An Apparatus for Non Destructive Study of Atom Transport in Liquids

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A description is given of a method developed for diffusion and electrotransport measurements in liquids, which permits several successive readings on a sample in uninterrupted anneal. Errors from solidification and sectioning are avoided, and the reproducibility of measured diffusion coefficients is better than two percent. Experimental results are given for gallium self-diffusion. The present apparatus can be conveniently applied to many liquids solidifying below some 280 °C utilizing gamma tracers with energies in the range 0.2—2.0 MeV. The design can be modified for higher temperatures.

1. Introduction

Several standard methods exist, see e. g. Refs. [1, 2], for studying atom transport phenomena in liquids. Usually, stable or radioactive tracers are employed, and before evaluation a specimen has to be cooled, solidified, and sectioned. In the present case we have applied two less commonly exploited ideas to facilitate the study of liquid diffusion. Firstly, the geometry of the thin film method, common in measurements of tracer diffusion in solids (see e. g. Ref. [3]) has been used, in as far as a small indicated drop at one closed end of a capillary is made to diffuse into a several cm long column of inactive liquid. The justification of using this method is discussed in Section 3. Secondly, the activity distribution is measured without disturbing the sample. This latter method, applicable also to electro- and thermotransport of tracers, has several advantages. Freezing and sectioning are avoided, two processes which can introduce large errors[4]. Furthermore, several readings can be made on the same sample during one diffusion process.

2. Experimental Setup

The diffusion process takes place in a cell shown in Fig. 1, made of pyrex glass. The cells are manufactured at this institute from precision bore Veridia capillary tubes. The inner diameter of the capillary is 0.70 ± 0.01 mm and the length is about 10 cm. The cell is manufactured with a hole in the wall opposite the open end of the capillary, in order to facilitate the insertion of radioactive metal. The procedure of filling is discussed in Sect. 3.

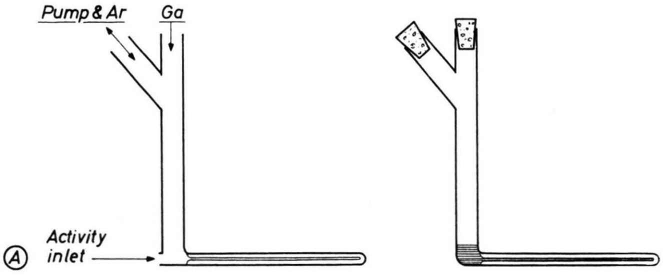

Fig. 1. Pyrex glass cell empty and filled. The insertion hole is placed at A.

The annealing temperature is achieved and stabilized by means of a regulated oil bath, a standard Lauda WB-20-S8, equipped with thyristor steering. The temperature, continuously read by a thermo-couple connected to a compensation bridge and a recording millivoltmeter, was found to be stable within 0.01 °C. The use of Dow Corning 710 silicone oil permits measurements up to 280 °C to be performed.

The cell is mounted on a slide which is moved by means of a screw. The position of the cell is controlled by a micrometer scale. Between the cell and the wall of the oil bath are two collimators consisting of 5 cm thick lead slabs with slits perpendicular to the direction of the liquid column. The collimators hang in chains on opposite sides of cog-wheels so that one is lowered when the other is lifted. In one position the slits coincide, permitting the radiation from a 2 mm long part of the cell to pass. In the other position 10 cm of lead almost completely stop gamma radiation from the cell. The difference in recorded gamma radiation between the two positions is a good measure of the activity concentration of the capillary part next to the slit. On the other side of the collimators and outside the wall, the gamma ray detector is situated. The detector consists of a 3 × 3″ NaI crystal with photomultiplier and preamplifier. The detector is heavily shielded by lead from

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[1] N. H. NACHTRIEB, Adv. Phys. **16**, 309 [1967].

[2] A. LODDING and A. OTT, Z. Naturforsch. **21 a**, 1344 [1966].

[3] P. G. SHEWMON, Diffusion in Solids, McGraw-Hill, New York 1963.

[4] A. NORDÉN and A. LODDING, Z. Naturforsch. **22 a**, 215 [1967].

scattered gamma rays and background radiation. The pulses from the detector are analysed in an RIDL single channel pulse height analyzer. Gate and window are chosen to give the best signal-to-background ratio (for Ga this corresponds to the energy interval 0.55 – 0.90 MeV). The analyzer is placed in another room to avoid gain shifts from temperature variations.

Figure 2 gives an overall view of the experimental setup, with the extra shielding demounted. Figures 3 and 4 show the geometry and the colimator arrangement in more detail.

In order to measure only the radiation from a well defined part of the sample, two precautions must be taken. Firstly, the collimator must be narrow and secondly the shielding of the other parts of the cell must be thick enough to transmit less than 10^{-4} of the gamma radiation. The effective distance between source and detector is therefore 20 cm and the solid angle only about 0.1 per cent. To obtain sufficient statistical certainty within reasonable measuring time, strong gamma sources have to be used (for further discussions see Sections 3 and 4).

The apparatus can be used for higher temperatures if the lead colimators are replaced by stainless steel and a liquid salt mixture is substituted for oil. Temperatures up to some 500 °C should then be feasible. For protection of the crystal a sheet of asbestos in front of the detector may be adequate.

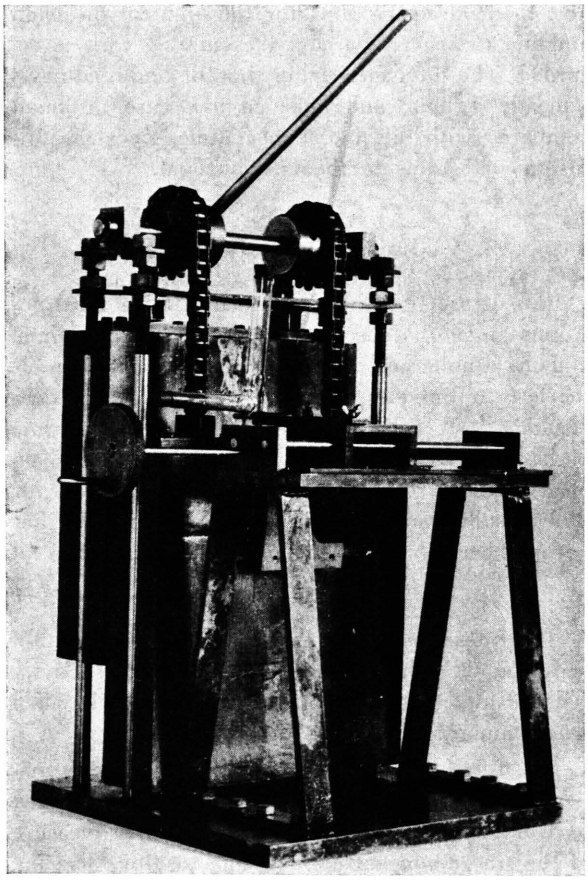

Fig. 2. Collimator arrangement (extra shielding demounted).

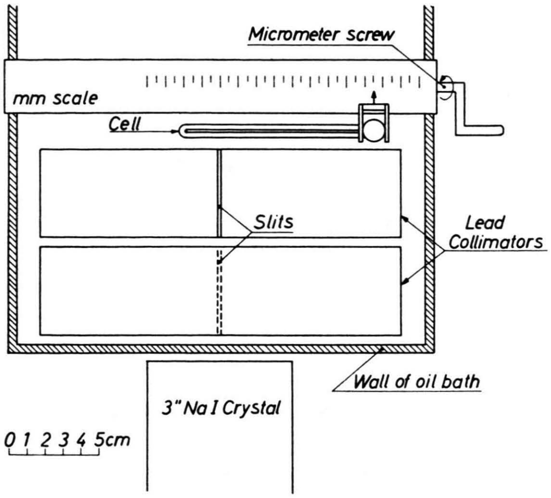

Fig. 3. Schematic drawing of apparatus, viewed from above at right angles to capillary.

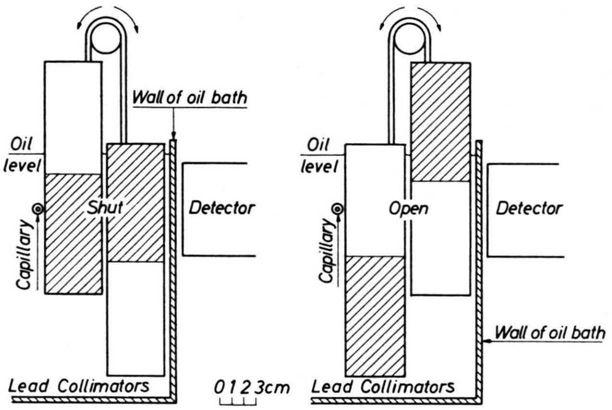

Fig. 4. Collimator arrangement viewed along capillary.

3. Production of Samples

We will here describe the production of gallium samples. Although some of the steps are specific for this metal, the general procedure is applicable also to other cases. For Ga, however, no special care to avoid corrosion has to be taken, as chemical reaction of gallium with air and glass is very slight even well above the highest temperatures of this investigation [5].

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[5] S. Larsson and A. Lodding, Proc. Thomas Graham Symp. "Diffusion Processes", 1969, Gordon Breach Publ., in press.

The presence of absorbing material between source and detector limits the number of useful radioactive isotopes. Thus, the source must emit gamma rays with energies above some 0.20 MeV. Furthermore, the half-life must not be too small. ^{72}Ga emits 0.69 and 0.84 MeV gamma rays with 14.1 hours' halflife and fulfills the requirements. The ^{72}Ga sources were produced by thermal neutron irradiation of 99.999% purity Ga metal (Koch Light Ltd) in the R2 reactor at Studsvik by AB Atomenergi. Typically 6 milligrams were irradiated for 14 h in a neutron flux of $2 \cdot 10^{12}$ neutrons cm^{-2} sec^{-1}, giving a specific activity immediately after irradiation of 1 mC/mg, which is sufficient for our purpose. No traces of impurity activities were found by neutron activation analysis [6]. Typical delay time between irradiation and experiment corresponded to about one halflife.

The diffusion process takes place in the glass cell shown in Fig. 1. In order to avoid contamination of capillary wall during insertion, radioactive liquid gallium is brought to the far end of the capillary by means of a syringe. About 0.5 mm of the capillary is thus filled with radioactive gallium, corresponding to an activity of 0.3 mC.

Inactive gallium is then filled into the capillary according to the following procedure. The hole is closed by fusing the walls together. After placing a piece of solid inactive gallium at the bottom, the cell is connected via a three way valve to a vacuum pump. When a pressure of 10^{-4} Torr is reached in the large tube the gallium is melted by means of a Bunsen burner outside the cell. Then argon gas is slowly let into the cell through the valve, and the inactive liquid gallium is pressed into the capillary. Since the initial vacuum in the capillary is certainly better than 10^{-1} Torr, complete contact between the active and inactive gallium is obtained. The cell is sealed with a rubber plug and mounted in the oil bath.

The use of the thin film solution (3) of Fick's second law is justified since the diffusivity is about 10^4 times greater in the liquid than in the solid. The penetration depth is proportional to $D^{1/2}$, so 0.5 mm of active liquid at the end of a 10 cm long inactive column corresponds to a surface layer of only about 5 micron thickness on the butt end of a solid cylinder with one mm available depth.

4. Measuring Method

The method employed permits several consecutive readings of the activity at different places in the capillary during one annealing run. Thus, the diffusion process can be followed until the equilibrium state is reached, which is in contrast to conventional methods.

When the cell is put in place the position of the contact layer between active and inactive metal is determined visually. Temperature equilibrium between cell and bath is obtained after $1-2$ min and does not have to be corrected for. Readings are normally taken after 10 and after 20 hours. The comparatively short halflife of ^{72}Ga prevents statistically accurate readings after more than about 30 hours. In each reading the column is scanned at 0.5 cm intervals and at each point a minimum of $4 \cdot 10^3$ counts is collected, giving a statistical accuracy of about 1.5%. In order to avoid systematic errors, points are usually in random order. To be able to make corrections for the ambient diffusion and the radioactive decay, the running time is recorded. The total measuring time of one reading is typically 1 hour and must in any case be small compared with the total anneal time, since the diffusion corrections are theory dependent.

5. Analysis of Data. Corrections

Raw data consist of a table which for several positions along the specimen gives the running time, and the number of counts for the two positions of the lead collimators, together with measuring time (usually kept constant). Furthermore, a separate background measurement is done without the cell in place. Afterwards, the activities are corrected for this constant background. Furthermore the activities have to be corrected for radioactive decay:

$$I = I' \exp\{+\lambda t\} . \qquad (1)$$

I' is the measured activity corrected for the constant background, t the running time and I the activity reduced to zero time. The decay constant λ is taken from standard tables.

The difference between the thus corrected activities with and without lead in front of the considered part of the specimen gives a good relative measure of the tracer concentration in this section. The log of the difference plotted against x^2, where x equals

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[6] C. Larsson and L. Broman, J. Inorg. Nucl. Chem. **31**, 3692 [1969].

the distance between the contact layer and the middle of the actual section, yields the preliminary penetration profile.

There are, however, three factors that can affect the slope of the profile and have to be taken into account. The first and most important is the continuous diffusion, i. e. gradual change of activity during the measurement.

The activity I_0 at the time $t = t_0$ is given by the equation

$$I_0 = \text{const} \cdot (D\,t_0)^{-1/2} \exp\{-x^2/4\,D\,t_0\}\,. \tag{2}$$

Here, x is the same as above, D the diffusion coefficient, and t_0 the time elapsed between the start of the diffusion and the start of the measurement. Since the activity is actually measured at the effective time $(t_0 + \Delta t)$, Eq. (2) is changed into

$$I = \text{const}[D(t_0 + \Delta t)]^{-1/2} \exp\{-x^2/4\,D(t_0 + \Delta t)\}. \tag{3}$$

I is the recorded intensity defined above. The time Δt is different for different values of x, and therefore the different I values have to be reduced to the corresponding I_0 values. The relation between I_0 and I becomes

$$I_0 = I\left(1 + \frac{\Delta t}{t}\right)^{1/2} \exp\left\{-\frac{x^2\,\Delta t}{4\,D\,t_0(t_0 + \Delta t)}\right\}. \tag{4}$$

Equation (4) can for $\Delta t \ll t_0$ be reduced to

$$I_0 \approx I\left(1 + \frac{\Delta t}{2\,t_0} - \frac{x^2\,\Delta t}{4\,D\,t_0^2}\right). \tag{5}$$

In the present case (Ga) $D \approx 5 \cdot 10^{-5}\ \text{cm}^2\ \text{sec}^{-1}$ and the total measuring time is about one hour. This gives a difference between I and I_0 of less than 10%. It introduces a substantial correction. Fig. 5 shows an example of preliminary and corrected diffusion profiles.

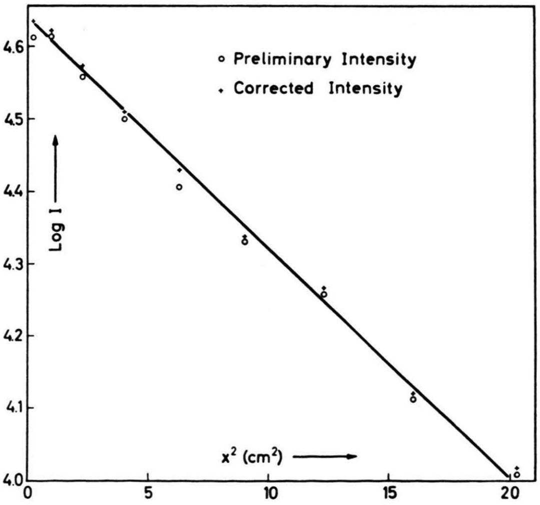

Fig. 5. Typical diffusion profile before and after corrections.

The second factor that might affect the diffusion profiles is the finite resolution of the collimators depending on the finite transmission through the lead shield. Contributions from nearby parts of the radioactive column increase the measured activity. This can be a problem, since the extra activity from one side is larger than from the other, giving an asymmetric yield curve. This can be written as

$$i(x) = c(x)\,f(x) \tag{6}$$

where $c(x)$ equals the concentration distribution in the sample and $f(x) = \exp\{k\,|x - x_0|\}$ is the yield curve from a point source located at x_0. The value of the constant k is measured to $(-4.96)\ \text{cm}^{-1}$ for the present setup. We therefore make an error when we measure the gamma intensity as the area under the asymmetric curve $i(x)$ instead of under the symmetric curve $f(x)$. It can be shown that the relative difference for two extreme values of x_0 introduces an error in the slope of the diffusion profile of about 1.0% for the slit width and collimator thickness of the present setup. This is taken into account by systematically adding 0.5% to the measured value of D; 0.5% being a mean value of the introduced error. The calculations are presented elsewhere[7].

A third error arises from the estimation of the position of the original contact layer between active and inactive metal i. e. of $x = 0$. The slope of a diffusion profile is described by the linear relation

$$\ln I_0 = a\,x^2 + b \tag{7}$$

arrived at by least squares analysis. An error δx in the contact layer position gives another slope a^1, since Eq. (7) changes into

$$\ln I_0 = a^1 (x + \delta x)^2 + b^1. \tag{8}$$

Using the standard statistical formula for a, the relative difference of a and a^1 can be shown to amount

$$\frac{a - a^1}{a} = \frac{2\,n\,\delta x \sum x_i^3 - 2\,\delta x \sum x_i \sum x_i^2}{n \sum x_i^4 - (\sum x_i^2)^2} \tag{9}$$

where x_i are the coordinates for the n different measuring points along the specimen. Inserting $x_i = 5, 10, \ldots, 100$ mm and $\delta x = 0.15$ mm, which

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[7] C. ROXBERGH, unpublished.

are typical experiment values, Eq. (9) gives the experimental error due to the uncertainty of the contact layer position, equal to 0.5%.

6. Example of Measurements

We have studied self-diffusion in liquid gallium metal. Results from this study are collected in an Arrhenius plot, Fig. 6. The diffusion coefficient was measured twice for each temperature using the same cell. As is clearly demonstrated in the figure, the agreement between points in each pair is very good and well within the calculated statistical limits. We observed no tendency of recorded D-values to vary with anneal time.

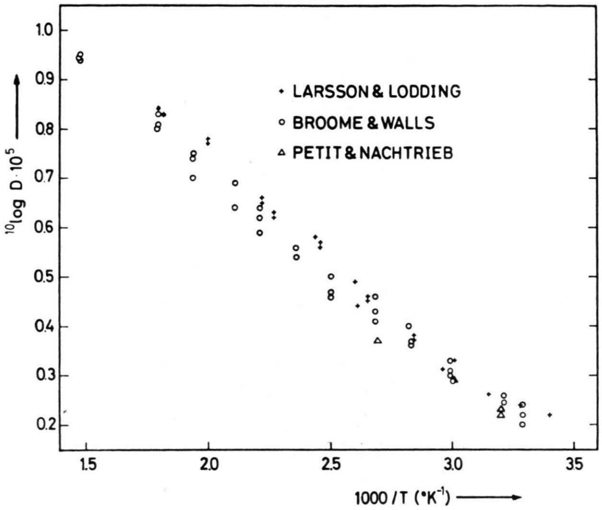

Fig. 6. Experimental temperature dependence of D in Ga, obtained by PETIT and NACHTRIEB [8], BROOME and WALLS [9] and by the present team.

The experimental error in each point is a combination of several effects. The dominant error in the evaluations of the penetration curves arises from the statistical uncertainties in preliminary data. Estimation by least squares analysis has amounted to 2% on an average. The error in the determination of the position of the contact layer is about 0.5%. The finite resolution introduces a further error of about 0.5%. The maximal estimated random error is thus certainly less than 4% while the reproducibility is as good as about 2%. Preliminary data of these experiments have been presented elsewhere [5], and a more detailed discussion of the Ga results is under preparation. The agreement with an early investigation by PETIT and NACHTRIEB [8] is good. Recently another investigation of self-diffusion in Ga, using a "shear-cell", has been published [9]. The results closely agree with ours at low temperatures (see Fig. 6), while a systematic difference begins to appear above some 150 °C. At the highest temperatures the shear cell results give D-values lower by some 6% than our results. The scatter of the individual shear cell points is however quoted to be as high as some 10%.

Acknowledgements

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[8] J. PETIT and N. H. NACHTRIEB, J. Chem. Phys. **24**, 1027 [1956].

[9] E. F. BROOME and M. A. WALLS, Trans. Met. S. AIME **245**, 739 [1969].