Arsenic Triselenide: Preparation and Electrical Conductivity at High Temperatures

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Arsenic triselenide and other chalcogenide glasses have been prepared rapidly from the elements by heating at temperatures in the range 900—1500 °C under argon at high pressure in an internally heated pressure vessel. The electrical conductivity of liquid arsenic triselenide has been measured over the temperature range 187—1425 °C under a high pressure of argon. Below 600 °C, the plot of log σ against $1/T$ is linear and confirms semiconductive behaviour. In the range 600—1425 °C, the conductivity initially shows a marked increase with temperature, but near 1400 °C it tends to become constant. The explanation offered qualitatively for the high-temperature behaviour, is that the selenide changes from a semiconductor to a metallic conductor as the polymeric structure of the liquid is thermally destroyed. The results are compared with those for liquid selenium.

ARSENIC TRISELENIDE can exist either as a glass or as a crystalline solid; the latter state can be obtained if the liquid is cooled extremely slowly, but Goriunova has shown that for cooling rates greater than 1 °C per min, the glassy form is always obtained.[1] This glass, in common with other chalcogenide glasses, is a semiconductor in the solid state and is technologically important.[2-4]

Preparation of arsenic triselenide and other chalcogenide glasses is carried out usually by heating reactants together for several hours in sealed quartz bulbs; the temperature must be raised slowly as the reaction proceeds to prevent excess pressures of selenium, *etc.* from building up.

One aim of the present work has been to prepare arsenic triselenide and similar glasses by heating the elements together under argon at a pressure greater than the expected vapour pressure of the most volatile constituent. Temperatures in the range 900—1500° can be used which allows a faster reaction rate and also facilitates the incorporation of high melting elements if required. Arsenic melts at *ca.* 820 °C under a reported pressure of 36·5 atm,[5] so that by use of pressure and temperatures greater than these values, the arsenic is liquefied and this also assists the reaction. The reaction vessel is a quartz bulb having a narrow tubular outlet, mounted in an internally heated pressure vessel. As the quartz vessel is open, it cannot burst, but the high pressure argon in the tubular outlet acts as a diffusion barrier and virtually eliminates vaporisation loss.

In addition to exhibiting semiconductivity in the solid state, arsenic triselenide shows this property in the liquid state. As the compound is rather volatile, however, measurements of the temperature conductivity relation for the liquid have so far been made only up to 730 °C.[6] Measurements at high temperatures must, therefore, be made under a high applied pressure of argon to prevent the liquid boiling off. Such measurements represent the second aim of this work, the conductivity measurements under pressure being made in a similar manner to those for liquid selenium.[7]

EXPERIMENTAL

Apparatus.—The high-pressure furnace used for the preparation and electrical measurements on the selenide is shown in Figure 1. The alumina furnace tube had a bore of 2·5 cm; the lengths of the main winding and top booster winding were respectively 30 and 7 cm. Both

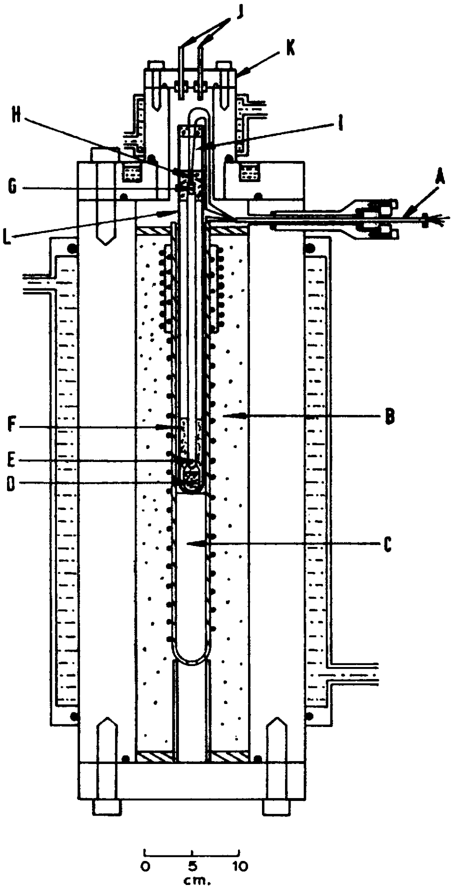

FIGURE 1 A, Thermocouple conduit (Johnson Matthey). B, Alumina powder. C, solid alumina baffle. D, Reactants. E, Thermojunction. F, Silica granules. G, Silica thermocouple sheath. H, Refractory fibre. I, Silica gel. J, Terminals for conductivity measurements. K, Perspex lid. L, Silica safety tube

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[1] N. A. Goriunova and B. T. Kolomiets, *Soviet Phys. Tech. Phys.*, 1958, **3**, 1766.

[2] A. D. Pearson, 'Modern Aspects of the Vitreous State,' Butterworths, London, 1964, vol. 3, p. 29.

[3] S. R. Ovshinsky, *Phys. Rev. Letters*, 1968, **21**, 1450.

[4] R. Pinto, *Thin Solid Films*, 1971, **7**, 391.

[5] S. Horiba, *Z. phys. Chem.*, 1923, **106**, 295.

[6] J. T. Edmond, *Brit. J. Appl. Phys.*, 1966, **17**, 979.

[7] E. H. Baker, *J. Chem. Soc.* (*A*), 1968, 1089.

windings were made from an alloy of platinum + 10% rhodium. Power terminals for carrying current through the vessel walls to the windings were of the ' spark-plug ' type and have been previously described.[8] At the pressures used here, heat loss tended to be greater in the upper part of the furnace tube. This loss could be compensated for by adjustment of the power input to the booster winding thus enabling a good constant-temperature zone to be obtained in the region of the sample. The constant-temperature zone was 5 cm long and was monitored with a thermocouple *ca.* 3 cm above the sample.

The vessel for preparation of the selenide was made of clear silica, the reaction bulb being 4 cm long and 1·9 cm in diam.; the tubular portion was 34 cm long and 9 mm in diam. A thermocouple (Pt–Pt + 13% Rh) was placed just above the sample to determine its temperature. The sample was made up from the stoicheiometric proportions of arsenic and selenium to yield *ca.* 20 g of the selenide. To prevent loss of the components by volatilisation, it is essential that the annular clearance between the thermocouple sheath and the outer tube be small; the thermocouple sheath was, therefore, selected so that this clearance was about 0·1 mm. The silica safety-tube was incorporated in case the bulb cracked when the sample solidified. Gas turbulence, above and below the sample, was prevented respectively by the packed silica granules and the solid-alumina support.

For the conductivity measurements, U-shaped conductivity cells were used. These were made of clear silica and were of similar design to those employed for the conductivity studies of liquid selenium.[7] The U-shaped capillary portion of each cell had a total length of *ca.* 7·5 cm with a bore of 1 mm or less. The cylindrical electrode chambers were 16 cm long and 0·7 cm in diam. Specpure graphite rods (Johnson Matthey) 3 mm in diam. were used for the electrodes. Although the resistance of this type of cell is determined almost entirely by the capillary portion, irregularities in the latter necessitated determination of the cell constant with 0·1M-potassium chloride solution. For the five cells used, the constants ranged from 100 to 5976; the cells with the highest constants were used at the highest temperatures, where the conductivity was greatest.

A cell was positioned in the silica safety-tube so that the capillary portion was in the constant-temperature zone. Connection to the graphite electrodes was made by stout platinum wires, which were, in turn, connected to the brass terminals in the Perspex lid at the top of the pressure vessel. The residual resistance of the leads and electrodes was *ca.* 1 Ω. A Wayne Kerr bridge (type B221) operating at 1592 Hz, was used for the conductivity measurements.

Materials.—The purities of the arsenic and selenium used were respectively 99·9999% and 99·999%; high-purity argon was the pressure medium.

Preparation of Arsenic Triselenide.—To remove air, the pressure vessel was flushed twice with argon, evacuated to 10^{-3} atm, and flushed once again. It was then pressurised to the working pressure and the temperature raised. Working pressures of 70—100 atm and temperatures of 900—1000° were found to be satisfactory. The molten reactants were kept at temperature for 1 h and then allowed to cool under pressure. The total time required for the preparation was *ca.* 3 h.

At 1000°, the vapour pressure of selenium is 20 atm,[7] whilst data for arsenic triselenide (to be published) show its vapour pressure to be *ca.* 4 atm at this temperature. The vapour pressures of arsenic at temperatures around 900° are uncertain, but would appear to be less than the applied pressures of argon because vaporisation loss of material was negligible; in each of four preparations of the selenide, only a faint film of condensate was found in the upper tubular portion of the silica vessel.

Ingots of arsenic triselenide prepared as above, were dark with a metallic lustre, and examination by optical microscopy showed them to be completely homogeneous. They were also free of voids, which suggests that argon solubility in the material is negligible. Since the cooling rate in the preparation was *ca.* 1° per min below 400°, it was expected that the material would be a glass;[1] this conclusion was confirmed by *X*-ray powder photographs which showed only diffuse patterns.

Preparation of other Chalcogenide Glasses.—A large number of these glasses can be made by this method; two examples are the electronically important materials $As_{50}Te_{40}Ge_{10}$ and $As_{30}Te_{48}Si_{12}Ge_{10}$. These were made under virtually loss-free conditions by direct combination of the elements, the melts in both cases being kept for 1 h under 70 atm of argon at a high temperature, then cooled under pressure. The temperature used for the first glass was 1100 °C, but for the silicon-containing glass, 1460 °C was used; this ensured that the silicon was molten. The total time for each preparation was *ca.* 3 h. *X*-Ray powder photographs showed that these materials, as prepared, were in the glassy state.

Conductivity of Liquid Arsenic Triselenide.—The space between each graphite electrode and the silica limb of the conductivity cell was packed with the powdered selenide to a depth of 6 cm. The cell was set up in the pressure vessel, the latter was then flushed with argon and pumped down to a pressure of 2 mmHg. The furnace temperature was raised until the temperature of the selenide column was 450 °C and then argon was slowly admitted until a pressure of 70 atm was attained. This completely filled the capillary portion of the cell with the liquid selenide and reduced any bubbles in the latter to minute size. In fact, no bubbles were observed in the capillary at the end of any run.

A heating rate of 10 °C per min was employed during a run, but whilst the conductivity was being measured, the temperature was kept constant manually within ±1 °C; 15 min were required for the temperature to stabilise. Some d.c. conductivities were obtained by occasionally connecting the cell to an Avometer; within the experimental errors, however, the d.c. and a.c. values were the same. Measurements were made up to 1425 °C.

As the cells could not be designed to prevent vaporisation loss, the level of the arsenic triselenide in the electrode chambers fell by *ca.* 0·3 cm during runs at the highest temperatures. This, however, had no measurable effect on the conductivity values because the latter were principally defined by the capillary portion of the cell.

Some measurements were made at lower temperatures by cooling back; the lowest temperature employed was 187°, where the selenide was virtually a solid glass.

RESULTS AND DISCUSSION

In Figure 2 is shown the variation of conductivity (σ) as a function of temperature for the range 187—

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[8] E. H. Baker, *J. Chem. Soc.*, 1962, 464.

1425°. The average accuracy of the results after consideration of the errors in the measurements and in the cell constants is *ca.* 4%.

The linear nature of the plot for the temperature range 187—600 °C (AB) is characteristic of intrinsic behaviour, which, from the thermoelectric measurements of Edmond appears to be mainly dependent on positive-hole conduction.[6] In this region, the conductivity plot is virtually identical with that obtained by the above author. The results in this region can be expressed by the relation:

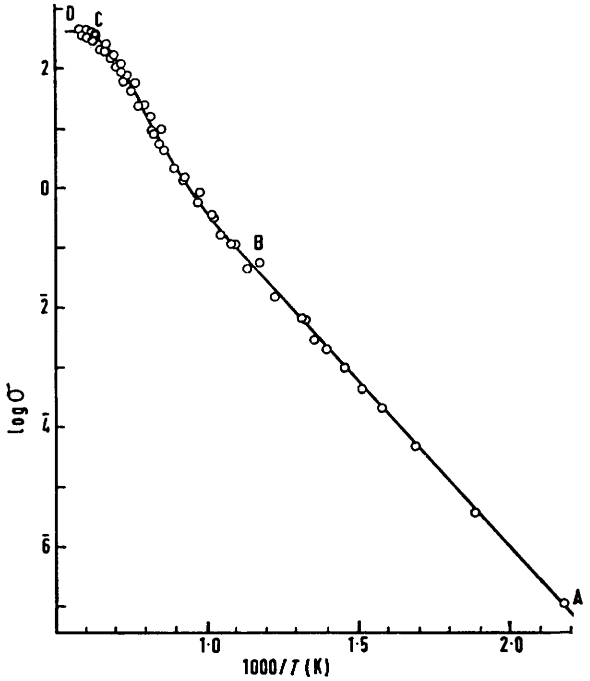

FIGURE 2 Conductivity–temperature relation for arsenic triselenide

$$\sigma = \sigma_0 \exp(-\Delta E/2kT) \qquad (1)$$

where σ_0 has the value $6{\cdot}86 \times 10^4\ \Omega^{-1}\ \text{cm}^{-1}$, and ΔE, the activation energy for the conduction process has the value 2·15 eV.

With increasing temperature, this energy gap should diminish according to a Kirchoff-type relation,[6,9] *i.e.* approximately as a linear function of temperature; this cannot be related to the marked change in conductivity at higher temperatures (BC) observed here, because the plot shows an upward curvature. Although the tangent, at any point on the conductivity plot, yields an activation energy, in the region BC, the variation of the activation energy with temperature indicates that a complex process is involved. This must entail not only a semiconductive process, but also an increased chemical breakdown with temperature of the chain or layer structure of the liquid into smaller molecules and atoms; the liquid, thus, becomes increasingly metallic in character. Mott[10] has suggested that the hole-type conduction should be carried over into this region, but the increasing metallic nature will result also in an increasing contribution of free electrons to the conduction.

At higher temperatures, where the polymer content is greatly diminished, further changes in constitution of the liquid with increasing temperature become less, and the conductivity tends to a roughly constant value (CD). At the point D (1425 °C) the liquid will contain only small molecules and atoms, and will resemble a liquid metal. Liquid metals have small temperature coefficients of conductivity (*ca.* 0·05% per degree), which are usually negative. The near constancy of the conductivity above 1400 °C is in keeping with metallic behaviour, but owing to the experimental difficulties in this region, the conductivity relation could not be resolved accurately. However, in the case of liquid tellurium which can be studied at lower temperatures and pressures, a small negative temperature coefficient of conductivity has been found above 1000°, showing the liquid to be entirely metallic (to be published).

For the semiconducting regions, the activation energy for liquid arsenic triselenide is about the same as that for liquid selenium [7] in which hole conductivity also predominates; σ_0 for arsenic triselenide, is *ca.* 10 times the value for selenium; the two materials do not differ all that much.

Hole mobilities are not apparently available for liquid arsenic triselenide, but Edmond quotes some evidence from Hall effect measurements on As_2Se_2Te and As_2SeTe_2 that the mobilities in these liquids vary little with temperature;[6] a similar property would be expected for liquid arsenic triselenide. It appears that for these materials in the semiconducting region, the temperature variation of conductivity is determined principally by change in the number of holes, in a conventional manner. In contrast, Aliev *et al.*,[11] from some Hall effect measurements on ultra-pure liquid selenium, in the range 300—500 °C, report that the Hall constant varies little with temperature and conclude that the σ–T relation is determined mainly by an increase in hole mobility (μ). At 400 °C, on the assumption that the relation, $\mu = \sigma \times$ Hall constant, applies to the liquid, the hole mobility becomes *ca.* $2\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$, which appears reasonable as it is near the region of values given for vitreous selenium,[12] *i.e. ca.* $0{\cdot}15\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ at room temperature and above. However, an exponential σ–T relation which is largely mobility controlled seems unusual for these high temperatures, and more detailed Hall-effect measurements are required to ascertain if the semiconducting mechanism for liquid selenium does, in fact, differ from that for the arsenic selenides.

Although selenium and arsenic are in the fifth series

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[9] N. B. Hannay, 'Semiconductors,' Reinhold, New York, 1960, p. 332.

[10] N. F. Mott, *Phil. Mag.*, 1971, **24**, 1.

[11] G. M. Aliev, S. I. Mekhtieva, and D. S. Abdinov, *Vyosokomol. Soed.*, 1966, **8**, 1659.

[12] H. P. Grunwald and R. M. Blakney, *Phys. Rev.*, 1968, **165**, 1006.

of the Periodic Table, arsenic lies in the direction of increasing metallicity. At temperatures above the semiconducting region, where the polymeric nature of these liquids is greatly diminished, their behaviour would be expected to relate more to atomic properties. Intuitively, one would therefore expect the presence of arsenic in selenium to make the liquid more metallic. This is, in fact, observed; arsenic triselenide becomes metallic at 1425 °C whilst a temperature of *ca.* 1680 °C (extrapolated) is required for selenium to reach this state.[7]

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