Part II: Analytic Equation of State of Polar Fluids

Variational inequality minimization (VIM) theory of statistical mechanics is used to derive analytic equations of state for polar fluids. For the pair-intermolecular potential energy function in the formulation of this theory, the Lennard-Jones, dipolar, quarupolar, and dipolar-quadrupolar interactions are used. For the three-body potential Axilrod-Teller function is used. The VIM theory has made it possible to derive algebraically analytic expressions for the thermodynamic functions of polar fluids. Thermodynamic properties of carbon dioxide, methyl chloride, ethane, hexane, iso-butane, and sulfur dioxide in the liquid and vapor phases are predicted with the use of the VIM equation of state. The results of the predictions are shown to be in very good agreement with the experimental data for majority of the fluids which are studied.

SCOPE

The objective of this study has been to develop algebraically analytic equations of state for polar fluids (vapors and liquids) through the applications of modern theories of statistical mechanics and consideration of polar intermolecular potential energy functions. This would allow the prediction of thermodynamic properties of fluids of industrial importance such as carbon dioxide, methyl chloride, sulfur dioxide, and others accurately by merely knowing their intermolecular potential energy parameters. It will also enable the applied scientists and practicing engineers to quantitatively take into account the contributions of nonpolar and polar intermolecular potential energies in their system design calculations. In addition, it will give us the opportunity to develop universal equations of state for the polar fluids for which limited experimental thermodynamic data are available.

The previous research activities in the development of equations of state of polar fluids can be divided into two categories. One category is the efforts made in correlating thermodynamic properties of polar fluids through empirical algebraic expressions. The other category consists of the rigorous statistical mechanical studies of polar fluids without any consideration for the development of equations of state. The present study is aimed to bridge the gap between these two categories of research by applying the modern theories of statistical mechanics for the development of analytic equations of state which could be applied in correlation and prediction of thermodynamic properties of polar fluids applicable for chemical engineering design calculations.

CONCLUSIONS AND SIGNIFICANCE

The VIM equation of state which was previously developed for nonpolar fluids is successfully applied for correlation and prediction of thermodynamic properties of polar fluids. It is demonstrated that by consideration of nonpolar, dipolar, quadrupolar and dipolar-quadrupolar interaction it is possible to derive equations of state which are accurate and simple enough to be used for engineering design calculations. Application of the VIM equation of state for the prediction of thermodynamic properties of carbon dioxide, methyl chloride, ethane, iso-butane, and sulfur dioxide has been successful. It is expected that the VIM equation of state will be equally successful for pre-

diction of thermodynamic properties of other polar fluids. The VIM equation of state is not expected to be accurate enough in correlation and prediction of thermodynamic properties of polar and associated molecular fluids like water. For such fluids contributions of the hydrogen bondings between the molecules of the fluid must be taken into account in formulation of their equations of state. However, the availability of the VIM equation of state for polar and nonassociated molecular fluids which is introduced in this paper is a prerequisite for its extention to the case of polar and associated molecular fluids.

BACKGROUND AND THEORY

In Part I, the groundworks for the development of analytic VIM equations of state based on the variational inequality minimization (VIM) theory of statistical mechanics were set and the resulting equations of state were successfully applied for nonpolar fluids. In this paper, application of the VIM theory of equation of state will be extended for polar fluids such as carbon dioxide, methyl chloride, iso-butane, and sulfur dioxide.

According to the VIM theory, when we consider pair- and triplet-intermolecular potential energy functions for the interaction of molecules of a fluid, the following inequality for the Helmholtz free energy will be derived

$$A \leq A_o + A_{2b} + A_{3b},\qquad(1)$$

where

$$A_o = A^{ig} + RT\eta(4 - 3\eta)/(1 - \eta)^2 \qquad(2)$$

is the hard-sphere fluid Helmholtz free energy function,

$$A_{2b} = \iint g_{o2}(r_{12})\phi(r_{12}\omega_1\omega_2)d\,r_1d\,r_2 \qquad(3)$$

is the contribution of the pair-interaction energy, and

$$A_{3b} = \iiint g_{o3}(123)\psi(123)d\,r_1d\,r_2d\,r_3 \qquad(4)$$

is the contribution of the three-body interaction energy to the Helmholtz free energy. In the above relations

$$\eta = \frac{\pi}{6}\rho N_o d^3$$

	Carbon Dioxide	Methyl Chloride
a_o	3.2868	3.6951
a_1	0.01349	−0.18508
a_2	342.973	−1.69349
a_3	−10.757	5.1704
RMSD	0.016	0.026
Fluid Entropy Data	(i)	(iii)
Ideal Gas Entropy Data	(ii)	(iv)

(i) Vargaftik (1975) and Rowlinson et al. (1980). (ii) Rowlinson et al. (1980). (iii) Hsu et al. (1964). (iv) Rodgers et al. (1974).

is a dimensionless density expression with d being the diameter of the hard-sphere reference fluid, g_{o2} and g_{o3} are the hard-sphere fluid pair- and triplet-distribution functions, respectively; $\phi(r_{12}\omega_1\omega_2)$ is the orientation-dependent pair-interaction potential energy function of polar molecules and $\psi(123)$ is the triple-interaction potential energy function.

In utilizing the VIM equation of state for calculation of thermodynamic properties the righthand side of inquality (Eq. 1) is minimized with respect to the hard-sphere reference diameter d according to the following conditions:

$$A' = (\partial A_o/\partial d)_{\rho,T} + (\partial A_{2b}/\partial d)_\rho + (\partial A_{3b}/\partial d)_\rho = 0, \quad (5)$$

$$A'' = (\partial^2 A_o/\partial d^2)_{\rho,T} + (\partial^2 A_{2b}/\partial d^2)_\rho + (\partial^2 A_{3b}/\partial d^2)_\rho \geq 0. \quad (6)$$

This calculation will result in an equality relation for the Helmholtz free energy and an expression for the hard-sphere reference diameter which will be a function of density and temperature. In Part I we demonstrated that minimization of the righthand side of inequality (Eq. 1) will produce a simple relation for the entropy,

$$S(\rho,T) = S^{ig} - R\eta(4 - 3\eta)/(1 - \eta)^2 = S_o(\eta) \quad (7)$$

which is identical with the hard-sphere fluid entropy. This simple relation has provided us with the incentive to calculate the hard-sphere reference diameter of different fluids using entropy data and solution of Eq. 7 for η (or d). Our computations for a variety of nonpolar and polar fluids have indicated that d is linearly dependent on both density and inverse temperature which can be accurately correlated to (see note added to the proof)

$$d = a_o + a_1\rho + a_2/T + a_3\rho/T. \quad (8)$$

Numerical values of a_i's for argon and methane were reported in Part I and for carbon dioxide and methyl chloride are reported in Table 1. In the present report, we develop the VIM equation of state of polar fluids with the consideration of dipole and quadrupole interaction energies of molecules. The resulting analytic VIM equation of state and the hard-sphere diameter are then represented in dimensionless (universal) forms which are then applied for prediction of thermodynamic properties of a variety of other polar fluids.

The pair-intermolecular potential energy function of polar molecules may be represented by the Lennard-Jones potential function together with the contributions of dipole, quadrupole and dipole-quadrupole interactions (Rasaiah et al., 1975; Stell et al. 1974; Massih and Mansoori, 1982),

$$\phi(r_{12}\omega_1\omega_2 = 4\epsilon[(\sigma/r_{12})^{12} - (\sigma/r_{12})^6] + \phi\mu\mu(r_{12}\omega_1\omega_2) + \phi\mu Q(r_{12}\omega_1\omega_2) + \phi QQ(r_{12}\omega_1\omega_2), \quad (9)$$

where, for interacting molecules of the same kind

$$\phi\mu\mu(r_{12}\omega_1\omega_2)$$
$$= -\mu^2[2 \cos\omega_1 \cos\omega_2 - \sin\omega_1 \sin\omega_2 \cos(\omega_1 - \omega_2)]/r_{12}^3, \quad (10)$$

$$\phi\mu Q(r_{12}\omega_1\omega_2)$$
$$= \frac{3}{4}\mu Q[\cos\omega_1 \cos\omega_2 - \sin\omega_1 \sin\omega_2 \cos(\omega_1 - \omega_2)]/r_{12}^4, \quad (11)$$

and,

$$\phi QQ(r_{12}\omega_1\omega_2) = \frac{3}{16} Q^2[1 - 5 \cos^2\omega_1 - 5 \cos^2\omega_2$$
$$- 15 \cos^2\omega_1 \cos^2\omega_2 + 2\{\sin\omega_1 \sin\omega_2 \cos(\omega_1 - \omega_2)$$
$$- 4 \cos\omega_1 \cos\omega_2\}^2]/r_{12}^5. \quad (12)$$

In the above equations ϵ and σ are the energy and length parameters of the Lennard-Jones potential function, μ is the dipole moment and Q is the quadrupole moment.

In the formulation of this potential energy function contributions of the induced dipole interacting with permanent dipole or permanent quadrupole are neglected by considering them to be very small so long as $\mu \leq 2.0 \times 10^{-18}$ erg$^{0.5}$ cm$^{1.5}$, which is the case for all the molecular fluids considered in this work.

In order to derive an analytic expression for the Helmholtz free energy of polar fluids we need to introduce the configurational angle-averaged potential energy function for polar interactions as originally introduced by Cook and Rowlinson (1953). See also Massih and Mansoori (1982):

$$\langle\phi\mu\mu(r_{12})\rangle_\omega = -\frac{1}{3}\mu^4/(kTr_{12}^6) \quad \text{for } \mu^4/(3kTr_{12}^6) < 1, \quad (13)$$

$$\langle\phi\mu Q(r_{12})\rangle_\omega = -\mu^2 Q^2/(kTr_{12}^8) \quad \text{for } \mu^2 Q^2/(kTr_{12}^8) < 1, \quad (14)$$

and

$$\langle\phi QQ(r_{12})\rangle_\omega = -\frac{7}{3}Q^4/(kTr_{12}^{10}) \quad \text{for } 6Q^2/(kTr_{12}^5) < 1. \quad (15)$$

Then, the angle-averaged pair-potential energy function of two identical polar molecules will be

$$\langle\phi(r_{12})\rangle_\omega = 4\epsilon\left[(\sigma/r_{12})^{12} - \frac{7}{20}(7Q_*^4/T^*)(\sigma/r_{12})^{10}\right.$$
$$\left. - \frac{1}{4}(\mu_*^2 Q_*^2/T^*)(\sigma/r_{12})^8 - \{1 + \mu_*^4/(12T^*)\}(\sigma/r_{12})^6\right] \quad (16)$$

where

$$\mu* = \mu/(\epsilon^{1/2}\sigma^{3/2}) \quad (17)$$

and

$$Q* = Q/(\epsilon^{1/2}\sigma^{5/2}) \quad (18)$$

For the three-body potential function we use the Axilrod-Teller triple-dipole function

$$\psi(123) = \nu(1 + 3 \cos\Theta_1 \cos\Theta_2 \cos\Theta_3)/(r_{12}r_{13}r_{23})^3, \quad (19)$$

as in the case of the nonpolar fluids. By replacing Eqs. 16 and 18 in Eqs. 3 and 4, respectively, and then replacing Eqs. 2–4 in Eq. 1 when the inequality sign is replaced by an equality sign we derive the analytic expression for the Helmholtz free energy of a polar fluid

$$A/RT = A^{ig}/RT + \eta(4 - 3\eta)/(1 - \eta)^2$$
$$+ \frac{48\eta}{T^*}\left[c^{-12}I_{12}(\eta) - \frac{7}{20}c^{-10}(Q_*^4/T^*)I_{10}(\eta)\right.$$
$$\left. - \frac{1}{4}c^{-8}(\mu_*^2 Q_*^2/T^*)I_8(\eta) - c^{-6}\{1 + \mu_*^4/(12T^*)\}I_6(\eta)\right]$$
$$+ \frac{\nu*}{T^*}c^{-9}(f_1/f_2). \quad (20)$$

where

$$\vartheta* = \frac{\nu}{\epsilon\sigma^9}, \quad c = \frac{d}{\sigma}$$

$$f_1 = 5.17184\eta + 6.16139\eta^2 - 2.19927\eta^3 \quad (21)$$

$$f_2 = 1 - 1.12789\eta + 0.73166\eta^2 \quad (22)$$

and

TABLE 2. INTERMOLECULAR POTENTIAL ENERGY PARAMETERS OF POLAR FLUIDS CALCULATED THROUGH VIM THEORY AND EXPERIMENTAL DIPOLE MOMENT DATA (SMYTH, 1955): ϵ/k IS IN K; σ IS IN 10^{-10}m]; Q IS IN [erg$^{0.5}\cdot$cm$^{2.5}$]; ν/k IS IN [10^{-90}m$^9\cdot$K]; AND μ IS IN [erg$^{0.5}\cdot$cm$^{1.5}$]

Substance	ϵ/k	σ	$Q \times 10^{26}$	$(\nu/k) \times 10^{-4}$	$\mu \times 10^{18}$
Carbon Dioxide	194.64	3.984	5.162	124.10	0.0
Methyl Chloride	389.40	4.730	1.202	103.633	1.8
Ethane	197.32	4.537	0.55	33.12	0.0
Hexane	401.65	7.301	2.35	43.29	0.0
Heptane	413.21	8.018	3.12	68.110	0.0
Isobutane	287.30	5.326	2.345	19.68	0.1
Sulfur Dioxide	352.37	4.102	4.12	87.631	1.7

TABLE 3. UNIVERSAL COEFFICIENTS α_{ij} OF EQ. 30

	$j = 0$	$j = 1$	$j = 2$	$j = 3$
$i = 0$	0.958047	−2.666531	0.217005	−0.0661946
$i = 1$	−0.236503	15.527093	−0.511675	−0.2453656
$i = 2$	0.124900	−6.568512	−0.215738	0.4858472
$i = 3$	−0.095197	4.553687	0.225446	−0.3861569
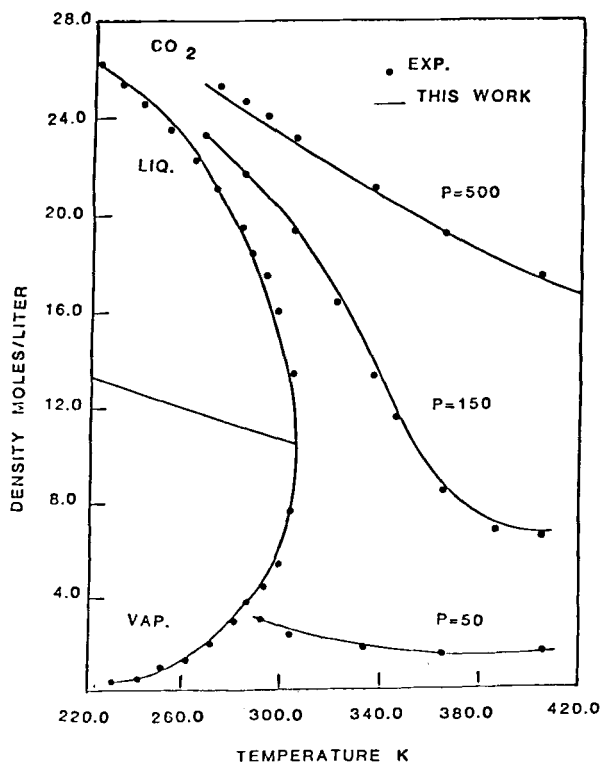
Figure 1. Isobaric saturation curve of carbon dioxide with different isobars at 50 × 10⁵, 150 × 10⁵, and 500 × 10⁵ Nm⁻² as calculated by the VIM equation of state and compared with the experimental data reported by Rowlinson et al. (1980).
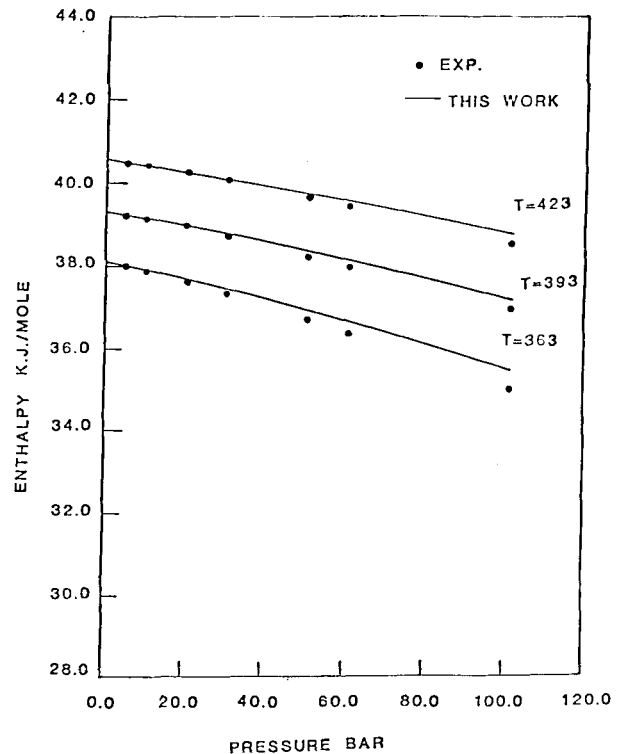

Figure 2. Enthalpy of carbon dioxide in the dense gas phase as calculated by the VIM equation of state and compared with the experimental data reported by Raznjevic (1976) at different temperatures.

$$I_n(\eta) = \sum_{i=0}^{5} C_{ni}\eta^i. \tag{23}$$

The procedure for derivation of Eq. 20 is already explained in Part I. Coefficients C_{ni} appearing in Eq. 23 are reported in Part I for different values of $n(=6, 8, 10, 12$ and $14)$. Equation 20 can be used for derivation of analytic expression of the other thermodynamic functions of polar fluids such as compressibility factor, internal energy, and enthalpy.

By using the relationship between pressure and the Helmholtz free energy

$$P = \rho^2(\partial A/\partial\rho)_T$$

and application of condition 14, the following analytic expression for the compressibility factor of polar fluids will be derived

$$Z = P/\rho RT = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3$$
$$+ \frac{48}{T^*}\left[c^{-12}\{I_{12}(\eta) + J_{12}(\eta)\} - \frac{7}{20}c^{-10}(Q_*^4/T^*)\{I_{10}(\eta) + J_{10}(\eta)\}\right.$$
$$\left. - \frac{1}{4}c^{-8}(\mu_*^2 Q_*^2/T^*)\{I_8(\eta) + J_8(\eta)\} - c^{-6}\{1 + \mu_*^4/(12T^*)\}\{I_6(\eta)\right.$$
$$\left. + J_6(\eta)\}\right] + \frac{\nu^*}{T^* c^9}\left(\frac{f_1 f_2 - f_1 f_2}{f_2^2}\right) \tag{24}$$

where

$$J_n(\eta) = \sum_{i=0}^{5} iC_{ni}\eta^i, \tag{25}$$

$$f_1 = 5.17184 + 12.32278\eta - 6.59781\eta^2, \tag{26}$$

and

$$f_2 = 1.12789 + 1.46332\eta \tag{27}$$

In a similar manner as in the case of the VIM equations of state of nonpolar fluids (Part I) intermolecular potential parameters ϵ, σ, and can be calculated by minimization of the following expression

$$\sum_{j=1}^{n}(Z_j^{\text{exptl}} - Z_j)^2 + \lambda\sum_{j=1}^{n}A_j' = \text{minimum}, \tag{28}$$
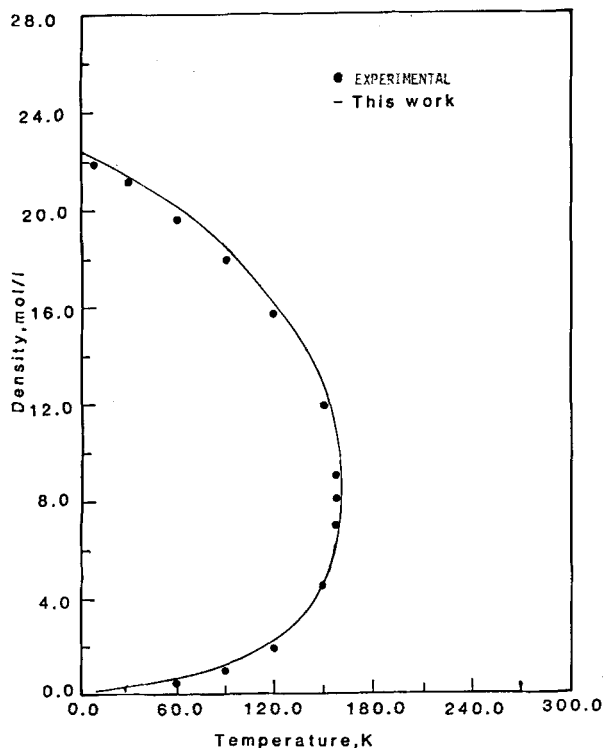
Figure 3. Isobaric saturation curve of sulphur dioxide calculated by the VIM equation of state and compared with the experimental data of Kang et al. (1961).

TABLE 4. DENSITY AND COMPRESSIBILITY OF METHYL CHLORIDE AS CALCULATED BY VIM EQUATION OF STATE, EQ. 24, AND COMPARED WITH EXPERIMENTAL DATA OF HSU et al. (1964).

T [K]	P [Nm^{-2}] $\times 10^5$	ρ_{exptl} [mol/L]	ρ_{cal} [mol/L]	Z_{exptl}	Z_{cal}
323.15	6.14	0.250	0.246	0.914	0.927
323.15	10.36	0.445	0.442	0.866	0.872
373.15	6.26	0.211	0.210	0.956	0.958
373.15	31.54	1.487	1.486	0.684	0.684
416.25	41.54	1.640	1.629	0.732	0.737
416.25	51.72	2.380	2.361	0.628	0.633
448.15	51.56	1.848	1.835	0.749	0.754
448.15	81.45	3.994	3.967	0.547	0.551
498.15	209.25	9.470	9.443	0.534	0.535
498.15	315.67	11.806	11.725	0.646	0.650

TABLE 5. DENSITY AND COMPRESSIBILITY OF HEXANE AS CALCULATED BY VIM EQUATION OF STATE, EQ. 24, AND COMPARED WITH EXPERIMENTAL DATA REPORTED BY VARGAFTIK (1975).

T [K]	P [Nm^{-2}] $\times 10^5$	ρ_{exptl} [mol/L]	ρ_{cal} [mol/L]	Z_{exptl}	Z_{cal}
343.15	50.0	7.203	6.467	0.243	0.271
343.15	300.0	7.555	8.082	1.392	1.301
373.15	100.0	6.957	6.591	0.463	0.489
373.15	300.0	7.280	7.965	1.328	1.214
433.15	100.0	6.269	5.933	0.443	0.468
433.15	300.0	6.759	6.850	1.232	1.216
473.15	50.0	5.385	4.725	0.236	0.269
473.15	300.0	6.426	6.945	1.187	1.098
483.15	50.0	5.160	4.526	0.241	0.275
483.15	300.0	6.345	6.728	1.177	1.110

TABLE 6. DENSITY AND COMPRESSIBILITY OF ISOBUTANE AS CALCULATED BY VIM EQUATION OF STATE, EQ. 24, AND COMPARED WITH EXPERIMENTAL DATA REPORTED BY VARGAFTIK (1975).

T [K]	P [Nm^{-2}] $\times 10^5$	ρ_{exptl} [mol/L]	ρ_{cal} [mol/L]	Z_{exptl}	Z_{cal}
313.15	40.0	8.866	9.311	0.173	0.165
393.15	40.0	6.886	6.836	0.178	0.179
313.15	80.0	9.490	9.483	0.324	0.324
393.15	80.0	7.353	7.530	0.333	0.325
313.15	120.0	10.003	9.622	0.461	0.479
393.15	120.0	7.453	7.929	0.493	0.463
293.15	160.0	9.940	10.130	0.660	0.648
373.15	160.0	8.582	8.638	0.601	0.597
393.15	160.0	7.999	8.199	0.612	0.597
293.15	200.0	10.464	10.219	0.784	0.803
313.15	200.0	10.034	9.861	0.766	0.779
353.15	200.0	9.451	9.168	0.721	0.743

with respect to these coefficients. In Eq. 28 λ is the Lagrangian multiplier and n is the number of experimental compressibility data. For polar molecules usually there is reliable dipole moment data available in the literature. However, the quadrupole moment data for molecules are rather scarce and varying according to various sources. Due to this problem Eq. 28 should be actually used for calculation of ϵ, σ, ϑ, and Q.

CALCULATION OF THERMODYNAMIC PROPERTIES

In applying the VIM equation of state for calculation of thermodynamic properties of polar fluids we will need to construct a dimensionless relationship for the reference hard-sphere diameter, Eq. 8, with respect to temperature and density. Coefficients a_i ($i = 0,1,2,3$) of Eq. 8 for argon and methane (which are non-polar fluids) are already reported in Part I. We have also calculated these coefficients for carbon dioxide which is a quadrupolar fluid (with zero dipole moment) and methyl chloride which is a dipolar fluid (with nonzero dipole and quadrupole moments) and they are reported in Table 1. With the availability of coefficients a_i of Eq. 8 for carbon dioxide and methyl chloride we are now able to calculate ϵ, σ, ν, and Q for these fluids through constrained Lagrangian minimization of Eq. 28 with respect to these parameters. Coefficients ϵ, σ, ν and Q for carbon dioxide and methyl chloride as calculated through Eq. 28 are reported in Table 2. Also reported in this table are the experimental dipole moment data for these fluids.

In order to express the hard-sphere reference diameter in a universal (dimensionless) form as

$$c = \frac{d}{\sigma} = \alpha_0 + \alpha_1\rho^* + \alpha_2/T^* + \alpha_3\rho^*/T^* \qquad (29)$$

where $T^* = kT/\epsilon$, $\rho^* = N_o\rho\sigma^3$, we need to express α_i ($i = 0,1,2,3$) with respect to ν^*, μ^*, Q^* as the following

$$\alpha_i = \alpha_{i0} + \alpha_{i1}\nu^* + \alpha_{i2}\mu^* + \alpha_{i3}Q^*, \quad (i = 0,1,2,3). \quad (30)$$

From argon and methane hard-sphere diameter data we have already calculated values of α_{i0} and α_{i1} ($j = 0,1,2,3$) which were reported in Part I. From the hard-sphere diameter data and potential energy parameters of carbon dioxide (for which $\mu = 0$) we can also calculate α_{i3} ($i = 0,1,2,3$). Then, by knowing α_{i0}, α_{i1}, and α_{i3}, and application of the hard-sphere diameter data and potential energy parameters of methyl chloride we can calculate α_{i2} ($i = 0,1,2,3$). All the values of universal coefficients α_{ij} ($i,j = 0,1,2,3$) as calculated by this procedure are reported in Table 3. With the availability of these universal coefficients the VIM equation of state can be used for calculation of thermodynamic properties of other polar fluids provided that their potential energy parameters are already known.

With the application of Eq. 29 in Eq. 24 and minimization of Eq. 28 we have derived the potential energy parameters of a number of other polar molecules as reported in Table 2.

TABLE 7. DENSITY AND COMPRESSIBILITY OF SULFUR DIOXIDE AS CALCULATED BY VIM EQUATION OF STATE, EQ. 24, AND COMPARED WITH EXPERIMENTAL DATA OF KANG et al. (1961).

T [K]	P $[Nm^{-2}] \times 10^5$	ρ_{exptl} [mol/L]	ρ_{cal} [mol/L]	Z_{exptl}	Z_{cal}
323.15	100.33	20.611	21.329	0.181	0.175
323.15	257.18	21.182	21.130	0.452	0.453
323.15	310.43	21.356	21.387	0.541	0.540
348.15	41.46	19.150	19.922	0.075	0.072
348.15	100.86	19.453	19.366	0.179	0.180
348.15	282.82	20.277	20.003	0.482	0.488
373.15	28.045	17.370	17.010	0.052	0.053
373.15	153.98	18.407	18.291	0.270	0.271
373.15	309.91	19.227	19.216	0.519	0.520
398.15	74.44	16.082	16.082	0.140	0.140
398.15	180.38	17.307	17.303	0.315	0.315
398.15	307.97	18.237	18.276	0.510	0.509
430.15	76.14	6.474	6.377	0.329	0.334
430.65	76.73	6.655	6.534	0.322	0.328
430.65	148.15	14.422	14.327	0.287	0.289
430.65	296.93	16.271	16.292	0.610	0.509
473.15	118.52	6.264	6.186	0.481	0.487
473.15	222.22	12.758	12.581	0.443	0.449
473.15	311.21	14.211	14.051	0.557	0.563

TABLE 8. PREDICTION OF INTERNAL ENERGY OF ETHANE USING VIM EQUATION OF STATE, EQ. 31, AND COMPARED WITH EXPERIMENTAL DATA REPORTED BY GOODWIN et al. (1976).

T [K]	P $[Nm^{-2}] \times 10^5$	ρ_{exptl} [mol/L]	U_{exptl} [J/mol]	U_{cal} [J/mol]
100.0	60.0	21.404	5,928.9	6,026.3
180.0	60.0	18.458	11,444.6	11,619.9
240.0	60.0	15.854	15,939.9	16,173.6
100.0	100.0	21.454	5,898.8	5,996.2
180.0	100.0	18.569	11,366.5	11,541.8
240.0	100.0	16.101	15,767.4	16,001.1
100.0	200.0	21.573	5,827.5	5,924.9
180.0	200.0	18.824	11,189.7	11,365.0
240.0	200.0	16.607	15,415.4	15,649.1
100.0	300.0	21.687	5,761.3	5,858.7
150.0	300.0	20.039	9,046.2	9,192.2
250.0	300.0	16.657	15,843.3	16,086.7
100.0	400.0	21.796	5,699.6	5,797.0
150.0	400.0	20.200	8,941.0	9,087.0
250.0	400.0	17.028	15,589.4	15,832.8

From the analytic expressions of the Helmholtz free energy and compressibility factor analytic expression for the other thermodynamic functions can be derived. For internal energy we get

$$U/RT = U^{ig}/RT + \frac{48\eta}{T^*}\left[c^{-12}I_{12}(\eta) - \frac{7}{20}c^{-10}(Q_*^4/T^*)I_{10}(\eta)\right.$$

$$\left. - \frac{1}{4}c^{-8}(\mu_*^2 Q_*^2/T^*)I_8(\eta) - c^{-6}\{1 + \mu_*^4/(12T^*)\}I_6(\eta)\right]$$

$$+ \frac{\nu^*}{T^*}c^{-9}(f_1/f_2). \quad (31)$$

For enthalpy of polar fluids we obtain

$$H/RT = H^{ig}/RT + 2\eta(2 - \eta)/(1 - \eta)^3 + \frac{48\eta}{T^*}\left[c^{-12}\{I_{12}(\eta)\right.$$

$$+ J_{12}(\eta)\} - \frac{7}{20}c^{-10}(Q_*^4/T^*)\{I_{10}(\eta) + J_{10}(\eta)\}$$

$$- \frac{1}{4}c^{-8}(\mu_*^2 Q_*^2/T^*)\{I_8(\eta) + J_8(\eta)\} - c^{-6}\{1 + \mu_*^4/(12T^*)\}\{I_6(\eta)$$

$$\left. + J_6(\eta)\}\right] + \frac{\nu^*}{T^*}[(f_1 f_2 - f_1' f_2 + f_1 f_2')/f_2^2] \quad (32)$$

Thermodynamic properties of a number of polar fluids are calculated by the VIM equation of state and they are reported here. In Figure 1 the saturation and isobaric curves of carbon dioxide as calculated by the VIM equation of state are reported along with the experimental data. In Figure 2 the saturation and isothermal curves of carbon dioxide are reported. Figure 3 consists of comparison of carbon dioxide enthalpy prediction by the VIM equation of state for different isotherms. According to these figures the results of the VIM equation of state are in good agreement with the available experimental data of carbon dioxide. It should be also pointed out that the results of the predictions by the VIM equation of state are in agreement with the IUPAC correlation of carbon dioxide due to Rowlinson et al. (1980).

In Figure 4 saturation curve of sulfur dioxide as predicted by the VIM equation of state is compared with the experimental saturation data. Again, according to this figure the VIM equation of state predictions are in good agreement with the experimental data. Thermodynamic property predictions of methyl chloride, hexane, iso-butane, sulfur dioxide, and ethane by the VIM equation of state are reported in Tables 4 to 8. According to these tables for most of the fluid which are studied, except probably for hexane, the VIM

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In Figure 3 saturation curve of sulfur dioxide as predicted by the VIM equation of state is compared with the experimental saturation data. Again, according to this figure the VIM equation of state predictions are in good agreement with the experimental data. Thermodynamic property predictions of methyl chloride, hexane, iso-butane, sulfur dioxide, and ethane by the VIM equation of state are reported in Tables 4 to 8. According to these tables for most of the fluid which are studied, except probably for hexane, the VIM prediction are in agreement with the experimental data. Table 9 consists of the critical constants of a number of polar fluid calculated via the VIM equation and compared with the experimental data. This table indicates good agreement between the results of the VIM equation and the experimental data.

TABLE 9. CRITICAL CONSTANTS OF CARBON DIOXIDE, METHYL CHLORIDE, ETHANE, AND SULFUR DIOXIDE AS CALCULATED BY VIM EQUATION OF STATE AND COMPARED WITH EXPERIMENTAL DATA

Substance	T_c[K]		P_c[10^{-5}Nm^{-2}]		V_c[cc/mol]	
	VIM	Exptl.	VIM	Exptl.	VIM	Exptl.
Carbon Dioxide	304.9	304.2	76.30	73.76	92.6	94.0
Methyl Chloride	412.2	416.3	80.25	66.77	126.3	139.0
Ethane	309.8	305.4	48.23	48.84	146.8	148.0
Sulfur Dioxide	433.6	430.8	80.35	78.83	123.6	122.0

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NOTATION

a_i	= coefficients defined in Eq. 8
A	= Helmholtz free energy
$c = d/\sigma$	= cut-off parameter
C_{ni}	= coefficients defined in Eq. 23
d	= hard-sphere diameter
f_i	= defined by Eqs. 21 and 22
g_{o2}	= hard-sphere fluid pair-distribution function
g_{o3}	= hard-sphere fluid triplet-distribution function
H	= enthalpy
I_n	= defined by Eq. 23
J_n	= defined by Eq. 25
k	= Boltzmann constant
N	= number of molecules
N_a	= Avogadro's number
P	= pressure
Q	= quadrupole moment
r_{ij}	= intermolecular distance
r_i	= molecular position vector
R	= universal gas constant
S	= entropy
T	= absolute temperature
U	= internal energy
V	= volume
$x = r/d$	= dimensionless intermolecular distance
$Z = PV/NkT$	= compressibility factor

Greek Letters

α_i	= coefficients defined in Eq. 29
λ	= Lagrangian multiplier
ρ	= molar density
ϕ	= pair intermolecular potential energy function
ψ_{ijk}	= triplet intermolecular potential energy function
η	= dimensionless density
σ	= Lennard-Jones length parameter
ϵ	= Lennard-Jones energy parameter
ν	= Axilrod-Teller energy parameter
Θ_i	= angle between r_{ij} and r_{ik}
ω_i	= polar angle
μ	= dipole moment

Subscripts

$2b$	= due to pair interactions
$3b$	= due to triplet interactions
c	= critical property
o	= hard-sphere reference fluid

Superscripts

exptl	= experimental property
ig	= ideal gas property
$*$	= dimensionless property

Note added to the proof: Our recent and more accurate hard-sphere diameter calculations from the entropy data indicate that eq. (8) is valid at high temperatures. However, for the purpose of the VIM equation of state eq. (8) seems sufficient for correlation of the hard-sphere diameter data.

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