

Thermodynamic and Transport Properties of Liquid HFC-227ea

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The thermal conductivity and heat capacity of liquid 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) have been studied by a high-frequency thermal-wave method over the temperature range of 294 to 345 K at pressures up to 2.8 MPa. The purity of the samples used throughout the measurements is 99.99 mol%. The experimental uncertainties of the thermal conductivity and heat capacity measurements were estimated to be within ± 1.5 and $\pm 2\%$, respectively. The thermal conductivity of HFC-227ea in the liquid phase decreases as temperature increases, while the pressure has an opposite effect.

KEY WORDS: heat capacity; HFC-227ea; high-frequency thermal-wave; liquid phase; thermal conductivity.

1. INTRODUCTION

The partially fluorinated hydrocarbon, 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), is considered an alternative ecologically safe working substance for high-temperature heat pumps. However, reliable experimental information about the thermodynamic properties of this substance is still very limited. Measurements of the thermal conductivity of liquid HFC-227ea over a wide range of temperature and pressure have not yet been performed, to the best of our knowledge. In the present paper, we report new experimental data on the thermal conductivity, λ , and heat capacity, C_p , of liquid 1,1,1,2,3,3,3-heptafluoropropane over the temperature range from 294 to 345 K and at pressures up to 2.8 MPa.

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2. EXPERIMENTAL

The thermal conductivity, thermal diffusivity, a , and volumetric heat capacity of HFC-227ea were measured by the method of high-frequency thermal waves [1]. This method allows us to determine a number of the liquid characteristics (λ and a , or λ and ρC_p , or a and ρC_p) in one experiment. Using the data on the density, ρ , one can subsequently determine the mass heat capacity. The principle of the method of high-frequency thermal waves [2, 3] consists of measuring the amplitude and phase of temperature oscillations of a low-inertia probe (a thin wire 5 to 20 μm in diameter) immersed in a liquid under study and heated by an alternating current (20 to 200 Hz). We used an indirect procedure of these measurements based on the equivalent-impedance technique previously developed by Kraftmakher [4] for measuring the heat capacity of wire samples. One of its features is the fact that, in studies of semitransparent media (such as the majority of organic liquids), it becomes possible to suppress the radiative heat-flux component and to measure directly the molecular thermal conductivity [2, 3]. The latter circumstance seems to be of great significance, since optical characteristics of newly synthesized substances, as a rule, are unknown, and the contribution of radiation to heat transfer cannot be reliably estimated by computation. The investigation of the liquid density has been performed by the gamma-ray attenuation technique previously described [5]. Details of the experimental equipment and procedures have been described elsewhere [1, 6].

The high-pressure measurement cell (up to 10 MPa) used in the present study was made of stainless steel. The internal elements were fabricated from fluoroplastics. The probe (platinum wire 20 μm in diameter) was installed horizontally inside a narrow (2 mm) slot 1 mm from the top fluoroplastic lid. As experiments showed, this design ensured effective suppression of convection, while simultaneously enabling measurements of low-viscosity liquids. The cell was immersed in a thermostatic bath. The temperature in the bath was held to within ± 10 mK throughout the measurements. The temperature was measured with a mercury thermometer. The uncertainty in the temperature measurement was estimated to be ± 0.05 K.

The pressure was produced by means of a thermal compressor which has been connected to the measurement cell by a thin capillary. The thermal compressor containing HFC-227ea was immersed in another thermostatic bath. The pressure was calculated from the temperature in the thermostatic bath and information on the saturated vapor pressure [5]. The estimated uncertainty in the pressure did not exceed 0.15%.

To estimate the instrumental error of the measurements, test experiments have been performed on liquids with well-known heat capacities and

molecular thermal conductivities (toluene, n-heptane). The results obtained from these experiments differ from the most reliable data [7–9] by no more than 1.3% and 1.8% for λ and C_p , respectively.

The HFC-227ea sample was supplied by the Russian Scientific Center “Applied Chemistry” (St. Petersburg) with a stated minimum purity of 99.99 mol per cent. Before the experiments were made, the initial product was purified by removing water and volatile components. For this purpose, HFC-227ea was kept in a vessel with silica gel activated at 393 K. Then, it was passed into another, preliminary evacuated vessel (thermal compressor), where it was cooled by liquid nitrogen and purified removing low-molecular-mass components by long evacuation followed by cyclic remelting of the sample.

3. RESULTS AND DISCUSSION

The molecular thermal conductivity and volumetric heat capacity of liquid HFC-227ea has been measured along eight isotherms from 294 to

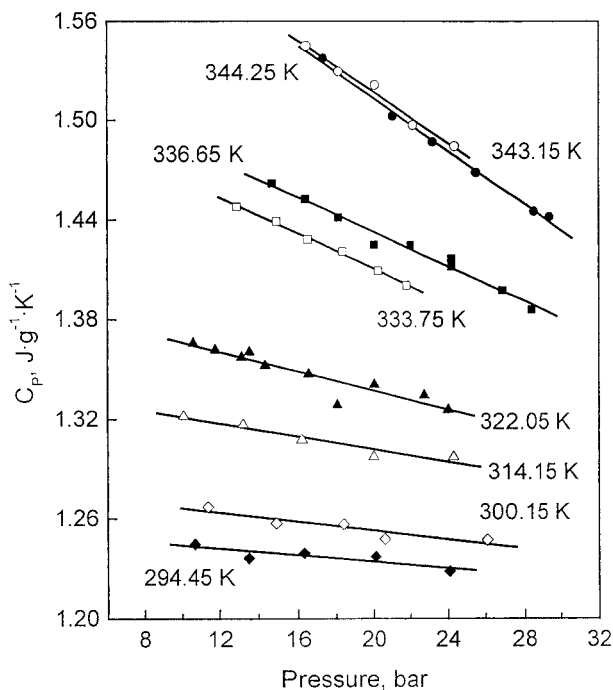


Fig. 1. Experimental heat capacity isotherms for liquid HFC-227ea.

345 K (Table I). Our data on the liquid density [5] were used for the mass heat capacity calculation. The experiments have shown that $C_p(T)$ and $\lambda(T)$ of HFC-227ea varies linearly with pressure (Figs. 1 and 2):

$$C_p(T) = C_0(T) + C_1(T) P \quad (1)$$

$$\lambda(T) = \lambda_0(T) + \lambda_1(T) P, \quad (2)$$

where P is the pressure in bar. The values of λ_1 ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), λ_0 ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1} \cdot \text{bar}^{-1}$), C_0 ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$), and C_1 ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1} \cdot \text{bar}^{-1}$), to within

Table I. Experimental Liquid Thermal Conductivity and Heat Capacity of HFC-227ea

P (bar)	C_p ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$)	λ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	P (bar)	C_p ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$)	λ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
$T = 294.45 \text{ K}$			$T = 333.75 \text{ K}$		
10.7	1.245	59.8	12.89	1.448	48.5
13.5	1.236	60.2	14.94	1.439	48.7
16.3	1.239	60.3	16.51	1.428	49.0
20.1	1.237	60.5	18.35	1.421	49.2
24.1	1.228	60.9	20.26	1.410	49.4
$T = 300.15 \text{ K}$			21.81	1.401	49.7
11.4	1.267	58.0	$T = 336.65 \text{ K}$		
14.9	1.257	58.4	14.73	1.462	47.9
18.4	1.257	58.5	16.39	1.453	47.9
20.6	1.248	58.6	18.15	1.442	48.2
26.1	1.247	58.9	20.05	1.425	48.6
$T = 314.15 \text{ K}$			22.04	1.425	48.7
10.1	1.322	54.1	24.22	1.417	48.9
13.2	1.317	54.3	24.22	1.412	48.9
16.2	1.308	54.6	26.9	1.398	49.2
20.0	1.297	55.0	28.4	1.386	49.6
24.3	1.297	55.2	$T = 343.15 \text{ K}$		
$T = 322.05 \text{ K}$			17.33	1.538	45.8
10.62	1.366	51.7	21.07	1.503	46.3
11.81	1.362	51.8	23.25	1.487	46.7
13.54	1.361	52.0	25.52	1.469	47.0
13.13	1.357	52.0	25.53	1.469	47.0
14.36	1.352	52.2	28.52	1.445	47.4
16.54	1.347	52.3	29.38	1.442	47.5
18.07	1.329	52.6	$T = 344.25 \text{ K}$		
20.05	1.341	52.6	16.43	1.545	45.7
22.78	1.335	52.8	18.16	1.530	46.0
24.03	1.326	53.1	20.09	1.521	46.3
			22.18	1.497	46.6
			24.37	1.485	46.9

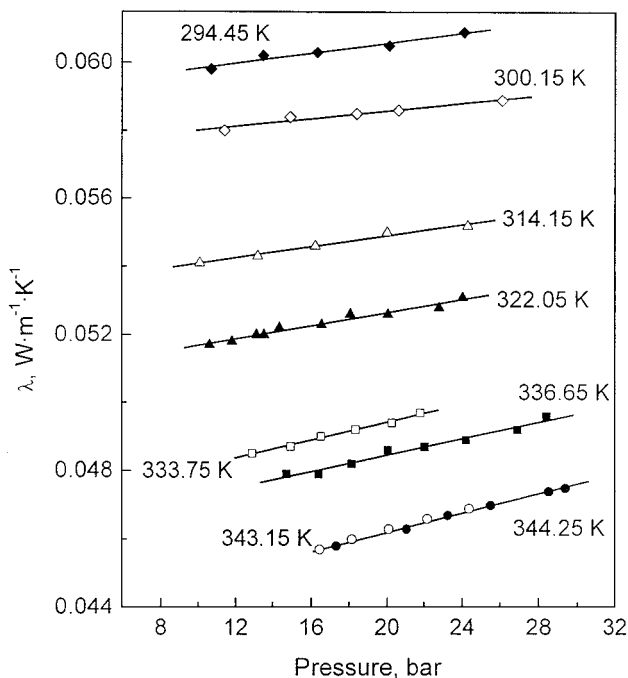


Fig. 2. Experimental thermal conductivity isotherms for liquid HFC-227ea.

the measurement error, are described by the following equations (Figs. 3 and 4):

$$C_0(T) = (1.137 \pm 0.025) + (55.155 \pm 3.0)(T_C - T)^{-4/3} - (7.28 \pm 4.5) \times 10^{-8}(T_C - T)^3 \quad (3)$$

$$C_1(T) = (0.00191 \pm 0.0003) - (0.9976 \pm 0.05)(T_C - T)^{-4/3} \quad (4)$$

$$\lambda_0(T) = (3.318 \pm 0.03) \times 10^{-2} + (3.208 \pm 0.05) \times 10^{-4}(T_C - T), \quad (5)$$

$$\lambda_1(T) = (2.967 \pm 0.55) \times 10^{-4} - (7.613 \pm 3.0) \times 10^{-6}(T_C - T) + (5.29 \pm 3.0) \times 10^{-7}(T_C - T)^{1.5}, \quad (6)$$

where $T_C = 375.95$ K is the critical temperature [10, 11]. In Fig. 5, the percentage deviations of the measured heat capacity data from Eq. (1) are shown. The average deviations of the experimental data from Eqs. (1) and (2) are about 0.25 and 0.50%, respectively.

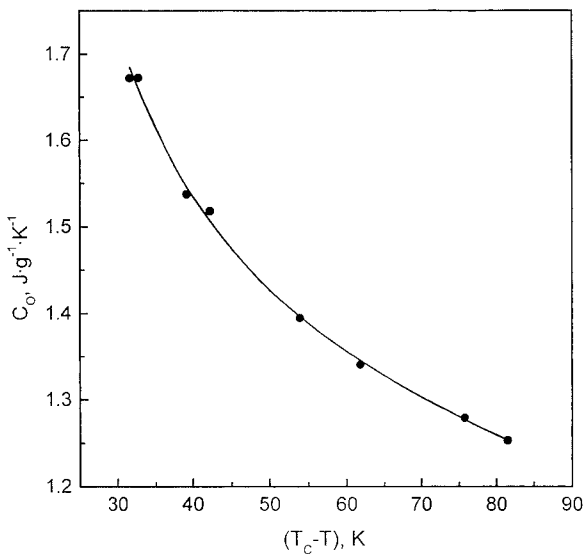


Fig. 3. Temperature dependence of the coefficient C_0 . Points are the values calculated from Eq. (1) along the isotherms; curve is Eq. (3).

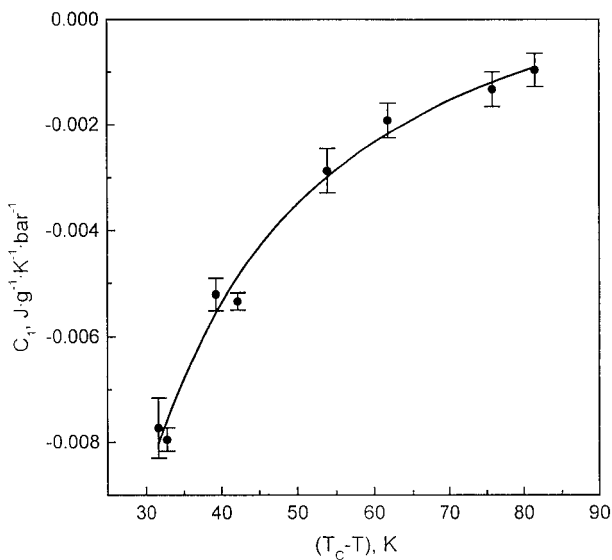


Fig. 4. Temperature dependence of the coefficient C_1 . Points are the values calculated from Eq. (1) along the isotherms; curve is Eq. (4).

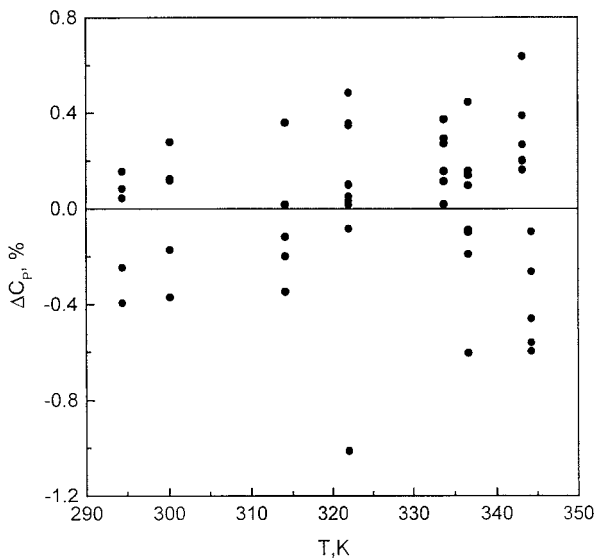


Fig. 5. Deviations of the experimental data for heat capacity from Eq. (1).

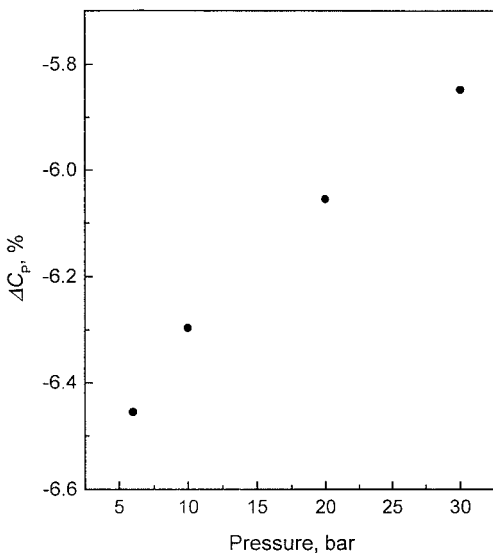


Fig. 6. Deviation of our heat capacity data from the data of H. Wirsber et al. [12] along the isotherm of 303.15 K; $\Delta C_p = [C_p([12])/C_p(\text{Eq. (1)}) - 1] \times 100\%$.

The heat capacity and thermal conductivity of saturated liquid were determined by extrapolation of Eqs. (1) and (2) to the coexistence curve. The data were fitted by the equations

$$C_p^S(T) = (1.347 \pm 0.003) + (28.476 \pm 0.15)(T_C - T)^{-4/3} - (2.18 \pm 0.03) \times 10^{-3}(T_C - T) \quad (7)$$

$$\lambda_s(T) = (4.025 \pm 0.025) \times 10^{-2} + (6.27 \pm 1.5) \times 10^{-5}(T_C - T) + (1.94 \pm 0.15) \times 10^{-5}(T_C - T)^{1.5} \quad (8)$$

Figure 6 shows the deviations of the data of Wirsber et al. [12] from Eq. (1). Their data are always smaller than our values, as calculated by Eq. (1). The deviations decrease when the pressures increase; they reach -6.5% at 6 bar and -5.8% at 30 bar.

4. CONCLUSION

Measurements of the thermal conductivity and heat capacity of HFC-227ea in the liquid phase are reported. The experiments were performed by a high-frequency thermal-wave method. The measurements were carried out in the temperature range of 294 to 345 K at pressures up to 2.8 MPa. The average deviations of the measured thermal conductivity and heat capacity data from values calculated by the fitting equations are about 0.5% and 0.25%, respectively. The overall uncertainty of our measurement is better than 2%.

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