that are not thermodynamically consistent. However, the computed saturation properties are within $\pm 0.5\%$ of the Maxwell criterion values, except near the critical point.

2. EXPERIMENTAL DATA FOR ETHANOL

The available experimental data for ethanol are summarized in Tables I and II. Table I lists the single-phase data, and Table II shows data for the saturation properties and the ideal gas heat capacity. Not all of the data listed in Tables I and II were used in the development of the formulation. However, all data listed in Tables I and II are compared to values calculated with the formulation. The data used to develop the formulation are indicated with asterisks in Tables I and II. Also listed in Tables I and II are columns that indicate the absolute average deviation (AAD) between values computed by a formulation and experimental data. The AAD for any property, X, is defined as,

$$\mathrm{AAD} = \frac{1}{n} \sum_{i=1}^{n} |(\% \Delta X)_i| \tag{1}$$

where $\% \Delta X$ represents the percent deviation between the calculated property and the experimental data, defined by,

$$\% \Delta X = 100 \left(\frac{X_{\text{data}} - X_{\text{calc}}}{X_{\text{data}}} \right) \tag{2}$$

In the formulation presented here, the critical parameters of the fluid are used as reducing parameters. The critical parameters were selected after evaluating the existing reported values. There is a significant range in the

Table I. Single Phase Data for Ethanol

Reference[a]	Points	Pressure (MPa) min	Pressure (MPa) max	Temperature (K) min	Temperature (K) max	AAD
		Pressure-Density-Temperature				
*Bich et al. [1]	34	0.04	0.17	348	631	0.071
Golubev et al. [2]	106	1.00	50.00	200	570	0.620
Gupta and Hanks [3]	24	2.76	22.06	273	363	0.067
Hawley et al. [4]	8	0.10	478.76	303	303	0.161
Hilczer and Goc [5]	6	8.11	44.58	298	298	0.322
Hu et al. [6]	5	0.10	0.10	298	303	0.059
Kalafati et al. [7]	216	0.87	21.47	423	573	8.829
Kubota et al. [8]	46	0.10	310.40	298	323	0.307
*Lo and Stiel [9]	162	8.27	68.95	473	623	0.286
Nikam et al. [10]	5	0.10	0.10	298	313	0.067
Ozawa et al. [11]	41	9.90	196.20	298	348	0.083
*Sauermann et al. [12]	97	0.10	56.70	263	483	0.079
Sun et al. [13]	120	0.10	280.00	193	263	0.153
*Takaguchi and Uematsu [14]	116	0.02	200.01	310	363	0.059
Tammann and Ruhenbeck [15]	113	0.04	96.52	293	673	8.900
Tanaka et al. [16]	44	7.01	310.38	298	323	0.315
Tu et al. [17]	3	0.10	0.10	298	318	0.036
Wilson et al. [18]	65	0.06	0.39	373	473	0.627
TOTAL	**1211**	**0.02**	**478.76**	**193**	**673**	
		Isobaric Heat Capacity (C_p)				
Counsell et al. [19]	25	0.03	0.10	330	475	6.746
Dong et al. [20]	24	0.03	0.10	331	424	8.811
Pedersen et al. [21]	16	0.10	0.10	301	344	5.626
Sinke and DeVries [22]	9	0.10	0.10	354	437	7.624
Stromsoe et al. [23]	12	0.10	0.10	357	651	8.000
Sun et al. [13]	120	0.10	280.00	193	263	2.759
TOTAL	**206**	**0.03**	**280.00**	**193**	**651**	
		Isochoric Heat Capacity (C_v)				
Sun et al.	120	0.10	280.00	193	263	3.048
		Speed of Sound				
Carnevale and Litovitz [24]	5	0.10	196.13	303	303	0.671
Eden and Richardson [25]	3	0.00	98.07	293	293	2.817
Hawley et al. [4]	8	0.10	478.76	303	479	1.383
*Sun et al. [13]	120	0.10	275.93	193	263	0.663
*Wilson and Bradley [26]	48	0.10	96.53	273	323	0.924
TOTAL	**184**	**0.00**	**478.8**	**193**	**479**	

[a] * = Data used in correlation procedures.

Table II. Saturation Data and Ideal Gas Heat Capacity Data for Ethanol

Vapor Pressure		P (MPa)		T (K)		AAD	
Reference[a]	Points	min	max	min	max	Fund Eq.	Eq. (3)
*Ambrose and Sprake [27]	25	0.006	0.179	293	367	0.439	0.029
*Ambrose et al. [28]	23	0.168	6.148	365	514	0.412	0.051
Aucejo et al. [29]	22	0.030	0.130	324	358	0.694	0.451
Dulitskaya [30]	3	0.008	0.089	298	348	0.703	0.234
Figurski and Malanowski [31]	17	0.013	0.098	307	351	0.515	0.089
Khurma et al. [32]	3	0.008	0.505	298	399	0.240	0.242
*Kretschmer and Wiebe [33]	8	0.002	0.102	273	352	0.697	0.112
Lee and Hu [34]	6	0.075	0.159	344	363	0.129	0.132
Lydersen and Tsochev [35]	12	2.660	6.165	469	515	2.439	1.651
Mischienko and Subbotina [36]	22	0.002	0.024	277	319	1.065	0.283
Mousa [37]	33	0.020	6.325	319	516	5.793	5.362
Sauermann et al. [12]	21	0.048	2.959	334	473	0.299	0.072
TOTAL	**195**	**0.002**	**6.325**	**273**	**516**		

Saturated Liquid Density		D ($\mathrm{mol \cdot dm^{-3}}$)		T (K)		AAD	
Reference	Points	min	max	min	max	Fund Eq.	Eq. (4)
Fiock et al. [38]	14	15.0	17.5	273	393	0.135	0.085
*Golick et al. [39]	8	15.7	17.1	293	363	0.039	0.019
*Hales and Ellender [40]	13	12.9	17.1	293	455	0.089	0.011
Mousa [37]	16	5.9	15.0	417	516	10.985	11.506
TOTAL	**51**	**5.9**	**17.5**	**273**	**516**		

Saturated Vapor Density		D ($\mathrm{mol \cdot dm^{-3}}$)		T (K)		AAD	
Reference	Points	min	max	min	max	Fund Eq.	Eq. (5)
*Fiock et al. [38]	14	0.001	0.145	273	393	1.426	0.236
Mousa [37]	16	0.653	5.917	417	516	19.165	17.610
TOTAL	**30**	**0.001**	**5.917**	**273**	**516**		

Ideal Gas Heat Capacity		c_p^0 ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)		T (K)		AAD	
Reference	Points	min	max	min	max	Fund Eq.	Eq. (8)
*Brickwedde et al. [41]	14	73.6	167.7	298	1499	–	0.012

[a] * = Data used in correlation procedures.

measured critical parameters mostly attributed to a wide variation in ethanol purity (from 90 to 99.99%). One of the reasons for this variation in purity is ethanol's high affinity for water. If the sample is not highly purified, the data will be compromised by the presence of the water. In addition, if the experimental apparatus contains traces of water vapor, a highly purified sample will become contaminated and render the data uncertain. With this in mind, the measured values of critical temperature and pressure of Ambrose et al. [28], and the critical density predicted with a corresponding states method of Ambrose and Walton [42] were used to define the critical point for this work,

$$P_c = 6.148\ \text{MPa}, \qquad \rho_c = 5.991\ \text{mol}\cdot\text{dm}^{-3}, \qquad \text{and} \qquad T_c = 513.9\ \text{K}.$$

Other constants required by the formulation are the molar mass of ethanol, 46.06844 $\text{g}\cdot\text{mol}^{-1}$ after Coplen [43], and the universal gas constant, 8.314472 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ after Mohr and Taylor [44].

3. ANCILLARY FUNCTIONS FOR ETHANOL

Ancillary functions for the vapor pressure, saturated liquid density, and saturated vapor density have been developed. These equations are not required for property calculations. However, they do provide excellent estimates for the iterative solution of calculations requiring the application of the Maxwell criterion. The ancillary equations were developed using the selected experimental data designated with asterisks in Table II.

The vapor pressure of ethanol is given by

$$\ln \frac{P}{P_c} = \frac{T_c}{T}\left(-0.0514771\theta^{1/2} - 8.27075\theta - 5.49245\theta^3 + 5.64829\theta^{11/2}\right) \tag{3}$$

where $\theta = 1 - T/T_c$. This equation can be used to predict vapor pressure values for ethanol to within $\pm 0.4\%$.

The saturated liquid density of ethanol is represented by

$$\frac{\rho'}{\rho_c} = 1 + 2.22195\theta^{1/3} - 0.0469268\theta + 10.3036\theta^{5/3} - 17.2305\theta^2 + 8.23564\theta^{8/3} \tag{4}$$

where θ is defined as in Eq. (3). Equation (4) represents the selected experimental data to within $\pm 0.2\%$

There are little reliable data for the saturated vapor density of ethanol. The data of Fiock et al. [38] were used in the limited range from 273 to 393 K. The final ancillary equation for the saturated vapor density was determined by fitting data from the intersection of the equation of state with the vapor pressure equation. The resulting equation for the saturated vapor density is

$$\ln\left(\frac{\rho''}{\rho_c}\right) = -8.35648\theta^{2/3} - 2.38722\theta^{5/3} - 39.6946\theta^{10/3} - 9.991134\theta^{16/3} \tag{5}$$

where θ is defined as in Eq. (3).

4. THE FUNDAMENTAL EQUATION FOR ETHANOL

The functional form of the fundamental equation used for this formulation was developed by Jacobsen et al. [45]. This equation is a potential function explicit in dimensionless Helmholtz energy with reduced density and reciprocal reduced temperature as independent variables. The form of the fundamental equation is

$$\alpha(\delta, \tau) = \alpha^0(\delta, \tau) + \bar{\alpha}(\delta, \tau) \tag{6}$$

where $\delta = \rho/\rho_c$, $\tau = T_c/T$, and $\alpha = a/RT$. The superscript "0" signifies the ideal gas contribution to the dimensionless Helmholtz energy, and the overbar is the real fluid residual.

The ideal-gas reduced Helmholtz energy can be derived from fundamental thermodynamic relationships for the ideal gas, and is given by

$$\alpha^0(\delta, \tau) = \frac{h_0^0\tau}{RT_c} - \frac{s_0^0}{R} - 1 + \ln\frac{\delta\tau_0}{\delta_0\tau} - \frac{\tau}{R}\int_{\tau_0}^{\tau}\frac{c_p^0}{\tau^2}\,d\tau + \frac{1}{R}\int_{\tau_0}^{\tau}\frac{c_p^0}{\tau}\,d\tau \tag{7}$$

where $\delta_0 = \rho_0/\rho_c$ and $\tau_0 = T_c/T_0$. The value of ρ_0 is determined from the ideal gas density at T_0 and P_0. The reference values are arbitrary. In this work, the values of $P_0 = 0.001$ MPa and $T_0 = 273.15$ K were adopted. The reference enthalpy and entropy values are also arbitrary, and were computed to eliminate negative property values within the limits of the fundamental equation. The resulting values are $h_0^0 = 45800\ \mathrm{J\cdot mol^{-1}}$ and $s_0^0 = 180\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$.

In order to complete the ideal gas calculation in Eq. (7), an equation for the isobaric ideal gas heat capacity is required. Ethanol has 21 vibrational frequencies. There are several sources that report vibrational wave numbers including Green [46], Brickwedde et al. [41], and Barrow [47]. Even though these sources were available for the wave numbers, a purely empirical representation was chosen. This was done to reduce the number of terms in the equation. The empirical form used in this work represents the theoretical behavior of the ideal gas heat capacity, and is given by

$$\frac{c_p^0}{R} = d_1 + \sum_{i=2}^{5} d_i \frac{(\theta_i/T)^2 \exp(\theta_i/T)}{[\exp(\theta_i/T) - 1]^2} \tag{8}$$

In Eq. (6), $d_1 = 6.41129$, $d_2 = 1.95989$, $d_3 = 7.60084$, $d_4 = 3.89583$, $d_5 = 4.23238$, $\theta_2 = 694$, $\theta_3 = 1549$, $\theta_4 = 2911$, and $\theta_5 = 4659$. These d_i and θ_i values were determined by fitting the functional form of Eq. (8) to the data reported by Brickwedde et al. [41]. Equation (8) is valid up to 1500 K and reproduces the Brickwedde et al. [41] data to within ±0.02%.

The real-fluid residual dimensionless Helmholtz energy is given by

$$\bar{\alpha}(\delta, \tau) = \sum_{k=1}^{m} N_k \delta^{i_k} \tau^{j_k} \exp(-\gamma \delta^{l_k}) \tag{9}$$

where N_k are the coefficients of the residual function and γ is set equal to zero (when l_k is zero) or a value of one (when l_k is non-zero). The values of i_k, j_k, and l_k are arbitrary; however, it is generally expected that i_k is an integer, j_k is a real number, and l_k is an integer greater than or equal to zero.

The value of the coefficients and exponents N_k, i_k, j_k, l_k, and the number of terms, m, were determined by a linear regression to selected experimental data. An initial comprehensive function containing 100 terms was used to represent Eq. (9). A step-wise linear least-squares algorithm incorporating a search procedure based on statistical parameters was then utilized to determine the final function. The selected data used to determine the value of the coefficients and exponents are indicated by asterisks in Table I. These data were fit simultaneously, thus ensuring proper slope and curvature behavior of the fundamental equation. This multi-property fitting procedure provides for thermodynamically consistent property calculation from the fundamental equation. The nonlinear data representing the speed of sound were linearized using a previously developed fundamental equation. Each time the fundamental equation was updated, the speed-of-sound data were recomputed to be used in the next regression. Saturation values computed from a previous fundamental equation were used as Maxwell criterion data in the regression. Similar to the speed of sound, these calculated data were recomputed after each regression. The resulting values of N_k, i_k, j_k, and l_k are summarized in Table III.

The thermodynamic properties of a fluid are determined by differentiation of the fundamental equation. The properties common to engineering

Table III. Coefficients and Exponents of the Fundamental Equation for Ethanol

k	N_k	i_k	j_k	l_k
1	$1.14008942201 \times 10^{1}$	1	-0.5	0
2	$-3.95227128302 \times 10^{1}$	1	0	0
3	$4.13063408370 \times 10^{1}$	1	0.5	0
4	$-1.88892923721 \times 10^{1}$	1	1.5	0
5	4.72310314140	1	2	0
6	$-7.78322827052 \times 10^{-3}$	1	5	0
7	$1.71707850032 \times 10^{-1}$	2	-0.5	0
8	-1.53758307602	2	1	0
9	1.42405508571	2	2	0
10	$1.32732097050 \times 10^{-1}$	3	0	0
11	$-1.14231649761 \times 10^{-1}$	3	2.5	0
12	$3.27686088736 \times 10^{-6}$	6	6	0
13	$4.95699527725 \times 10^{-4}$	7	2	0
14	$-7.01090149558 \times 10^{-5}$	8	2	0
15	$-2.25019381648 \times 10^{-6}$	8	4	0
16	$-2.55406026981 \times 10^{-1}$	1	5	2
17	$-6.32036870646 \times 10^{-2}$	3	3	2
18	$-3.14882729522 \times 10^{-2}$	3	7	2
19	$2.56187828185 \times 10^{-2}$	6	5.5	2
20	$-3.08694499382 \times 10^{-2}$	7	4	2
21	$7.22046283076 \times 10^{-3}$	8	1	2
22	$2.99286406225 \times 10^{-3}$	2	22	4
23	$9.72795913095 \times 10^{-4}$	7	23	4

design are summarized in the following equations using density and temperature as independent variables.

pressure:
$$\frac{P}{\rho RT} = 1 + \delta\left(\frac{\partial\bar{\alpha}}{\partial\delta}\right)_{\tau} \tag{10}$$

internal energy:
$$\frac{u}{RT} = \tau\left[\left(\frac{\partial\alpha^{0}}{\partial\tau}\right)_{\delta} + \left(\frac{\partial\bar{\alpha}}{\partial\tau}\right)_{\delta}\right] \tag{11}$$

enthalpy:
$$\frac{h}{RT} = \tau\left[\left(\frac{\partial\alpha^{0}}{\partial\tau}\right)_{\delta} + \left(\frac{\partial\bar{\alpha}}{\partial\tau}\right)_{\delta}\right] + \delta\left(\frac{\partial\bar{\alpha}}{\partial\delta}\right)_{\tau} + 1 \tag{12}$$

entropy:
$$\frac{s}{R} = \tau\left[\left(\frac{\partial\alpha^{0}}{\partial\tau}\right)_{\delta} + \left(\frac{\partial\bar{\alpha}}{\partial\tau}\right)_{\delta}\right] - \alpha^{0} - \bar{\alpha} \tag{13}$$

isochoric heat capacity:
$$\frac{c_v}{R} = -\tau^{2}\left[\left(\frac{\partial^{2}\alpha^{0}}{\partial\tau^{2}}\right)_{\delta} + \left(\frac{\partial^{2}\bar{\alpha}}{\partial\tau^{2}}\right)_{\delta}\right] \tag{14}$$

Table IV. Sample Table of Thermodynamic Properties of Ethanol

Pressure[a] (MPa)	T (K)	Density ($\mathrm{kg \cdot m^{-3}}$)	Enthalpy ($\mathrm{kJ \cdot kg^{-1}}$)	Entropy ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	C_v ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	C_p ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	Speed of Sound ($\mathrm{m \cdot s^{-1}}$)
0.1	350	737.85	259.95	1.0363	2.6542	3.1707	964.32
0.1 SL	351.05	736.78	263.30	1.0459	2.6614	3.1818	960.72
0.1 SV	351.05	1.6269	1113.8	3.4687	1.5894	1.8044	260.21
0.1	375	1.5114	1158.1	3.5908	1.6788	1.8887	269.72
0.1	400	1.4087	1206.2	3.7148	1.7504	1.9535	279.09
0.1	425	1.3202	1255.8	3.8351	1.8187	2.0165	287.96
0.1	450	1.2431	1307.0	3.9521	1.8859	2.0799	296.42
0.1	500	1.1144	1414.2	4.1778	2.0168	2.2058	312.39
0.1	550	1.0108	1527.5	4.3938	2.1411	2.3272	327.36
0.1	600	0.9253	1646.8	4.6013	2.2581	2.4425	341.55
0.1	650	0.8534	1771.7	4.8011	2.3679	2.5512	355.10
1	250	825.84	1.2861	0.1732	1.6648	2.0320	1330.0
1	275	805.37	55.119	0.3783	1.9324	2.2900	1227.0
1	300	784.72	116.16	0.5905	2.2122	2.5948	1137.9
1	325	762.88	184.79	0.8101	2.4569	2.8927	1054.4
1	350	739.00	260.59	1.0347	2.6530	3.1665	970.98
1	375	712.24	342.92	1.2618	2.8014	3.4173	884.40
1	400	681.60	431.37	1.4900	2.9087	3.6590	791.85
1 SL	423.85	647.20	521.57	1.7090	2.9808	3.9104	694.41
1 SV	423.85	15.246	1207.3	3.3267	1.9648	2.4277	260.65
1	425	15.169	1210.0	3.3333	1.9685	2.4265	261.42
1	450	13.736	1270.3	3.4711	2.0217	2.3954	276.50
1	500	11.778	1389.6	3.7224	2.1045	2.3895	300.64
1	550	10.439	1510.2	3.9524	2.1985	2.4426	320.26
1	600	9.4314	1634.2	4.1681	2.2968	2.5191	337.33
1	650	8.6290	1762.3	4.3730	2.3943	2.6038	352.77
10	250	831.84	9.4714	0.1625	1.6724	2.0325	1372.8
10	300	792.50	124.00	0.5786	2.2095	2.5799	1189.5
10	350	749.65	267.18	1.0190	2.6424	3.1291	1033.3
10	400	697.79	435.07	1.4667	2.8899	3.5720	872.36
10	500	530.74	840.27	2.3662	3.0457	4.8198	464.50
10	600	129.00	1474.5	3.5258	2.7347	4.0688	273.66
100	250	877.47	92.779	0.0753	1.7375	2.0655	1697.5
100	300	847.15	206.47	0.4886	2.2031	2.5117	1558.1
100	350	817.12	343.69	0.9108	2.5870	2.9583	1448.3
100	400	784.52	500.06	1.3279	2.8005	3.2736	1348.2
100	500	709.84	845.18	2.0968	2.8698	3.5670	1166.1
100	600	626.59	1204.7	2.7521	2.7297	3.5932	1015.1

[a] SL = Saturated Liquid, SV = Saturated Vapor.

$$\text{isobaric heat capacity:}\quad \frac{c_p}{R}=\frac{c_v}{R}+\frac{\left[1+\delta\left(\dfrac{\partial\bar{\alpha}}{\partial\delta}\right)_\tau-\delta\tau\left(\dfrac{\partial^2\bar{\alpha}}{\partial\delta\,\partial\tau}\right)\right]^2}{1+2\delta\left(\dfrac{\partial\bar{\alpha}}{\partial\delta}\right)_\tau+\delta^2\left(\dfrac{\partial^2\bar{\alpha}}{\partial\delta^2}\right)_\tau} \tag{15}$$

$$\text{speed of sound:}\quad \frac{w^2}{RT}=\left(\frac{c_p}{c_v}\right)\left[1+2\delta\left(\frac{\partial\bar{\alpha}}{\partial\delta}\right)_\tau+\delta^2\left(\frac{\partial^2\bar{\alpha}}{\partial\delta^2}\right)_\tau\right] \tag{16}$$

Table IV presents a sample table of thermodynamic properties of ethanol computed with the formulation described above. This table provides values that can be used to verify computer programs based on this formulation.

5. ACCURACY ASSESSMENT OF THE FUNDAMENTAL EQUATION

The accuracy of the fundamental equation was determined by statistical comparisons (both graphical and tabular) of property values calculated with the fundamental equation to experimental data. The percent deviation in any property, X, given by Eq. (2), forms the basis for graphical comparisons. Deviation plots showing percent deviation in density, heat capacity, and velocity of sound were constructed and reviewed to assess the accuracy of the fundamental equation. Summary deviation plots are shown in Figs. 1 through 3. Figures 1 and 2 display the percent deviation in density, and Fig. 3 shows the percent deviation in the speed of sound. The tabular results of the statistical analyses are summarized in Tables I and II in the AAD columns. The AAD is the absolute average deviation of any property, X, defined by Eq. (1). In Table I, the AAD is computed for all data. Asterisks indicate those data used to develop the fundamental equation. In Table II, there are two AAD columns. The first column indicates the AAD for the property computed directly from the fundamental equation by invoking the Maxwell criterion. The second column is the AAD for the property computed from the ancillary equations. In the case of the ideal gas heat capacity, the AAD is based upon values computed from Eq. (8).

Even though the single-phase data extend to a low temperature of 193 K, the lowest temperature for the saturation data is 273 K. The lack of saturation data below 273 K, particularly vapor pressure data, makes extrapolation somewhat uncertain. The form of the vapor pressure equation used in this work is based on the well-known Wagner form, and is fairly simple; possessing only four terms. Because of this, the authors feel comfortable declaring a lower limit of 250 K on this formulation.

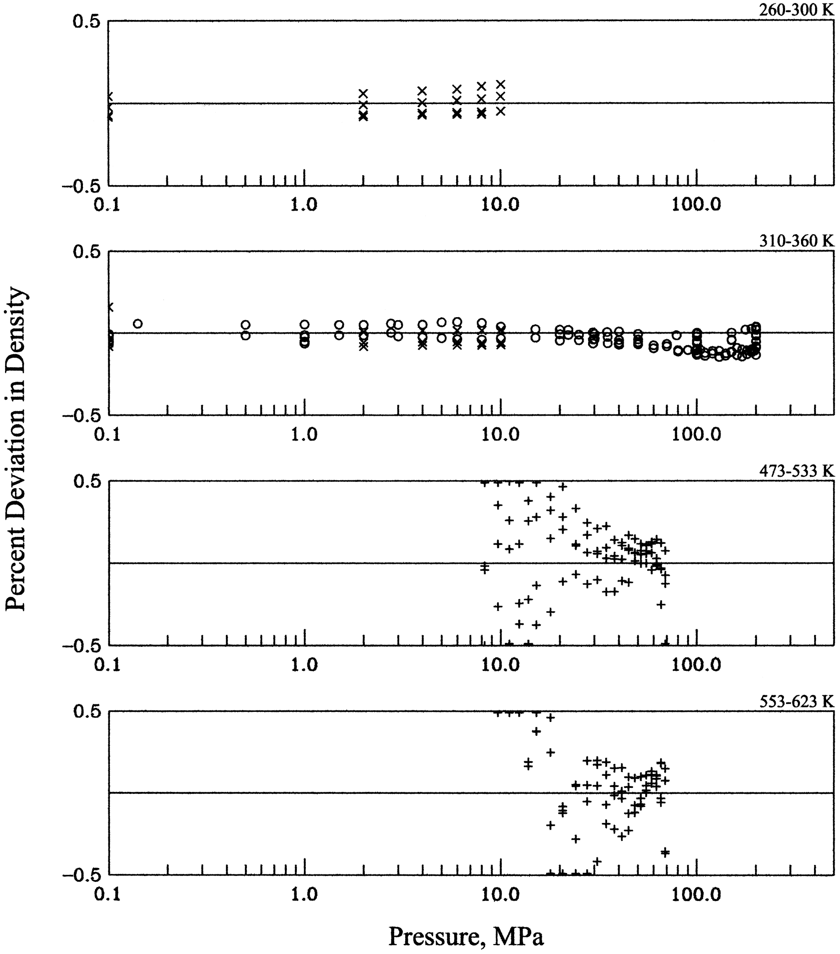

Fig. 1. Comparison of ethanol densities calculated with the fundamental equation to selected experimental data measured on isotherms. (+, Lo and Stiel [9]; ○, Takaguchi and Uematsu [14]; ×, Sauermann *et al.* [12])

The upper temperature limit of the formulation (650 K) is a slight extrapolation beyond the the vapor phase data of Bich et al. [1]. The data of Tammann and Ruhenbeck [15] extends to 673 K, but were found to be inconsistent with other data. The upper limit in pressure is 280 MPa, based on the speed of sound data of Sun et al. [13]. The data of Hawley et al. [4] extend to 479 MPa, and are represented by the fundamental equation, but these eight data points are on one isotherm (303 K).

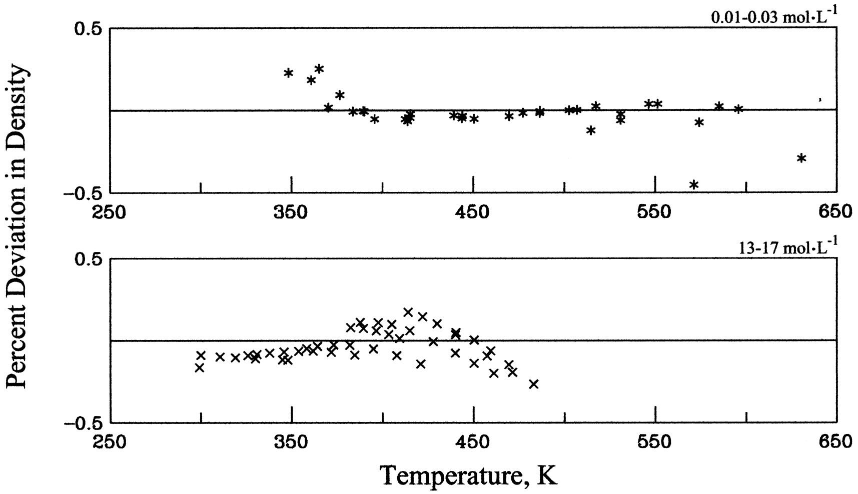

Fig. 2. Comparison of ethanol densities calculated with the fundamental equation to selected experimental data measured on isochores. (×, Sauermann *et al.*; ∗, Bich *et al.* [1])

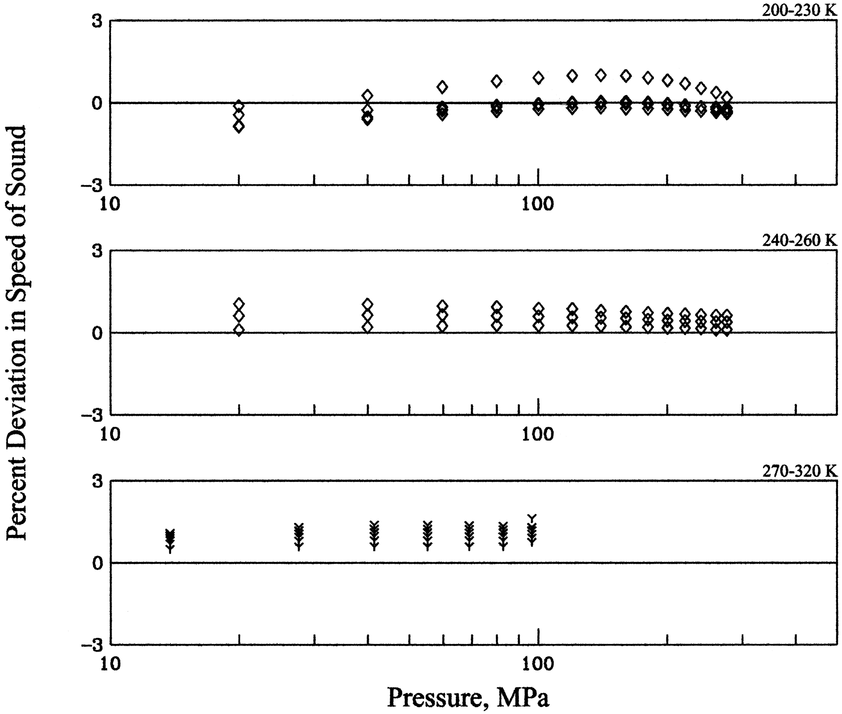

Fig. 3. Comparison of ethanol speed of sound calculated with the fundamental equation to selected experimental data. (◇, Sun *et al.* [13]; Y Wilson and Bradley [26])

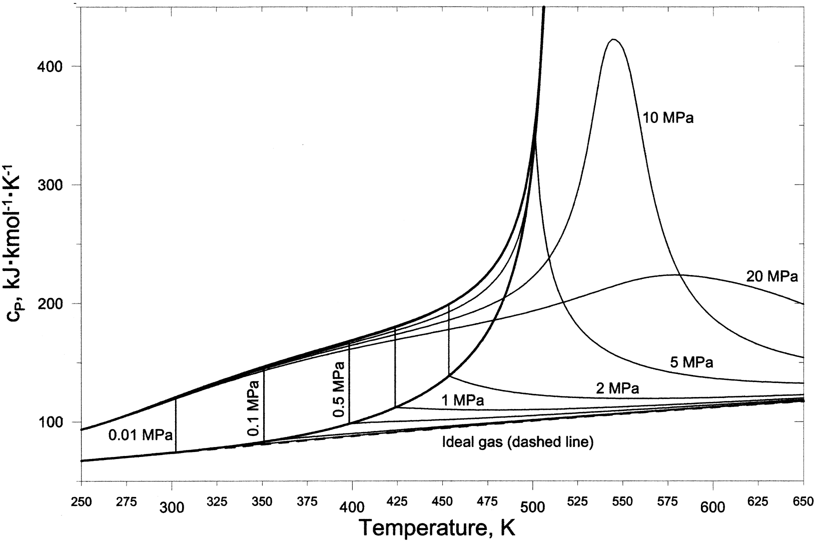

Fig. 4. c_p-T plot for ethanol computed from the fundamental equation.

Based upon the statistical analysis (both graphical and tabular), the formulation presented here can be used to compute the thermodynamic properties of ethanol to within ±0.2% in density, ±3% in heat capacity, and ±1% in speed of sound. Saturation values of the vapor pressure and saturation densities are represented by the fundamental equation to within ±0.5%, except near the critical point.

An indication of the qualitative accuracy of any equation of state can be seen in property plots. In plots like these, it is easy to pick out uncharacteristic behavior. Figure 4 shows a plot of isobaric heat capacity versus temperature with several isobars included. This figure shows correct physical behavior of this property. Equation (15) indicates that the isobaric heat capacity is a function of both first and second derivatives of the fundamental equation. Since Fig. 4 indicates proper physical behavior of the isobaric heat capacity, it can be concluded that heat capacity, speed of sound, and first derivative properties, such as internal energy, enthalpy, and entropy, calculated from this formulation may be considered to be reliable.

6. CONCLUSIONS

The fundamental equation presented in this paper represents the current state of the art concerning the thermodynamic properties of ethanol. While this equation can be used with confidence to compute thermodynamic properties of ethanol in the specified range, this equation can be improved with additional experimental data.

In general, further measurements of the thermodynamic properties of ethanol are required to both extend the range of the equation, and to improve the accuracy of the heat capacity calculations. P-ρ-T measurements in the vapor phase to accompany the data of Bich et al. [1] would be helpful in extending the equation to higher temperatures. An intensive experimental study of the isochoric heat capacity, especially in the liquid phase, would be very helpful to improve the accuracy of the heat capacity calculations. Saturation data, especially low-temperature vapor pressure and saturated vapor density, along with saturation heat capacities are needed to make the low-temperature limit of the fundamental equation consistent with the low-temperature speed-of-sound data of Sun et al. [13].

REFERENCES

1. E. Bich, M. Ramsdorf, and G. Opel, *Z. Phys. Chem. (Leipzig)* **265**:401 (1984).
2. I. F. Golubev, T. N. Vasil'kovskaya, and V. S. Zolin, *Inzh.-Fiz. Zh.* **38**:668 (1980).
3. A. C. Gupta and R. W. Hanks, *Thermochim. Acta* **21**:143 (1977).
4. S. Hawley, J. Allegra, and G. Holton, *J. Acoust. Soc. Am.* **47**:137 (1970).
5. T. Hilczer and R. Goc, *Bull. Soc. Sci. Lett. Poznan* **16**:201 (1961).
6. J. Hu, K. Tamura, and S. Murakami, *Fluid Phase Equilib.* **131**:201 (1977).
7. D. D. Kalafati, D. S. Rasskazov, and E. K. Petrov, *Teploenergetika* **14**:77 (1967).
8. H. Kubota, Y. Tanaka, and T. Makita, *Int. J. Thermophys.* **8**:47 (1987).
9. H. Y. Lo and L. I. Stiel, *Ind. Eng. Chem. Fundam.* **8**:713 (1969).
10. P. S. Nikam, L. N. Shirsat, and M. Hasan, *J. Chem. Eng. Data* **43**:732 (1998).
11. S. Ozawa, O. Noriyuki, Y. Masashi, S. Honmo, and Y. Ogino, *J. Chem. Thermodyn.* **12**:229 (1980).
12. P. Sauermann, K. Holzapfel, J. Oprzynski, F. Kohler, W. Poot, and T. W. de Loos, *Fluid Phase Equilib.* **112**:249 (1995).
13. T. F. Sun, J. A. Schouten, P. J. Kortbeek, and S. N. Biswas, *Phys. Chem. Liq.* **21**:231 (1989).
14. Y. Takiguchi and M. Uematsu, *Int. J. Thermophys.* **16**:205 (1995).
15. G. Tammann and A. Ruhenbeck, *Ann. Physik* **13**:63 (1932).
16. Y. Tanaka, T. Yamamoto, Y. Satomi, H. Kubota, and T. Makita, *Rev. Phys. Chem. Jpn.* **47**:12 (1977).
17. C. Tu, H. Ku, W. Wang, and Y. Chou, *J. Chem. Eng. Data* **46**:317 (2001).
18. K. S. Wilson, D. D. Lindley, W. B. Kay, and H. C. Hershey, *J. Chem. Eng. Data* **29**:243 (1984).
19. J. F. Counsell, J. O. Fenwick, and E. B. Lees, *J. Chem. Thermodyn.* **2**:367 (1970).
20. J. Q. Dong, R. S. Lin, and W. H. Yen, *Can. J. Chem.* **66**:783 (1988).
21. M. J. Pedersen, B. K Webster, and H. C. Hershey, *J. Chem. Thermodyn.* **7**:1107 (1975).
22. G. C. Sinke and T. De Vries, *J. Am. Chem. Soc.* **75**:1815 (1953).
23. E. Stromsoe, H. G. Ronne, A. L. Lydersen, and T. F. Sun, *J. Chem. Eng. Data* **15**:286 (1970).

24. E. H. Carnevale and T. A. Litovitz, *J. Acoust. Soc. Am.* **27**:547 (1955).
25. H. F. Eden and E. G. Richardson, *Acustica* **10**:309 (1960).
26. W. Wilson and D. Bradley, *J. Acoust. Soc. Am.* **36**:333 (1964).
27. D. Ambrose and C. H. S. Sprake, *J. Chem. Thermodyn.* **2**:631 (1970).
28. D. Ambrose, C. H. S. Sprake, and R. Townsend, *J. Chem. Thermodyn.* **7**:185 (1975).
29. A. Aucejo, S. Loras, R. Munoz, and L. M. Ordonez, *Fluid Phase Equilib.* **156**:173 (1999).
30. K. A. Dulitskaya, *Zh. Obshch. Khim.* **7**:185 (1945).
31. G. Figurski and S. K. Malanowski, *Fluid Phase Equilib.* **148**:161 (1998).
32. J. R. Khurma, O. Muthu, S. Munjal, and B. D. Smith, *J. Chem. Eng. Data* **28**:100 (1983).
33. C. B. Kretschmer and R. Wiebe, *J. Am. Chem. Soc.* **71**:1793 (1949).
34. M. J. Lee and C. H. Hu, *Fluid Phase Equilib.* **109**:83 (1995).
35. A. L. Lydersen and V. Tsochev, *Chem. Eng. Tech.* **13**:125 (1990).
36. K. P. Mishchienko and V. V. Subbotina, *Zh. Prikl. Khim.* **40**:1156 (1967).
37. A. H. N. Mousa, *J. Chem. Eng. Jpn.* **20**:635 (1987).
38. E. F. Fiock, D. C. Ginnings, and W. B. Holton, *J. Res. Nat. Bur. Stand.* **6**:881 (1931).
39. A. Z. Golik, Y. I. Shimanskii, and N. M. Kobiichuk, *Ukr. Fiz. Zh.* **3**:537 (1958).
40. J. L. Hales and J. H. Ellender, *J. Chem. Thermodyn.* **8**:1177 (1976).
41. F. G. Brickwedde, M. Moskow, and J. G. Aston, *J. Res. Nat. Bur. Stand.* **37**:263 (1946).
42. D. Ambrose and J. Walton, *Pure Appl. Chem.* **61**:1395 (1989).
43. T. B. Coplen, *J. Phys. Chem. Ref. Data* **30**:701 (2001).
44. P. J. Mohr and B. N. Taylor, *J. Phys. Chem. Ref. Data* **28**:1713 (1999).
45. R. T Jacobsen, R. B. Stewart, M. Jahangiri, and S. G. Penoncello, *Adv. Cryo. Eng.* **31**:1161 (1986).
46. H. S. Green, *Trans. Faraday Soc.* **57**:2132 (1961).
47. G. M. Barrow, *J. Chem. Phys.* **20**:1739 (1952).