

Conductivity measurements on liquid sulphur

E. H. BAKER, T. G. DAVEY

Nuffield Research Group in Extraction Metallurgy, Imperial College, London, UK

The electrical conductivity of liquid sulphur has been measured from the melting point to 900° C, evaporation of the sulphur being prevented by use of an atmosphere of argon at elevated pressure. With rise in temperature, the conductivity increases except at the polymerization maximum near 170° C where a minimum in the conductivity is confirmed. Above 400° C the plot of $\log \sigma$ versus $1/T$ is linear, and on the assumption that the conductivity at these temperatures is intrinsic, a value of ~ 3.1 eV is obtained for the energy gap. Although the rise in conductivity above 400° C is accompanied by a decrease in mean chain length in the liquid, there is no simple relationship between the two properties. The behaviour of sulphur is compared with that of liquid selenium.

1. Introduction

Although sulphur is an important constituent of both crystalline and glassy semiconductors, its electrical properties in the liquid state have not been greatly studied, possibly owing to its molecular complexity and low conductivity. Also it is only in recent years that sulphur of satisfactory purity has been available for conductivity studies.

In 1964, Feher and Lutz [1] measured the conductivity of high-purity liquid sulphur from its melting point to 260° C. The conductivity was found to increase with temperature except near 170° C where the polymerization maximum occurs and a distinct minimum was observed. At this temperature the liquid, which is composed mainly of S_8 rings, polymerizes to give a mixture of long chains with a mean chain length of about 10^6 atoms [2]. The conductivity phenomenon has also been observed by Vezzoli [3]. The conductivity minimum in this region has been ascribed by Vezzoli *et al.* [4] to be due more to scattering of current carriers by the long chains than by a depletion of carriers by chain formation. This seems reasonable, particularly since the conductivities are $< 10^{-11} \Omega^{-1} \text{cm}^{-1}$, where there will be a high contribution to conduction by impurity ions.

Feher and Lutz considered that in the range 200 to 260° C, the effect of impurities was small

and the increasing conduction was of an intrinsic type, determined by break-up of the chains; a value of 2.9 eV was found for the energy gap. Later work by Watanabe and Tamaki [5] showed a linear relation between $\log \sigma$ and $1/T$ which yielded an intrinsic gap value of ~ 3 eV. This, however, was observed in the higher temperature range of 300 to 450° C. A linear relation of similar slope but with conductivities lower by a factor of 10^2 was also obtained by Steunenber *et al.* [6] for the range 350 to 435° C.

The main aim of the present work has been to obtain conductivity data in the apparently unstudied temperature region above the normal boiling point of sulphur (445° C). This necessitates the use of argon at elevated pressure over the conductance cell, the pressure being slightly greater than the vapour pressure of sulphur at each temperature. To complete the study, conductivity measurements have also been made at lower temperatures.

2. Experimental

Sulphur of purity 99.9999% supplied by Halewood Chemicals was used; high-purity argon was the pressure medium.

For measurements where the vapour pressure of sulphur exceeded atmospheric, i.e. above 445° C, an internally heated pressure vessel was used,

which incorporated a platinum alloy resistance furnace. This apparatus was employed for studies of arsenic triselenide and has been described in detail [7, 8].

The silica cell used for conductance measurements under pressure is shown in Fig. 1a. Gold rods welded to gold wires were used as electrodes because gold does not appear to form a stable solid or liquid sulphide at high temperatures.

After charging the cell with dried sulphur, the latter was melted and the cell positioned in the pressure vessel; the furnace temperature was $\sim 150^\circ\text{C}$. After flushing several times with argon the apparatus was filled to the required pressure and the temperature raised. The pressure was chosen so that it was about 20 atm. above the expected vapour pressure at each temperature of measurement [9]. The maximum pressure required was 100 atm. at $\sim 900^\circ\text{C}$. The narrow tubular limbs of the cell were designed to prevent dissolved argon from reaching the electrode chamber. The conductance became constant well within the 20 minute period required to stabilize the temperature at each pressure. A Wayne Kerr bridge, type B221, operating at 1592 Hz and a Keithley Electrometer Type 610C were used respectively for the a.c. and d.c. measurements. Some measurements taken on cooling showed conductance values similar to those obtained on heating up, indicating that the chain length equilibrium is established quite rapidly at the higher temperature.

A preliminary plot of the results showed that at temperatures below 500°C where the conductivities were $< 10^{-8}\ \Omega^{-1}\text{cm}^{-1}$, the slope of the $\log \sigma$ versus $1/T$ relation was much less than at higher temperatures. From this it was concluded that there was a marked contribution to the conduction by impurities at the lower temperatures. It was therefore decided to use freshly-distilled sulphur for the lower temperature measurements.

The silica cell used at the lower temperatures incorporated square platinum electrodes and is shown in Fig. 1b. To remove any hydrocarbon contaminants, the cell was heated at 800°C for 8 h. The platinum wires were then sealed into the ends of the side-arms with minute beads of Araldite and the sulphur sealed in the reservoir. The cell was then evacuated to a pressure of a few millimetres, and the sulphur heated at 120°C until evolution of dissolved gases ceased. The tempera-

ture was then raised and the requisite amount of sulphur distilled into the electrode chamber. For the conductance measurements, a positive pressure of dry argon was maintained in the cell.

A chain of resistors having a maximum value of $10^8\ \Omega$ was connected in series with the cell and a d.c. potential of 100 V was applied across the whole. The voltage across the resistor chain was measured mainly with a Keithley Electrometer Type 615; for the lowest conductances a Vibron Electrometer, Type 33B-2 was used.

Since the conductance in the temperature region of the polymerization maximum ($\sim 170^\circ\text{C}$) varies with field strength [1] the latter was kept at $\sim 90\ \text{V cm}$. A slow heating rate of $\sim 0.5^\circ\text{C min}^{-1}$ was used in this temperature region; above 200°C the heating rate was 2°C min^{-1} . During the measurements, the potential was periodically reversed to reduce polarization.

Measurements were also made by this procedure with a similar silica cell which incorporated rods of Specpure graphite as electrodes; in this case, the electrodes were cleaned prior to use by heating briefly at 800°C prior to assembly in the baked-out cell.

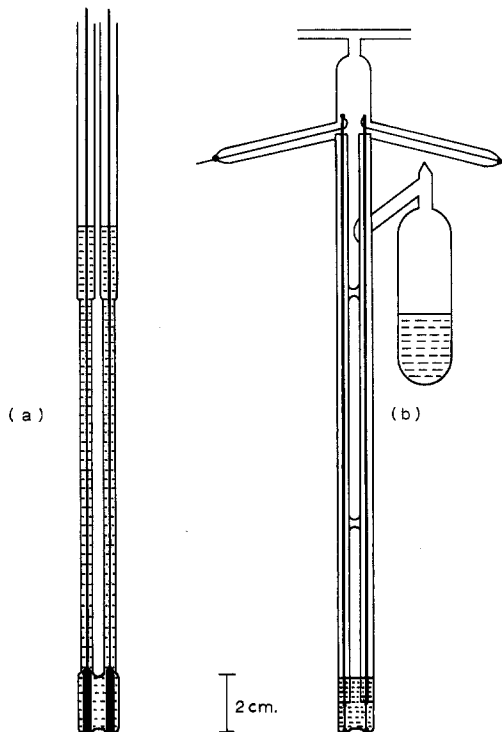


Figure 1 Silica conductance cells (a) with Au rods and wires for high temperatures; (b) with platinum plates and wires for lower temperatures.

After the measurements, the cells were dismantled and cleaned, and their constants determined with 10^{-2} molar KCl solution. For the cells with gold, platinum and graphite electrodes the constants were 0.41, 0.50 and 0.26 respectively.

3. Results and discussion

3.1. Results of conductivity measurements

Conductivity values as a function of temperature from the melting point to 900°C are plotted in Fig. 2. The values of σ at the lower temperatures are those which were obtained on heating up.

For temperatures near the conductivity minimum, the values of σ are about 50 times higher than those obtained by Feher and Lutz [1], but whether multiple distillation of the sulphur used here would have led to substantially lower conductivities is purely conjecture. At the end of the measurements the platinum electrodes were found to be slightly tarnished; a phenomenon which does not appear to have been reported previously. Analysis of the sulphur by X-ray fluorescence showed that any dissolved platinum was below the limit of detection, i.e. well under 50 p.p.m. However, with conductivities of around $10^{-11} \Omega^{-1} \text{cm}^{-1}$ there will undoubtedly be a high sensitivity to impurities, so that variations in the results from different investigations are to be expected. The minimum in the conductivity plot in Fig. 2 near 170°C where the polymerization maximum occurs, is nevertheless well confirmed.

Above 200°C the plots in Fig. 2 are similar in form to that obtained by Watanabe and Tamaki [5] but their values of σ are about 10^2 times higher than those found here.

The values of σ obtained with graphite electrodes are higher than those obtained with platinum electrodes for temperatures above 300°C . At first this was thought to be due to a leaching out of impurities, but it was found that on cooling back, the values at lower temperatures became near to those obtained with platinum. The reason for this behaviour with graphite at higher temperatures is unclear but it suggests that graphite may not be a satisfactory electrode material for temperatures above 300°C .

Analysis (XRF) of the sulphur after measurements at the highest temperatures showed the gold content to be virtually undetectable, certainly less than 50 p.p.m. In this region the linearity of the plot in Fig. 2 indicates that the effect of impurities is small, and the conductivity can be considered to be dependent mainly on changes in liquid structure.

3.2. Conductivity and chain length

The σ -values for the linear portion of the plot in Fig. 2 can be expressed by the relation

$$\sigma = \sigma_0 \exp(-E/kT) \quad (1)$$

which leads to a value of the apparent activation energy E , of $\sim 1.55 \text{ eV}$.

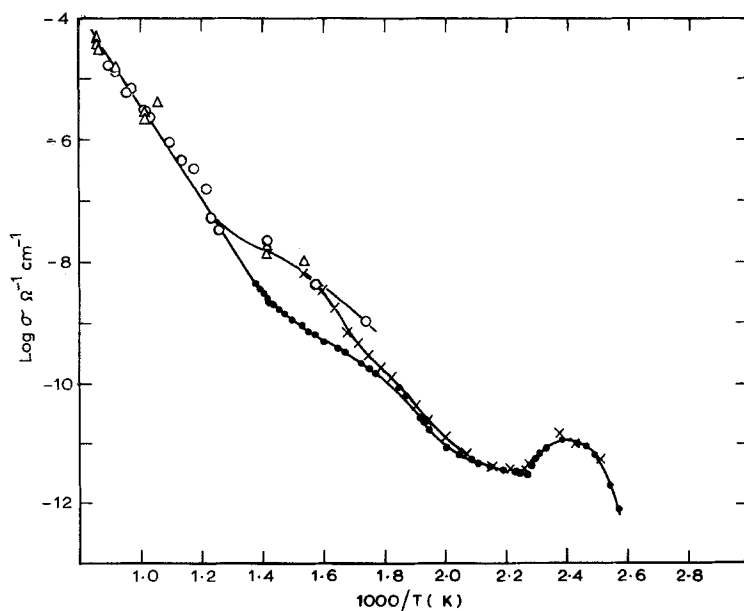
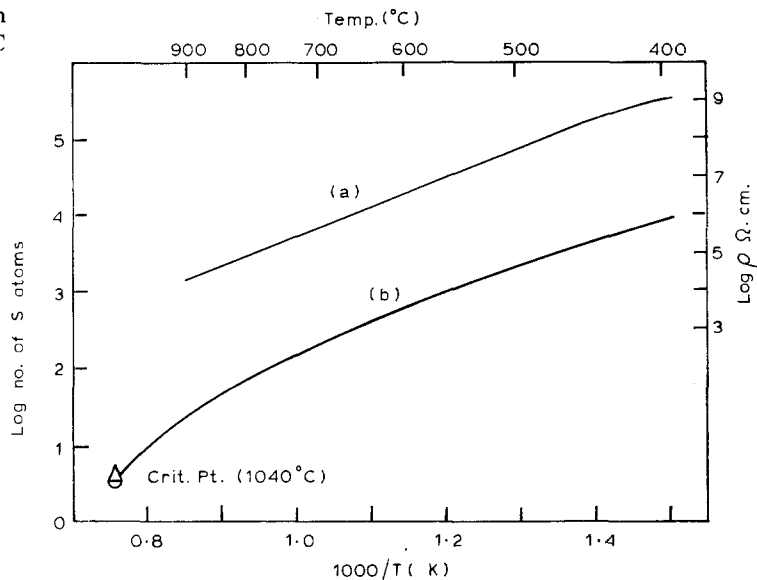


Figure 2 Conductivity of liquid sulphur up to 900°C . Undistilled sulphur with Au electrodes: (Δ), a.c. measurements; (\circ) d.c. measurements. Distilled sulphur, d.c. measurements: (\bullet), Pt electrodes; (\times) graphite electrodes.

Figure 3 Resistivity and mean chain length for temperatures above 400°C (a) resistivity; (b) chain length.



For liquid chalcogenide glasses which seem usually to be of p-type at lower temperatures, it is suggested that the activation energy E , can be interpreted as $(E_F - E_V)$ where E_F is the Fermi energy. The energy level E_V lies near the extremity of the density of states curve for the valence band, and the space between E_V and the band extremity is occupied by localized states. At E_V the hole mobility is considered to show a sharp transition, exhibiting a "mobility shoulder" so that E could be regarded as involving a "mobility activation". The value of E is about half that for the optical gap and diminishes markedly with rise in temperature [10].

For sulphur, intrinsic conduction is normally assumed at higher temperatures, [1, 5] so that Equation 1 becomes

$$\sigma = A \exp(-\Delta E/2kT) \quad (2)$$

In this case, the temperature variance of the pre-exponential term, A , which entails the carrier mobilities is considered to have a relatively small effect on the slope of the $\log \sigma$ versus $1/T$ plot. Unlike the chalcogenide glasses, only one element is involved and scission of the sulphur chains might well produce equal numbers of electrons and holes; there is at present no evidence to the contrary, so that tentatively an intrinsic type of conduction could be accepted. Thermopower measurements are not available for liquid sulphur at high temperatures, but for such a material [11] the mobilities would be expected to be $< 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$. This, and the fact that marked

changes in liquid structure occur, shows that there is no real analogy with an intrinsic semiconductor such as pure crystalline germanium.

The value of 3.1 eV for ΔE is about the same as that obtained by Watanabe and Tamaki, and also by Steunenber *et al.* [6]; it is an approximate one for the temperature range because the temperature coefficient of the gap is unknown.

Accepting that Equation 2 is determined principally by the numbers of carriers released, then a rough relationship might be expected between the conductivity and the mean chain length in the liquid. The mean chain length expressed as the number of sulphur atoms is plotted as a function of temperature in Fig. 3. Below 600°C the values have been obtained from the magnetic susceptibility measurements of Poulis and Massen [12] which agree well with those from viscosity determinations [2]. At the critical point (1040°C) the molecular composition of the liquid and vapour become identical. Baker [13] from vapour pressure measurements in this region in conjunction with mass spectrograph data at low pressures, estimated the mean molecularity at the critical point to be $S_{3.4}$. Rau *et al.* [14] from vapour density studies at high pressures obtained $S_{2.78}$. The latter value is likely to be the more accurate but both points lie close together as shown in Fig. 3.

To assist comparison with the conductivity data, the σ -values have been converted to values of resistivity (ρ) and plotted on an arbitrary ordinate scale. Although there is some similarity of trend of

the two properties, the values of ρ and the mean chain length drop by factors of about 10^5 and 600 respectively over the range 400 to 900°C. There is clearly no simple relationship between resistivity and mean chain length. Possibly the resistivity drops sharply because charge transfer takes place mainly via the shortest chains, the concentration of which multiplies rapidly with rise in temperature.

3.3. Comparison with liquid selenium

In the temperature range 350 to 600°C the plot of $\log \sigma$ versus $1/T$ for selenium is linear. However, the interpretation of the energy gap from the plot is uncertain as in the case of sulphur. Intrinsic semiconduction is usually assumed, so that for comparison with sulphur it is convenient to retain this assumption. On this basis the value of ΔE is found to be 2.1 to 2.4 eV [15–18]. Above about 600°C the rate of increase of σ with temperature becomes greater, which would appear to be related to the selenium becoming n-type [11]. Baker [17] found that at above about 1150°C, the rate of change of σ with temperature then diminished, and extrapolation beyond 1420°C indicated that σ would reach a maximum limiting value of around $10^2 \Omega^{-1} \text{cm}^{-1}$ between 1600 and 1700°C, where a substantial metallic contribution to the conduction would be present. Since it was suspected that this was the region of the critical point, this imposed uncertainties on the extrapolation. Later work by Hoshino *et al.* [19] showed the critical point to lie at $\sim 1600^\circ\text{C}$, the maximum conductivity under slightly supercritical conditions being about $10^2 \Omega^{-1} \text{cm}^{-1}$. In this region the selenium was considered to be more molecular than metallic in character. This is quite feasible, because a significant degree of covalency would still be expected to be present, so that the “metallic” nature in this region is to be taken in its broadest sense from the level of conductivity and the absence of an exponential conductivity–temperature relationship.

From 400 to 600°C where both sulphur and selenium are assumed intrinsic, the values of σ for sulphur are around 10^3 times lower than those for selenium; it is thus to be expected that addition of selenium to sulphur increases its conductivity [5]. Magnetic susceptibility measurements [20] indicate that in this temperature region the mean chain lengths for selenium are about twice those for sulphur, whilst extrapolated viscosity data [2]

show them to be about one tenth of the values for sulphur. Shorter chains in selenium implies a larger number of carriers in the latter compared with sulphur, which would be in accordance with the lower value for ΔE of 2.3 eV for selenium compared with 3.1 eV for sulphur.

At 900°C the conductivity of sulphur is $5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$, while that of selenium is $10^{-1} \Omega^{-1} \text{cm}^{-1}$ [17]. In its critical region of $\geq 1600^\circ\text{C}$, selenium approaches a metallic level of conduction, but for sulphur as its critical temperature of 1040°C is approached, the conductivity will not increase much above the value at 900°C. In fact, in the vicinity of the critical point where the density decreases sharply, a fall-off in conductivity is possible. Any significant increase in the conductivity of sulphur must presumably be sought under supercritical conditions. The reason for not studying the critical region in the present work, was that attack of the gold electrodes above 900°C was anticipated; also the critical temperature is near the melting point of gold. If an electrode material resistant to sulphur at these temperatures could be found, it is improbable that even at supercritical pressures and temperatures a metallic level of conductivity would be detected.

Acknowledgements

We thank Dr J. A. Savage for reading the manuscript, also the Ministry of Defence (Department of Components, Valves and Devices) and the Science Research Council, for financial support.

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Received 9 December 1977 and accepted 19 January 1978.