An Equation of State for 1,1,1-Trifluoroethane (R-143a) [1]

J. Li [2,4], R. Tillner-Roth [3], H. Sato [2] and K. Watanabe [2]

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[2] Department of System Design Engineering, Faculty of Science and Technology, Keio University, 3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223, Japan.

[3] Institute of Thermodynamics, University of Hannover, Callinstrasse 36, 30167 Hannover, Germany.

[4] To whom correspondence should be addressed.

ABSTRACT

A fundamental equation of state has been developed for 1,1,1-trifluoroethane (R-143a) in the form of dimensionless Helmholtz free energy. The experimental thermodynamic property data which cover temperatures from the triple-point (161 K) to 433 K and pressures up to 35 MPa are used to develop the present equation, and they are represented by the present equation within their reported experimental uncertainties: 0.1% in density both for vapor and liquid phase P-ρ-T data, 1% in isochoric specific heat-capacities, and 20 ppm in vapor phase speed-of-sound data. The range of validity of the present model is confirmed to cover temperatures 160 to 650 K and pressures up to 50 MPa according to an excellent thermodynamic behavior of the isobaric specific heat-capacity values in entire fluid phase which are derived from the developed equation of state.

KEY WORDS: alternative refrigerant, equation of state, R-143a, thermodynamic property modeling, 1,1,1-trifluoroethane.

1. INTRODUCTION

The binary and ternary refrigerant mixtures containing 1,1,1-trifluoroethane (R-143a) are the most promising candidates to replace a conventional azeotropic refrigerant R-502 which is currently being used exclusively for low-temperature refrigeration systems. The equation of state for R-143a is urgently needed not only to represent the thermodynamic properties for the pure refrigerant of R-143a, but also, as a basic equation, to develop a thermodynamic model for refrigerant mixtures containing R-143a. Like other HFC refrigerants considered as substitutes for CFC's and HCFC's, the thermodynamic properties of R-143a have been investigated rather extensively in recent years. Available experimental data include 874 points of P-ρ-T data in vapor phase, 1535 in liquid phase, 460 points of essential thermodynamic property data along the coexistence curve and 854 points of caloric property data. The temperature and pressure ranges of the experimental thermodynamic properties accumulated are wide enough, and the uncertainties of those data are reliable enough to develop a so-called wide-range equation of state.

In this paper, an equation of state explicit in the dimensionless Helmholtz free energy is presented. A regression analysis developed by Wagner [1] is used to find the suitable structure of the equation with respect to the linear data, while a nonlinear optimization method proposed by Ahrendts and Baehr [2] is adopted to modify the equation on the basis of available thermodynamic property data.

All the equations and the temperature values in this paper are given on the International Temperature Scale of 1990 (ITS-90).

2. EXPERIMENTAL DATA SOURCE

It is needless to mention that not all of the existing thermodynamic property data is selected as the input data to develop the present equation of state. A selection of the input data has been done on the basis of an analysis of the experimental uncertainties reported, the magnitude of their scatter and the thermodynamic consistency with other data sets.

The observed critical temperature and density values by Aoyama et al. [3], T^*=345.860.01 K, and ρ^*=4341 kgm^{-3}, are selected as the numerical constants to define the reduced density δ (=ρ/ρ^*) and inverse reduced temperature τ (=T^*/T) which are used as the independent variables in the present modeling.

Eight points of the ideal gas isobaric specific heat-capacity values, C_p^0, by Gillis [4] are used to establish a C_p^0 correlation at the ideal gas state. These data are derived from the speed-of-sound measurements for temperatures from 250 to 400 K. Taking into account the contribution of anharmonicities, Yokozeki et al. [5] recalculated the ideal gas isobaric specific heat-capacity values based on the spectroscopic data. The calculated results between 160 K (triple-point temperature) and 700 K are also selected as additional input data in the present study.

Five hundred and twenty-six vapor phase P-ρ-T data of de Vries [6], which cover the range of temperatures 263-433 K and pressures 0.02-20.6 MPa, are selected as the basic data for vapor phase. On the other hand, in the liquid phase, 536 P-ρ-T data of de Vries are used which cover the range of 243-393 K and 1.48-18.1 MPa. In addition, 102 P-ρ-T data of Magee [7] beyond the range in which de Vries' data exist are used too.

The vapor-pressure data observed by de Vries [6] are selected to represent the thermodynamic properties at saturation. The measurements by Russel et al. [8] are also added so as to represent the behavior at lower temperatures where no other data exist. The input data thus selected from those by de Vries and Russel et al. cover the temperature range of 173-345 K.

One hundred and fifty-one isochoric specific heat-capacity data in liquid phase as well as those at the saturated-liquid condition from triple-point to critical temperature both reported by Magee [7] are also selected as the input data. Eighty-five speed-of-sound measurements in vapor phase by Gillis [4] are also included among the input data sets for the present purpose.

3. EQUATION OF STATE

The developed equation of state for R-143a given in the dimensionless Helmholtz free energy, $\Phi(\tau,\delta)$, is splitted into two parts: an ideal part, Φ^0, which describes the ideal gas behavior and a residual part, Φ^r, which is responsible for the representation of thermodynamic behavior of the real fluid, as given below ;

$$\Phi(\tau,\delta) = \frac{A}{RT} = \Phi^0(\tau,\delta) + \Phi^r(\tau,\delta)$$

(1)

where A is the specific Helmholtz free energy. $R = R_m / M$ is the gas constant of R-143a with the universal gas constant R_m = 8.31451 Jmol^{-1}K^{-1} and molar mass M = 0.084041 kgmol^{-1} . τ and δ are the independent variables mentioned previously.

The ideal part, $\Phi^0(\tau,\delta)$, of the present equation of state is given by

$$\Phi^0(\tau,\delta) = \ln(\delta) + a_1^0 + a_2^0\tau + a_3^0 \ln(\tau) + a_4^0\tau^{-3/2} + a_5^0\tau^{5/4} + a_6^0\tau^{-1}$$

(2)

The first term comes from the ideal gas law, i.e., $p = \rho RT$. The next two constants a_1^0 and a_2^0 in Eq. (2) are adjusted so that the saturated liquid enthalpy and entropy values calculated from Eq. (1) at 273.15 K are 200 kJkg^{-1} and 1 kJkg^{-1}K^{-1} , respectively. These two numerical constants are naturally determined after establishing the residual part of the equation of state. The last 4 terms in the right-hand side of Eq. (2) are related to an empirical correlation of the ideal gas isobaric specific heat-capacity, $C_p^0(T)$. Initially, Eq. (2) has been developed based on the selected C_p^0 data. Later, the coefficients a_3^0, a_4^0, a_5^0 and a_6^0 are slightly readjusted simultaneously with the optimization of the residual part Φ^r in order to take into account the caloric property behavior of the real fluid. The final values of these coefficients thus determined are: a_1^0=-0.5556942E+0, a_2^0= 0.8937480E+1, a_3^0=-0.8999794E+0, a_4^0= 0.1652398E+1, a_5^0=-0.6827433E+0, a_6^0=-0.8113464E+1. Equation (2) is valid for temperatures from 100 to 700 K.

Two optimization strategies have been employed to establish the residual part $\Phi^r(\tau,\delta)$ of the present model. The first one consists of the regression analysis developed by Wagner [1] in which essential terms of significant importance are selected

from a bank of large number of terms. For R-143a, such an initial bank of terms is given by the following expression:

$$\Phi^r(\tau,\delta) = \sum_i a_i \delta^{d_i} \tau^{t_i} + \sum_i a_i \delta^{d_i} \tau^{t_i} e^{-\delta^{c_i}} \tag{3}$$

It consists of polynomial terms of δ and τ and supplementary terms associated with an exponential function, exp($-\delta^{c_i}$), where exponent c_i varies from 1 to 4. About 500 terms are taken into consideration regarding the bank of terms given by Eq. (3).

For the purpose of applying Eq. (3) to the regression of selected input data sets for various thermodynamic properties, they have to be divided into linear and nonlinear data sets. The linear data such as P-ρ-T properties and isochoric specific heat-capacities are used to find a suitable structure of the residual part $\Phi^r(\tau,\delta)$. Besides the linear experimental thermodynamic properties, two additional constraints are also included in the present regression analysis:

a) thermodynamic constraints at the critical point ;

$$(\partial p/\partial \rho)_{T|_{\rho=\rho_c}^{T=T_c}} = 0, \quad (\partial^2 p/\partial \rho^2)_{T|_{\rho=\rho_c}^{T=T_c}} = 0$$

(4)

b) the Maxwell relation regarding the saturation properties at a given temperature ;

$$\Phi^r(\tau,\delta') - \Phi^r(\tau,\delta'') = \frac{P_s}{RT}\left(\frac{1}{\rho''} - \frac{1}{\rho'}\right) - \ln\frac{\rho'}{\rho''}$$

(5)

where P_s denotes saturation pressure, ρ' and ρ'' are saturated liquid- and vapor-densities, respectively.

The method proposed in [2] is used for the nonlinear optimization as a next step to readjust the coefficients of the equation of state based on all of the selected linear and nonlinear experimental thermodynamic property data. The final form of the residual part $\Phi^r(\tau,\delta)$ thus established in the present study is

$$\Phi^r(\tau,\delta) = \sum_{i=1}^{5} a_i \delta^{d_i} \tau^{t_i} + \sum_{i=6}^{19} a_i \delta^{d_i} \tau^{t_i} \exp(-\delta^{c_i})$$

(6)

The numerical coefficients of a_i and exponents d_i, t_i and c_i are listed in Table I.

4. RESULTS AND DISCUSSIONS

The critical parameter values calculated from the present equation are: T_c=345.86 K, P_c=3.764 Mpa and ρ_c=434 kg/m^3. The critical temperature T_c and critical density ρ_c agree with the measurements by Aoyama et al. [3]. The critical pressure calculated from the present equation differs slightly from most of the reported values within ±5 kPa, which is, however, smaller than the uncertainty reported for the critical pressure values.

Two triple-point temperature measurements are reported by Magee [7] and Russel et al. [8], respectively, although no triple-point pressure and density data are reported. The triple-point pressure estimated by Tillner-Roth [9] is 1.091 kPa corresponding to the triple-point temperature T_t=161.34 K measured by Magee. At the same triple-point temperature, the present model yields T_t=161.34 K, ρ_t'=1329 kg·m^{-3}, ρ_t''=0.068 kg·m^{-3} and P_t=1.080 kPa which differs from the value by Tillner-Roth [9] only by 11 Pa.

Figure 1 shows the deviations of the reported ideal gas isobaric specific heat-capacity values from the present equation. The data by Gillis [4] are well represented by Eq. (1) within ±0.3%, whereas the results of Beckermann and Kohler [10] show a larger scatter up to ±1%. Theoretical values by Chen et al. [11] are represented within ±1% for temperatures 100 to 700 K, while the values by Yokozeki et al. [5] which include anharmonicity corrections are well represented within ±0.4% for temperatures 160 to 700 K.

For an easier comparison of the P-ρ-T properties, we divide entire fluid phase into following 4 regions since the quantity of data is too large.

vapor-phase region: T 344 K, $P < P_s$ and T 344 K, ρ 250 kgm^{-3}

liquid-phase region: T 344 K, $P > P_s$ and T 344 K, ρ 650 kgm^{-3}

near-critical region: 344 K < T 353 K and 250< ρ < 650 kgm^{-3}

supercritical region: T > 353 K and 250< ρ < 650 kgm^{-3}

Figure 2 gives the relative pressure deviations of measurements by de Vries[6] in vapor-phase region at different pressures. Most of the measurements are well represented by the present model within ±0.05%. The lowest three isothermal Burnett measurements which show a little different behavior from others are represented within ±0.1%. Several data in the liquid-phase region due to the vibrating tube densimeter are represented within ±0.2% as also shown in Fig. 2. Figure 3 shows the relative density deviations in the liquid-phase region at different pressures. Most of the liquid-phase measurements by de Vries[6] are satisfactorily represented within ±0.05% except several points near the saturation which have a large scatter up to ±0.1%. The liquid-phase P-ρ -T measurements by Magee[7] show a little higher positive deviation, but all of them are represented within 0.2%. Measurements of de Vries in near-critical region and supercritical region are also represented within ±0.4% in pressure deviation.

Figure 4 illustrates the vapor-pressure deviations with respect to temperature. The experimental vapor-pressure data by de Vries [6] are represented within ±0.035%, while those by Russel et al. [8] are represented with the deviations not more than ±50 Pa.

Figure 5 gives the deviations of isochoric heat-capacity data by Magee [7] in liquid-phase, where the measurements from triple-point to critical temperature are well represented within the deviation of ±1%.

Table II summarizes the result of statistic deviations analysis for all the thermodynamic properties compared. The statistic quantities are defined by the following expressions in which X stands for an arbitrary property. The bad data denoted by BAD in the right-hand column is defined when the deviation exceeds ±10%.

$$\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{N}\left|\{(\frac{X_{\exp,i} - X_{cal,i}}{X_{cal,i}})\cdot 100\%\}\right| \quad (7)$$

$$\mathrm{BIAS} = \frac{1}{N}\sum_{i=1}^{N}\{(\frac{X_{\exp,i} - X_{cal,i}}{X_{cal,i}})\cdot 100\%\} \quad (8)$$

$$\mathrm{RMS} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\{(\frac{X_{\exp,i} - X_{cal,i}}{X_{cal,i}})\cdot 100\%\}^2}$$

(9)

Figure 6 illustrates the isobaric heat-capacity behavior derived from the present equation of state for the range of temperatures from triple-point to 650 K and pressures from 0.05 to 50 MPa. This figure naturally confirms that the present model provides an excellent thermodynamic consistency including C_p behavior even in such an extensive range of temperatures and pressures.

5. ACKNOWLEDGMENTS

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Table I. Numerical Constants in Eq. (6)

i	a_i	c_i	t_i	d_i
1	0.1606645 E-1	-	0	5
2	0.4163515 E+1	-	0.5	1
3	-0.5031058 E+1	-	0.75	1
4	-0.1920208 E-1	-	2.5	2
5	0.1470093 E-2	-	2.5	4
6	0.1775429 E+0	1	0.25	3
7	-0.7316069 E-2	1	0.25	8
8	-0.9555916 E-1	1	2	3
9	-0.5822518 E+0	1	3	1
10	-0.4211022 E-3	2	3	10
11	-0.2059847 E-1	2	8	1
12	0.3711325 E-1	2	8	4
13	0.1799723 E-3	2	8	8
14	-0.4145922 E-1	2	10	2
15	0.7682566 E-4	3	8	12
16	-0.2089695 E-2	3	17	8

17	0.1958633 E-2	3	20	2
18	-0.3198325 E-5	3	35	5
19	-0.5376561 E-2	4	27	3

Table II. Statistic Analysis of Experimental Thermodynamic Properties

Author	Year	Points	AAD	BIAS	RMS	MAXDEV	BAD
$X = P$							
deVries	1996	536	0.036	0.002	0.096	1.522	2
Fujiwara and Piao	1995	40	0.357	0.344	0.426	0.990	0
Giuliani et al.	1994	14	0.103	0.103	0.115	0.233	0
Giuliani et al.	1995	62	0.099	0.020	0.347	2.679	0
Mears et al.	1955	21	1.250	-1.039	1.428	2.608	0
Weber and Defibaugh	1996	117	0.049	-0.015	0.065	0.117	0
Zhang et al.	1995	84	0.063	0.001	0.079	0.193	0
$X = \rho$							
deVries	1996	526	0.134	0.054	0.542	7.112	0
Defibaugh	1996	855	0.307	0.307	0.807	6.821	3
Magee	1996	154	0.085	0.085	0.092	0.233	0
$X = C_p^0$							
Beckermann and Kohler	1995	9	0.479	0.461	0.531	0.832	0
Chen et al	1975	10	0.541	0.533	0.610	1.008	0
Gillis	1994	8	0.083	-0.037	0.106	-0.229	0

Mears et al.	1955	6	1.501	-0.889	1.591	-1.880	0
Smith et al.	1952	4	0.658	0.567	0.786	1.097	0
Yokozeki et al.	1997	28	0.127	-0.019	0.153	0.349	0
$X = C_v$							
Magee	1996	159	0.511	0.348	1.120	5.999	0
$X = C_p$							
Mukoyama et al.	1996	4	0.520	-0.391	0.714	-1.323	0
$X = w$							
Beckermann and Kohler	1995	246	0.027	-0.012	0.032	-0.079	0
Gillis	1994	85	0.005	0.004	0.007	0.018	0
Takagi	1996	188	0.473	-0.026	0.593	2.584	2
X = B							
Bignell and Dunlop	1993	3	0.659	-0.659	0.742	-1.087	0
Beckermann and Kohler	1995	9	1.564	-1.027	1.967	-3.625	0
Gillis	1994	13	1.314	1.220	1.365	1.856	0
Zhang et al.	1995	7	0.480	-0.313	0.528	-0.929	0

Table II. Statistic Analysis of Experimental Thermodynamic Properties (continued)

Author	Year	Points	AAD	BIAS	RMS	MAXDEV	BAD
$X = P_s$							
deVries	1996	59	0.009	-0.001	0.013	-0.041	0
Doering	1992	31	0.305	0.166	0.383	0.998	0
Fujiwara and Piao	1995	23	0.128	0.128	0.130	0.213	0
Fukushima	1993	18	0.095	-0.024	0.167	-0.628	0
Giuliani et al.	1994	60	0.096	-0.066	0.135	-0.461	0
Giuliani et al.	1995	33	0.083	0.045	0.100	0.174	0
Mears et al.	1955	7	0.377	0.280	0.508	1.141	0
Nagel and Bier	1996	26	0.246	0.246	0.247	0.293	0
Russel et al.	1944	9	0.095	0.052	0.113	-0.197	0
Takashima and Higashi	1995	12	0.197	-0.065	0.228	-0.400	0
Wang et al.	1993	30	0.103	-0.100	0.117	-0.225	0
Weber and Defibaugh	1996	52	0.059	-0.059	0.066	-0.126	0
Widiatmo et al.	1994	12	0.324	0.324	0.388	0.774	0
Ye	1994	11	0.352	0.352	0.423	0.695	0
Zhang et al.	1995	11	0.136	0.136	0.140	0.199	0

X = r ’							
Defibaugh	1996	22	0.239	0.239	0.346	1.326	0
Doering	1992	4	2.214	2.214	2.361	3.396	0
Fukushima	1993	10	1.684	-1.684	1.722	-2.157	0
Mears et al.	1955	6	3.566	3.566	3.567	3.699	0
Widiatmo et al	1994	17	0.555	-0.555	0.579	-1.125	0
Yokoyama and Takahashi	1991	16	0.337	-0.336	0.383	-0.551	0
X = r ’’							
Aoyama et al.	1995	13	0.587	0.121	0.758	1.792	0
Fukushima	1993	7	3.838	-3.838	3.875	-4.697	0
Higashi and Ikeda	1995	5	0.764	0.289	0.937	1.681	0
$X = C_v$’							
Magee	1996	96	0.445	-0.219	0.792	-4.382	3
$X = C_p$’							
Russel et al.	1944	11	0.109	0.016	0.136	0.320	0

FIGURE CAPTIONS

Fig. 1. Deviations of ideal gas isobaric specific heat-capacity values from the present equation: () Gillis [4]; () Beckermann and Kohler [10]; () Chen et al.[11]; () Yokozeki et al.[5]

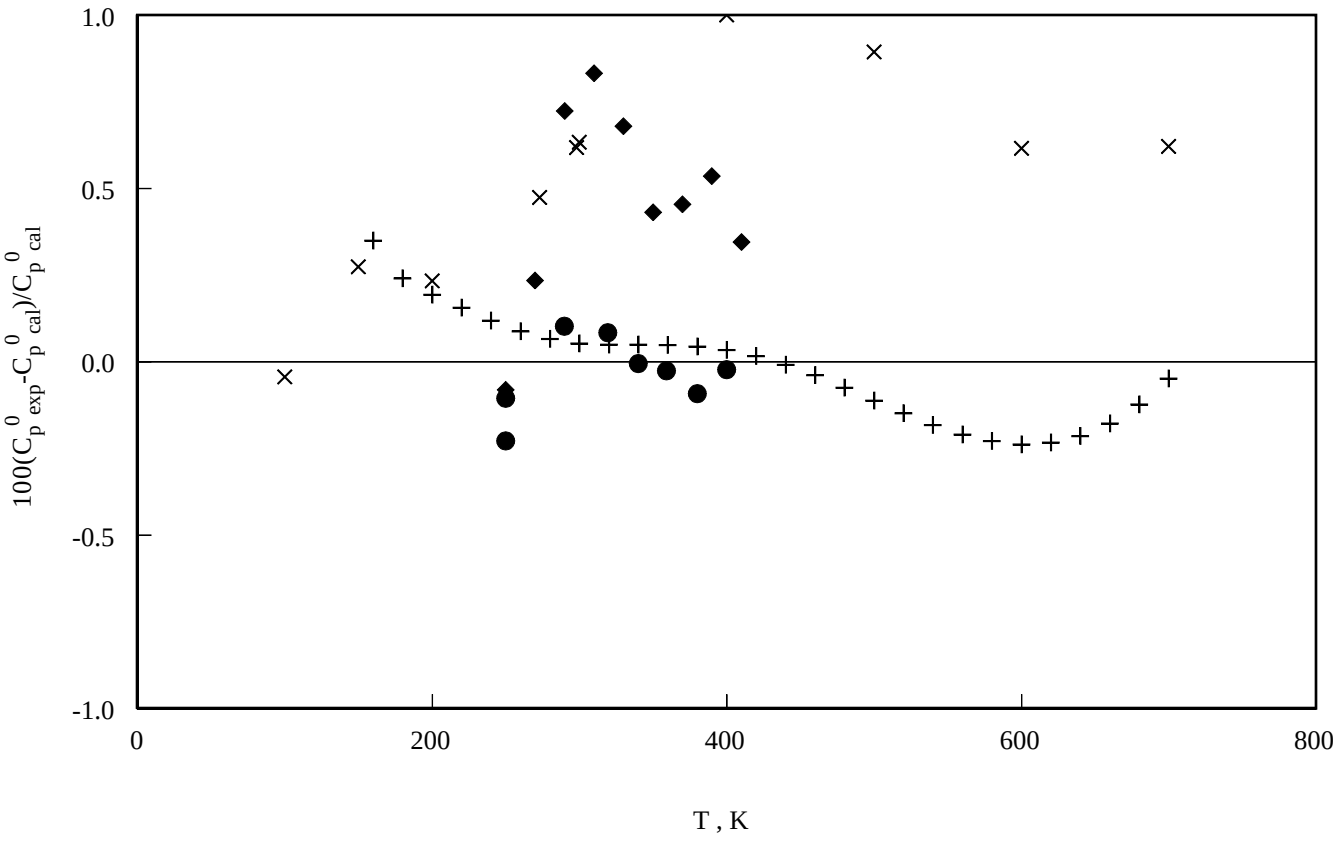
Fig. 2. Pressure deviations of P-r -t data in vapor-phase region: () de Vries (Burnett) [6]; () de Vries (Vibrating tube) [6].

Fig. 3. Density deviations of P-r -t data in liquid-phase region: () de Vries [6]; () Magee [7].

Fig. 4. Vapor-pressure deviations from the present equation: () de Vries [6]; () Russel et al. [8]; () Weber and Defibaugh [12]; () Giuliani et al. [13]; () Zhang et al. [14]

Fig. 5. Deviations of isochoric specific heat-capacities in liquid-phase region: () Magee [7].

Fig. 6. Isobaric specific heat-capacity behavior derived from the present model.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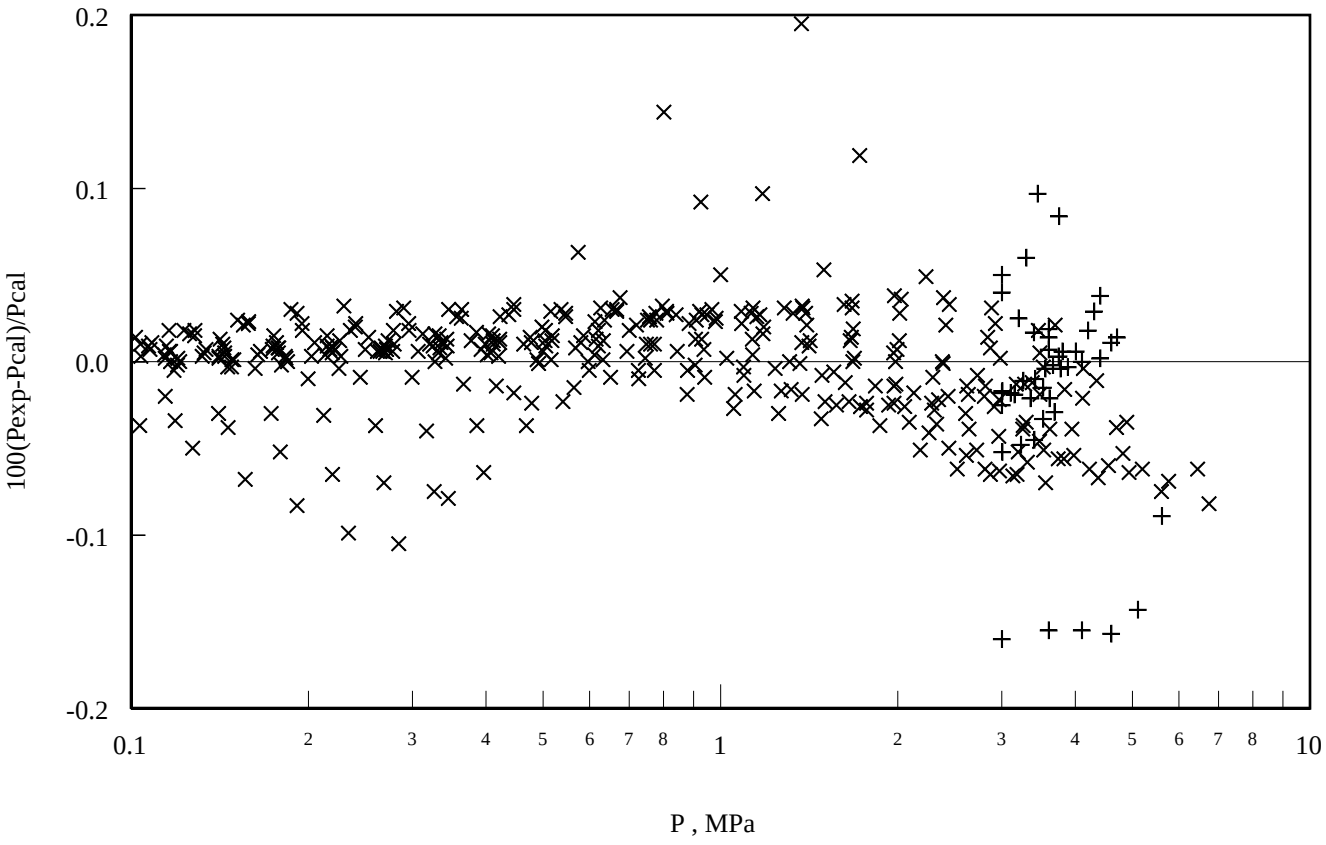
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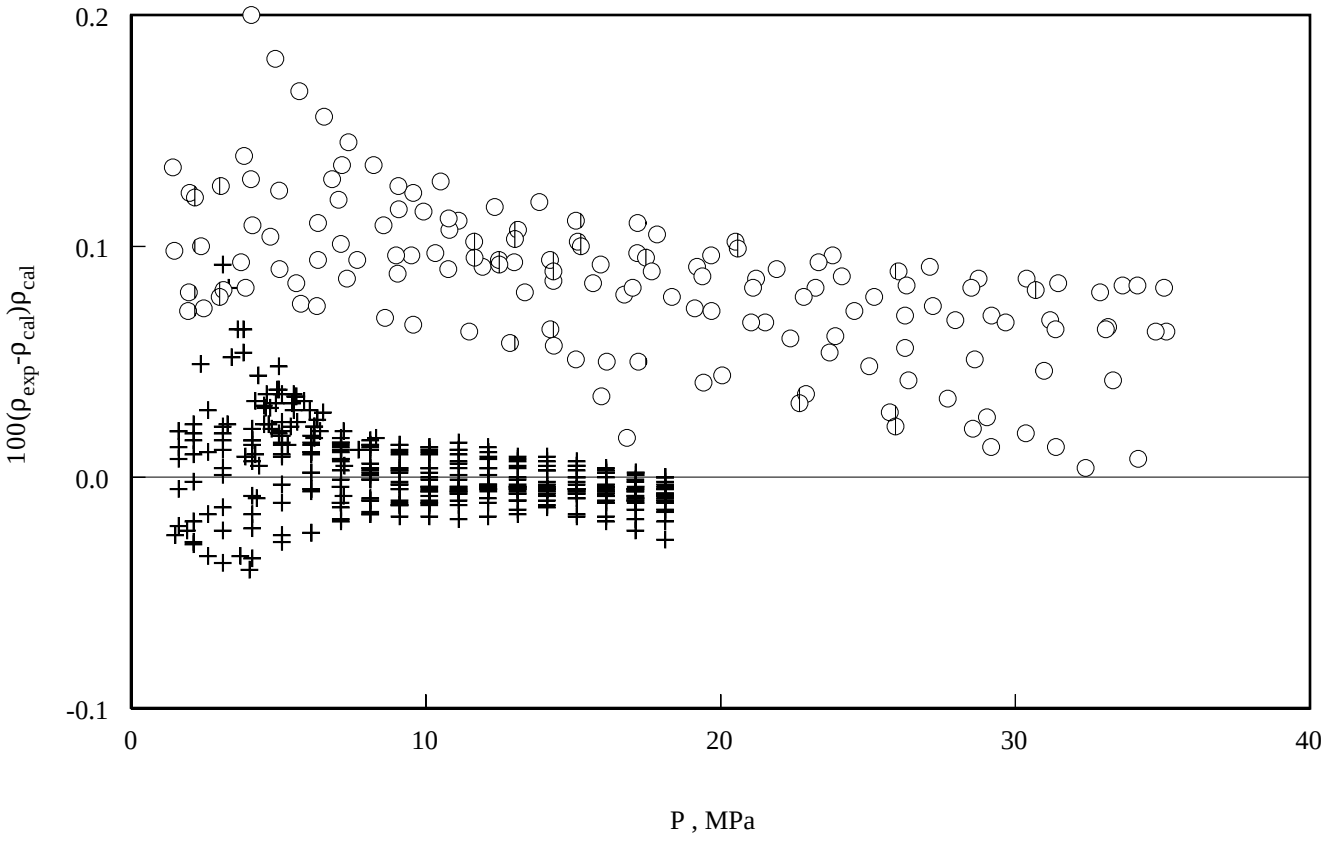
P , MPa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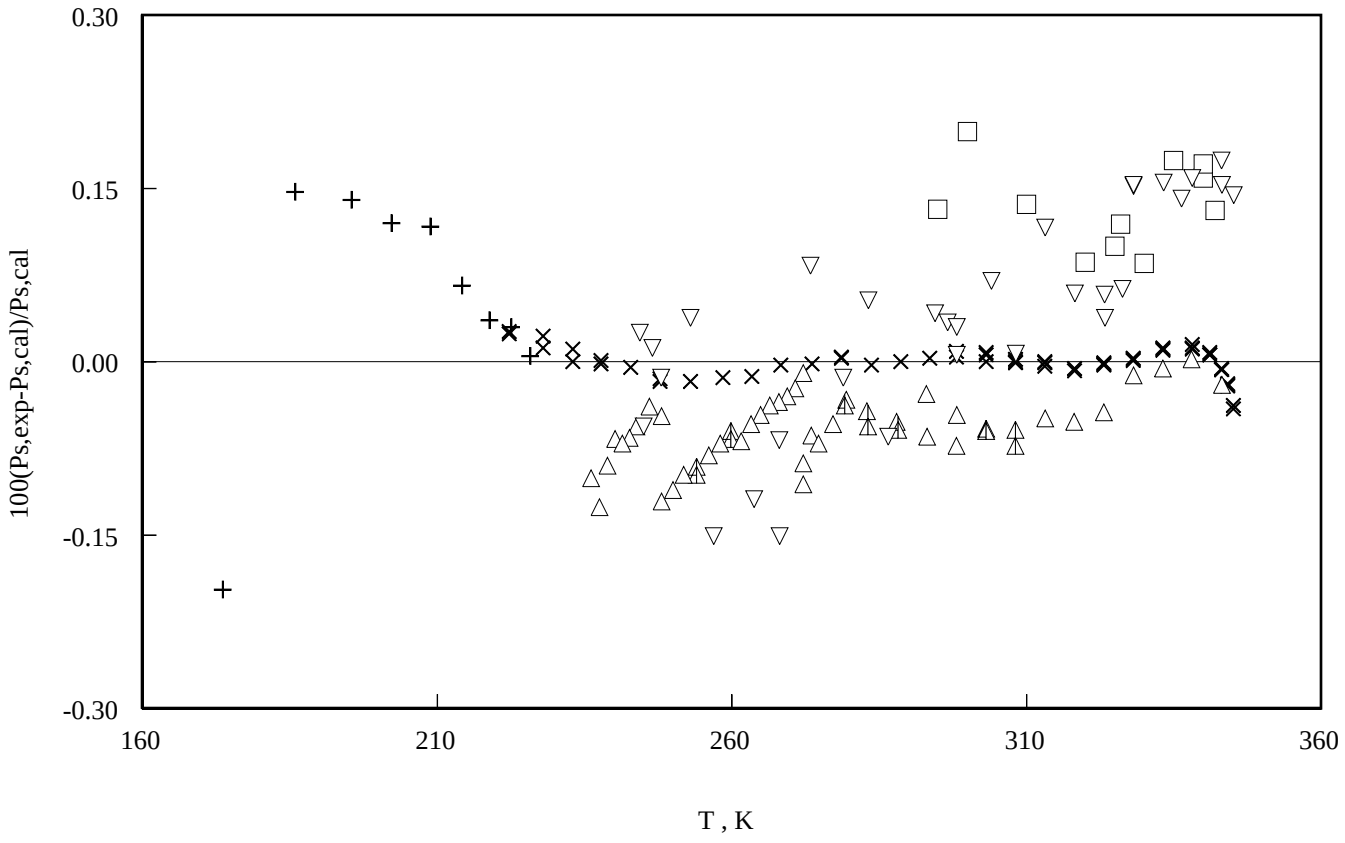
P , MPa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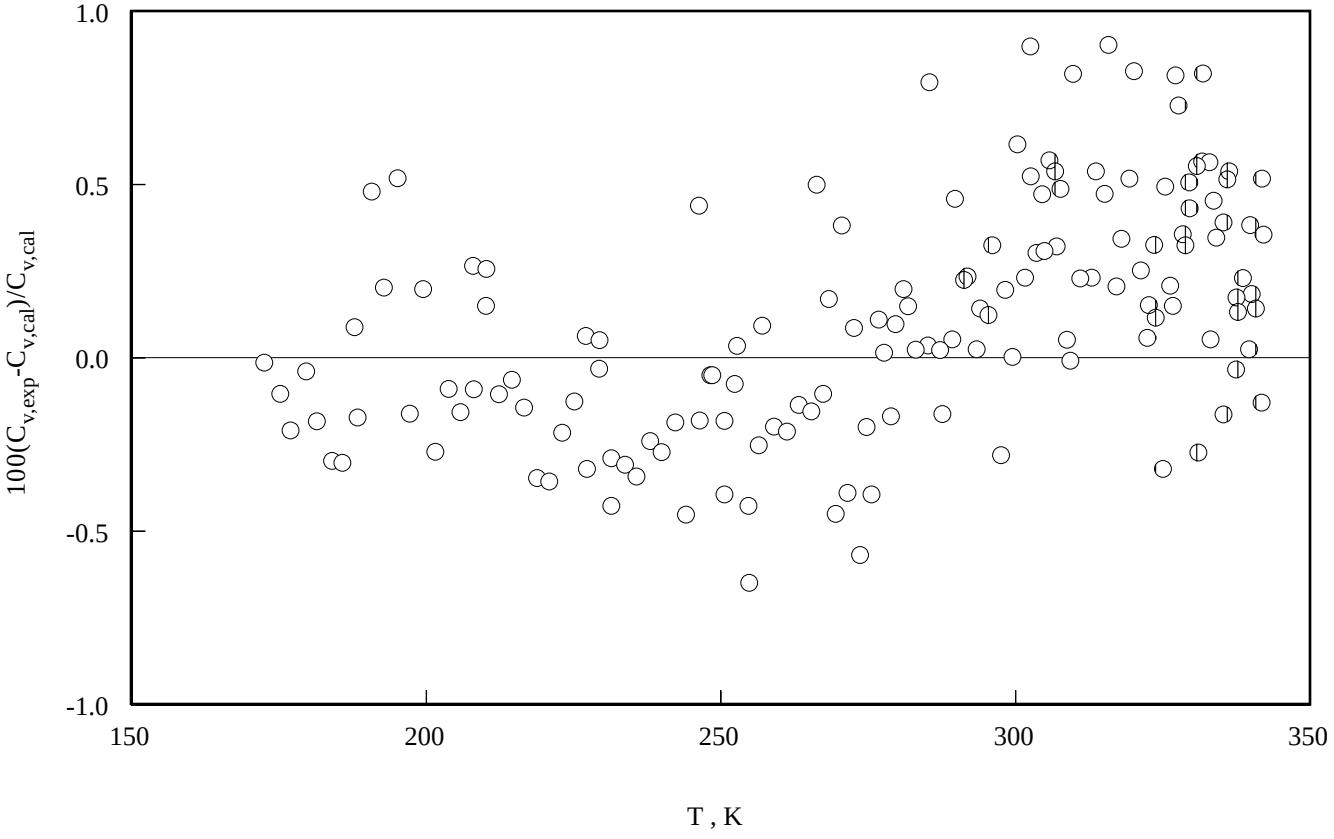
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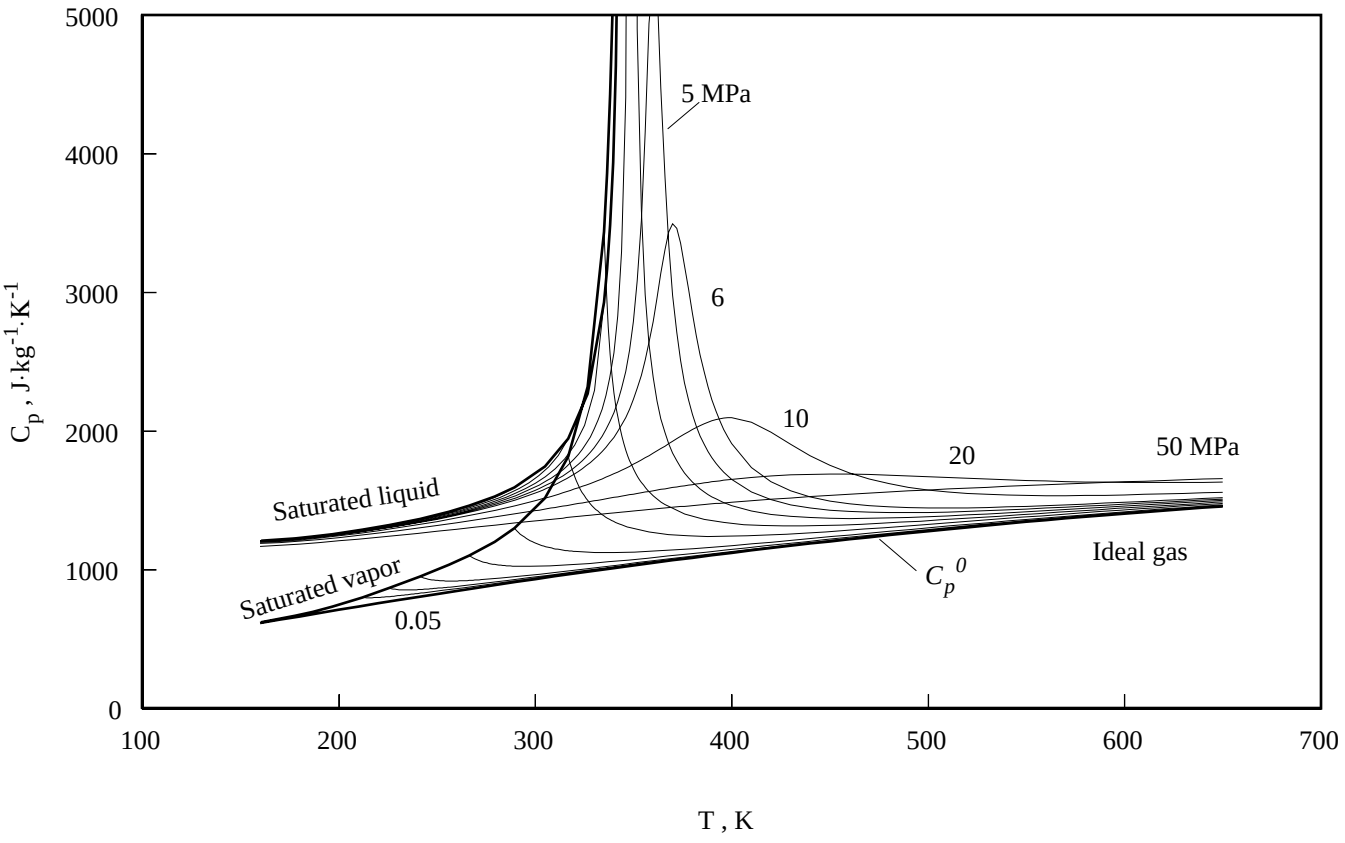
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6
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20
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Saturated liquid
Saturated vapor
0.05
C_p^0
Ideal gas