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# **Saturated Pressure Measurements of Dimethyl Ether at Temperatures from (219 to 361) K**

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## **Abstract**

The vapor pressure data of Dimethyl Ether (RE170), an ozone-friendly refrigerant, was measured using a constant volume apparatus. Measurements were carried out at temperatures from (219 to 361) K and at pressures from (22 to 2622) kPa. A total of 71 experimental points were obtained. The measurements were fitted to a Wagner type equation and an absolute deviation of 0.26 %. After a literature survey of the saturated pressure experimental findings, our experimental results were compared with the REFPROP 7.0 prediction together with the published data.

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## Introduction

Dimethyl Ether is an important chemical material and has many engineering applications. It is now developed as a substitute of engine fuel for gasoline, as assistant solvent and aerosol propellant.

It can be made from coal, natural gas, residual oil, oil coke, and other biological materials and its production cost is very low. In addition dimethyl ether has non-toxicity and non-carcinogenity.

Considering that dimethyl ether has zero Ozone Depletion Potential (ODP) and zero Global Warming Potential (GWP), and for its good thermodynamic properties, it was also suggested as an alternative refrigerant (RE170). In particular for air conditioning systems applications, the mixture of 60 % in mass of ammonia and 40 % in mass of dimethyl ether forms an interesting azeotrope (R723). For all these reasons, the study of its thermophysical properties is very important.

In the saturation region, excluding very old and less precise data,<sup>1,2</sup> accurate experimental data for RE170 are not very numerous. In fact, since last years a limited number of points was collected by different laboratories while studying the VLE of its binary systems.<sup>3-12</sup> Confirming the rising interest on this fluid, an intensive research was recently carried in terms of critical parameters,<sup>13</sup> surface tension,<sup>14</sup> viscosity,<sup>15</sup> thermal conductivity<sup>16</sup> by Wu and co-workers. Inside this research project, a quite large amount of vapor pressure data at temperatures from (233 to 399) K were collected by the same authors.<sup>17</sup>

Furthermore, large differences among the published experimental vapor pressure data are evident.

For these reasons, 71 experimental points were collected in the two phase region in a temperature range spanning from (219 to 361) K. Experimental observations were regressed with a Wagner-type equation. A comparison of all the available data through the REFPROP 7.0<sup>18</sup> prediction in a special version for this specific fluid<sup>19</sup> was also carried out.

## Experimental Section

**Materials.** The sample was provided by Aldrich Inc., USA. It was de-aerated by immersion in liquid nitrogen and evacuation. Its purity was checked by gas chromatography using a thermal

conductivity detector and was found to be better than 99.8 % in molar basis by analysis of peak area.

**Apparatus.** The new experimental set-up is illustrated in Figure. 1. The basic experimental set-up has already been described elsewhere,<sup>20</sup> so it is only briefly outlined here. Two twin thermostatic baths were filled with different silicone oils (Baysilone M10 and Baysilone M100, Bayer). After charging with the sample, the set-up could be operated over two temperature ranges, approximately from (210 to 290) K and from (290 to 360) K, depending on which bath was used. The two silicone oils have different kinematic viscosity values (10 and 100 cSt at room temperature, respectively). The one with lower kinematic viscosity, due to its higher volatility, was applied only for the low temperature range, while that with a greater viscosity was applied only at high temperatures. The thermostatic baths were easy to move thanks to the new system configuration. The spherical cells and pressure transducer are immersed in one of the two thermostatic baths. An auxiliary thermostat was used to reach below-ambient temperatures. The cell volume was estimated to be  $(273.5 \pm 0.3)$  cm<sup>3</sup> at room temperature<sup>20</sup> and the cell volume change with temperature was taken into account.<sup>21</sup> The pressure and temperature data acquisition systems were identical to those of the previous apparatus.<sup>21,22</sup> A PID device was used to control the temperature, which was measured using a calibrated resistance thermometer; the total uncertainty of the temperature measurements was  $\pm 0.02$  K. The uncertainty in the pressure measurements stems from the uncertainty of the transducer and null indicator system, and the pressure gauges. The uncertainty of the digital pressure indicator (Ruska, mod. 7000) is  $\pm 0.003$  % of its full scale. Temperature fluctuations due to bath instability can also affect the total uncertainty in the pressure measurement, which was nonetheless found to be less than  $\pm 1$  kPa. The charging procedure by gravimetric method has been described elsewhere.<sup>23</sup>

## Results and Discussion

**Vapor pressure.** The experimental vapor pressures at temperatures in the range (219 K to 361) K are given in Table 1. Experimental data were fit to the four-parameter Wagner equation,

$$\ln \frac{P}{P_c} = \frac{T_c}{T} [A_1 \tau + A_2 \tau^{1.5} + A_3 \tau^2 + A_4 \tau^5] \quad (1)$$

where  $\tau = (T_c - T)/T_c$ ; the critical temperature  $T_c = 400.1$  K.<sup>18</sup>

The following values were found for the parameters:  $A_1 = -7.40714$ ,  $A_2 = 3.42409$ ,  $A_3 = -2.97850$ ,  $A_4 = -3.43070$ . From the fitting procedure, the critical pressure was fixed to be  $P_c = 5370.2$  kPa.<sup>18</sup>

Defining the deviations in pressure as

$$dP = \frac{1}{n} \sum_{i=1}^n [(P_{\text{exp}} - P_{\text{calc}}) / P_{\text{exp}}] \cdot 100 \quad (2)$$

$$|dP| = \frac{1}{n} \sum_{i=1}^n [(P_{\text{exp}} - P_{\text{calc}}) / P_{\text{exp}}] \cdot 100 \quad (3)$$

where  $n$  is the number of experimental points, the following values were found:  $dP = 0.16$  % and  $\text{abs}(dP) = 0.26$  %. The error distribution is shown in Figures 2 and 3. The absolute deviations were found to be well distributed within  $\pm 1$  kPa, while the relative deviations were found to be within  $\pm 1\%$ , excluding few points at the lower temperatures that, due to the very low experimental pressures, produced higher deviations in percent.

The experimental results were also compared with the published data in the literature. In figures 4 and 5 are reported absolute and relative deviations for the literature data<sup>3-12,17</sup> from equation 1.

Most of the deviations are well within  $\pm 10$  KPa, showing a general consistency between the sources; a systematic shift of 5 KPa was found only for one source,<sup>17</sup> while higher deviations were found at temperatures greater than 320 K for two sources.<sup>11,12</sup> The common trend but the systematic shift found with one source<sup>17</sup> could be due to the different sample purity.

Our experimental results were also compared with REFPROP 7.0 together with the published data in the literature. In Figure 6, the distribution of deviations between the literature sources and REFPROP 7.0 is shown. From figure 6 it is evident that the same trend (but with slightly shifted results) was obtained comparing the present work data with the more recent and numerous ones.<sup>11,12,17</sup> Excluding again one source,<sup>17</sup> a very good agreement for temperatures between 250 and 300 K was obtained.<sup>11,12</sup> An excellent agreement was also obtained with sources obtained by direct VLE measurements.<sup>6-10</sup> In general, agreement with REFPROP 7.0 was good, even if measurements with lower temperatures (less than 250 K) showed in Figure 7, again due to the very low experimental pressures, systematic negative relative deviations.

## **Conclusions**

The measurements of 71 experimental points for saturated pressure were obtained using a constant-volume apparatus for RE170. The experimental points taken within the VLE boundary were fitted with a Wagner type equation. The experimental VLE data were compared with the REFPROP 7.0 prediction and with recently-published data and a generally good consistency between the different sources was found.

## **Acknowledgement**

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## Figure captions

Figure 1. Schematic illustration of the apparatus.

- |                                     |  |
|-------------------------------------|--|
| 1. Constant volume spherical cell   | 12. Power system                               |
| 2. Auxiliary cell                   | 13. Cooling coil                               |
| 3. Magnetic pump                    | 14. Connections to auxiliary thermostatic bath |
| 4. Differential pressure transducer | 15. Acquisition system                         |
| 5. Electronic null indicator        | 16. Bourdon gage                               |
| 6. Charging system                  | 17. Dead weight gage                           |
| 7. Thermostatic baths               | 18. Vibrating cylinder pressure gage           |
| 8. Platinum thermo-resistances      | 19. Precision pressure controller              |
| 9. Thermometric bridge              | 20. Nitrogen reservoir                         |
| 10. Stirrer                         | 21. Vacuum pump system                         |
| 11. Heater                          |  |

Figure 2. Scatter diagram of the saturated pressure absolute deviations from the fit with the Wagner equation, eq 1.

Figure 3. Scatter diagram of the saturated pressure relative deviations from the fit with the Wagner equation, eq 1.

Figure 4. Vapor pressure absolute deviations of RE170 from eq. 1 and measurements published in the literature:

- |          |             |           |           |
|----------|-------------|-----------|-----------|
| ▽ Ref. 3 | ◇ Ref. 5    | ⊙ Ref. 11 | □ Ref. 17 |
| ⊙ Ref. 4 | △ Ref. 6-10 | ○ Ref. 12 |           |

Figure 5. Vapor pressure relative deviations of RE170 from eq.1 and measurements published in the literature:

- |          |             |           |           |
|----------|-------------|-----------|-----------|
| ▽ Ref. 3 | ◇ Ref. 5    | ⊙ Ref. 11 | □ Ref. 17 |
| ⊙ Ref. 4 | △ Ref. 6-10 | ○ Ref. 12 |           |

Figure 6. Vapor pressure absolute deviations of RE170 from REFPROP 7.0 and measurements published in the literature:

- |                |          |             |           |
|----------------|----------|-------------|-----------|
| ● Present work | ◊ Ref. 4 | △ Ref. 6-10 | ○ Ref. 12 |
| ▽ Ref. 3       | ◇ Ref. 5 | ⊙ Ref. 11   | □ Ref. 17 |

Figure 7. Vapor pressure relative deviations of RE170 from REFPROP 7.0 and measurements published in the literature:

- |                |          |             |           |
|----------------|----------|-------------|-----------|
| ● Present work | ◊ Ref. 4 | △ Ref. 6-10 | ○ Ref. 12 |
| ▽ Ref. 3       | ◇ Ref. 5 | ⊙ Ref. 11   | □ Ref. 17 |



## References

1. Cardoso, E.; Bruno, A. Recherches experimentales sur quelques proprietés termique des gaz – elements critiques et tensions de vapeur de l'oxyde de methyle *J. Chim. Phys.* **1923**, *20*, 347-351 (in French).
2. Kennedy, R. M.; Sagenkahn, M.; Aston, J. G. The heat capacity and entropy, heats of fusion and vaporization, and the vapor pressure of dimethyl ether, the density of gaseous dimethyl ether. *J. Am. Chem. Society* **1941**, *63*, 2267-2272.
3. Horstmann, S.; Birke, G.; Fischer, K. Vapor-Liquid Equilibrium and Excess Enthalpy for the binary System Propane + Dimethyl Ether and Propene + Dimethyl Ether at Temperatures from (298 to 323) K. *J. Chem. Eng. Data* **2004**, *49*, 38-42.
4. Noles, J. R.; Zollweg, J. A. Vapor-liquid Equilibrium for Chlorodifluoromethane + Dimethyl Ether from 283 to 395 K at Pressures to 5.0 MPa. *J. Chem. Eng. Data* **1992**, *37*, 306-310.
5. Jonasson, A.; Persson, O.; Fredenslund, A. High-Pressure Solubility of Carbon Dioxide and Carbon Monoxide in Dimethyl Ether. *J. Chem. Eng. Data* **1995**, *40*, 296-300.
6. Bobbo, S.; Fedele, L.; Camporese, R.; Stryjek, R. Isothermal Vapor Liquid Equilibrium for the Three Binary Systems 1,1,1,2,3,3-Hexafluoropropane with Dimethyl Ether or Propane, and 1,1,1,3,3,3-Hexafluoropropane with Dimethyl Ether. *Fluid Phase Equilib.* **2000**, *174*, 3-12.
7. Bobbo, S.; Stryjek, R.; Camporese, R. (Vapor + liquid) Equilibrium Measurements and Correlations of the Refrigerant Mixture {dimethylether (RE170) + 1,1,1,3,3,3-Hexafluoropropane (R236fa)} at the Temperatures (303.68 and 323.75) K. *J. Chem. Thermodyn.* **1998**, *30*, 1041-1046.
8. Bobbo, S.; Fedele, L.; Stryjek, R.; Camporese, R. Hydrogen Bonding of HFCs with Dimethyl Ether: Evaluation by Isothermal VLE Measurements. *Fluid Phase Equilib.* **2002**, *199*, 153-160.
9. Bobbo, S.; Fedele, L.; Scattolini, M.; Camporese, R.; Stryjek, R. Isothermal Vapor + Liquid Equilibrium Measurements and Correlation for the Dimethyl Ether + 1,1,1,2,3,3,3-

- Heptafluoropropane and the Propane + 1,1,1,2,3,3,3-Heptafluoropropane Systems. *Fluid Phase Equilib.* **2004**, *224*, 119-123.
10. Fedele, L.; Bobbo, S.; De Stefani, V.; Camporese, R.; Stryjek, R. Isothermal VLE Measurements for Difluoromethane + Dimethyl Ether and an Evaluation of Hydrogen Bonding. *J. Chem. Eng. Data* **2005**, *50*, 128-132.
  11. Valtz, A.; Gicquel, L.; Coquelet, C.; Richon, D. Vapour-liquid equilibrium data for the 1,1,1,2 tetrafluoroethane (R134a) + dimethyl ether (DME) system at temperatures from 293.18 to 358.15 K and pressures up to about 3 Mpa. *Fluid Phase Equilib.* **2005**, *230*, 184-191.
  12. Yasumoto, M.; Uchida, Y.; Ochi, K.; Furuya, T.; Otake, K. Critical Properties of Three Dimethyl Ether Binary Systems: Dimethyl Ether (RE-170) + Propane (HC-290), Butane (HC-600), and 2-Methyl Propane (HC-600A). *J. Chem. Eng. Data* **2005**, *50*, 596-602.
  13. Wu, J. T.; Liu, Z. G.; Wang, B.; Pan, J. Measurements of critical parameters and saturated densities of dimethyl ether. *J. Chem. Eng. Data* **2004**, *49*, 704-708.
  14. Wu, J. T.; Liu, Z. G.; Wang, F. K.; Ren, C. Surface tension of dimethyl ether from (213 to 368) K. *J. Chem. Eng. Data* **2003**, *48*, 1571-1573.
  15. Wu, J. T.; Liu, Z. G.; Bi, S. S.; Meng, X. Y. Viscosity of saturated liquid dimethyl ether from 227 to 343 K. *J. Chem. Eng. Data* **2003**, *48*, 426-429.
  16. Wu, J. T.; Liu, Z. G.; Jin, X. G.; Pan, J. The thermal conductivity of some oxygenated fuels and additives in the saturated liquid phase. *J. Chem. Eng. Data* **2005**, *50*, 102-104.
  17. Wu, J. T.; Liu, Z. G.; Pan, J.; Zhao, X. M. Vapor pressure measurements of dimethyl ether from (233 to 399) K. *J. Chem. Eng. Data* **2004**, *49*, 32-34.
  18. Lemmon, E.W.; McLinden, M.O.; Huber, M.L. NIST Standard Reference Database 23, NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP), Version 7.0 (Gaithersburg: National Institute of Standards and Technology), **2002**.
  19. Lemmon, E.W. Private communication.

20. Di Nicola, G.; Polonara, F.; Ricci, R.; Stryjek, R. *PVTx* Measurements for the R116 + CO<sub>2</sub> and R41 + CO<sub>2</sub> Systems. New Isochoric Apparatus. *J. Chem. Eng. Data* **2005**, *50*, 312-318.
21. Giuliani, G.; Kumar, S.; Polonara, F. A Constant Volume Apparatus for Vapour Pressure and Gas Phase *P-v-T* Measurements: Validation with Data for R22 and R134a. *Fluid Phase Equilib.* **1995**, *109*, 265-279.
22. Giuliani, G.; Kumar, S.; Zazzini, P.; Polonara, F. Vapor Pressure and Gas Phase PVT Data and Correlation for 1,1,1-Trifluoroethane (R143a). *J. Chem. Eng. Data* **1995**, *40*, 903-908.
23. Di Nicola, G.; Giuliani, G.; Polonara, F.; Stryjek, R. Saturated pressure and *P-V-T* measurements for 1,1,1,3,3,3-hexafluoropropane (R-236fa). *J. Chem. Eng. Data* **1999**, *44*, 696-700.

Ta

Table 1. Experimental Saturation Pressures  $P$  at Temperature  $T$  for RE170

$T_{90}/\text{K}$	$P/\text{kPa}$	$T_{90}/\text{K}$	$P/\text{kPa}$
219.15	22.3	293.08	508.9
221.13	25.2	295.07	540.0
223.11	28.3	297.07	573.0
224.88	31.5	299.08	606.9
226.88	35.4	301.11	643.1
228.85	39.5	303.08	680.2
230.86	43.9	305.07	718.4
232.86	48.7	307.07	758.8
234.85	54.1	309.06	800.7
236.85	59.8	311.07	844.2
239.14	66.3	313.06	889.5
241.14	73.2	315.06	936.6
244.14	84.0	317.04	985.3
247.13	96.1	319.03	1036.0
249.13	104.9	321.03	1088.7
251.14	114.3	323.02	1143.3
255.13	135.1	325.02	1200.6
257.12	146.6	327.13	1262.3
259.14	159.0	329.02	1319.9
261.13	171.8	331.11	1385.3
263.13	185.6	333.11	1450.6
265.13	199.8	335.11	1518.8
267.13	215.5	337.10	1588.4
269.13	231.8	339.10	1660.3
271.13	248.9	341.08	1733.3
273.13	266.8	343.09	1811.3
275.04	285.1	345.09	1891.2
277.02	305.0	347.08	1972.8
279.02	326.4	349.08	2057.4
281.02	348.8	351.07	2144.3
283.02	372.3	353.05	2232.7
285.01	397.0	355.05	2326.0
287.00	422.8	357.05	2421.9
288.99	449.8	359.05	2520.3
290.99	478.4	361.04	2621.5

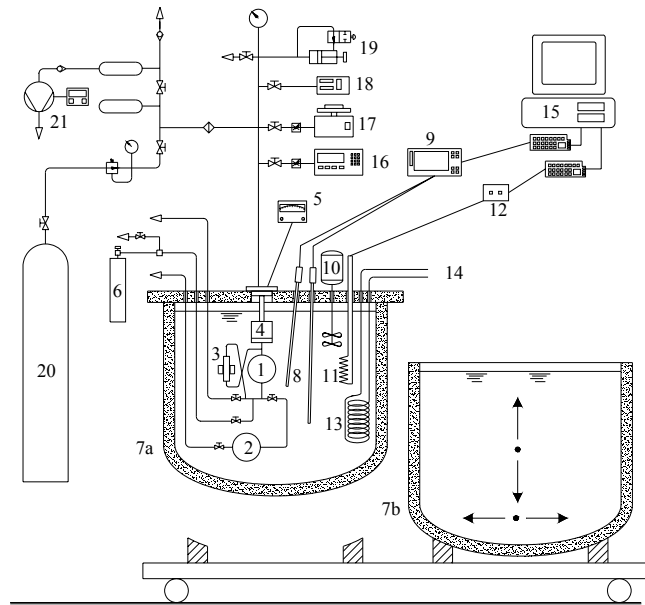


Figure 1

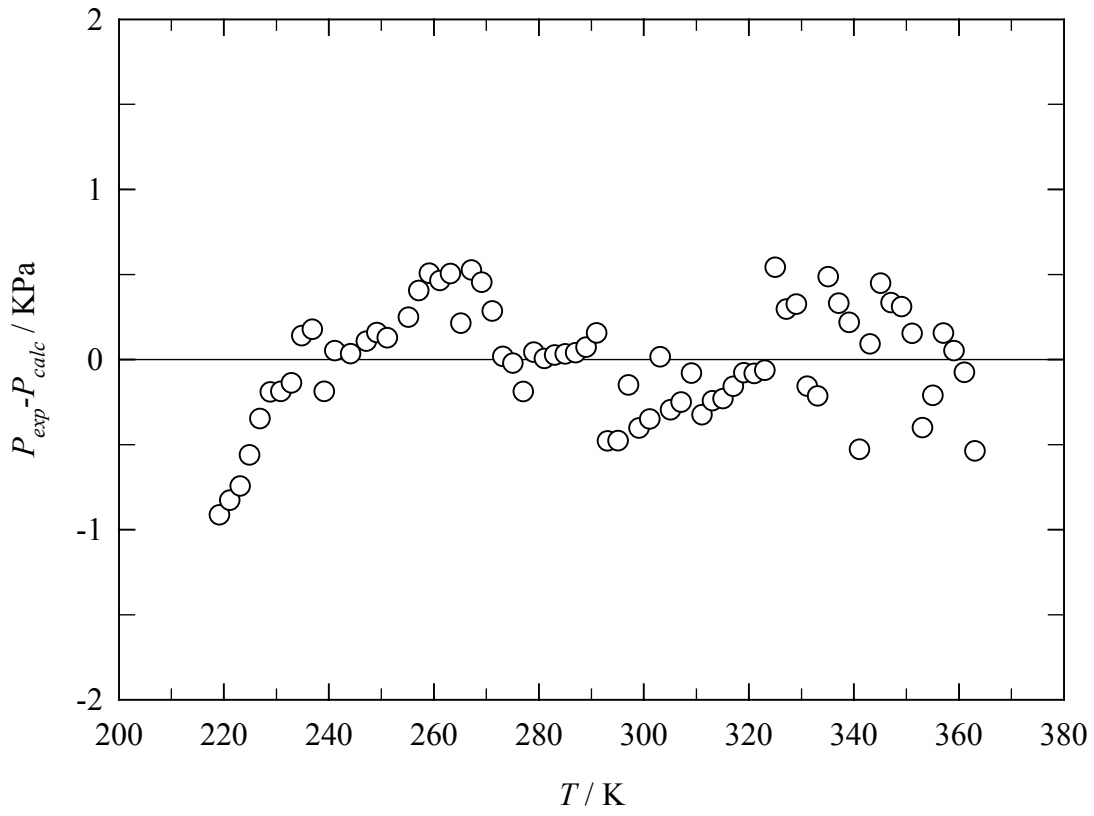


Figure 2.

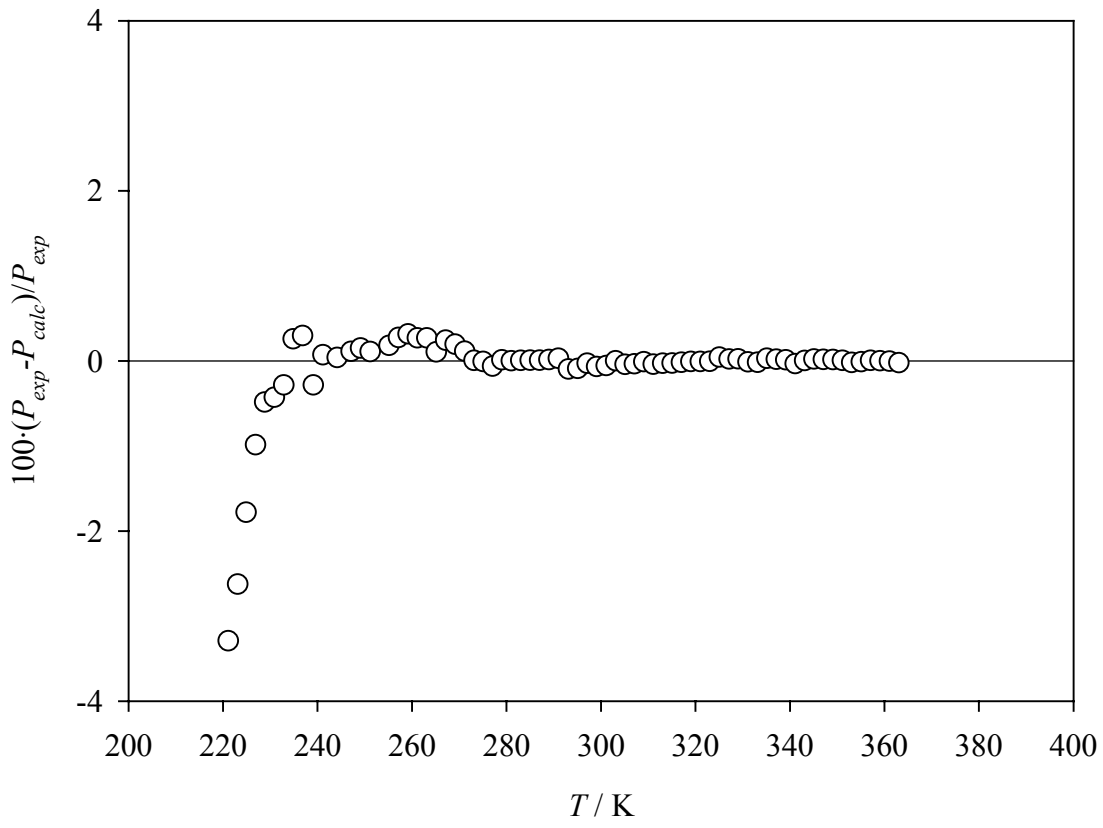


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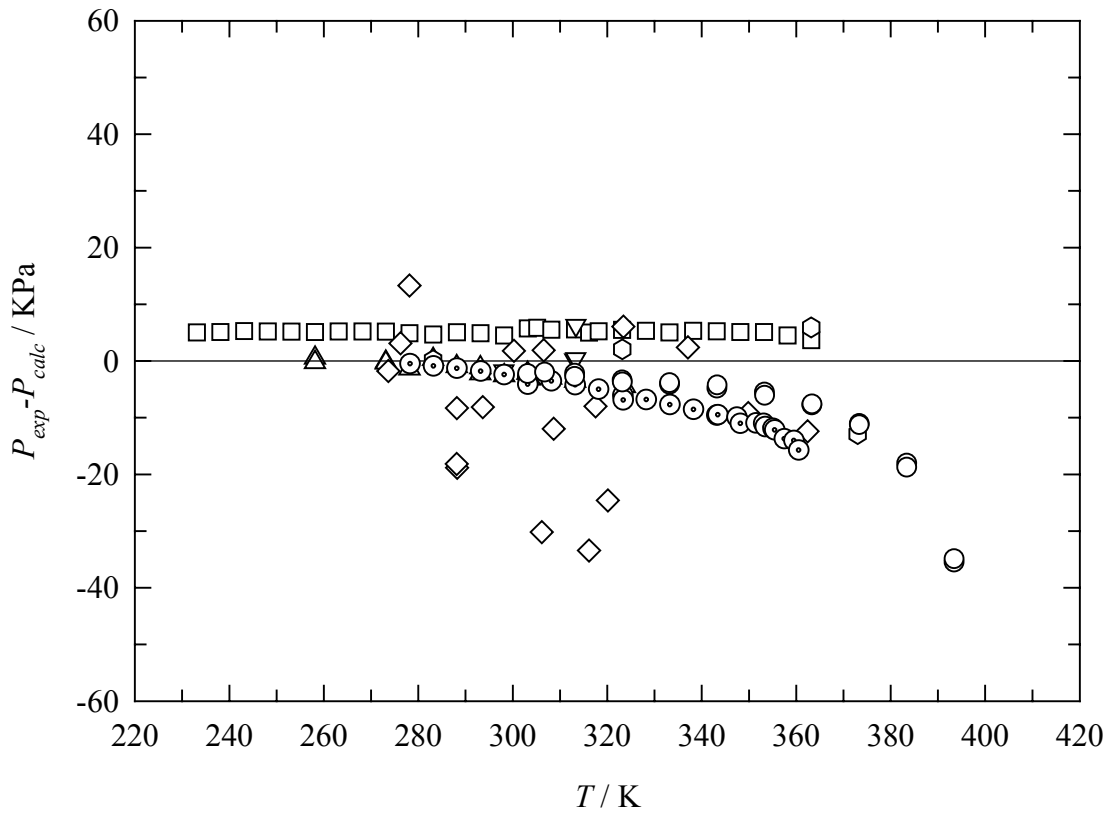


Figure 4.



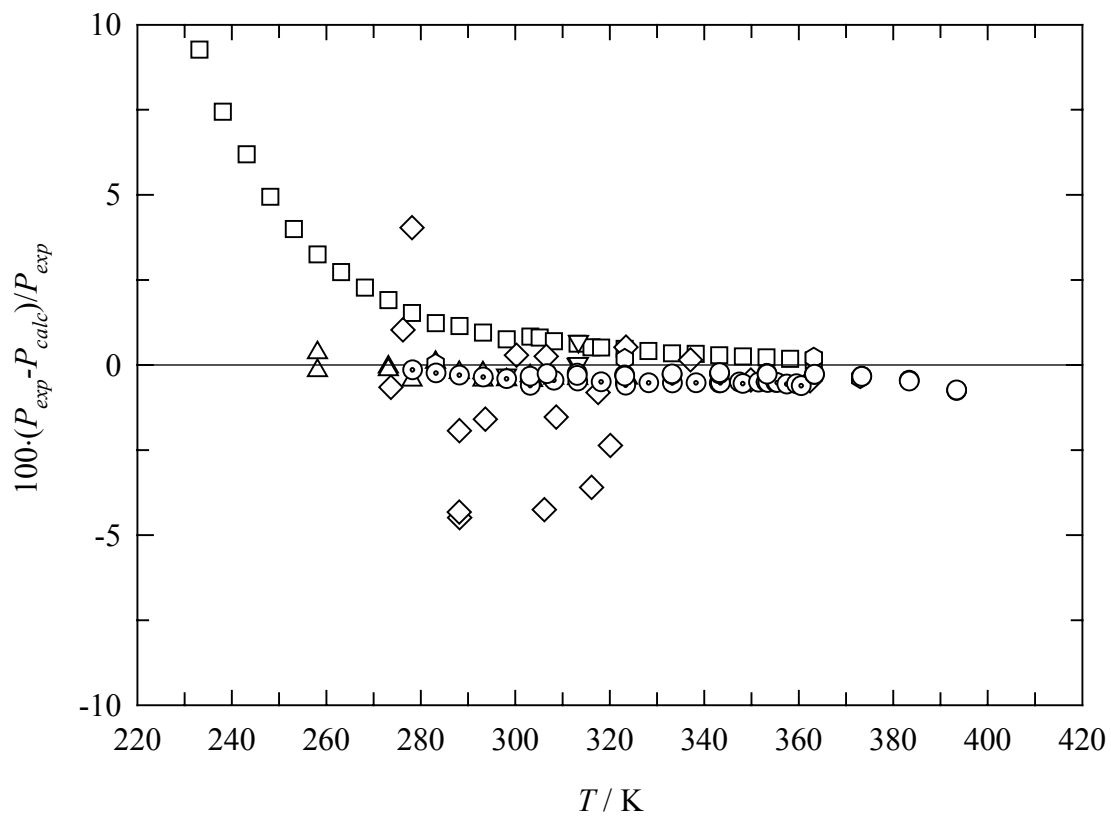


Figure 5.

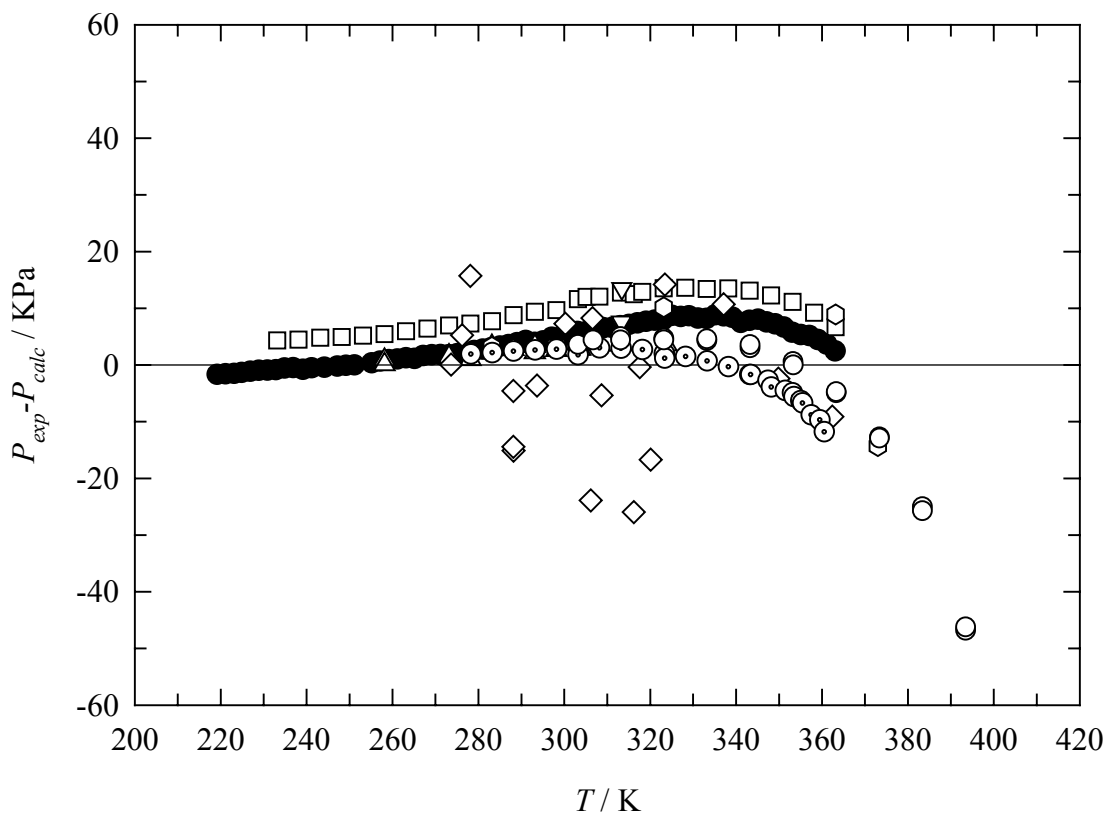


Figure 6.

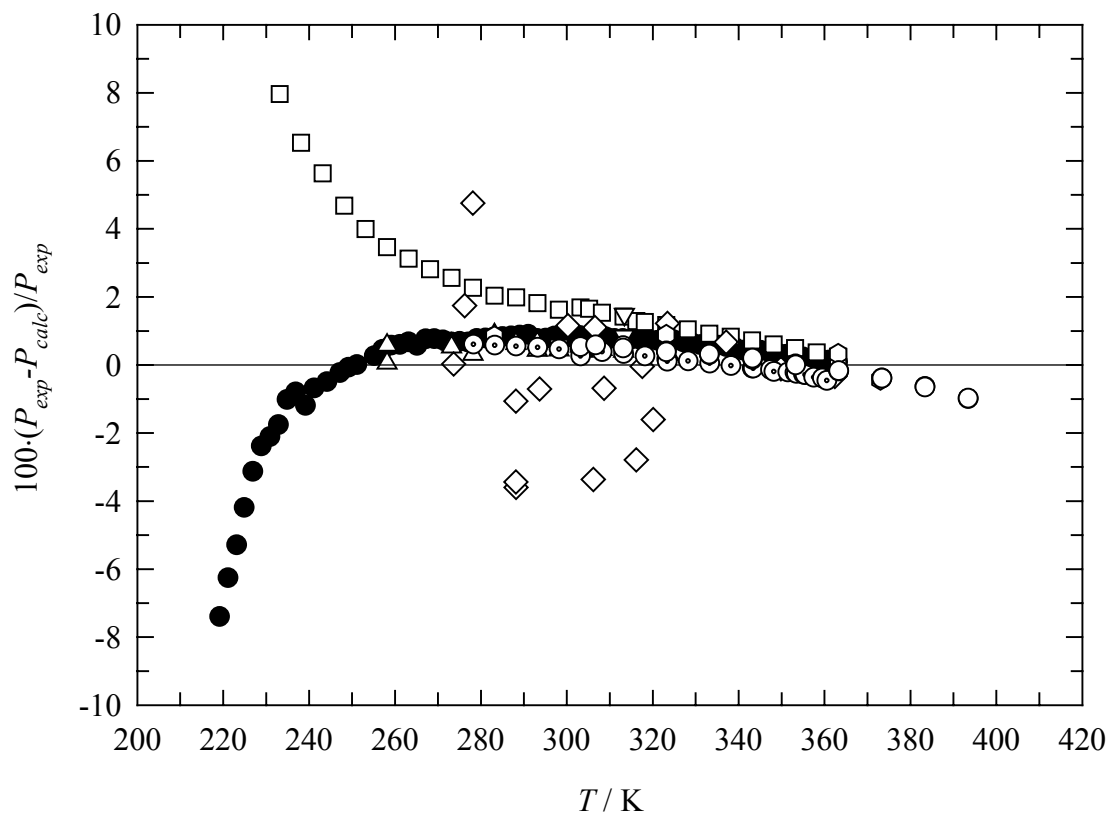


Figure 7.