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Measurement of Thermal Conductivity, Heat Capacity, and Thermal Diffusivity of Sulfur and Selenium in the Liquid State

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The thermal properties (thermal activity, heat capacity, thermal conductivity, and thermal diffusivity) of liquid sulfur and selenium were measured in the temperature range 160–400°C. These measurements were performed using an experimental apparatus, based on the ac heated-wire (strip) technique. Liquid sulfur shows a second order phase transition at 225°C. The present study has considered four different mechanisms of heat transfer: conduction, electrons, internal electromagnetic radiation, and convection. The results showed that heat transfer is mainly due to conduction, whereas that due to electrons and electromagnetic radiation is very small indeed. Suppression of convection by the cell configuration was studied, as well as the effect of locating the strip or the wire in horizontal form, which permits heat flow in one direction. Moreover, stability of the third harmonic shows that there is no hydrodynamic flow inside the liquid, which means that the convection is taken in consideration within the time of measurements.

KEY WORDS: heat capacity; selenium; sulfur; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

The present work deals with semiconductor elements belonging to main group VIB in the periodic table. These are classified under substances having the ability to retain their semiconducting properties even after melting. Sulfur and selenium possess thermoelectric and photoelectric properties which are of practical significance. They have been studied in the solid phase at moderate temperatures [1]. Sulfur is an element which is solid

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up to 120°C and consists mainly of S_8 rings. These rings are also stable in the liquid phase. Its viscosity rises by a factor 10^4 when the temperature exceeds 159°C. This phenomenon is commonly explained by the so-called λ-transition.

Knowledge of the behavior of liquid selenium is much more limited, despite the wide industrial use of this semiconducting element. It is known that the viscosity is high at the melting point (218°C) and decreases at higher temperatures. Measurements of the thermal properties of liquid semiconductors with temperature will help our understanding of the structure and heat transfer mechanisms of such materials in the liquid state.

2. EXPERIMENTS

An ac-heated wire technique has been previously developed [2] to measure the thermal activity (b), heat capacity (ρC_p), thermal diffusivity (a), and thermal conductivity (λ). In the present experiments, measurements on sample materials (S, Se) of purity 99.99% were performed in a cylindrical pyrex flask cell. The electrodes were made of molybdenum due to the high corrosive nature of the samples, especially at high temperatures, and were interconnected with a platinum wire or strip. The tested pure materials were prepared by direct fusion in an evacuated furnace (0.1333 Pa).

The required thermals were determined with chromel-alumel thermocouples, which were immersed in the investigated liquids. The experimental system was calibrated before the measurements. The reproducibility of the data was checked over several experimental runs with increasing and decreasing temperatures. The total systematic error for measuring thermal activity is 3–4%; for thermal conductivity and diffusivity coefficients, it is 5–7%; while for heat capacity it is estimated to be in the range 5–7%.

3. RESULTS AND DISCUSSION

The thermal properties of sulfur and selenium were measured at different temperature ranges starting from the melting point of the investigated liquid.

3.1. Thermal Properties of Liquid Sulfur

The temperature dependence of the molecular complexity of sulfur, particularly in the liquid phase, has received considerable attention. Viscosity, static susceptibility, optical absorption, and heat capacity support the

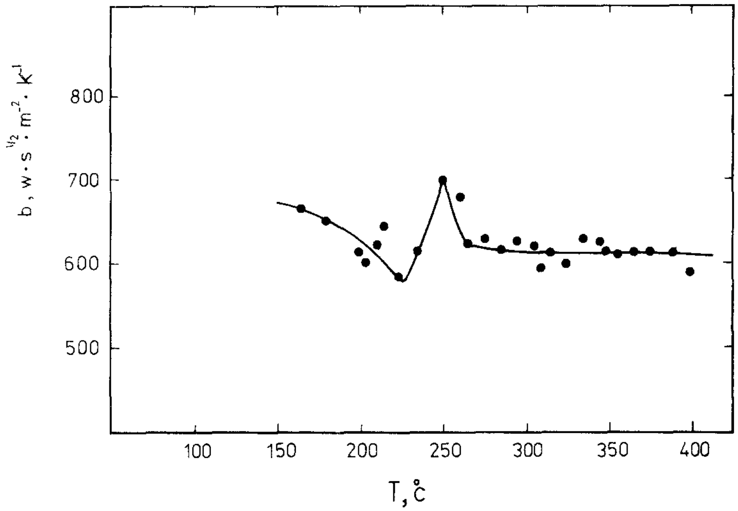

Fig. 1. The thermal activity of liquid sulfur.

concept of the existence of equilibrium between discrete S_8 molecules and the long chain sulfur polymer S_n in the liquid phase. Evidence for polymer formation in these systems is derived mainly from viscosity [3] and thermal measurements [4].

Figure 1 shows the variation of thermal activity *b* with temperature. An increase of 16% in thermal activity at 250°C is detected. The change in heat capacity ρC_p of liquid sulfur is shown in Fig. 2; ρC_p decreases with temperature in the range 165–225°C; then increases until it reaches a peak value at 250°C. Above this temperature ρC_p decreases as the temperature increases. This peak value lies in a narrow range of temperature from 225 to 250°C. According to Bacon and Fanelli [5], the viscosity data near the melting point showed that sulfur is a moderately mobile liquid. As the temperature increases its viscosity initially decreases up to 157°C, then it rises rapidly at 187°C. With a further increase in temperature, the viscosity of the melt decreases slowly. The sudden rise in viscosity is attributed to the appearance of long chain sulfur molecules. As temperature increases, the concentration of polymeric sulfur continues to increase. This is accompanied by a gradual decrease in viscosity in the temperature range 187°C to the boiling point. A color change was noticed between 187°C and the boiling point.

Parallel to the behavior of viscosity, the heat capacity also changes; this is caused by the polymerization equilibrium of sulfur, which is initiated by ring scission. At the melting point, liquid sulfur consists of free S_8 units.

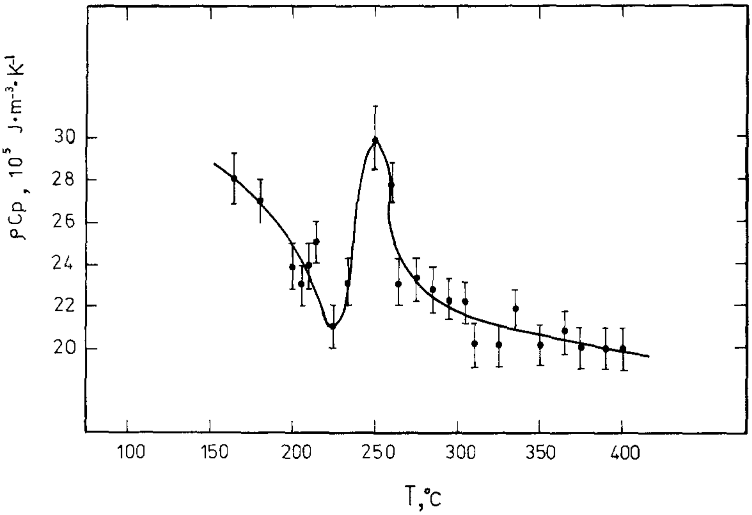

Fig. 2. The heat capacity of liquid sulfur.

These will form chains with up to 10^5 S_8 units [6]. The point appeared as a peak or a reversal in the sign of the characteristic curve of the heat capacity; this sign is repeated at 225°C. These changes indicate that polymerization and depolymerization of liquid has occurred. This behavior was proved in a study of the electrical conductivity by Vizzoli et al. [7], who indicated that these structural transitions occur at 166 and 212°C. Polymerization and depolymerization of liquid sulfur refers, respectively, to the process of chain growth and chain scission promoted by changing thermodynamic conditions.

Figure 3 shows the variation of the thermal conductivity of sulfur with temperature; it may be seen that thermal conductivity increases with temperature. In the same figure, data reported by Sugawara [8], Mogilevsky and Chudnovski [9], and Fedorov [10] are also presented. The total thermal conductivity can be expressed as follows:

$$\lambda_{\text{total}} = \lambda_M + \lambda_e \tag{1}$$

where λ_M is the molecular thermal conductivity, and λ_e is the electronic part. Fedorov [10] showed that, moving away from the melting point, the molecular rings are broken and the number of carriers are increased as manifested by an increase in the thermal conductivity.

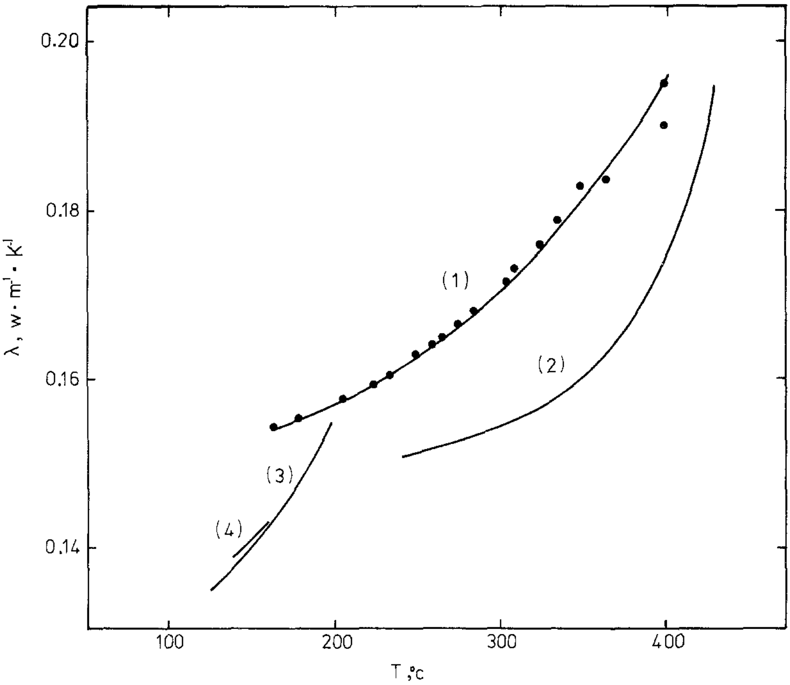

Fig. 3. The thermal conductivity of liquid sulfur: (1) present work; (2) data reported in ref. 8; (3) data reported in ref. 9; (4) data reported in ref. 10.

In order to calculate λ_e it is possible to use the Wiedemann-Franz relation:

$$\lambda_e = L\sigma T \tag{2}$$

where L is the Lorenz number, and σ is the electrical conductivity. At high temperatures, the mole fraction of the polymer increases, but the average chain length decreases [11]. The two ends of each chain give rise to unpaired localized electrons [12]. This means that the number of electrons in the liquid sulfur is very small. This gives some insight into the mechanism of heat transfer by electrons, which is calculated, based on the data reported in the literature [13], to yield $\lambda_e = 8.8 \times 10^{-7}\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$. This indicates that the main transport mechanism is due to the conduction. The effect of the radiative part can be estimated in the same way as discussed in ref. 2; it has been found that the radiative part of the thermal conductivity is negligible in this range of temperature.

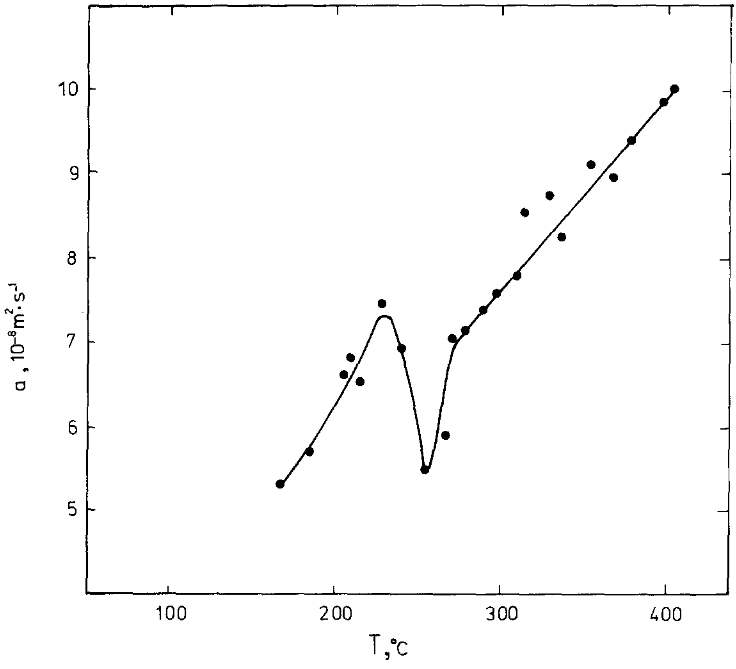

Fig. 4. The thermal diffusivity of liquid sulfur.

The thermal diffusivity of liquid sulfur is shown in Fig. 4. Diffusivity increases until it reaches a peak at 225°C, and then it continues to increase with temperature. This behavior can be explained in terms of the change of heat capacity with temperature at 225°C, above which sulfur depolymerizes, causing a change in the heat capacity. Thermal diffusivity is expressed according to the equation

$$a = \frac{\lambda}{\rho C_p} \tag{3}$$

Measured thermal properties data of the liquid sulfur are shown in Table I.

3.2. Thermal Properties of Liquid Selenium

Eisenberg and Tobolosky [14] showed that near the melting point, liquid selenium consists of a mixture of Se_8^R that these chains have a major influence on the physical properties and are responsible for the extraordinary viscosity of Se. The average chain length at this temperature was

Table I. Thermal Properties of Liquid Sulfur

T (°C)	b ($\mathrm{W \cdot s^{1/2} \cdot m^{-2} \cdot K^{-1}}$)	λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)	a ($\mathrm{10^{-8}\ m^2 \cdot s^{-1}}$)	ρC_p ($\mathrm{10^5\ J \cdot m^{-3} \cdot K^{-1}}$)
165	667	0.154	5.33	28.0
180	650	0.155	5.68	27.0
200	612	0.157	6.58	23.8
205	603	0.157	6.82	23.0
210	619	0.158	6.50	24.0
215	639	0.158	6.15	25.0
225	582	0.159	7.46	21.0
235	609	0.160	6.89	23.0
250	699	0.163	5.44	29.9
260	676	0.164	5.88	27.8
265	620	0.165	7.02	23.0
275	624	0.166	7.12	23.3
285	614	0.168	7.35	22.8
295	623	0.169	7.57	22.3
305	616	0.171	7.75	22.1
310	592	0.173	8.54	20.2
325	596	0.176	8.72	20.1
335	625	0.179	8.20	21.8
350	607	0.183	9.08	20.1
365	613	0.183	8.96	20.5
375	612	0.187	9.38	19.9
390	612	0.192	9.84	19.5
400	584	0.195	10.00	19.5

calculated to be 10^4 atoms [14]. But the study of Keezer and Baiely [16] indicates that the actual length may be in the range 10^5–10^6 atoms. The structure of liquid Se is strongly affected by temperature changes. The mean chain length decreases rapidly as the temperature increases [15].

Figure 5 shows the variation of thermal activity of Se with temperature, while Fig. 6 represents the variation of thermal conductivity with temperature. In Fig. 6 the results reported by other investigators [9, 17, 18] are also shown. The maximum discrepancy among the results is about 4–10%. From the figure it was found that thermal conductivity increases with temperature; this was due to rapid breakdown of the long chain. Evidence of this was provided by the nature of the chain in the viscosity and velocity of sound measurements [19, 20].

The charge carrier density increases with temperature due to the rapid breakdown of the Se chains. The effect of an increase in the charge carrier density is greater than the effect of an increase in the amount of carrier scattering. Therefore, thermal conductivity of liquid selenium increases with temperature. To investigate the electronic component of thermal conductiv-

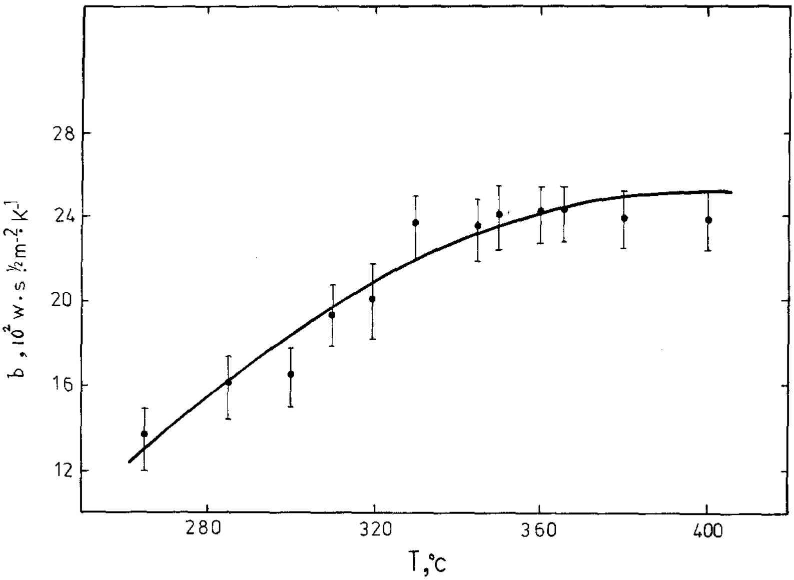

Fig. 5. The thermal activity of liquid selenium.

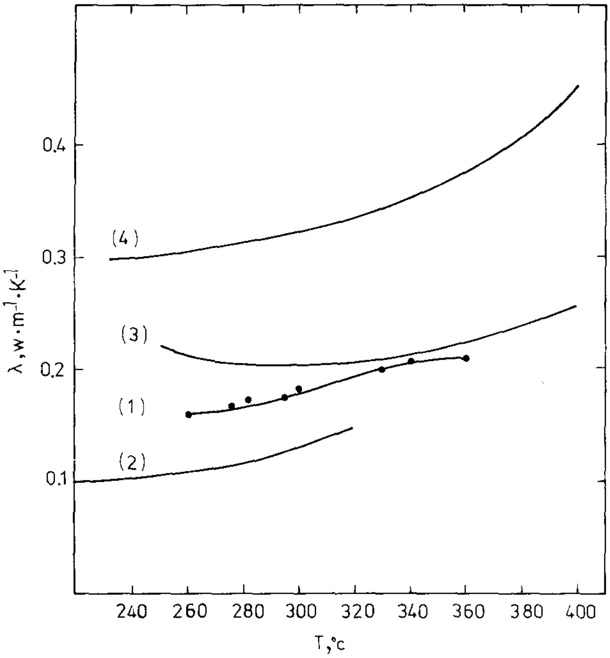

Fig. 6. The thermal conductivity of liquid selenium: (1) present work; (2) data reported in ref. 9; (3) data reported in ref. 17; (4) data reported in ref. 18.

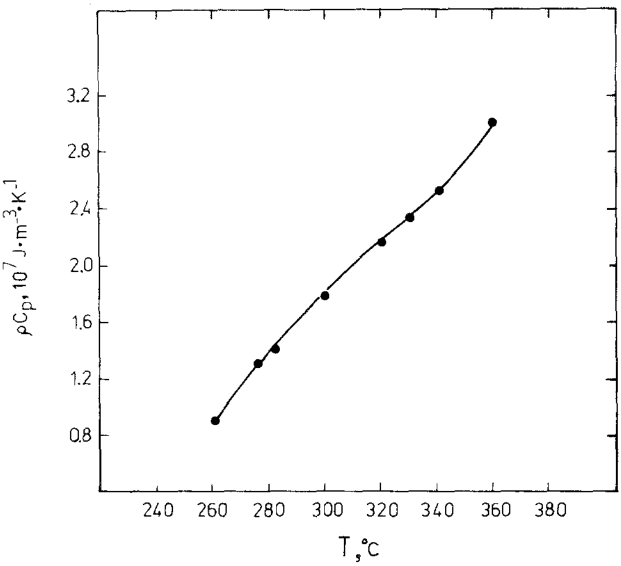

Fig. 7. The heat capacity of liquid selenium.

ity of Se, we use the electrical conductivity data by Glazov et al. [15] at 220°C. It was found that the electronic part (λ_e) of the thermal conductivity is very small, $\sim 10^{-10}$ $W \cdot m^{-1} \cdot K^{-1}$. This means that the electronic component in thermal conductivity is negligible. Heat transfer in Se is mainly due to conduction, which is attributed to molecular activity.

The change of heat capacity of liquid selenium with temperature is shown in Fig. 7. The ρC_p of Se increases with increasing temperature. The molecular structure is shown by the ring-chain equilibrium described by the reaction:

$$Se_8^R \rightleftharpoons Se_8 \tag{4}$$

$$Se_n \rightleftharpoons Se_{n-m} + Se_m \tag{5}$$

The initiation, Eq. (4), describes the opening of eight membered rings (Se_8^R) to form linear chains (Se_8). The propagation reaction given in Eq. (5) describes the formation of n membered chains containing $n - m$ and m atoms.

The change in thermal diffusivity of liquid selenium with temperature is shown in Fig. 8. Thermal properties of selenium are given in Table II.

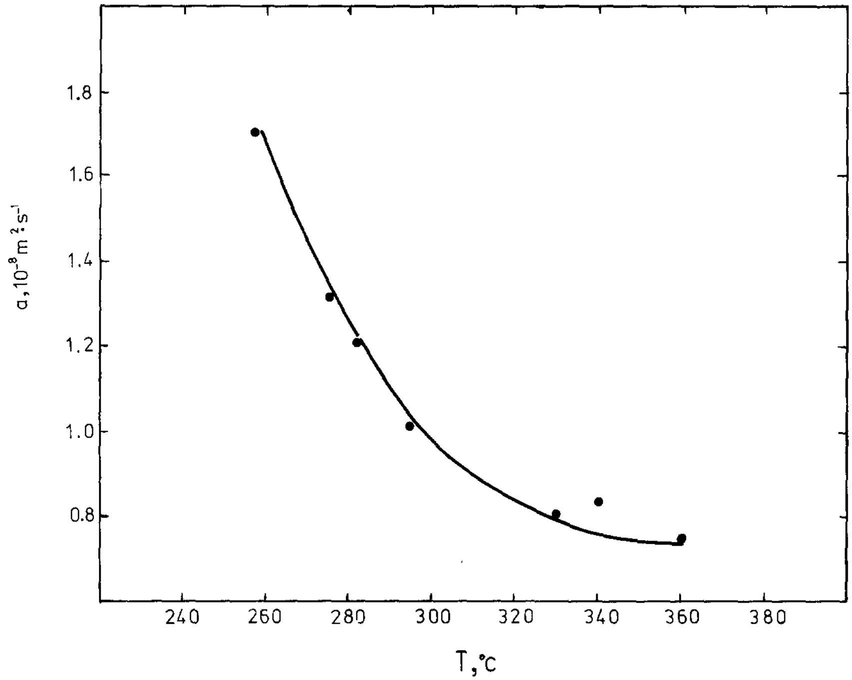

Fig. 8. The thermal diffusivity of liquid selenium.

Table II. Thermal Properties of Liquid Selenium

T (°C)	b ($W \cdot s^{1/2} \cdot m^{-2} \cdot K^{-1}$)	λ ($W \cdot m^{-1} \cdot K^{-1}$)	a ($10^{-8}\ m^2 \cdot s^{-1}$)	ρC_p ($10^7\ J \cdot m^{-3} \cdot K^{-1}$)
260	1240	0.160	1.70	0.90
276	1480	0.170	1.30	1.30
282	1580	0.173	1.20	1.40
295	1760	0.175	0.98	1.46
300	1820	0.183	1.03	1.79
330	2120	0.189	0.80	2.36
340	2300	0.204	0.83	2.53
365	2440	0.210	0.70	3.00

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