



Thermodynamic Property Model of Wide-Fluid Phase Propane

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Abstract. A new thermodynamic property model for propane is expressed in form of the Helmholtz free energy function. It consists of eight terms of the ideal-gas part and eighteen terms of the residual part. Accurate experimental data of fluid properties and theoretical approach from the intermolecular potential were simultaneously considered in the development to insure accuracy and to improve reliability of the equation of state over wide range of pressures and temperatures. Based on the state range of experimental data used in the model development, the validity range is judged from the triple-point of 85.48 K to temperature of 450 K and pressure up to 60 MPa. The uncertainties with respect to different properties are estimated to be within 0.03% in ideal-gas isobaric specific heat, 0.2% in liquid phase density, 0.3% in gaseous phase density 1% in specific heats, 0.1% in vapor-pressure except at very low temperatures, 0.05% in saturated-liquid density, 0.02% in speed of sound of the gaseous phase and 1% in speed of sound of the liquid phase.

Keywords: *equation of state; propane; hydrocarbon; Helmholtz free energy; thermodynamic properties.*

1 Introduction

Propane has notable interest in industrial and scientific sectors due to this fluid is a major constituent in natural gases. Applications of propane as working fluid in thermal systems beside as fuel in power plants and heating systems in residential houses need information of its properties for thermal design and analysis. Prospective implementation of the fluid as substitution for replacing some ozone depleting fluids in thermal systems is also interesting to be studied in advance. Hydrocarbons are considered as environmentally safe substance due to its zero ozone-depletion potential and very small global-warming potential. Unfortunately, flammability of propane imposes limitation for the amount of fluid used in most applications since it has high risk operations and high maintenance costs. Restriction for applications as working fluid may be reduced by mixing propane with other non-flammable substances. Furthermore, high economic values of the fluid in any application require further study of the fluid.

Several thermodynamic property models for fluid-phase propane have been proposed, i.e. Helmholtz equation of state by Miyamoto and Watanabe [1], and the modified Benedict-Webb-Rubin (MBWR) equation of state by Younglove and Ely [2]. Newer equation of state for propane was proposed in 2003 by Span and Wagner [3] to make general functional form of equation of state for group of the polar fluid. Even MBWR model of Younglove and Ely [2] was developed based on older experimental data and the temperature scale IPTS-68. Until now it is used in the previous version of REFPROP software, version 6.01 released by NIST (National Institute of Standard and Technology, USA) [4]. On the other hand, thermodynamic property model of Miyamoto and Watanabe [1] is currently used in a famous thermophysical properties database software, REFPROP version 7.0 [5]. Their model was established with base of measurement data mostly used in this study, except the sets newly available after its publication.

Assessment of Miyamoto and Watanabe's model found that this model has lack on representation of Joule-inversion curve. This may be caused by functional form used in their equation of state. This behavior was not considered in the development. Therefore, improvement of thermodynamic property model for propane is important to be conducted. This paper reports the result of a research relating to development of thermodynamic equation of state for propane. Most recent paradigm on thermodynamic property model development for difluoromethane (R-32) previously reported by Astina and Sato [6] are considered.

2 Data and Modeling

Reliable input data for the thermodynamic property modeling contribute on the accuracy or data reproducibility from the model. Experimental data are very important for thermodynamic modeling of empirical equation of state. New data were found such as reported by Kitajima et al. [7], Kayukawa et al. [8] in 2003 and Gloss et al. [9] in 2004. Assessments of experimental data were carefully performed through literature survey to find the reliable data set. All data were prepared in the same unit system and scale. Data with temperature standard older than ITS-90 were converted into ITS-90. The distributions of available experimental data for the propane are illustrated in Figure 1. The experimental data either pvT or caloric properties are very scarce at low pressures and temperatures. Specific heats in gaseous phase are also unavailable. These all are caused by difficulty in measuring the properties at those ranges.

New experimental data and all data used to fit the model in the work of Miyamoto and Watanabe [1] are selected to be the input data for developing the new thermodynamic property model in this study. Thermodynamic property

model of propane that has been developed uses the reference values of specific enthalpy of $200 \text{ kJ}\cdot\text{kg}^{-1}$ and specific entropy of $1.0 \text{ kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ for the saturated-liquid state at 273.15 K . This reference state has been chosen in accordance with a convention recommended by International Institute of Refrigeration [4, 5].

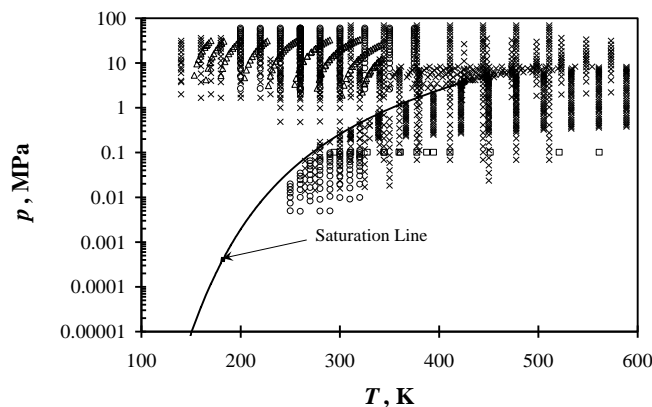


Figure 1 Distribution of available data for propane. (\times) $p\rho T$; (Δ) c_v ; (\square) c_p ; (\circ) w .

Physical parameters and ancillary equations are needed for development and implementation of the thermodynamic property model. Dimensionless thermodynamic properties are introduced to avoid unit errors in both thermodynamic model development and implementation of the equation of state. The equation of state is explicitly given in the two dimensionless independent parameters, reduced density, $\delta = \rho / \rho_c$, and inverse reduced temperature, $\tau = T_c / T$. Critical parameters used for propane are the critical temperature of 369.825 K [10], the critical density of $218.5 \text{ kg}\cdot\text{m}^{-3}$ [10], and the critical pressure of 4.24709 MPa derived from the extrapolation of the vapor-pressure equation. This extrapolation is needed due to the measurement uncertainties are large in the most critical point. Other parameters are the triple-point temperature of 85.48 K [11], the universal gas constant of $8.314472 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ [12], and the molar mass of $0.04409562 \text{ kg}\cdot\text{mol}^{-1}$ [13].

Complexity of thermodynamic property relation and shortcomings on measurements of thermodynamic properties have caused thermodynamic modeling paradigm continuously change in accordance with comprehension of thermodynamic properties either empirical or theoretical approaches can be achieved. Accuracies and thermodynamic consistencies are two important judgments on their assessment. Thermodynamic consistencies include critical constraints, behavior of ideal curves, and consistencies with other equation of

state with theoretical approaches. Reasonable mathematical and physical backgrounds were included in thermodynamic modeling. Reducing the degrees of freedom of the equation is important in multi property regression, especially on development of the residual part. Biological evolutionary process was considered to develop an optimization program code, which was originally developed by the first author [14], in order to get suitable structural form for the thermodynamic model either for ancillary equations or Helmholtz equation of state. Further information on the optimization procedure can be found in a published paper of Astina and Sato [15].

3 Ancillary Equations

Three ancillary equations, which have function of temperature, are formulated for three properties at saturation boundary (p_s , ρ' and ρ''). The equations are valid from triple-point temperature up to critical-point temperature. Ancillary equations are used to generate isothermal data of p_s , ρ' and ρ'' that are needed in development of the fundamental equation of state. This should be conducted since the data are commonly available at different temperatures. The specified structural forms of each equation were fitted to the measurement data of each property. The structural forms of the equations are predefined by considering scaling law so that the representation of the respective properties which are very difficult to measure at low temperatures and at the vicinity of the critical point can be improved.

Three ancillary equations for the vapor pressure and saturated-vapor and liquid densities from the triple point to the critical point were developed in this work in accordance with the optimization procedure in ref. [14, 15]. The vapor-pressure equation can be written as,

$$\ln \frac{p_s}{p_c} = \frac{T_c}{T} \sum_{i=1}^4 N_i \left(1 - \frac{T}{T_c}\right)^{t_i}, \quad (1)$$

where $N_1 = -6.785441$, $t_1 = 1$, $N_2 = 1.736759$, $t_2 = 1.5$, $N_3 = -1.363097$, $t_3 = 2.2$, $N_4 = -2.372037$, and $t_4 = 5$. The saturated-liquid density equation can be expressed as,

$$\frac{\rho'}{\rho_c} - 1 = \sum_{i=1}^4 N_i \left(1 - \frac{T}{T_c}\right)^{t_i}, \quad (2)$$

where $N_1 = 1.338996$, $t_1 = 0.3$, $N_2 = 1.14031485$, $t_2 = 0.6$, $N_3 = 0.1000498$, $t_3 = 1.5$, $N_4 = 0.1971671$, and $t_4 = 3.6$. The saturated-vapor density equation can be expressed as,

$$\ln \frac{\rho''}{\rho_c} = \sum_{i=1}^5 N_i \left(1 - \frac{T}{T_c} \right)^{t_i}, \quad (3)$$

where $N_1 = -0.5885818$, $t_1 = 0.3$, $N_2 = -3.235032$, $t_2 = 0.5$, $N_3 = -10.88160$, $t_3 = 1.8$, $N_4 = -43.95392$, $t_4 = 5.4$, $N_5 = -114.482$, and $t_5 = 13.9$.

4 New Equation of State

As a Helmholtz equation of state, the thermodynamic property model for propane is given in a combination of two separated parts. The ideal-gas part, α^0 , covers the ideal behavior of fluid and the so-called residual part, α^r , represents the residual behavior of real fluid. The ideal-gas isobaric specific heat equation was initially established and then the ideal-gas part can be obtained by integrating the specific heat equation with respect to selected reference state.

The ideal-gas part was derived by means of integration of the ideal-gas isobaric specific heat equation. This specific heat equation was established by fitting to theoretical values derived by Chao et al. [16], Dailey and Felsing [17] and Sage et al. [18]. The terms were selected in accordance with an original genetic optimization method, which was developed in the first application for difluoromethane [6]. The integral boundary condition was defined with a reference state in accordance with International Institute of Refrigeration. The ideal-gas part is written as,

$$\alpha^0(\delta, \tau) = \ln \delta + N_0^0 + N_1^0 \tau + N_2^0 \ln \tau + \sum_{i=3}^6 N_i^0 \ln \left\{ 1 - \exp(-\eta_i^0 \tau) \right\} \quad (4)$$

Numerical coefficients and parameters for this equation are given in Table 1.

Table 1 Coefficients and parameters of the ideal-gas part.

i	η_i^0	N_i^0
0	-	-4.992828913
1	-	4.290868000
2	-	3.021340195
3	1.048289299	2.890619390
4	3.052931786	4.463727599
5	11.41993237	8.143131355
6	5.039954185	10.48770680

The residual part was determined from a multi-property regression and genetic optimization for selecting terms in the equation. The residual part is written as,

$$\alpha^r = \sum_{i=1}^9 N_i \delta^{d_i} \tau^{t_i} + \sum_{i=10}^{13} N_i \delta^{d_i} \tau^{t_i} \exp(-\delta) + \sum_{i=14}^{16} N_i \delta^{d_i} \tau^{t_i} \exp(-\delta^2) + \sum_{i=17}^{18} N_i \delta^{d_i} \tau^{t_i} \exp(-\delta^3) \quad (5)$$

where the numerical coefficients and constants for this equation are given in Table 2.

Thermodynamic relation for each property when density and temperature are known are given in the following shorter descriptions. Unclear symbol can be referred to the nomenclature given at the end of this paper.

Compressibility and pressure:

$$Z(\tau, \delta) = p(\tau, \delta) / (\rho RT) = 1 + \delta \alpha_{\delta}^r$$

Saturation properties:

$$p_s(\tau, \delta') / (\rho' RT) = 1 + \delta' \alpha_{\delta'}^r$$

$$p_s(\tau, \delta'') / (\rho'' RT) = 1 + \delta'' \alpha_{\delta''}^r$$

$$p_s(\tau, \delta', \delta'') / (RT) (1/\rho'' - 1/\rho') - \ln(\delta' / \delta'') = \alpha^r(\delta', \tau) - \alpha^r(\delta'', \tau)$$

Virial coefficients:

$$B(\tau) \rho_c = \lim_{\delta \rightarrow 0} \alpha_{\delta}^r \quad C(\tau) \rho_c^2 = \lim_{\delta \rightarrow 0} \alpha_{\delta\delta}^r$$

Specific heats:

$$c_p^0(\tau) / R = 1 - \tau^2 \alpha_{\tau\tau}^0 = 1 + c_v^0 / R$$

$$c_v(\tau, \delta) / R = -\tau^2 (\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r)$$

$$c_p(\tau, \delta) / R = -\tau^2 (\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r) + \frac{(1 + \delta \alpha_{\delta}^r - \delta \tau \alpha_{\delta\tau}^r)^2}{(1 + 2\delta \alpha_{\delta}^r + \delta^2 \alpha_{\delta\delta}^r)}$$

Speed of sound:

$$w(\tau, \delta)^2 M / (\mathcal{R}T) = 1 + 2\delta \alpha_{\delta}^r + \delta^2 \alpha_{\delta\delta}^r + \frac{(1 + \delta \alpha_{\delta}^r - \delta \tau \alpha_{\delta\tau}^r)^2}{-\tau^2 (\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r)}$$

Internal energy: $u(\tau, \delta) / (RT) = \tau (\alpha_{\tau}^0 + \alpha_{\tau}^r)$

Enthalpy: $h(\tau, \delta) / (RT) = \tau (\alpha_{\tau}^0 + \alpha_{\tau}^r) + 1 + \delta \alpha_{\delta}^r$

$$\text{Entropy: } s(\tau, \delta) / R = \tau(\alpha_\tau^0 + \alpha_\tau^r) - (\alpha^o + \alpha^r)$$

Abbreviations:

$$\alpha_\tau = \frac{\partial \alpha}{\partial \tau}, \alpha_{\tau\tau} = \frac{\partial^2 \alpha}{\partial \tau^2}, \alpha_\delta = \frac{\partial \alpha}{\partial \delta}, \alpha_{\delta\delta} = \frac{\partial^2 \alpha}{\partial \delta^2}, \alpha_{\delta\tau} = \frac{\partial^2 \alpha}{\partial \delta \partial \tau}$$

Table 2 Coefficients and constants of the residual part.

i	d_i	t_i	N_i
1	1	0.5	4.351478882 $\times 10^0$
2	1	0.75	-5.303338979 $\times 10^0$
3	1	1.4	8.778030399 $\times 10^{-1}$
4	1	3.7	-4.698521308 $\times 10^{-2}$
5	1	3.875	4.011015086 $\times 10^{-2}$
6	2	1.375	-6.253587025 $\times 10^{-1}$
7	3	0.5	1.283811450 $\times 10^{-1}$
8	4	1.5	1.039006296 $\times 10^{-2}$
9	7	1	1.735220995 $\times 10^{-4}$
10	1	1.25	-8.445284479 $\times 10^{-1}$
11	2	5	-5.604721398 $\times 10^{-3}$
12	4	1.75	1.041801469 $\times 10^{-1}$
13	8	3.75	-1.741341952 $\times 10^{-5}$
14	1	3.5	-2.824024467 $\times 10^{-1}$
15	3	9.4	1.086225331 $\times 10^{-4}$
16	4	3.6	-4.532304594 $\times 10^{-2}$
17	3	19	-1.462184694 $\times 10^{-2}$
18	12	13	-1.564259451 $\times 10^{-4}$

5 Assessment and Discussion

Accurate reproducibility for reliable and well measured data of the equation of state is the first criteria to reveal its quality. Data groups of different thermodynamic properties are compared to the values calculated from new equation of state at the same state points. The calculated values are served as a base line in the comparisons to get better assessment of data from different sources. Relative deviations of measured data from the calculated data are

mostly used as comparative indicator. Statistical results of the equation of state to represent thermodynamic properties based on assessments of available experimental data are given in Tables 3 and 4. Statistical definitions used are: AAD – average of absolute deviation; BIAS – average of deviation; STD – standard deviation; and Max. Dev. - maximum deviation. Uncertainty is calculated based on two times the value of the standard deviation.

Table 3 Statistical results of the new equation of state at saturation.

First Author	Year	N	Prop.	AAD (%)	STD (%)	BIAS (%)	Max. Dev. (%)	N_{out}
Reamer [19]	1949	9	ρ'	14.3	1.32	14.3	17.8	0
Thomas [10]	1982	22	ρ'	0.37	1.12	0.20	5.2	0
Helgeson [20]	1967	16	ρ'	0.42	0.40	0.38	1.7	0
McClune [21]	1976	17	ρ'	0.04	0.014	0.04	0.06	0
Orrit [23]	1978	31	ρ'	0.055	0.081	-0.015	0.35	0
Ely [23]	1978	16	ρ'	0.037	0.036	0.028	0.11	0
Haynes [24]	1944	16	ρ'	0.097	0.097	0.032	0.11	0
Reamer [19]	1949	9	ρ''	15.2	2.9	12.2	16.1	0
Thomas [10]	1982	11	ρ''	0.39	0.43	-0.26	1.3	0
Helgeson [20]	1967	16	ρ''	0.61	0.96	-0.23	2.9	0
Glos [9]	2004	24	p_s	0.13	0.25	-0.03	1.0	3
Carruth [25]	1973	12	p_s	11.9	18.7	6.79	47.1	0
Thomas [10]	1982	24	p_s	0.067	0.073	-0.033	0.16	0
Reamer [19]	1949	9	p_s	0.34	0.76	-0.23	2.2	0
Helgeson [20]	1967	16	p_s	0.12	0.13	0.12	0.42	0
Kemp [26]	1938	12	p_s	0.12	0.13	0.11	0.40	0
Goodwin [11]	1982	78	c_s	0.38	0.46	-0.13	0.73	0

Assessment of reproduced ideal-gas isobaric specific heat c_p^o with the accurate reanalysis data of c_p^o is required for the assessment of ideal-gas properties. As shown in Figure 1, the ideal-gas isobaric specific heat of Chao et al. [16] are reproduced from 50 to 1500 K with uncertainty less than 0.1%. Miyamoto and Watanabe's model [1] from the new equation of state are also shown in the same figure for comparison. The equation of Miyamoto and Watanabe is observed to be less accurate compared to the new equation of state. The

extrapolated data of speed of sound as derived by Trusler and Zarari [30] have larger discrepancy in comparison to other data.

Table 4 Statistical results of the new equation of state in single phases.

First Author	Year	N	Prop.	Phase*	AAD (%)	STD (%)	BIAS (%)	Max. Dev (%)	N_{out}
Glos [9]	2004	27	ρ	G	0.089	0.12	-0.005	0.37	0
Glos [9]	2004	83	ρ	L	0.074	0.09	0.05	0.25	0
Glos [9]	2004	90	ρ	SC	0.28	0.29	0.11	0.75	0
Thomas [10]	1982	414	ρ	L	0.13	0.17	-0.01	-0.60	178
Reamer [19]	1949	116	ρ	G	0.13	0.19	0.085	0.95	0
Reamer [19]	1949	89	ρ	L	0.13	0.19	0.085	0.96	0
Straty [27]	1984	19	ρ	G	0.11	0.18	-0.036	0.48	0
Straty [27]	1984	123	ρ	SC	0.23	0.32	-0.15	1.8	0
Ely [22]	1978	222	ρ	L	0.051	0.078	0.049	1.1	0
Haynes [24]	1977	196	ρ	L	0.11	0.11	0.071	0.29	0
Kitajima [7]	2003	38	ρ	L	0.11	0.11	-0.04	0.69	0
Goodwin [28]	1978	58	c_v	L	0.89	0.47	0.88	1.97	0
Kitajima [7]	2003	38	c_v	L	5.4	5.6	-4.6	16.9	0
Ersnt [29]	1970	36	c_p	L	0.63	0.49	-0.64	2.7	0
Trusler [30]	1996	78	w	G	0.010	0.011	0.005	0.02	0
Niepman [31]	1984	89	w	L	0.18	0.24	-0.01	1.2	17
Younglove [33]	1981	180	w	L	0.30	0.25	0.27	1.1	10
Lancam [32]	1984	230	w	L	0.58	0.79	0.27	2.3	11

*L: liquid phase, G: gaseous phase, SC: supercritical region

The representation of the saturation properties can be assessed by comparing values calculated from the new equation of state with measurements of the vapor pressure and the saturated-liquid and vapor densities. Comparisons to the other models were also assessed. The deviations of vapor pressures are shown in Figure 3. It performs adequate accurate from low to high temperatures. Deviations for the saturated-liquid and vapor densities are given in Figures 4 and 5. Both the new model and also the older ones show larger discrepancies in density for the states near the critical point. The uncertainties are 0.1% for the vapor pressure, 0.08% for the saturation temperatures, 0.1% for the saturated-liquid densities, and 1% for the saturated-vapor densities. Available

experimental data for the saturated-vapor densities are very scarce at lower temperatures. Calculated values from the new equation of state for vapor pressures are very close to the data of Thomas and Harrison [10].

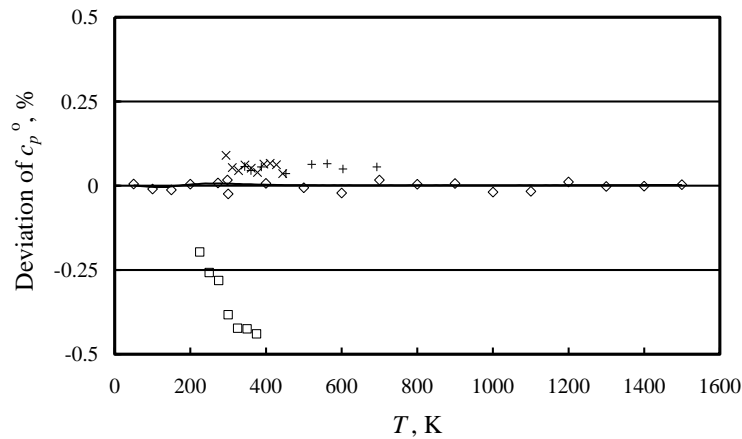


Figure 2 Deviation of ideal gas specific heat of propane from the new equation of state. (\diamond) Chao et al. [16]; (\times) Sage et al. [18]; (+) Dailey and Felsing [17]; (\square) Trusler and Zarari [30]; (—) Equation of Miyamoto and Watanabe [1].

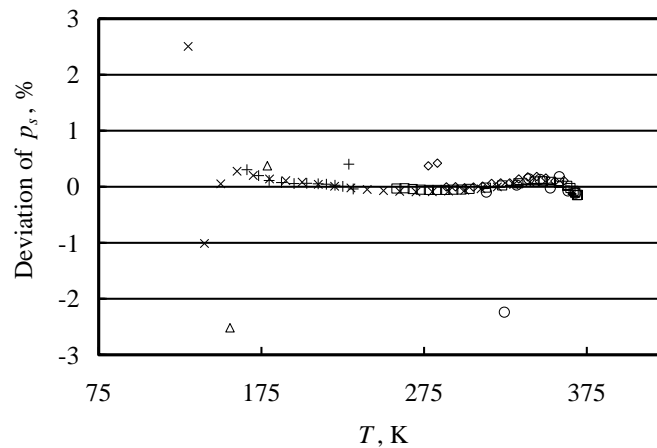


Figure 3 Deviation of vapor pressures of propane from the new equation of state. (\circ) Reamer et al. [18]; (Δ) Carruth and Kobayashi [24]; (\times) Glos et al. [9]; (+) Kemp and Egan [25]; (-) Kratkze [34]; (\square) Thomas and Harrison [9].

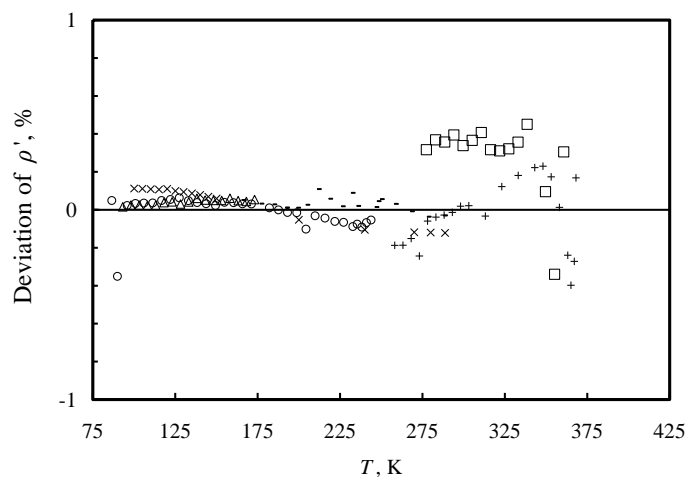


Figure 4 Deviation of saturated liquid density of propane from the new equation of state. (+) Thomas and Harrison [10]; (o) Orrit and Laupretre [38]; (-) Ely and Kobayashi [23]; (□) Helgeson and Sage [22]; (Δ) McClune [37].

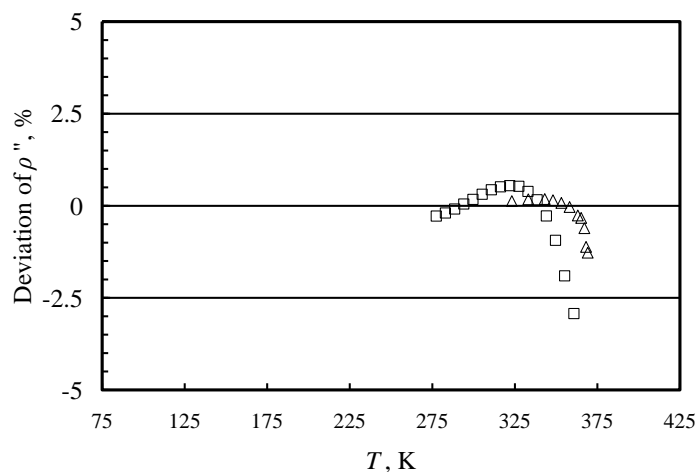


Figure 5 Deviation of saturated vapor density of propane from the new equation of state. (□) Helgeson and Sage [20]; (Δ) Thomas and Harrison [10].

Density deviations over a wide range of single-phases either in gaseous and liquid states are shown in Figures 6 and 7. The density deviation for the superheated-vapor phase is represented within 0.3%, that for the liquid phase is within 0.2% for good data, and that for the supercritical region is within 0.6%.

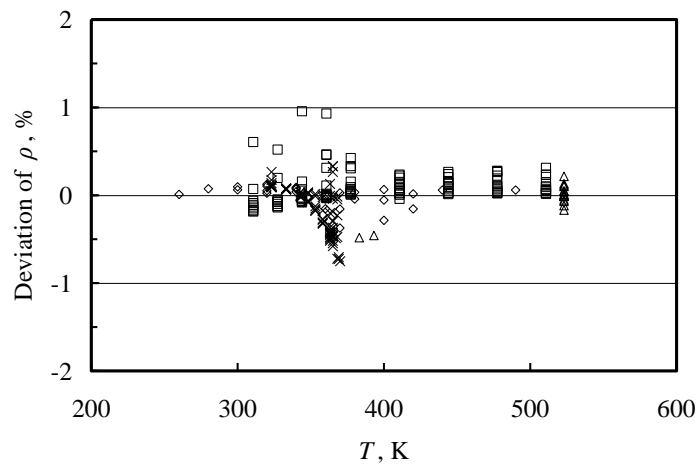


Figure 6 Deviation of density of propane in gaseous phase from the new equation of state. (◇) Glos et al. [9]; (Δ) Straty and Palavra [26]; (□) Reamer et al. [19].

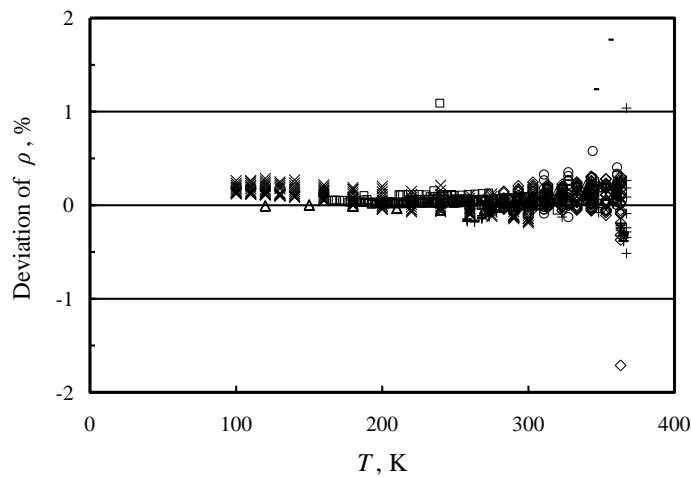


Figure 7 Deviation of density of propane in liquid phase from the new equation of state. (Δ) Glos et al. [9]; (◇) Dittmer et al. [35]; (□) Ely and Kobayashi [23]; (x) Haynes and Hiza [24]; (○) Reamer et al. [19]; (+) Thomas and Harrison [10].

Deviations of isochoric specific heat in liquid phase and liquid states are shown in Figure 8. Maximum deviation is 2% and it looks that bias exists for this property. Such as shown in Table 4, the data of Kitajima et al. [7] cannot be represented well by the new equation of state. The average absolute deviation is 5.4 % and bias is -4.6% . The data of Goodwin and Haynes [11] are represented

well. The uncertainty is less than 1%. The available experimental data for isobaric specific heat can be reproduced with uncertainty around 1% as indicated in the Table. Other specific heat comparison is given in Figure 9. This result shows deviation of saturated liquid specific heat from the new equation of state.

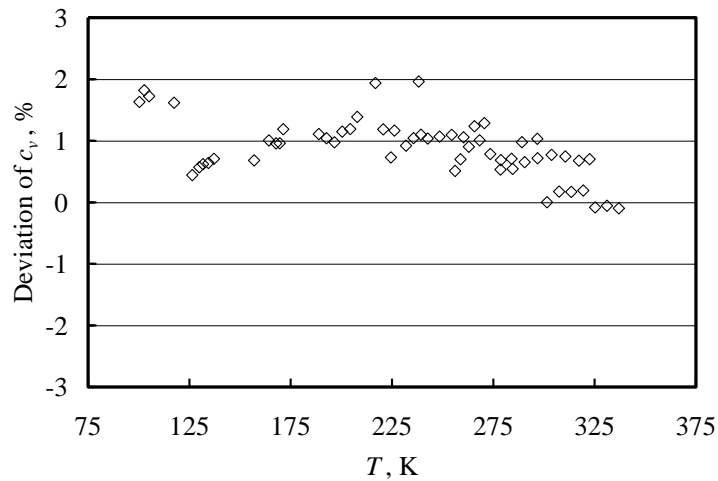


Figure 8 Deviation of specific heat of propane in liquid phase from the new equation of state. (\diamond) Goodwin [11].

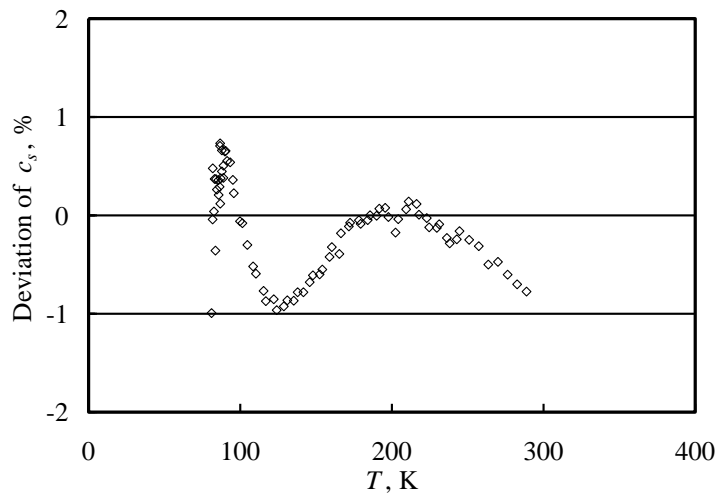


Figure 9 Deviation of saturated-liquid specific heat of propane from the new equation of state. (\diamond) Goodwin [27].

As shown in Figure 10, the speed of sound in the gaseous phase can reproduced with an uncertainty of 0.02%, while as shown in Figure 11, the speed of sound in the liquid phase is represented with an uncertainty of within 1.0%. As shown in the statistical results, most representation for speed of sound in the liquid phase is inferior to the gaseous phase. This relates to uncertainty of measurement for the speed of sound.

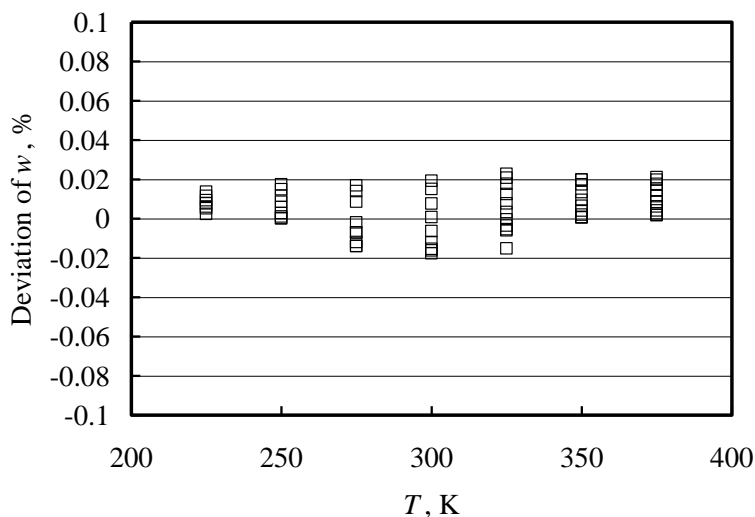


Figure 10 Deviation of speed of sound of propane in gaseous phase from the new equation of state. (□) Trusler and Zarari [30].

Critical parameters were determined from the new model. By setting first and second differentiation of pressure with respect to density at zero, critical density and temperature from the equation of state can be calculated. The calculated critical temperature and density are $218.5 \text{ kg}\cdot\text{m}^{-3}$ and 369.825 K . Using these values, the critical pressure calculated from the new model is 4.2562 MPa . This demonstrates that the fitting of the critical constraints in the regression adequately yields the critical parameters.

Thermodynamic consistency was assessed to find reliable equation of state and was viewed to reveal its ability in reproducing data beyond available experimental data. Consistency relations of fundamental equation of state to intermolecular energy are considered in assessment of behavior of the second and third virial coefficients. Behaviors of second and third virial coefficients are shown in Figures 12 and 13. Both coefficients perform correct behavior of intermolecular potential. The reliable values are still difficult to be judged since these properties are very difficult to measure. However, the present result

confirms good trend and consistency, especially, the third virial coefficient behavior that agrees with intermolecular potential behavior.

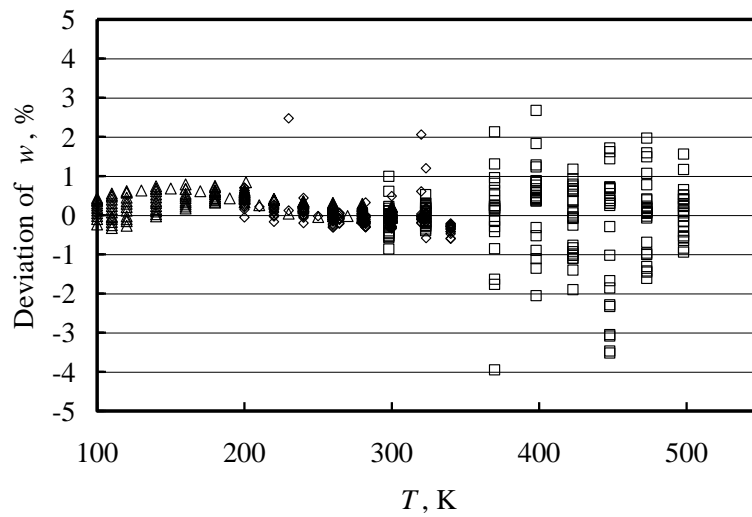


Figure 11 Deviation of speed of sound of propane in liquid phase from the new equation of state. (\diamond) Niemann [31]; (\square) Lancam [32]; (Δ) Younglove [33].

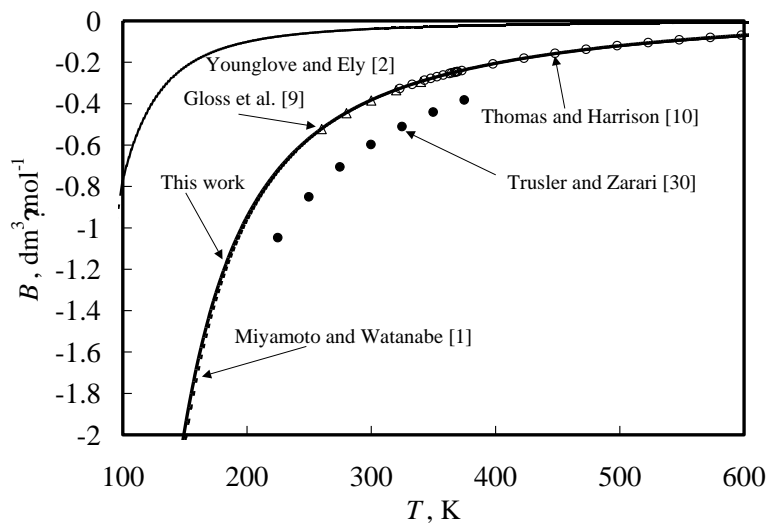


Figure 12 Second virial behavior derived from the new equation of state.

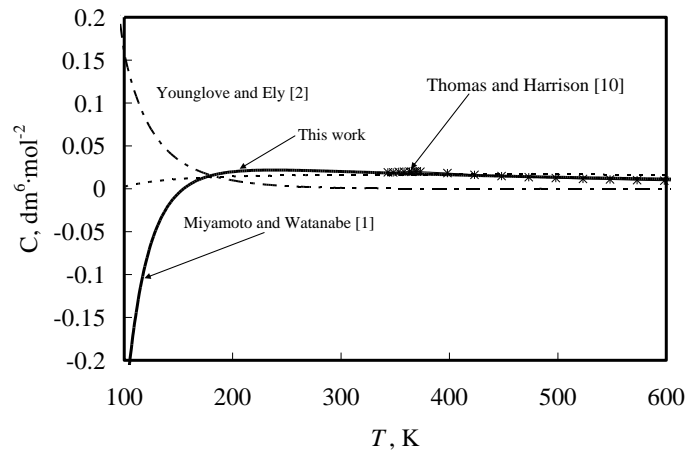


Figure 13 Third virial behavior derived from the new equation of state.

Assessment of thermodynamic surface from the new equation of state was conducted by plotting isothermal lines of pvT properties and isobaric lines of specific heat and speed of sound. The results show that the new equation of state perform the correct thermodynamic surface. The results are shown in Figures 14 to 17. Both isochoric and isobaric specific heat surfaces are performed in accordance with proper behavior. It appears that their values near critical point increase significantly. The proper behavior is also performed for the speed of sound. The lowest value is given in the critical point.

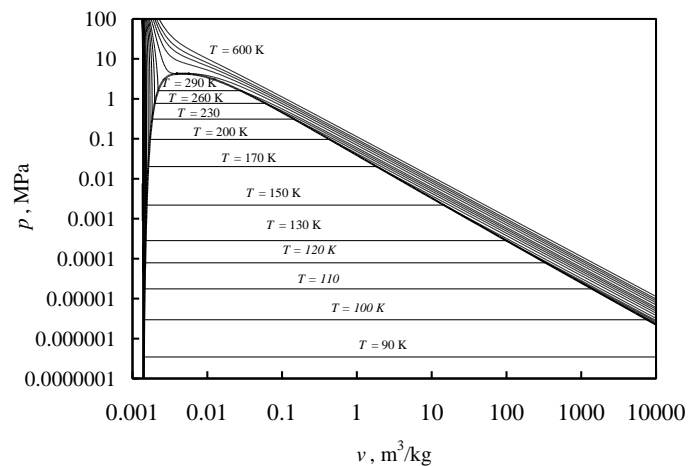


Figure 14 Isothermal lines of pvT properties from new equation state for propane.

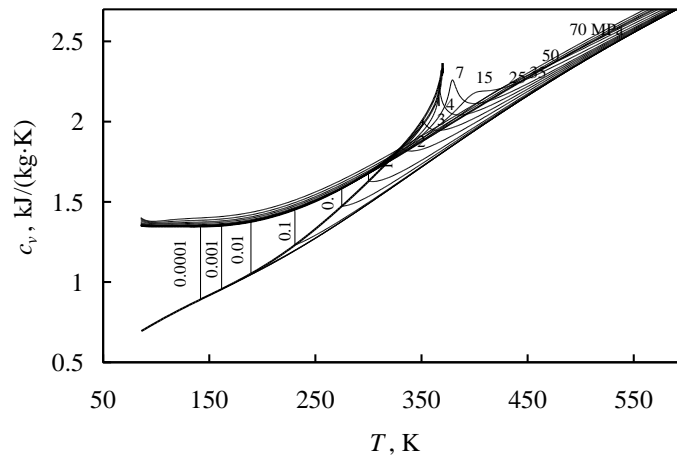


Figure 15 Isochoric lines of isochoric specific heat from new equation state for propane.

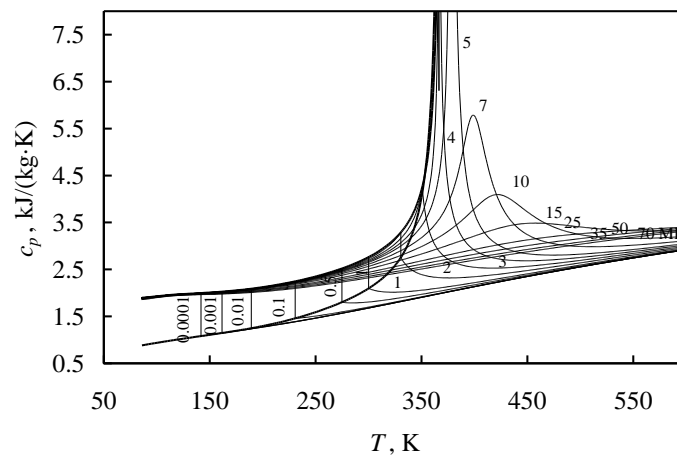


Figure 16 Isobaric lines of isobaric specific heat from new equation state for propane.

Ideal curves are considered to judge whether the fluid surface of an equation of state is reasonable or not. Reasonable behavior of thermodynamic surface of a fluid is necessary to be assessed for verifying the equation of state to adequately represent thermodynamic properties in wide-range fluid. Considering the reasonable behavior of ideal curves given by Span and Wagner [38] for simple fluid of nitrogen and carbon dioxide, unreasonable ideal curves will affect the

ability of the property representation at extreme temperatures and pressures. The assessment of ideal curves is important to confirm the goodness of the structural terms of the equation of state for wide-range of thermodynamic surface in the fluid phase.

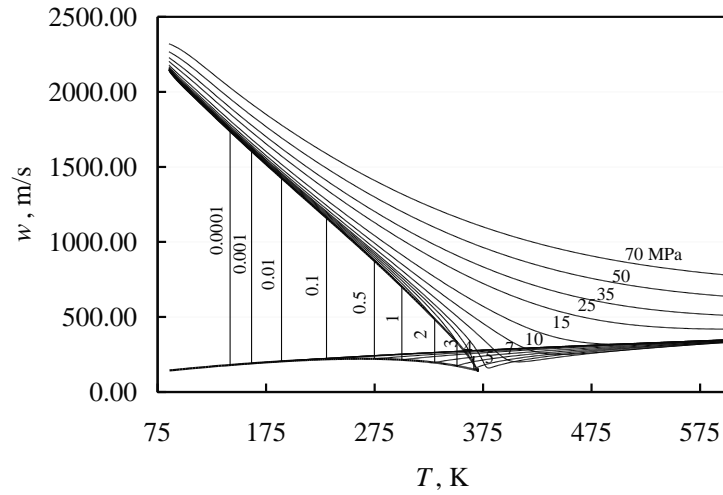


Figure 17 Isobaric lines of speed of sound from new equation state for propane.

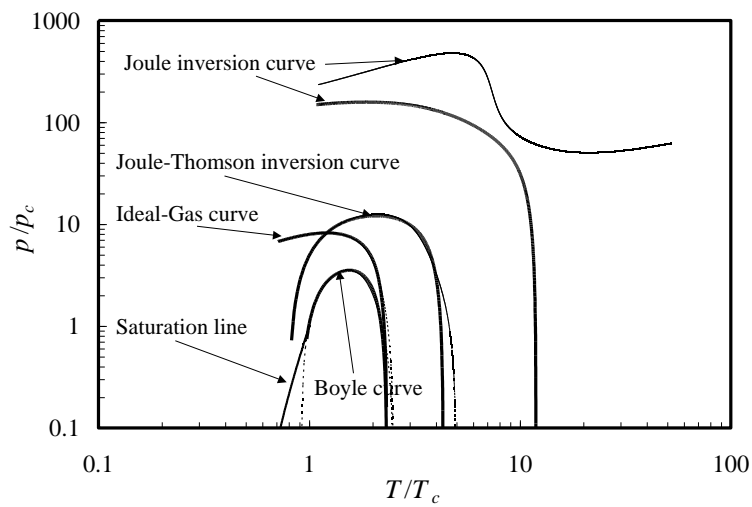


Figure 18 Ideal curves from new equation state for propane. (—) New equation of state; (---) Miyamoto and Watanabe [1].

Ideal curves are assessed to avoid unreasonable behavior in the region where no experimental data are available. This assessment is one of interesting in this study to find equation of state with reasonable behavior of the ideal curves. The comparative result is shown in Figure 18. Strictly different behavior is shown for Joule inversion curve of this work and the previously work by Miyamoto and Watanabe [1].

These results suggest that the theoretical intermolecular background is possible to be considered to improve the reliability of an equation of state for low temperatures, especially in the region near saturation. These behaviors are as consequence of higher degree of freedom for the thermodynamic model and scarce data near the saturation both pvT and caloric data used for the thermodynamic modeling. Consequently, intermolecular potential behavior is rationally considered as one of parameters on developing fundamental equations of state. This result is similar to the first publication [6] of serial results on thermodynamic modeling of this research group on hydrofluorocarbon and hydrocarbon fluids.

6 Conclusions

Thermodynamic property model for fluid-phase propane was established with rational thermodynamic behavior and consistencies. It is represented in Helmholtz free energy and has independent parameters of density and temperature. It can provide reliable thermodynamic properties even at very low temperatures and near saturation in the gaseous phase, liquid phase and supercritical region. The specific heat values in the gaseous phase near saturation are reasonably represented without any thermodynamic inconsistencies. Intermolecular potential behaviors of the fluids were represented well by performing the second and third virial coefficients. Ideal curves were also derived. It represents good agreements with all of the ideal curves consisting of ideal-gas curve, Joule-Thomson inverse curve, Boyle curve, and Joule inverse curve. Thermodynamic surfaces were assessed in these developments by plotting isothermal lines of pvT properties, isobaric lines of specific heat and speed of sound.

The equation of state for propane is valid in the fluid phase for temperatures from the triple point to 450 K and pressures up to 60 MPa. The second and third virial coefficients are in agreement with those derived in accordance with the intermolecular potential theory. The estimated uncertainties are 0.3% in density for the gaseous phase, 0.2% in density for the liquid phase, 0.6% in density for the supercritical region, 0.02% in speed of sound for the gaseous phase, 1% in speed of sound for the liquid phase, and 1% in isochoric specific heat for the liquid phase.

Acknowledgement

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Nomenclature

B	second virial coefficient
c	specific heat
C	third virial coefficient
M	molar mass
p	pressure
R	gas constant, which depends on other property unit in the equation
\mathfrak{R}	universal gas constant, 8,314472 kJ/(kmol·K)
T	temperature
v	specific volume
w	speed of sound
α	reduced Helmholtz free energy
δ	reduced density (ρ/ρ_c)
ρ	density
τ	inverse reduced temperature (T_c/T)

Subscripts

c	critical parameter
p	process at constant pressure
s	saturation
t	triple point
v	process at constant volume

Superscripts

o	ideal-gas part
r	residual part
s	saturated-liquid state
v	saturated-vapor state

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