Methods for calculating the heat capacity of decafluorobutane in a liquid

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Abstract. This work presents a comparison of the values of isochoric and isobaric heat capacities in a liquid in the range of parameters from 20°C to 140°C and pressures from 2 MPa to 10 MPa, obtained by two different methods. Under one of the proposed methods isobaric and isochoric heat capacities are obtained within joint thermal (pνT-dependence) and acoustic (speed of sound) measurements, the other method represents heat capacity values are obtained from a unified equation of state presented by the authors earlier based on the results of experimental and computational studies. New density measurements on 7 isotherms in the liquid and supercritical areas of state in the temperature range from 5°C to 141°C and pressure from 1.6 MPa to 10.9 MPa are presented. Estimation of the calculated based on experimental data for the isochoric heat capacity is ± 5%. The discrepancy between the calculated values of the heat capacity by both methods in the entire range of the studied temperatures reaches 30%, which is explained by the lack of experimental data on the heat capacity in the known literature.

1. Introduction

This work is a continuation of a cycle of complex studies to obtain databases on the thermophysical properties of some potentially promising fluorocarbon working fluids suitable for use as working fluids of modern power plants providing high thermodynamic efficiency [1]. Interest in the thermophysical properties of fluorocarbon working bodies arose in connection with the search for ways to improve nuclear and combined cycle plants. Working substances of fluorocarbon composition, due to a number of advantages, in the development of "organic Rankine cycles (ORCs)", are considered among the promising working substances of the power industry. These include such perfluoro compounds, for example, decafluorobutane (C₄F₁₀), which was previously used mainly as a refrigerant. Experimental data known to date on the thermal properties of liquid and gaseous C₄F₁₀ are published in [2-7]. New density measurements in recent years [8] have significantly expanded the range of experimentally investigated parameters and made it possible to proceed to the construction of a unified equation of state in order to obtain data on thermophysical properties necessary for calculating heat-power cycles and plant balances.

This work presents a comparison of the values of isochoric and isobaric heat capacities in a liquid in the range of parameters from 20°C to 140°C and pressures from 2 MPa to 10 MPa, obtained by two different methods.
2. Proposed method of calculating heat capacities

According to one of the methods (hereinafter referred to as proposed method 1) [9], for comparison, the data of isobaric and isochoric heat capacities obtained during joint thermal ($p\nu T$- or $p\rho T$-dependence) and acoustic (speed of sound) measurements are presented. A comprehensive study of thermodynamic properties, which includes measurements of the density of the working fluid and the speed of sound depending on pressure and temperature, as the properties studied most accurately, allows, using the mathematical apparatus of thermodynamics [10], to calculate other thermodynamic functions, for example, such as isochoric and isobaric heat capacities. The combined use of experimental data on the density of a substance and the speed of sound in it makes it possible to calculate the isobaric and isochoric heat capacities without invoking the values of ideal gas functions. For the joint use of data of substance’s speed of sound and density, it is necessary to describe with high accuracy the results of experimental studies by equations of the virial polynomial form (well amenable to differentiation).

3. Description of experimental data

Earlier the authors obtained new experimental data on the speed of sound of decafluorobutane by the pulse-frequency method in the temperature range $20\div170^\circ C$ and pressures up to 11 MPa [11]. The uncertainty of the experienced was no more than 0.2%. The obtained array of experimental data on the speed of sound is described by an equation of the form:

$$a = \sum_{i=0}^{m} \sum_{j=0}^{n} b_{ij} \left( T^{-i} p^j \right)$$

where $a$ is the speed of sound, m/s; $p$ - pressure, MPa; $T$ is temperature, K; $i, j$ - coefficient indices; $b_{ij}$ - coefficients of the polynomial at temperature $T$ and pressure $p$, respectively; $m, n$ are the maximum degrees of the polynomial.

As a result of the calculation according to the obtained equation (1), the standard deviation of the described data from the array of experimental data on the speed of sound was 0.048% (at $m = 4; n = 3$).

This paper presents the data of the next series of measurements of the density of decafluorobutane, obtained by the constant volume piezometer. The measurements were carried out over 7 isotherms in the liquid and supercritical areas of state. The range of the studied state parameters of the new series is shown in figure 1, its boundaries are from $5^\circ C$ to $141^\circ C$, and the pressure values are from 1.6 MPa to 10.9 MPa.

![Figure 1. The range of parameters for the obtained values of density of C$_4$F$_{10}$ in p-t diagram.](image)
In total 43 experimental points were obtained. The uncertainty of the experimental data was no more than 0.1%. For a comparative assessment of the experimental data obtained, a computational model was used, built using the similarity method, within the framework of NIST REFPROP 9.0 properties calculator software [12]. The disposition of the deviations is shown in figure 2.

The form of the relative deviations is quite natural: with an increase in temperature, an increase in deviations is observed. The values of the obtained deviations of the experimental data from the data [12] are within ± 0.4%. To assess the quality of the results of this series of measurements, the experimental data were described by a polynomial equation. In this case, it is advisable to represent density data in the form of an equation of state of the virial type:

\[
\rho = \sum_{i=0}^{m} \sum_{j=0}^{n} b_{i,j} \cdot p^i \cdot T^{-j}
\]  

(2)

where \( \rho \) is pressure, MPa; \( \rho \) is the density of the studied substance, kg/m\(^3\); \( T \) is temperature, K; \( i, j \) - coefficient indices; \( b_{i,j} \) - coefficients of the polynomial at temperature \( T \) and pressure \( p \), respectively; \( m, n \) are the maximum degrees of the polynomial.

The description of the obtained array of experimental data by an equation of the indicated form according to the equation (2), the calculation of the absolute and fractional deviations was carried out in the environment Wolfram Mathematica 10 [13]. As a result of the calculation according to the obtained equation with a degree of 6x6, the standard deviation of the described data from the array of experimental data did not exceed 0.067%. Despite the fact, that the density data are represented by an ordinary polynomial dependence, and not by a virial-type equation, the deviations of the experimental data from the calculated model did not exceed 0.07%. The surface shape of the resulting equation with the plotted experimental points is shown in figure 3.
4. Obtaining data of heat capacities

The data arrays obtained in the cross range of the state parameters of both the acoustic experiment and the data on density measurements were processed in accordance with the procedure for calculating the caloric properties [9]. Processing these data made it possible to obtain equations in the form of polynomials for calculating the isobaric and isochoric heat capacity. So, for example, to describe the array of obtained values of the isochoric heat capacity (135 points in total), the obtained equation was obtained for the dependence of the isochoric heat capacity \( c_v \) on temperature and pressure of degree 9x8. The surface shape of the obtained equation with the plotted points obtained by method 1 is shown in figure 4.

![Figure 4](image)

**Figure 4.** Graphical illustration of the surface \( c_v(T, p) \) with plotted points calculated by the method 1.

The equations for the isochoric \( (c_v) \) and isobaric \( (c_p) \) heat capacities obtained in the form (2) were described by equations with 72 and 81 coefficients with a standard deviation of 0.350% and 0.470%, respectively.

5. Obtaining data of heat capacities and evaluation its creditability

To assess the consistency and creditability of the proposed method 1, the values of isochoric \( (c_v) \) and isobaric \( (c_p) \) heat capacities obtained with its help were compared with the data from [12]. Deviations are shown in figure 5 and figure 6.

![Figure 5](image)

**Figure 5.** Deviations of \( c_v \) values calculated by method 1 compared with [12].

![Figure 6](image)

**Figure 6.** Deviations of \( c_p \) values calculated by method 1 compared with [12].
6. Comparison of the values of the heat capacities obtained by different methods

The obtained heat capacity values according to method 1, it is proposed to compare with the heat capacity values obtained according to method 2. According to method 2, the heat capacity values are obtained from a unified equation of state presented by the authors based on the results of experimental and computational studies [14]. On the basis of the unified equation of state presented in the work, the heat capacity values were also compared with [12]. The discrepancies in the calculated heat capacity values in the entire temperature range reach 11%, which is explained by the lack of experimental data on the decafluorobutane heat capacity in the known literature.

Comparisons of the obtained values of isochoric and isobaric heat capacities according to method 1 and method 2 for three isotherms 120°C, 130°C and 140°C are presented in table 1.

Table 1. Deviations of the obtained data of heat capacities from the data [12].

| Temperature (K) | Pressure (MPa) | Data obtained by method 1 | Data obtained by method 2 |
|----------------|----------------|---------------------------|---------------------------|
|                |                | $c_v$, J/kg·K $c_p$, J/kg·K | $\delta c_v$, % $\delta c_p$, % | $c_v$, J/kg·K $c_p$, J/kg·K | $\delta c_v$, % $\delta c_p$, % |
| 393.15        | 2              | 1053 1469 9.91 15.8       | 1015 1321 6.94 -6.80    |
| 393.15        | 4              | 1081 1482 9.42 -20.8      | 1000 1548 -2.14 12.8    |
| 393.15        | 6              | 1043 1121 7.40 -19.5      | 692 1005 18.4 10.8     |
| 393.15        | 8              | 1009 893 4.76 -19.5       | 620 950 25.5 8.91     |
| 393.15        | 10             | 1016 986 5.66 -20.1       | 584 910 19.1 9.07     |
| 403.15        | 2              | 1075 - 11.8 -            | 1011 - -6.60 3.20    |
| 403.15        | 4              | 1128 1277 12.3 -16.4      | 1081 1564 -9.29 10.6    |
| 403.15        | 6              | 1114 1201 12.3 -5.84      | 950 1245 2.80 9.73    |
| 403.15        | 8              | 1067 1250 9.09 -4.94      | 879 1119 9.35 7.39    |
| 403.15        | 10             | 1014 1232 4.76 -3.03      | 840 1049 13.0 9.20    |
| 413.15        | 2              | 1073 - 11.5 -            | 1007 1995 -6.04 -10.9 |
| 413.15        | 4              | 1075 1567 9.09 -12.7      | 1059 1603 -8.37 -9.96 |
| 413.15        | 6              | 1037 1233 4.76 -18.2      | 1070 1415 -8.36 -5.26 |
| 413.15        | 8              | 1027 1163 4.76 -15.5      | 1025 1306 -4.81 -1.32 |
| 413.15        | 10             | 1012 1055 3.85 -12.2      | - - - - - - |

As can be seen from Table 1, the obtained deviations from [12] are quite significant. At the same time, the data on heat capacity obtained by methods 1 and 2 are based on the calculated and experimental data, which are currently absent in the known literature.

7. Conclusion

The widely used equations of state in the form of reduced Helmholtz energy, laid down in [12], are very convenient for calculating the density, enthalpy, and entropy. However, to calculate the heat capacities using these equations, second-order differentiation is required. It is clear, that in this case the uncertainty of the calculated data on the heat capacity increases by an order of magnitude. In this regard, the use of data from [12], which are rather inhomogeneous and strongly fluctuate, especially in the supercritical region of parameters, raises certain doubts. Therefore, based on the results of the calculations, tables of thermophysical properties were obtained, including data on heat capacity, the use of which on an appropriate scale can be recommended for performing preliminary calculations of cycles of power plants using decafluorobutane as a working fluid. Despite the fact, that the density data were described by an ordinary polynomial dependence (not a reduced virial-type equation), the results obtained do not go beyond the total uncertainty of the data from the specified source. The author's estimate of the calculated and experimental data for the isochoric heat capacity is ± 5%. Uncertainty of data on heat capacity in the basic package [12] is not presented. The required uncertainty of the data, as a rule, used for the design of cycles and processes in power plants is in the range of 1.5-4%.

Also, in the presence of reliable data on the heat capacity and density of substances, the inverse problem can be solved. A formula can be derived from the known ratios and the speed of sound can be
calculated from it, which is very important for the range of parameters where experimental research is difficult, for example, in the gas phase.

Thus, the discrepancy between the calculated values of the heat capacity by both methods in the entire range of the studied temperatures reaches 30%, which is explained by the lack of experimental data on the heat capacity in the known literature. The resulting level of discrepancy takes place for both presented independent methods. This circumstance is of certain interest for further research.

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