An experimental *PVT* apparatus with a vibrating tube measurement cell[1]

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ABSTRACT

A new experimental apparatus based on the vibrating tube principle has been developed. The design of the apparatus was adapted for study of *PVT* properties of fluorocarbons and their mixtures. The experimental method was expanded for *PVT* measurements in both liquid and vapor phases. The operating range for the apparatus is between 260 and 400 K and up to 35 MPa. The potential sources of methodological uncertainties have been considered. The estimated accuracy of our measurements was ±0.05K for temperature, ±9 kPa and ±50 kPa for pressure from 0 to 7 MPa and from 7 to 35 MPa respectively. The systematic uncertainties of density determination did not exceed 0.4 kg/m^3 for vapor and 3 kg/m^3 for liquid phases. The reliability of the experimental *PVT* data has been verified by measurements on several fluorocarbons and comparisons with the literature data.

KEY WORDS: densimeter; fluorocarbons; *PVT* properties; vibrating tube.

1. INTRODUCTION

For over 20 years vibrating tube principle has been widely and successfully applied for the experimental study of *PVT* properties of various chemical compounds. High precision and applicability of this method for liquid density measurements in a wide temperature/pressure range made it attractive for experimenters and even competitive to the classical *PVT* methods. The present paper gives a detailed description of the experimental apparatus with a vibrating tube measurement cell. It was built for the purpose of study of *PVT* properties of fluorocarbon compounds and their mixtures in the liquid as well as in the vapor phase. Calibration procedure, potential sources of experimental and methodological uncertainties and results of the performance of the apparatus are carefully considered.

2. EXPERIMENTAL APPARATUS

New *PVT* apparatus shown schematically in Fig. 1 was built around a stainless steel vibrating tube densimeter (Anton PAAR Model DMA 512). The experimental cell consists of the stainless steel U-shaped hollow tube (S) which is enclosed in a steel temperature controlled jacket (K). The vibrating period of the cell is measured by accurate frequency-meter (J) (Model DMA-60).

The temperature of the cell (S) is regulated by circulating water/ethylene glycol mixture through the jacket (K) from the external temperature-controlled circulating bath RTE-111 (R). The temperature is measured by mercury thermometer (Q) with uncertainty 0.01K. To avoid temperature and concentration gradient in the measurement circuit (between valve V15, and pressure transducers (T) and (W)) its temperature is controlled by Cole-Parmer digital RTD proportional temperature controller (P) (Model R-600C) and variable autotransformer (Y) with heating tape within ±1K. The estimated accuracy of temperature measurements of the experimental cell is 0.05 K in the temperature range from 260 to 400K.

The measurement cell is connected on one end to the pressurizing cell (D) and HIP pressure generator (N) (Model 87-6-5). Pressurizing cell is double ended pressure vessel made of 304 stainless steel seamless tubing. It contains a piston to separate the investigated substance from the pressure-control gas (nitrogen) introduced at the bottom of it from the cylinder (B). The volume of the pressurizing cell is 850 cm^3 that is about 50 times larger than the volume of the rest of the system that allows to transfer the introduced amount of the sample in the liquid as well as in the gas phase in the entire temperature interval. The pressure generator serves for fine tuning of the pressure in the measurement circuit. The pressure gauge (A) is used to control the pressure of nitrogen before its introducing into the pressurizing cell. Gauge (I) controls the pressure at the entrance of the measurement. Depending on the pressure range the pressure of the investigated sample is measured by two Setra pressure transducers (T) and (W) (Model 204) in couple with the Setra DATUM 2000™ pressure readouts (U) and (X). The instrument uncertainties of pressure transducers (T) and (W) are 45 kPa and 8 kPa in the pressure range from 0 to 35 MPa and from 0 to 7 MPa respectively.

3. CALIBRATION OF THE EXPERIMENTAL CELL

The experimental cell was calibrated by measuring the period of oscillation under vacuum (≈10^{-2}Torr) and 1,1,1,2-tetrafluoroethane at pressures up to 32 MPa. Temperatures during the calibration ranged between 263 and 353 K.

The expression which relates the vibrating period τ to density of the sample ρ loaded into the experimental cell can be expressed by Eq.(1)

$$\rho = \frac{m_0}{V}\left(\frac{k}{k_0}\frac{\tau^2}{\tau_0^2} - 1\right) \qquad (1)$$

where τ_0 is a vibrating period of the cell measured under vacuum, k and k_0 are spring coefficients of the vibrating tube under the investigated fluid and vacuum, and m_0 is a mass of the tube of internal volume V.

Using assumption that spring coefficient k is constant for a given vibrating system over a range of thermodynamic parameters Eq.(1) is usually simplified in practice to

$$\rho = K\left(\frac{\tau^2}{\tau_0^2} - 1\right) \tag{2}$$

where K is coefficient determined from calibration.

The set of coefficients $K=K_{T,P}$ is established by the calibration for given reference substances at different temperatures and pressures. Since the typical way for measurements by vibrating method is isothermal, the correlations $K= K\ (P)_T$ were developed for each temperature of interest.

Combination of the Eqs.(1) and (2) lead to the following expression for calibration coefficient $K(P)_T$

$$K(P)_T = \frac{m_0}{V} = \frac{m_0}{V_0(1+BP)} = \frac{A}{1+BP} \tag{3}$$

where A and B are coefficients determined by calibration. Coefficient A is related to the mean density of the vibrating tube including the evacuated inner cavity. Coefficient B reflects the volume changes occuring in the stainless steel vibrating tube due to its mechanical elasticity.

Applying two-constant calibration dependence (3) is quite acceptable when the calibration and measurements are performed at the same thermodynamic parameters. However attempts to spread this correlation on the wide pressure range lead to significant uncertainties in density determination. These uncertainties caused by the pressure expansion of vibrating tube and by above assumption k=const (in reality, the spring coefficient k is function of moment of inertia of the cell and hence it depends on geometry and density distribution of the vibrating system). Significant improvement of calibration equation (3) can be achieved by introducing polynomial pressure dependence to the coefficient B. Thus, correlation for calibration coefficient can be expressed by following equation

$$K(P)_T = \frac{A}{1 + P\sum_{i=0}^{n} B_i P^i} \tag{4}$$

The accuracy of determination of coefficients $K_{T,P}$ is limited by the uncertainty of the reference data on 1,1,1,2-tetrafluoroethane [1], that is 0.05% for liquid densities. The deviations of coefficients $K_{T,P}$ from calibration dependence $K(P)_T$ (Eq.(4)) did not exceed 0.04% over the entire range of parameters studied.

4. EXPERIMENTAL AND METHODOLOGICAL UNCERTAINTIES

Since the present experimental method belongs to the propagation ones, first were determined the absolute uncertainties of measured parameters. It included the estimation of the systematic components of absolute uncertainties as well as the random ones. The systematic uncertainties in the present work have the following values: ΔT=0.05K, ΔP_{sys}=45 kPa and ΔP_{sys}= 8 kPa (for transducers (T) and (W), respectively), $\Delta\tau_{sys}=\Delta\tau_{0sys}$=0.5 μs. The composition X of investigated blends is determined by weighting of pure components. Taking into consideration the accuracy of analytical balances the uncertainties of weighting of single components ΔW_i and mixture ΔW_{mix} were 2 10^{-3} g and 4 10^{-3} g . Thus, the accuracy of the mixture concentration ΔX was determined as 2 10^{-3} . Systematic uncertainty of the calibration coefficient ΔK_{sys} was defined in the previous section and did not exceed 1.8 (about 0.04%).

The random uncertainties of pressure measurements ΔP_{ran} and calibration coefficient ΔK_{ran} were calculated by analyzing the data of calibrations of the pressure transducers and vibrating tube and by estimating their standard deviations from calibration dependencies. Combining random and systematic components in quadrature, the total experimental uncertainties of calibration and measurements of pressure come to the following values: ΔK= 4, ΔP= 50 kPa and ΔP= 9 kPa (for transducers(T) and (W) , respectively). The random

uncertainty in determination of the vibrating period $\Delta\tau_{ran}$ were within 10-30 μs (depending on particular region of thermodynamic surface measured). That is significantly higher then the systematic errors $\Delta\tau_{sys}$. Thus, the value of total experimental uncertainty of the vibrating period measurements $\Delta\tau$ were assumed equal to $\Delta\tau_{ran}$.

Using the Eq. (4) and results of error estimation in direct measurements, the systematic uncertainty in determining the density does not exceed 3 kg·m^{-3} for liquid and 0.4 kg·m^{-3} for vapor phase.

As with other experimental methods, vibrating method has specific methodological uncertainties that need to be taken into consideration before measurements, as well as for analysis of the experimental data. The basic assumption of the present method is postulating of only pressure dependence of calibration coefficient at constant temperature $K_T=K_T(P)$. Calibration coefficient is a function of geometry, physical properties of the cell and spring coefficient of the vibrating system k. Proposed Eq.(4) takes into account an integral effect of all above factors. However spring coefficient k is not only a function of thermodynamic parameters, but it also depends on moment of inertia of the whole vibrating system which includes as a vibrating tube itself as a fluid loaded in it. Thus, at the calibration and measurements, even at the same temperature and pressure, we deal with two different vibrating systems due to a difference of thermodynamic properties of reference and investigated fluids. In contrast to classical experimental methods such as variable volume or constant volume methods, calibration coefficient K is not only a function of mechanical properties of the experimental cell. In the present method coefficient K is related to the whole vibrating system and hence depends on specific thermodynamic properties of the reference substance.

Influence of considered methodological uncertainty is very insignificant on density measurements in the liquid phase and in the vapor phase at low pressures. However it can

contribute to a total density uncertainty at moderated and elevated pressures where the difference of thermodynamic properties of reference and investigated fluids is most substantial. Experimental *PVT* data for carbon dioxide and hexafluoroethane (present work , Fig. 2), carbon dioxide [2] and 1,1,1,2-tetrafluoroethane [1] at near-critical and super-critical isotherms are in agreement with corresponding EOS. However, errors in determination of super-critical densities of N_2, O_2, methane and helium ranged between 1 and 10% [2]. Thus, the contribution of the methodological component to a total systematic uncertainty varies with different fluids and thermodynamic conditions, that needs to be carefully considered in further analysis of the experimental results.

5. RESULTS OF PERFORMANCE OF THE EXPERIMENTAL APPARATUS

Measurements of *PVT* properties by the present experimental apparatus were performed as in a liquid phase as in a vapor phase for several single compounds (1,1,1-trifluoroethane, chlorodifluoromethane and 1,1,1,2-tetrafluoroethane) and mixture of difluoromethane and pentafluoroethane (concentration 50/50 wt.%). Obtained experimental results were compared with the literature data. Figs. 3 - 5 represent absolute deviations of our experimental densities from their values calculated from corresponding equations of state. For all investigated compounds the measured data are in a good agreement with their EOS within the experimental uncertainties.

Significant improvement of the accuracy of experimental data on vapor density was achieved by adjusting parameter τ_0 in Eq.(2). Due to possible adsorption of the sample by stainless steel vibrating tube during the measurements, the value of τ_0 is slightly changed. It does not influence on the results of measurements in the liquid phase where the ratio τ^2/τ_0^2 =1.2-1.6, but may cause additional uncertainty in the vapor phase. Since the meaning of τ_0 is vibrating period of the tube under vacuum, experimental values of τ in the vapor phase were extrapolated to the zero pressure. Obtained τ_0 by this extrapolation were

adjusted then in the limits of uncertainties of τ to the condition $\lim_{P \to 0} Z(P) \to 1$, where $Z(P)$ is compressibility factor calculated from the experimental data.

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FIGURE CAPTIONS

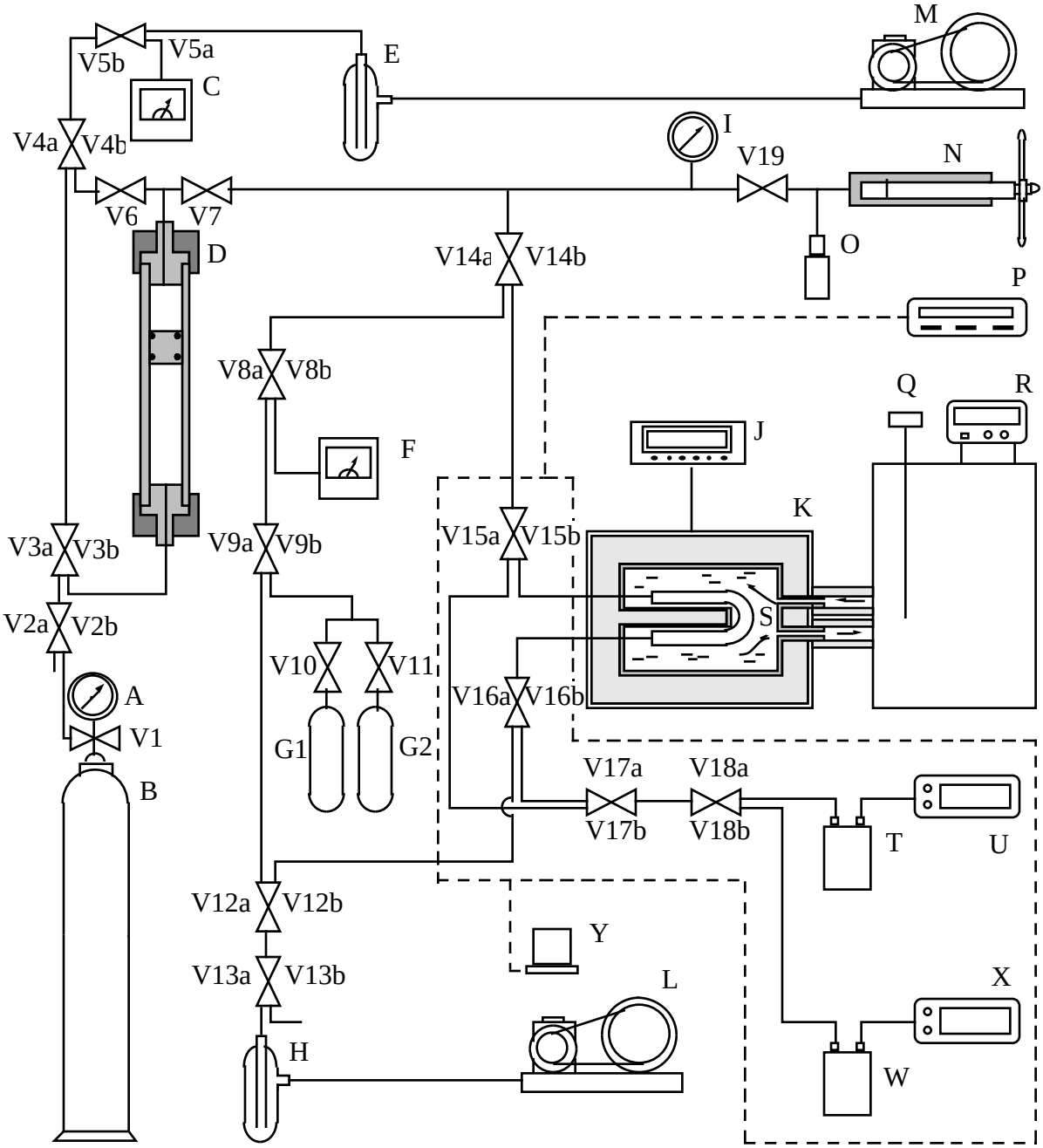
Fig. 1. Schematic diagram of *PVT* apparatus with a vibrating tube measurement cell: (A), (I) pressure gauges; (B) nitrogen cylinder; (C), (F) vacuum gauges; (D) pressurizing cell; (E), (H) vacuum traps; (G1), (G2) cells with a sample; (J) digital frequency meter; (K) temperature controlled jacket; (L) , (M) vacuum pumps; (N) pressure generator; (O) pressure relief device; (P) temperature controller with heating tape; (Q) thermometer; (R) temperature controlled circulating bath; (S) vibrating tube; (T), (W) pressure transducers; (U), (X) pressure manometers; (Y) variable autotransformer; (V1) - (V19) valves

Fig. 2. Deviations of experimental densities of hexafluoroethane and carbon dioxide from the reference EOS [3] and [5], respectively

Fig. 3. Deviations of experimental liquid densities of chlorodifluoromethane and experimental saturated liquid densities of difluoromethane/pentafluoroethane (50/50 wt.%) from the reference equations [6] and [8], respectively

Fig. 4. Deviations of experimental vapor densities of 1,1,1,2-tetrafluoroethane and 1,1,1-trifluoroethane from the reference EOS [1] and [7], respectively

Fig. 5. Deviations of experimental vapor densities of difluoromethane/pentafluoroethane (50/50 wt.%) from the reference EOS [9] (a) and [10] (b)


M
V5b
V5a
E
C
V4a
V4b
I
V19
N
V6
V7
D
V14a
V14b
O
P
V8a
V8b
Q
R
J
F
K
V3a
V3b
V9a
V9b
V15a
V15b
S
V2a
V2b
V10
V11
A
V16a
V16b
V1
G1
G2
V17a
V18a
B
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T
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V12b
Y
V13a
V13b
L
X
H
W

Fig. 1

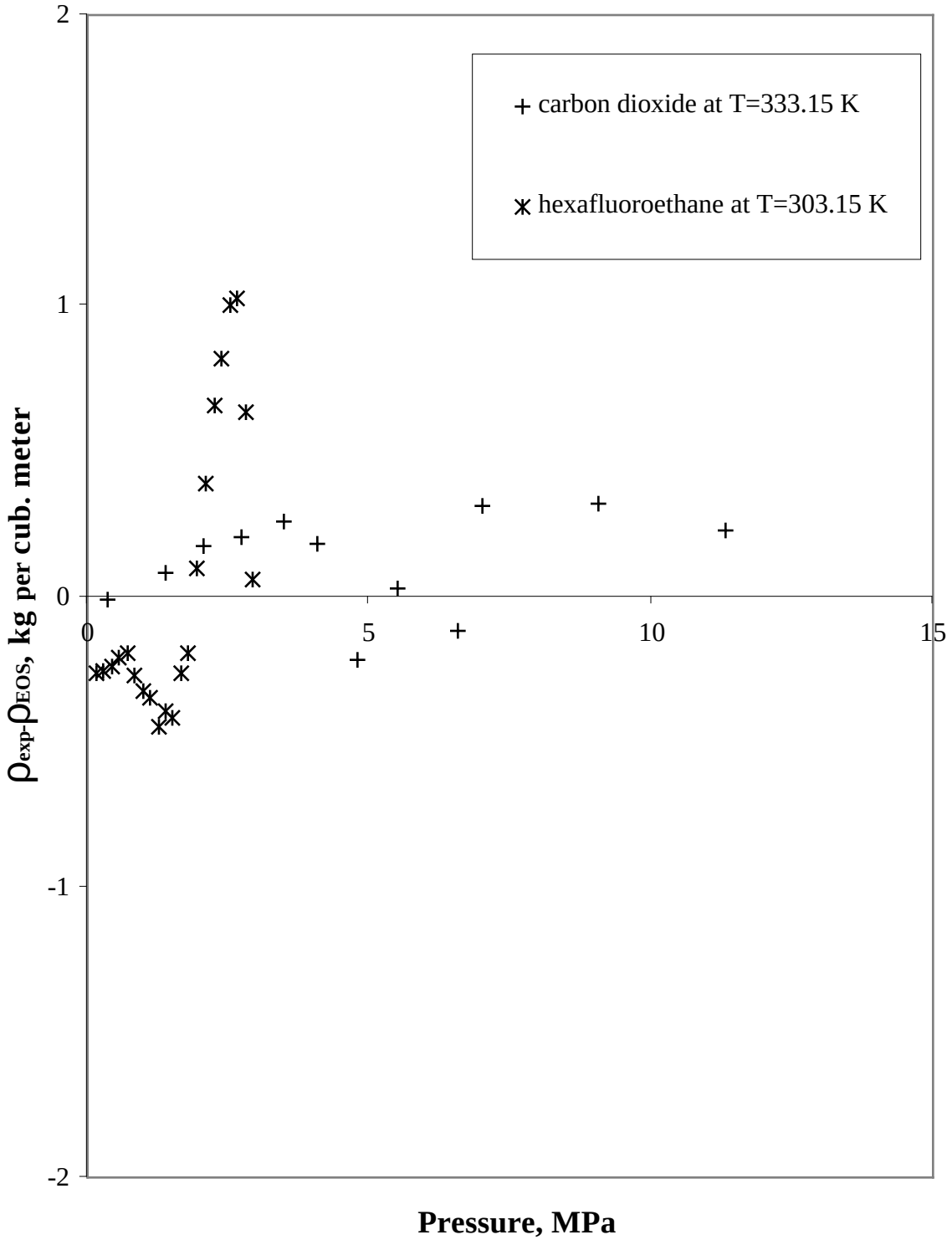
2
1
0
-1
-2
0
5
10
15
carbon dioxide at T=333.15 K
hexafluoroethane at T=303.15 K
ρexp-ρEOS, kg per cub. meter
Pressure, MPa

Fig. 2

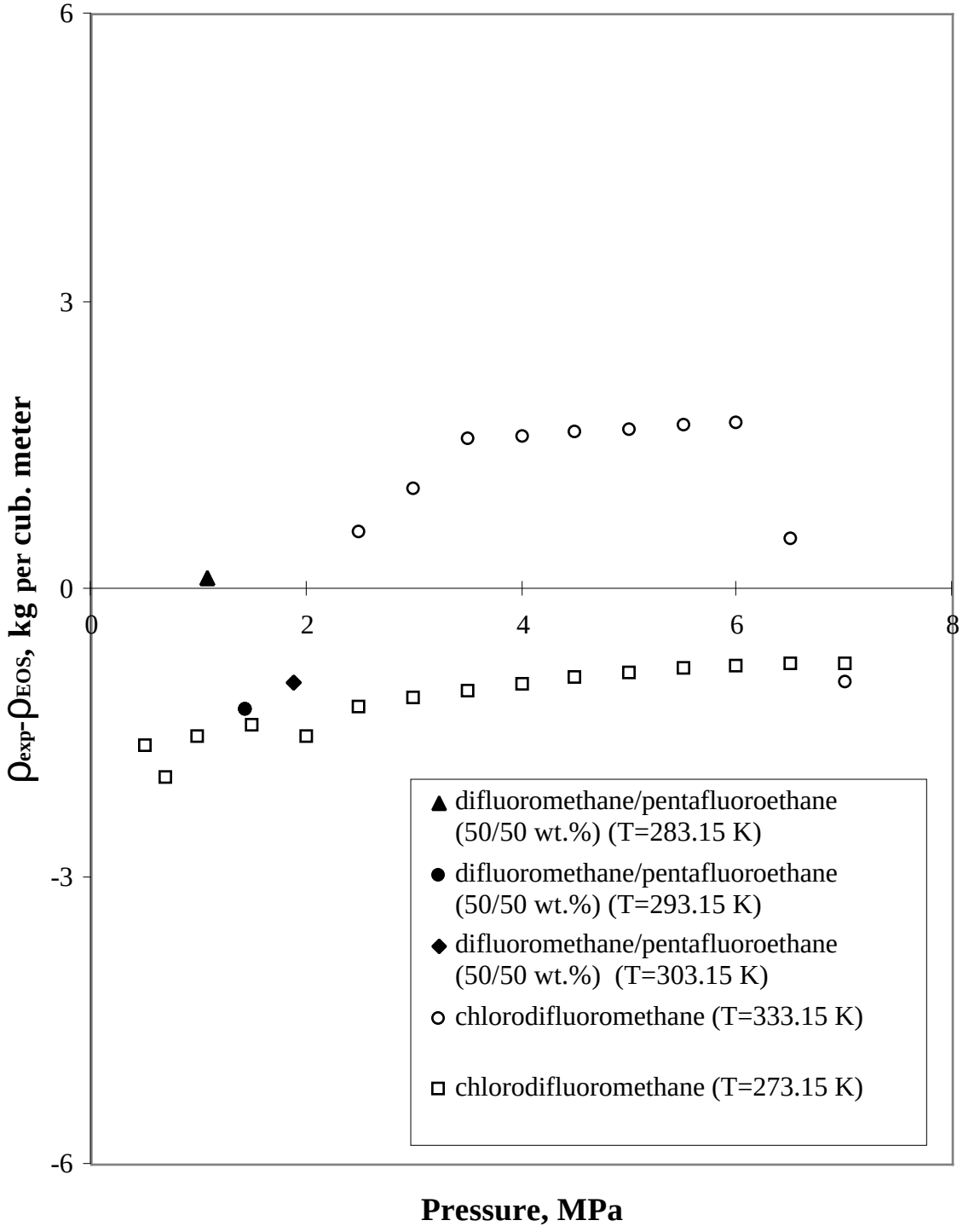
6
3
0
-3
-6
0
2
4
6
8
ρexp-ρEOS, kg per cub. meter
Pressure, MPa
difluoromethane/pentafluoroethane (50/50 wt.%) (T=283.15 K)
difluoromethane/pentafluoroethane (50/50 wt.%) (T=293.15 K)
difluoromethane/pentafluoroethane (50/50 wt.%) (T=303.15 K)
chlorodifluoromethane (T=333.15 K)
chlorodifluoromethane (T=273.15 K)

Fig. 3

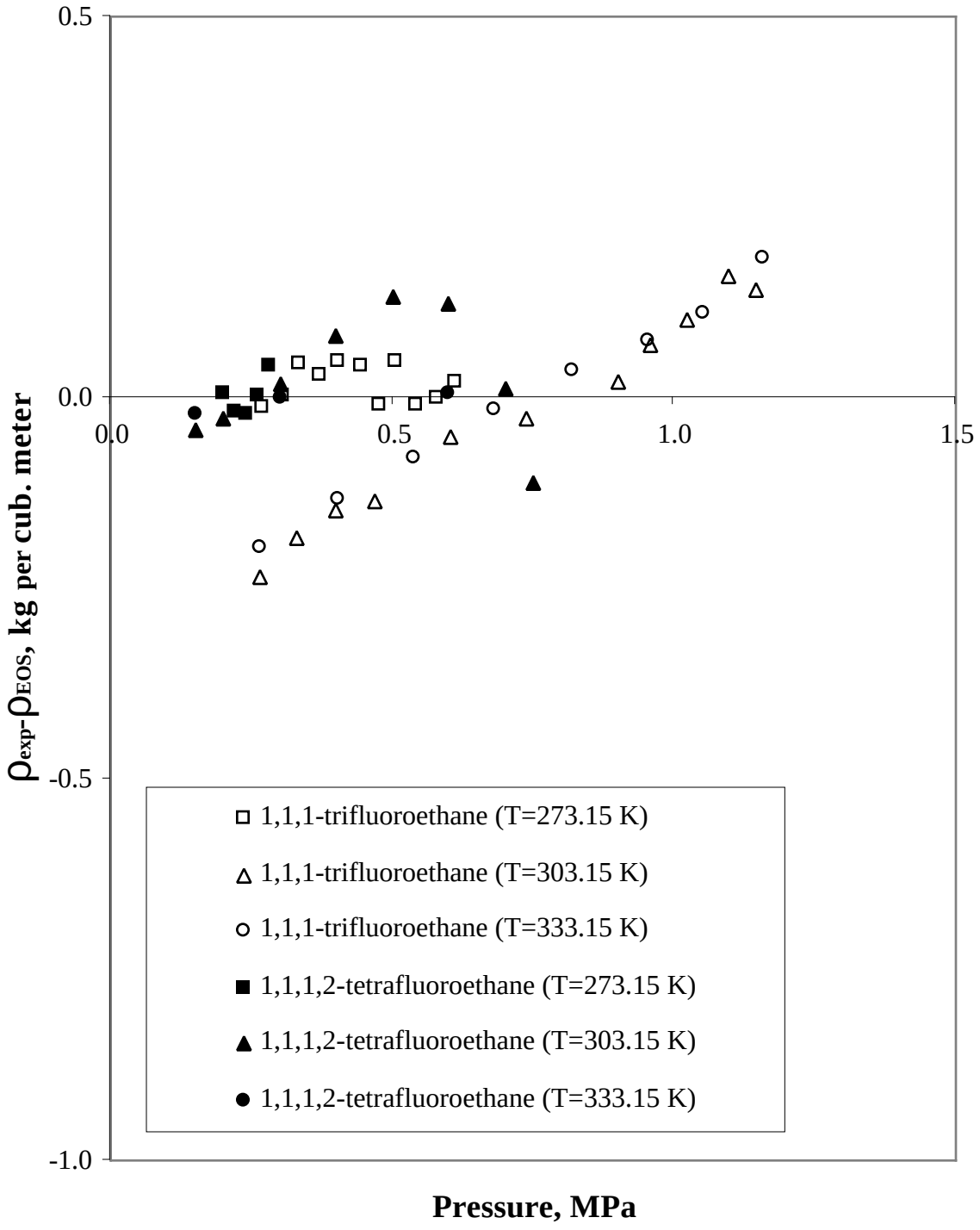
0.5
0.0
-0.5
-1.0
0.0
0.5
1.0
1.5
ρexp-ρEOS, kg per cub. meter
Pressure, MPa
1,1,1-trifluoroethane (T=273.15 K)
1,1,1-trifluoroethane (T=303.15 K)
1,1,1-trifluoroethane (T=333.15 K)
1,1,1,2-tetrafluoroethane (T=273.15 K)
1,1,1,2-tetrafluoroethane (T=303.15 K)
1,1,1,2-tetrafluoroethane (T=333.15 K)

Fig. 4

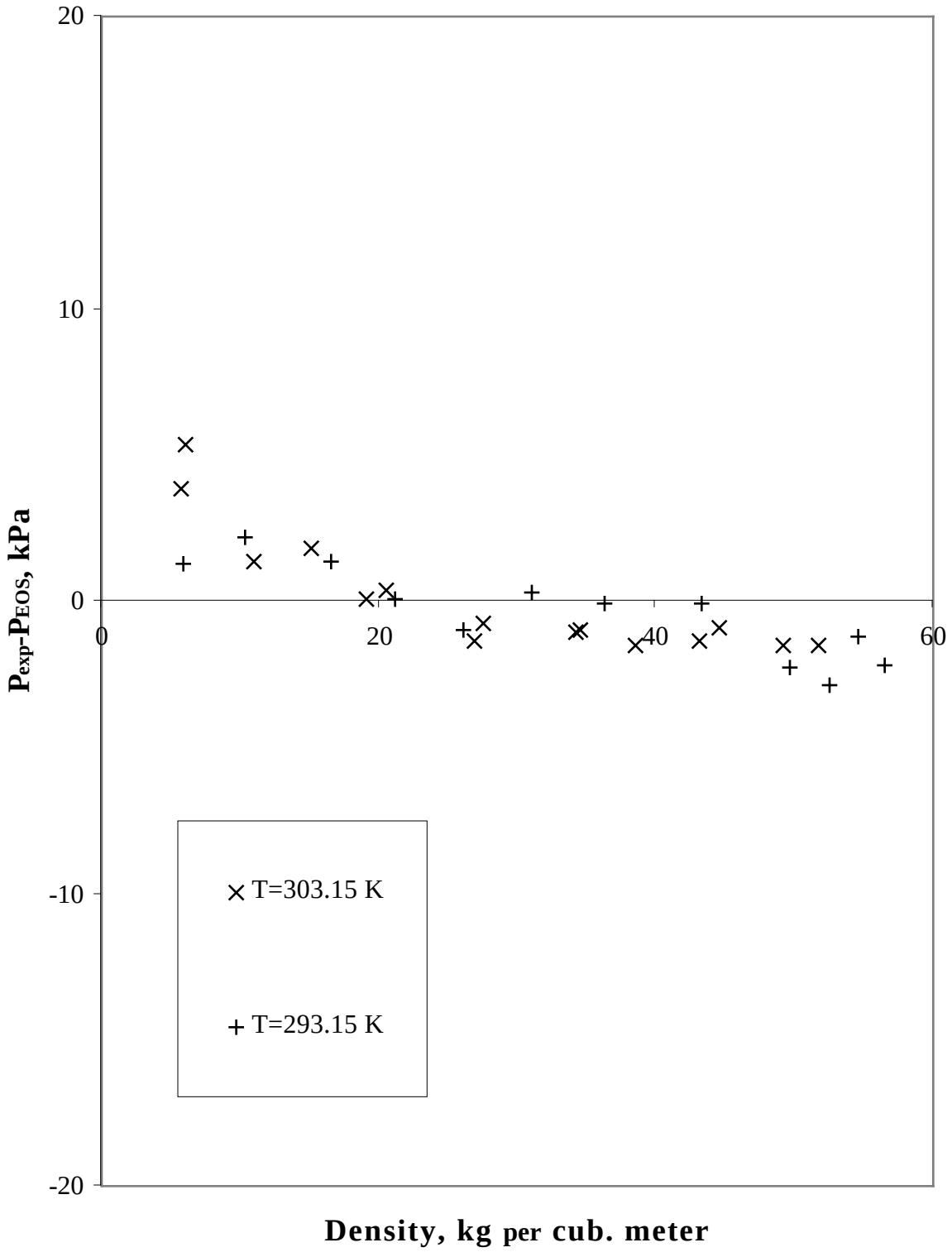
20
10
0
-10
-20
0
20
40
60
Pexp-PEOS, kPa
Density, kg per cub. meter
T=303.15 K
T=293.15 K

Fig. 5a

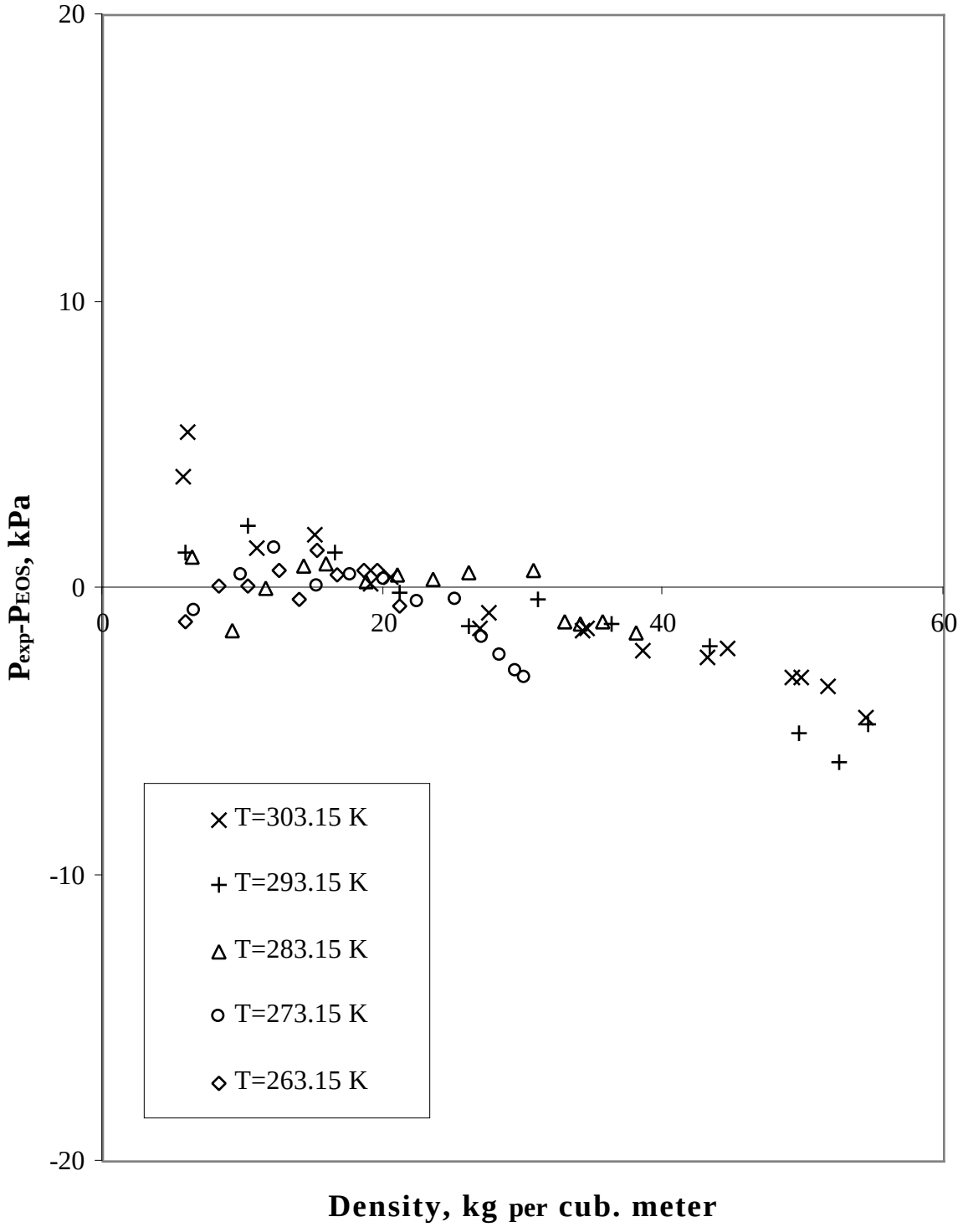
20
10
0
-10
-20
0
20
40
60
Pexp-PEOS, kPa
Density, kg per cub. meter
T=303.15 K
T=293.15 K
T=283.15 K
T=273.15 K
T=263.15 K

Fig. 5b