Short communication

Density of molten sulfur in the 334–508 K range

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Abstract

As the density of elemental sulfur was determined on slowly cooling from 508 K, it was unexpected for the metastable molten state to be maintained to temperatures as low as 334 K, thus expanding by about 20 K the T-range within which experimental data become available. In the 334–430 K range, the density ρ of the metastable molecular melt was fitted to ρ (g cm^{-3}) = 2.18835–0.00098187T (K), subsequently leading to volumic expansion coefficients $\alpha_V(T) = -(1/\rho(T))(\partial\rho/\partial T)_P$ of 5.28×10^{-4} K^{-1} at 334 K and 5.56×10^{-4} K^{-1} at 430 K.
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1. Introduction

In a recent paper [1], a simple method to determine the density of liquids as a function of the temperature was described and validated by applying it to molten *n*-alkanes and water.

In the present communication, results regarding molten sulfur are presented as another example of the practicality and feasibility of that method. More precisely, this work was undertaken to check whether the method was sensitive enough to reveal the change in density that accompanies the well-known λ-transition in molten sulfur. Surprisingly, molten sulfur was maintained in the metastable state to temperatures as low as 334 K, thus allowing a significant set of new data to be collected and compared with the values previously predicted by Kennedy and Wheeler [2] at temperatures lower than T_λ.

2. Materials and methods

Crystalline powder of elemental sulfur from Prolabo (>99.5%), France, was used as such after checking through high-resolution X-ray powder diffraction that it was made of the orthorhombic α-allotrope. Two samples of about 14 g of sulfur, weighed using a balance sensitive to 0.1 mg, were prepared as follows.

Powders were introduced in cylindrical silica tubes from Heraeus (Germany), maintained under a vacuum (about 10^{-3} Pa) for several days at room temperature then cautiously molten at a temperature not exceeding 430 K while maintaining a dynamic vacuum to evacuate possible adsorbed gases. Afterwards, crystalline samples, recovered after slowly cooling to room temperature, were weighed together with their containers of known mass.

Once sealed under a vacuum, the tubes were suspended in an XU 75/300 oven from Climats (France) whose inner temperature is usually controlled at ±1 K, and heated to a temperature not exceeding 508 K.

Prior to that, the inner diameters (d) of the silica tubes had been measured by means of an alesometer sensitive to 0.001 mm, and the height (h) of the melts measured by means of a cathetometer sensitive to 2 μm.

The specific volume of the melt, from which the density is obtained, is given by $v = \pi d^2 h/4m$ (m: mass of the melt), and the inaccuracy on v is calculated by $\Delta v/v \approx 2\Delta d/d + 2\Delta h/h + \Delta m/m$, where $2\Delta d/d \approx 0.06/5$, $2\Delta h/h \approx 0.06/80$ and $\Delta m/m \approx 4/1000$. It follows that $\Delta v/v$ is of about 1.5% neglecting the expansion of the silica glass proven negligible [3,4].

Data were collected on cooling from 508 K after 24 h isothermal steps (the difference in the temperature of two consecutive steps was about 1 K (tube 1) or 2 K (tube 2)).

In addition, it is worth noting that the furnace was placed on rubber blocks to prevent early crystallization that might be induced by external vibrations.

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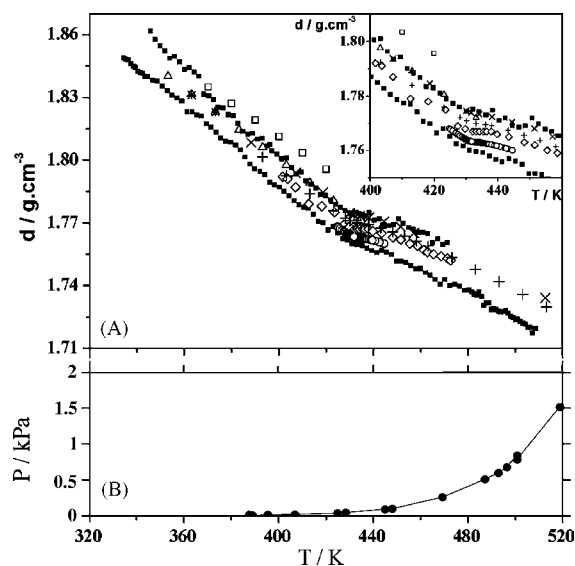
3. Results and comparison with data from the literature

The results of the two series of measurements (experimental values are compiled in Appendix A) are shown in Fig. 1A, in which data from the literature have been added for comparison.

This figure shows that: (i) most of the data range within the two series of results that differ from each other by about $0.02\,\mathrm{g\,cm^{-3}}$ only, and (ii) the change in density (inset in Fig. 1A) that accompanies the λ-transition is detected in the same temperature range as with other methods [5–7,9,11].

In addition, the color of the metastable melt darkened from pale yellow to red-brown while cooling.

Unexpectedly, the simple method used allows the temperature range within which the molecular melt can persist as a metastable phase to be expanded to $334\,\mathrm{K}$ instead of $353\,\mathrm{K}$ previously reached by Basin and Nenashev [12].

In the 334–430 K range, the data from series 1 fit to ρ_1 $(\mathrm{g\,cm^{-3}}) = 2.16525 - 0.000943738T$ (K) $(r^2 = 0.995)$, which leads to a volumic expansion coefficient $(\alpha_V)_1 = -(1/\rho(T))(\partial\rho/\partial T)_P$ of $5.10 \times 10^{-4}\,\mathrm{K^{-1}}$ at 334 K and $5.36 \times 10^{-4}\,\mathrm{K^{-1}}$ at 430 K. In the same range, the data from series 2 fit to ρ_2 $(\mathrm{g\,cm^{-3}}) = 2.21144 - 0.00102T$ (K) $(r^2 = 0.998)$, and lead to $(\alpha_V)_2 = 5.45 \times 10^{-4}\,\mathrm{K^{-1}}$ at 334 K and $5.75 \times 10^{-4}\,\mathrm{K^{-1}}$ at 430 K. Both series fit to ρ $(\mathrm{g\,cm^{-3}}) = 2.18835 - 0.00098187T$ (K) $(r^2 = 0.911)$, and the mean $\overline{\alpha_V}$ value is found to be $5.28 \times 10^{-4}\,\mathrm{K^{-1}}$ at 334 K and $5.56 \times 10^{-4}\,\mathrm{K^{-1}}$ at 430 K. This is quite different from the literature data in the same range [5–12] that fit to ρ $(\mathrm{g\,cm^{-3}}) = 2.24934 - 0.00113T$ (K) $(r^2 = 0.935)$ and lead to $\alpha_V = 6.04 \times 10^{-4}\,\mathrm{K^{-1}}$ at 334 K and $6.41 \times 10^{-4}\,\mathrm{K^{-1}}$ at

430 K, i.e. α_V values greater than the value of $4.5 \times 10^{-4}\,\mathrm{K^{-1}}$ reported by Shirai [10] in the temperature range from 363 to 453 K, and that remains greater than the values from the present work.

Zheng and Greer [11], who determined accurate density values for molten sulfur near the polymerization temperature T_p, observed small upward shifts in the values on cycling heating and cooling around T_p. These authors tentatively ascribed these shifts to the persistence of polymeric species as "impurities" in the hours spent for data collection. Since each series of present data was collected within about 2 months, the $S_8 = S_n$ equilibrium may be assumed more likely shifted left as the values were collected at the lowest temperatures reached.

Inaccuracy (about ±1.5%) in the density values from the present work is of the same magnitude as the scattering of the data from the literature. In spite of that, as regards the metastable molecular molten state of elemental sulfur in equilibrium with its vapor phase, the more time is spent collecting data, and the greater the T-range in which the data are collected, the better the knowledge of the volumic expansion coefficient is. It is important to note that the pressure remains very small in the T-range explored (see Fig. 1B in which data from Peng and Zhao [13] have been reported).

Lastly, Kennedy and Wheeler [2] modeled the dependence of the density on the temperature of molten sulfur according to a linear hypothesis in the T-range below the λ-transition. They based their modeling on Kellas' values [5] of the density at temperatures close to T_λ, the temperature of the λ-transition. These authors used two possible values of the volumic expansion coefficient α_λ $((\alpha_\lambda)_A = 4.89 \times 10^{-4}\,\mathrm{K^{-1}}$, $(\alpha_\lambda)_B = 5.5 \times 10^{-4}\,\mathrm{K^{-1}})$ for unpolymerized S_8 sulfur at T_λ. The data extracted from the straight lines drawn by these authors led to ρ_A $(\mathrm{g\,cm^{-3}}) = 2.1609 - 0.00088482T$ (K) and ρ_B $(\mathrm{g\,cm^{-3}}) = 2.208 - 0.00099385T$ (K), from which values of the volumic expansion coefficient, $(\alpha_V)_A = 4.74 \times 10^{-4}\,\mathrm{K^{-1}}$ at 334 K and $4.97 \times 10^{-4}\,\mathrm{K^{-1}}$ at 430 K, and $(\alpha_V)_B = 5.30 \times 10^{-4}\,\mathrm{K^{-1}}$ at 334 K and $5.58 \times 10^{-4}\,\mathrm{K^{-1}}$ at 430 K, are calculated. It may thus be concluded that $(\alpha_\lambda)_B$ from Kennedy and Wheeler's assumption B agrees fairly well with the mean values for α_V from the two series of experimental data of the present work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.03.016.

Fig. 1. (A) Density of molten sulfur as a function of the temperature. (Full squares) This work (series 1: upper curve; series 2: lower curve); (×) Ref. [5]; (diamond) Refs. [6,7]; (empty squares): Ref. [8]; (+) Ref. [9]; (*) Ref. [10]; (empty circles) Ref. [11]; (empty triangles) Ref. [12]. Inset: detail showing the density change in the T-range of the λ-transition. (B) Vapor pressure of sulfur, from data assessed by Peng and Zhao [13].

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