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UNIVERSITA' DI GENOVA  
Istituto di Fisica Sperimentale

FINAL TECHNICAL REPORT  
on  
DIFFUSION COEFFICIENT IN SOLID ARGON  
and  
THERMOCONDUCTIVITY OF SOLID ARGON

Contract No DA-91-591-EUC-2151

Period covered 1 March 1962 - 28 February 1963

Responsible: Giovanni Boato

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Genova, 26 March 1963

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### Summary

Reference is made to the first two final technical reports (contract No DA-91-391-EUC-1403 and - 1721) for the description of the apparatus for growing argon single crystals, for an exposition of the experimental set up for measuring the self diffusion coefficient in these crystals and for a thorough discussion of the first preliminary results.

Although a rough evaluation of  $D = D_0 \exp (-Q/RT)$  was possible, furnishing

$$D_0 = 350 \pm 150 \text{ cm}^2/\text{sec}$$

$$Q = 4150 \pm 150 \text{ cal/mole}$$

it was soon realized that large systematic errors were present in these measurements, affecting particularly the value of  $D_0$ . It was also realized that the tracer technique applied to large crystals could be hardly perfected and consequently it was hopeless to reduce drastically the errors. In order to obtain more precise information on the diffusion, it was decided to try a modified technique of measurement, using always the tracer method, but operating on thin polycrystalline layers of argon. It was thought that the effect due to the grain boundaries - which should be present in non negligible quantity in this case - was certainly much less important than other perturbing effects present when working with large crystals, namely extended distillation phenomena and partial detachment of the crystal from the walls of the crucible where it was prepared.

Transparent layers of solid argon of uniform thickness were prepared by slow condensation of the vapor on a cold wall, held at a constant temperature. On these layers, 10 to 80 microns thick, diffusion experiments were performed, using  $A^{36}$  as a tracer. The crystal was held in a strong temperature gradient. The penetration of the tracer into the crystal was followed continuously with a mass spectrometer. Penetration curves were obtained with the same procedure used in previous experiments.

A great improvement of the experimental results was observed: 1) the diffusion coefficient thus measured is 80 times smaller than that measured on large crystals 2) this change is

to be ascribed mostly to a strong reduction of  $D_0$ , while the activation energy was not remarkably affected 3) measurements could be performed in a more extended temperature range, namely down to 65°K 4) the penetration curves follow more closely the diffusion equation.

The experimental points are pretty well aligned in a  $\ln D$  versus  $1/T$  plot, although a slight bending of the curve seems to be present. As an average the following values were obtained

$$D_0 = 15 \pm 10 \text{ cm}^2/\text{sec}$$

$$Q = 4120 \pm 100 \text{ cal/mole}$$

It is seen that  $D_0$  differs by a factor 20 from the value previously obtained, while  $Q$  is only changed by one percent.

The observed reduction in  $D_0$  can be explained, if distillation of the large crystals during diffusion is taken into account.

The new values of  $D_0$  and  $Q$  are certainly affected by much smaller systematic errors; the accuracy now obtained is thought to be satisfactory, due to the difficulty of the experiment. The discussion of the results already given in the previous report is not altered by the new experiments. The discrepancy with the theoretical value is always present and the reasons for this are not clear.

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The measurement of the coefficient of thermal conductivity of solid argon was not yet completed. However a great progress was made in the design and the performance of the apparatus. The conditions for growing cylindrical rods of solid argon of good quality were understood. Many crystals were prepared, their change of hardness with decreasing temperature was studied. It was learned how to cool the crystals down to liquid helium temperature without damaging them. Clamps to hold tight the gas thermometer to the crystal were designed and checked at low temperature. On the basis of these studies, the final apparatus was completed. The first measurements of the thermoconductivity coefficient are under way. On the basis of these studies, the final apparatus was completed. The first measurements of the thermoconductivity coefficient are under way.

## DIFFUSION

### 1. Introduction

After several diffusion experiments, performed on large crystals of solid argon prepared by the Bridgman technique, which gave preliminary values for the self diffusion coefficient as a function of temperature from 78°K to 83°K (see final technical reports referring to Contracts No.s DA-91-591-EUC-1403 and -1721), it was realized that with the technique used it was hopeless to reduce drastically the large systematic errors, affecting particularly  $D_0$ , and consequently to obtain better overall results.

In fact, when a large crystal of argon - prepared in a crucible - is used to perform diffusion experiment, it is impossible to avoid completely 1) some detaching of the crystal from the walls 2) some redistillation of the crystal during diffusion. These phenomena are related to the high vapour pressure of solid argon in the temperature range interestin for diffusion and are complicated by the low thermal conductivity of the crystal. These same reasons make it practically impossible to use the standard sectioning technique so widely used for measuring diffusion coefficients.

To improve the reliability of the diffusion data, the technique used was somewhat changed. We gave up on trying to perform diffusion on single crystals (or assemblies of large size crystals) prepared by the Bridgman technique. A thin layer of polycrystalline argon was instead deposited on a cold flat wall of known surface area; the layer was slowly grown from the vapor phase, as to have a clear crystal and an even thickness. On the layer the diffusion experiment was then performed in the usual way (see preceding reports). A large gradient of temperature is maintained in the cell on top of the layer, as to avoid redistillation. The detaching phenomenon can thus be completely avoided. From the results obtained it is apparent, that no sizable effect was detected, due to the use of polycrystals instead of single crystals.

## 2. Experimental

2.1. The measuring cell - Two slightly different apparatuses were used to perform the experiments. They are shown in figure 1 and 2.

In the first apparatus, the cylindrical metallic cell is covered by an optical glass, used to observe the quality of the solid argon surface. The bottom of the cell is the upper part of a copper block immersed in liquid nitrogen; the temperature is thermo-regulated at  $\pm 0.01^\circ\text{K}$  by using a heater and a Pt thermometer just below the bottom of the cell. The lateral wall of the cell was made of stainless steel tubing, 0.1 mm thick. The volume of the cell was  $V=1.40 \text{ cm}^3$ , the height 1.5 cm and the diffusion area  $S=0.95 \text{ cm}^2$ ; along the cell a temperature gradient of about  $50^\circ\text{K/cm}$  was maintained. The significant quantity for calculating the diffusion coefficient from the experimental data is given by  $A \frac{V}{S}$ , where A is the ratio between the average number density in the vapor phase and the number density in the solid; in the first apparatus  $A \frac{V}{S}$  was equal to  $1.79 \cdot 10^{-3} \text{ cm}$  at  $T=80^\circ\text{K}$ . The gas inlet and outlet were two copper capillaries, 0.4 mm. inner diameter; the cell was connected to the mass spectrometer through a thin capillary of less than 0.07 mm. inner diameter. All the capillaries entered the cell from the lateral wall.

The second apparatus was built as to have a better defined diffusion surface and a smaller dead volume above the crystalline layer. This apparatus does not contain any looking glass, since observations of the crystal surface made with the first apparatus had shown that at small growing rate, the layer was always even and transparent. The bottom of the cell was again the upper part of an electrolytic copper block as in the first apparatus but it was more carefully polished and flattened. The lateral wall was made of a short length (0.62 cm) of stainless steel tubing the wall thickness being 0.6 mm. The vacuum tightness was assured not by a soldered joint, as in the first apparatus, but by a small indium O-Ring; in this way the diffusion surface was more clearly defined. The volume of the second cell is  $0.72 \text{ cm}^3$ , the diffusion surface  $1.16 \text{ cm}^2$ ; the temperature gradient is about  $10^\circ\text{K/cm}$ ; as a consequence the quantity  $A \frac{V}{S}$  has the more favorable value of  $1.01 \cdot 10^{-3} \text{ cm}$  at  $80^\circ\text{K}$ . The temperature of the copper block is held constant by thermoregulating the liquid nitrogen bath and by using

a heater supplied with a stabilized power supply. The temperature above the cell is held constant by using a small liquid oxygen trap and a thermoregulating unit. The temperatures above and below are both regulated within  $0.1^{\circ}\text{K}$ . The inlet and outlet capillaries enter the cell from above.

2.2 Experimental procedure - After having measured the temperature of the cell bottom and controlled its constancy, the argon was condensed by pushing gradually the gas into the cell with a metallic syringe. The rate of condensation corresponded to about 1 micron of crystal (in thickness) per minute. The layer was always condensed at the same temperature at which the diffusion was performed. The total thickness of the layer was always at least six times the average diffusion penetration depth, ranging from 30-40  $\mu$  below the triple point to about 10  $\mu$  at  $70^{\circ}\text{K}$ . The argon vapor pressure during condensation was measured with a mercury manometer of relatively small dead volume; and found to be constant within  $\pm 0.1$  mm Hg. The vapor pressure thus determined was used to calculate the temperature during each diffusion experiment.

When the condensation is completed, the cell is closed and some time is allowed to elapse for conditioning; about  $1.7\text{cm}^3$  of  $\text{A}^{36}$  tracer is then introduced at the working pressure, by the same method described in the preceding report; the introduction lasted about one minute; the  $\text{A}^{36}$  concentration in the tracer was 1.1%, against 0.337 in the atmospheric argon. The diffusion time was never longer than 75 minutes; the decrease of  $\text{A}^{36}$  in concentration in the vapor was continuously followed with the mass spectrometer. The gas used for the analysis was always less than 1% of the total amount of argon in the vapor overlying the crystal. After diffusion was completed, the crystal was gradually evaporated by using the syringe and the concentration decrease again followed with the mass spectrometer. The evaporation was certainly occurring by parallel layers (except probably for a small region at the border). The better reliability of the evaporation process to obtain penetration curves - in comparison with previous experiments - was confirmed by the experimental

results, which are much more self consistent than in diffusion runs using large size crystals. A complete plot of the concentration change, as recorded by the mass spectrometer is shown in fig.3. It is seen that the delay time in the response of the analysing capillary - due to its dead volume - is 90 to 100 seconds and that the time needed to reach the maximum concentration is 3 to 5 minutes (measured from the beginning of the tracer introduction). The initial concentration  $c_0$  in the vapor above the crystal - necessary for calculating the diffusion coefficient - was evaluated roughly from the balance of the isotopic species. The final value of  $c_0$  - used for calculation - was obtained by best fitting the experimental diffusion curves with calculated ones.

### 2.3 Results

The measurements of the self diffusion coefficient were performed in the temperature range between triple point (35.3°K) and 65°K; it is seen that a large improvement was obtained by using the new method, as far as the extension of the explored temperature range is concerned. On the other hand, we had trouble with thermostat regulation just below the triple point, due to the high vapor pressure and to the necessity of using thicker layers of argon (above 30  $\mu$ ). Runs carried out very near to the triple point were not reproducible and gave large apparent diffusion coefficient ( $5 \cdot 10^{-9}$   $\text{cm}^2/\text{sec}$ ). Therefore the measurements above 80°K are not reliable.

Between 80°K and 65°K the self diffusion coefficient decreases from about  $10^{-10}$  to  $10^{-12}$   $\text{cm}^2/\text{sec}$ . The diffusion coefficient was calculated from the law of disappearing of the tracer from the vapour phase. The values of D calculated from the penetration curves are not always in agreement with these values but, as a rule, the penetration curves follow the corrected trend for a diffusion law down to zero tracer concentration.

In fig.4 all reliable values of D measured until the present moment are collected. They are grouped as follows

1) First series of measurements made on large crystals, already published; these values were slightly corrected, in order to take into account approximately the effect of the detaching of crystal

from the wall. For this reason the free surface 3 of the crystal was evaluated to be  $1.1 \text{ cm}^2$  instead of  $0.5 \text{ cm}^2$ . Consequently the  $D_0$  value is decreased from  $350 \text{ cm}^2/\text{sec}$  to  $75 \text{ cm}^2/\text{sec}$ .

2) Second series of measurements made on large crystals. The diameter of the crucible was about the same as in 1) but the dead volume was a few times smaller. In these runs the surface of the crystal was found to be slightly bend; the phenomenon of detaching was more extended than in 1).

3) First series of measurements made on thin layers; the first apparatus described in this report was used.

4) Second series of measurements made on thin layers; second apparatus used.

It is seen that the diffusion coefficient measured on thin layers is about 30 times smaller than that previously measured. The points relative to 4) are slightly higher than those relative to 3).

The points obey an approximately linear relationship in a  $\ln D - 1/T$  diagram. However, a slight bending of the curve is apparent, giving a higher activation energy at higher temperature. Since the point at the highest temperatures are certainly affected by errors, we are not sure as yet if the bending of the curve represents a real effect. The point at  $65^\circ\text{K}$  appears to lie outside of the linear law.

From the complete collection of data shown in fig.4, one sees clearly that the value of  $D_0$  <sup>is changed</sup> as the apparatus used is modified, while  $Q$  is not strongly affected, ranging, in different runs, from 3800 to 4200 cal/mole.

As an average the results obtained on thin layers give approximately, from  $80^\circ\text{K}$  to  $70^\circ\text{K}$ ,

$$D_0 = 15 \pm 10 \text{ cm}^2/\text{sec}$$

$$Q = 4120 \pm 100 \text{ cal/mole}$$

These values are in good agreement with those derived, by using the theorem of corresponding states, from Yen's measurements on Xe. It is possible that these values are still affected by small systematic errors and that the true  $D_0$  value is still lower.



In conclusion, we point out that we have finally obtained reliable values of the self-diffusion coefficient of solid argon; these values are still in strong disagreement with those calculated from the activation state theory by Fieschi, Hardelli and Repanai. The reasons for the disagreement are not yet understood.

## THERMAL CONDUCTIVITY

### 1. Introduction

In the final report of the preceding contract, the reasons for carrying out the experiment and the plan of measurements were already discussed. We only want to remind the reader that the experiment is worth to be performed only if one can be sure of the good quality of the crystal. This involves the following problems.

- a) to prepare cylindrical rod of crystalline argon made of a single crystal or at least of a few crystals having a size of the order of the lateral dimension of the rod.
- b) to cool such a rod to the helium temperature without spoiling or damaging the crystal.
- c) to learn how to handle the crystal at low temperature and how to attach to it the heater and the thermometers to be used for the measurement.

For this purpose we had made a preliminary design of the apparatus, which was illustrated in the previous report.

In the present contracting year we were involved in checking the performance of the various parts of the apparatus. These parts were built and checked separately, as described in detail in the following. The final version of the apparatus - as a product of these studies - was finally constructed. No direct measurements of the thermal conductivity coefficient were carried out as yet.

### 2. Experimental

#### a) Purification of argon.

We had first to face the problem of the purification of argon, in order to get a gas having a total impurity content as low as 10 p.p.m. This was accomplished by using very pure argon as a start and by purifying it further by gettering methods. Ba getters were found to be the best purifying agent. Analysis were made by using an ATLAS  $\text{CH}_4$  mass spectrometer. This instrument allows easily to see impurities of water, carbon monoxide and nitrogen, but it is not able to detect oxygen, which reacts completely inside the mass spectrometer, if present in small amounts. Many analyses were carried out to learn out to use the

instrument; we think we are now able to detect impurities (exception made for oxygen) in amounts as low as 10 p.p.m. Further studies are planned in connection with the measurement of thermal conductivity of impure crystals. To avoid contamination of the pure argon, the vacuum and handling line should be very clean; no solvent should be used to avoid contamination of the vacuum grease; a static vacuum of the order of  $10^{-4}$  mmHg must be kept in the line for more than 48 hours. This was accomplished by building a vacuum line, half metallic and half pyrex, easily demountable for cleaning purposes and containing the minimum number of stopcocks and C-rings.

#### b) Preparation of crystals

The part of the apparatus used for preparing the cylindrical rod of crystalline argon was built and checked separately. The method for growing the crystal is based on the same principles already used in the diffusion experiment. The pyrex crucible, 6 to 7 cm. long, 0.57 cm inner diameter, is thermally anchored at both ends to a metal envelope, made of copper, where the thermal gradient, needed for growing the crystal, is established. The gradient is maintained by a small heater situated in the upper part of the metal envelope; the lower part of the envelope is attached to a copper rod which is immersed in liquid nitrogen. The regulation and programming of the temperature is piloted by the same thermoregulating unit already used for the diffusion experiment. The temperature can be held constant within  $\pm 0.02^\circ\text{K}$ . The crystal is grown from the liquid at a rate of 1-2 mm. per hour in a gradient of temperature of about  $1^\circ\text{K}$  per cm. The liquid layer above the growing crystal was several millimeter high, in order to obtain a surface convex toward the top of the crucible.

Good clear specimen of solid argon were prepared in this way, but we were not able as yet to obtain a single crystal in the form of a rod. The best samples were obtained with the slowest growing rates and with the purest argon; in this case, the grain size was about 3 to 4 mm.; the grain boundaries were viewed from the side, after detaching the crystal from the wall

and effecting a thermal attack.

The crystalline rods, prepared as described above, can be detached from the walls of the crucible by slightly pumping above the crystal, provided that the temperature is made uniform throughout the length.

Once the crystal is detached, it can be slipped out from the crucible by pulling it up with the use of an anchor embedded in the upper part of the crystal. The crystal can thus be handled without subjecting it to any strain whatsoever.

c) Cooling of the crystal to helium temperature.

A few runs were performed to study the behaviour of the crystal during the cooling process. It is to be reminded that, since the expansion coefficient of solid argon is high, the crystal must be cooled to helium temperature before the connections to the thermometers are made. It is hoped that with this precaution the thermal contacts, made by using spring clamp, will remain good during the measurement at temperatures above 4°K.

Once the crystal was prepared, it was pulled out of the crucible and suspended in the middle of a glass container situated on top of the crucible, in such a way that its behaviour could be followed by eye from the outside.

The temperature was initially that of boiling liquid nitrogen; the liquid nitrogen was then pumped out at the lowest possible temperature and its evaporation favoured by means of a heater. During this stage the crystal was at an approximate temperature of 65°K, surrounded by its own vapor, at a pressure of 2 cm Hg. It was observed that at this temperature the crystal did not change its shape, while at temperatures nearer to triple point, a deformation of the crystal occurred at the level of the anchor, under its own weight. Before the outer liquid nitrogen was totally evaporated, 10 to 20 cm. of pure helium were introduced in the glass container in order to favor heat exchange and avoid distillation to colder wall as much as possible.

Once the nitrogen had completely evaporated, the liquid helium transfer was immediately started in the dewar. First the

whole apparatus was slowly cooled using the cold helium vapor and finally the dewar was filled with liquid helium. During this process the qualities of the crystal were not appreciably changed; we did not observe any opacity or deterioration of the crystal caused by its high vapor pressure. At helium temperature the rod was still cylindrical in shape, transparent and clear; the diameter was found to be reduced of 2-3 tenths of a millimeter, since some argon did evaporate during the cooling, distilling as a white opaque layer to the surrounding colder walls. The use of helium gas as an evaporation inhibiting agent has given us the means of avoiding the deteriorating effect of a sudden drop of temperature as observed by other authors on crystal with high vapor pressure.

During these experiments, the hardness of the crystal was checked by using a fine needle operated from outside. Just below the melting point, solid argon is very soft, just like butter; it is easily punctured and, if suspended it deforms slowly under its own weight; on the contrary at the helium temperature solid argon is pretty hard and the testing needle hardly penetrates into the crystal.

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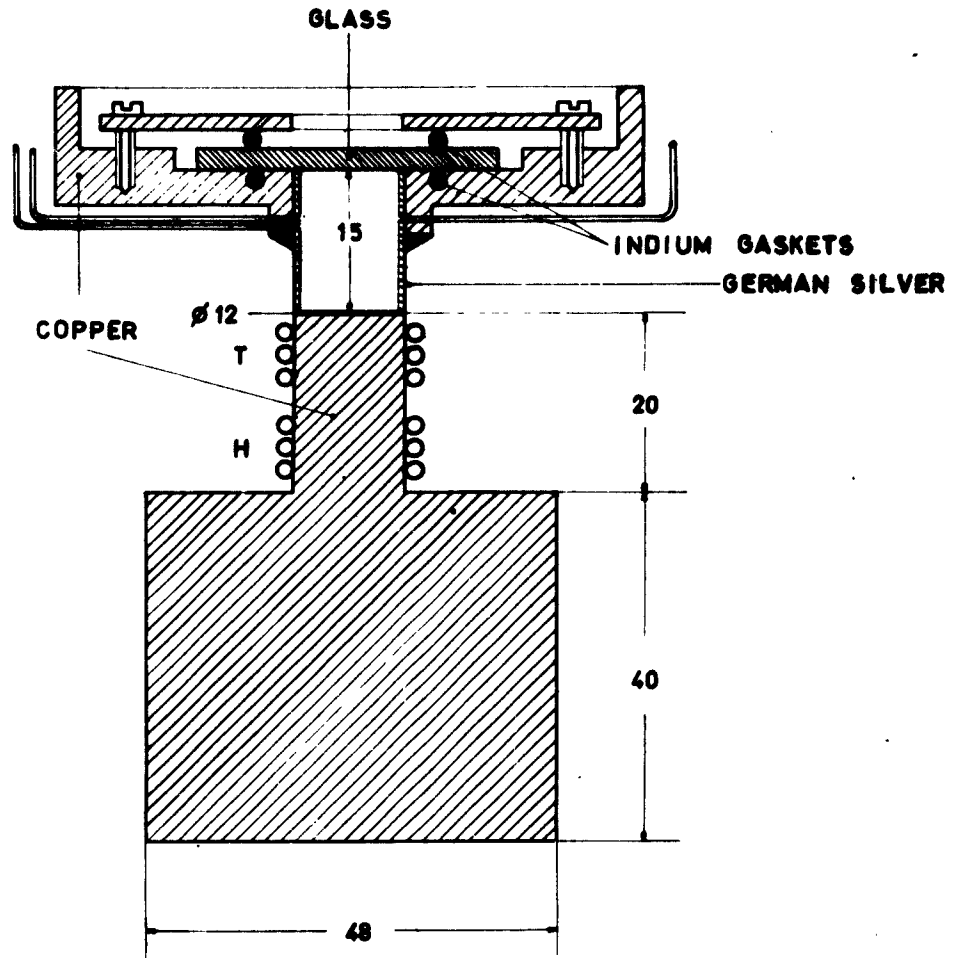
The experiments above described have allowed us to construct the whole apparatus and to plan the experiment to the minor details. The apparatus is now ready; the measurements will be started in the new contracting period.

References

- R. Fieschi, G.F. Hardelli and A. Repanai  
Chiarotti - Phys. Rev. 123, 141 (1961)
- W.H.S. Yen - Thesis (Saint Louis 1962)
- A. Bernè, G. Boato and M. De Pas -  
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Nuovo Cimento (to be published)
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Canadian Journal of Physics.

Figure captions

- Fig. 1. The first apparatus for measuring diffusion coefficient in thin layers.
  
- Fig. 2. The second apparatus for measuring diffusion coefficient in thin layers.  $C_1$   $C_2$   $C_3$  inlet and outlet capillaries;  $T_1$   $T_2$  platinum thermometers;  $R_1$   $R_2$   $R_3$  heaters; A measuring cell; E indium gaskets
  
- Fig. 3. A typical experimental diffusion curve as recorded by the mass spectrometer (second apparatus used). The broken curve shows the theoretical curve from which D is calculated. The penetration curve is obtained from the evaporation curve after making corrections for delay in the capillary and for mixing in the vapor.
  
- Fig. 4. Plot of all values of D, as a function of temperature
  - + First series of measurements on large crystals (corrected surface)
  
  - X Second serie of measurements on large crystals (corrected surface - smaller dead volume)
  
  - ∩ Measurements on thin layers; first apparatus.
  
  - Measurement on thin layers; second apparatus.
  
  - — — — — Yen's results on xenon, after reduction of  $D_0$  and Q values by means of theorem of corresponding states.
  
  - . . . . — Theoretical calculation by Fieschi, Nardelli and Repanai.



H = HEATER

T = THERMOMETER

FIG.1



LIQUID  
NITROGEN  
LEVEL

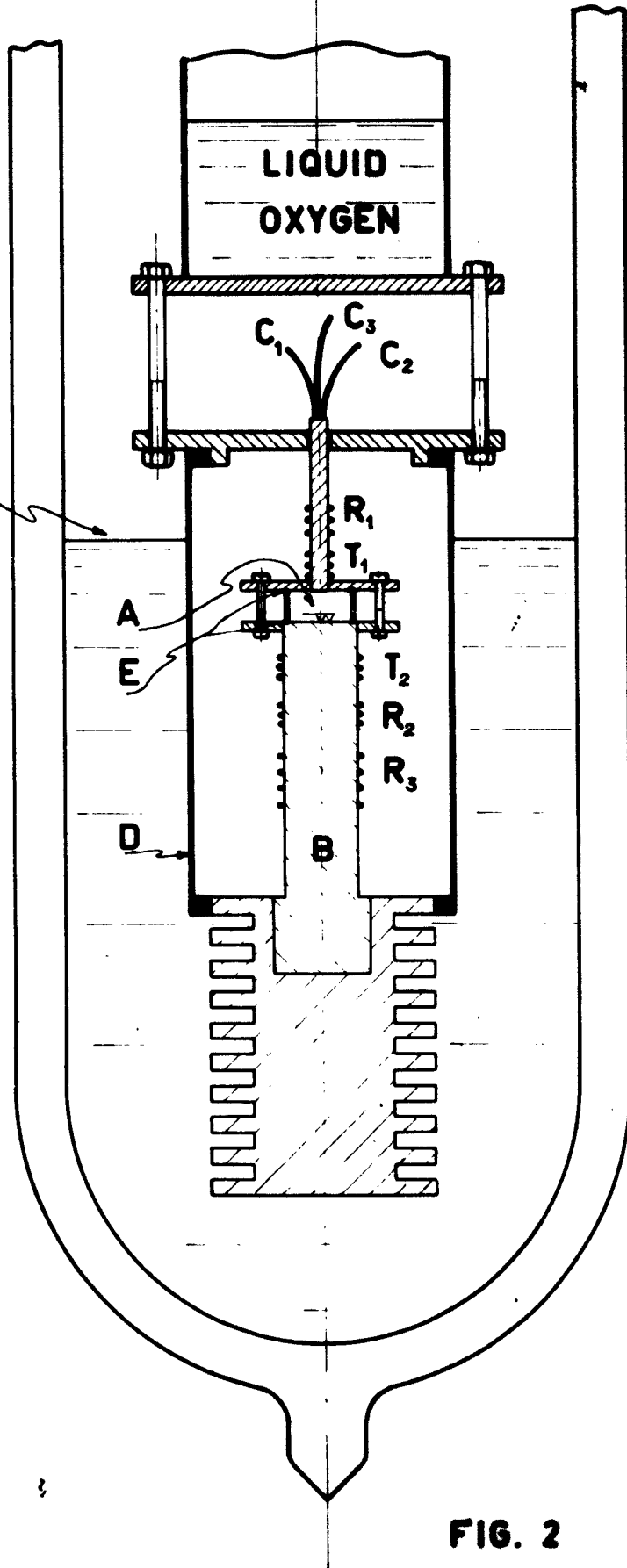


FIG. 2

$C_v C_n$

400

360

320

280

240

200

160

120

80

40

theoretical curve

1

0

4

8

12

16

20

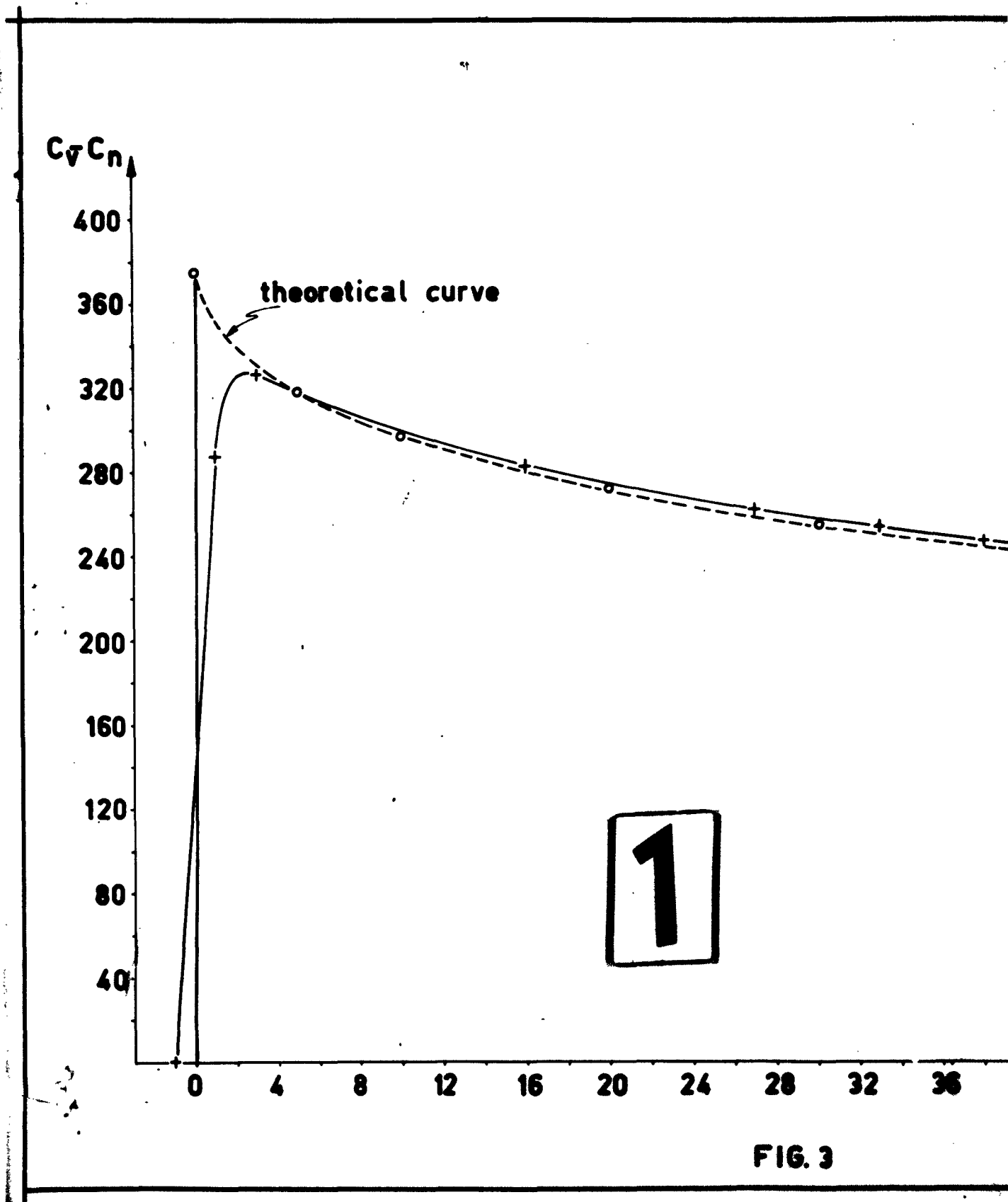
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28

32

36

FIG. 3



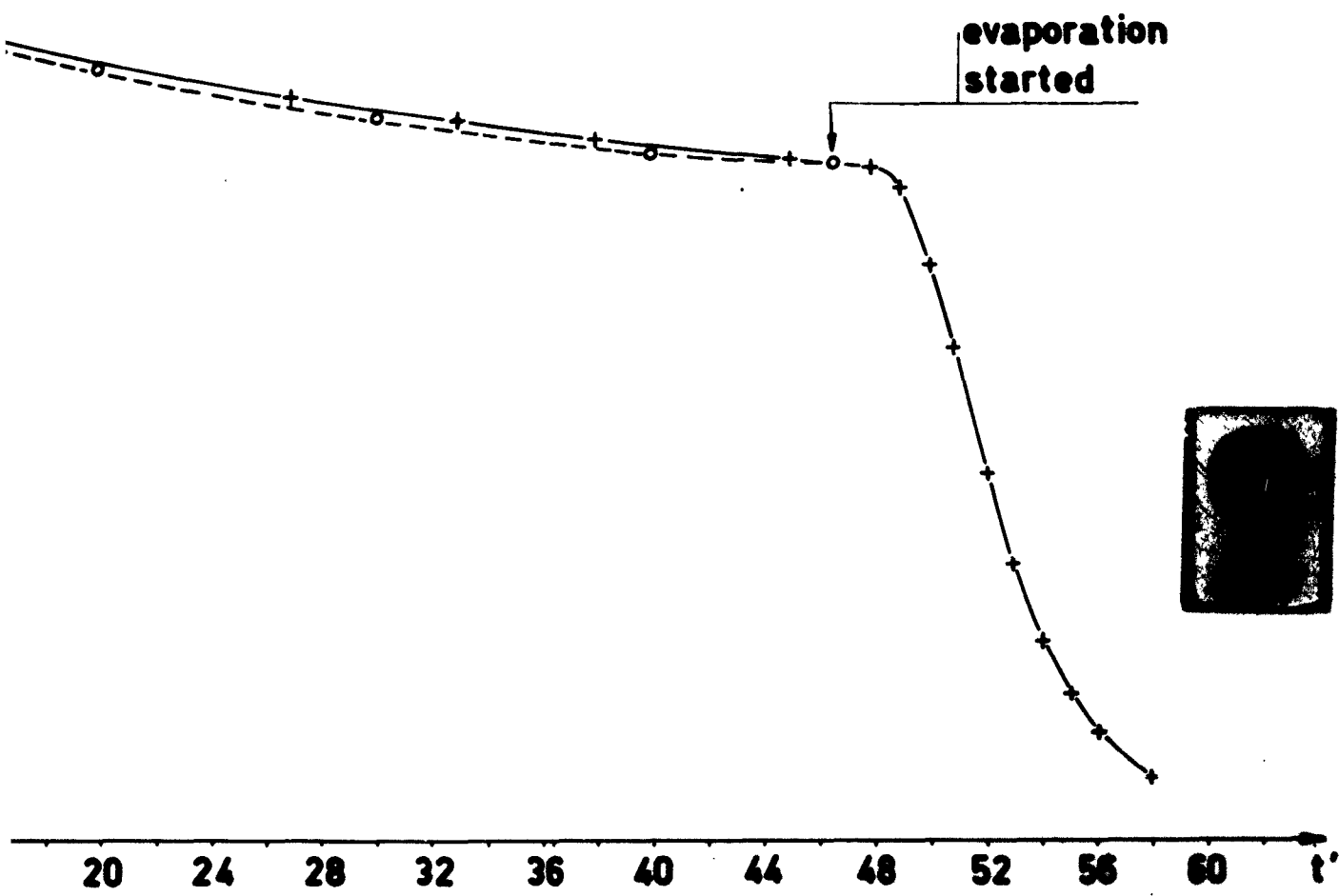


FIG. 3

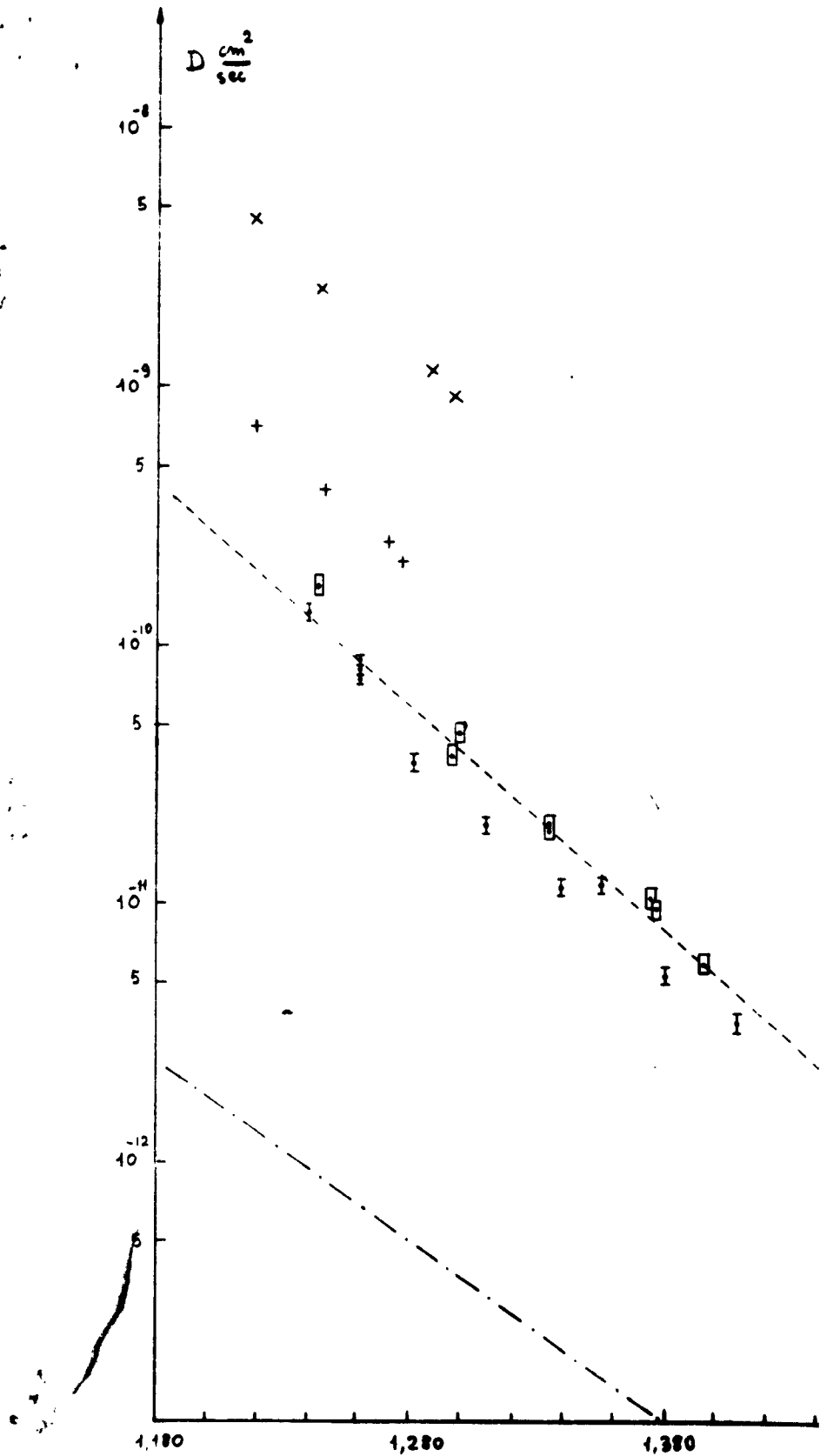


Fig. 4

A N N E X

Personnel utilized during the reporting period

Dr. G. Boato, Dr. L. De Pas and Dr. A. Bernè have continued their part-time activity in this program. In the last six months Dr. De Pas took complete charge of the diffusion experiment; at first the thermal conductivity experiment was care of Mr. Tonti, who took a thesis in the subject. Unfortunately Mr. Tonti left the group in September; after that Dr. Bernè took complete charge of the thermo-conductivity experiment and is now aided by Mr. Pesce, a graduate student. The technicians Mr. Parodi and Mr. Castoldi built mechanical and electronic devices; Mr. Pozzo helped in the diffusion experiment and carried out the mass spectrometric analyses. Dr. Casanova and Dr. Hardelli took part in theoretical discussions of the experiments.

Expenses (unofficial summary)

Dr. L. De Pas	Lit. 1.200.000
Dr. A. Bernè	Lit. 1.200.000
Mr. A. Pozzo	Lit. 1.200.000
Dr. G. Casanova	Lit. 400.000
Dr. G. Hardelli	Lit. 200.000
Mr. A. Parodi	Lit. 200.000
Materials and expendable supplies	Lit. 2.000.000
Administrative services, general expenses, etc.	Lit. 600.000

TOTAL Lit. 7.000.000