A SUMMARY OF THE THESIS
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A study of self-diffusion in plastic crystals has been carried out using radioactive tracer techniques. Single crystals of cyclohexane and pivalic acid were used for the experiments.

The choice of the above compounds was made because of the cubic symmetry of their crystal structures, and because activation energy values for self-diffusion in them had already been published. It was hoped to compare these results, which had been obtained from nuclear magnetic resonance measurements, with those of the present study. The cubic symmetry of the crystals would eliminate the problem of diffusion anisotropy.

Methods were developed for the growth of large single crystals of cyclohexane and pivalic acid from the melt, based on the Bridgman technique. Radioactive forms of the two compounds were evaporated onto the end surfaces of cylindrical portions of their corresponding single crystals and allowed to diffuse. The radioactive cyclohexane was a carbon-14 form, obtained commercially. Tritiated pivalic acid was made by an exchange technique, using pivalic acid and tritiated water. The diffusion periods were, for cyclohexane, 2 to 50 hours in the temperature range -30°C to -60°C and, for pivalic acid, 1 to 2 hours in the range 7°C to 22°C. The crystals were then sectioned parallel to the initial active face, using a calibrated microtome. The quantity of radioactive material which had diffused into each section was determined by liquid scintillation counting techniques. Penetration was found to a depth of 5×10^{-2} cm., in

some cases. The rate of self-diffusion in cyclohexane was also measured by the surface-decrease technique. A thin end-windowed G.M. counter was placed over the initially radioactive face of the crystal and the decrease in surface activity with time was measured.

It was found that the diffusion processes in cyclohexane and pivalic acid, within the temperature ranges studied, could be described by the equations:-

$$D = (6. \pm 3.\ ) \times 10^{6}\ \mathrm{EXP} - \left[\frac{16500 \pm 300}{RT} \right] \mathrm{cm}^{2}\ \mathrm{sec}^{-1}$$

and $$D = (2.25 \pm 1.25)\ \mathrm{EXP} - \left[\frac{10000 \pm 300}{RT} \right] \mathrm{cm}^{2}\ \mathrm{sec}^{-1}$$

respectively. These equations were thought to represent bulk-diffusion in both cases. The pre-exponential factor and activation energy for self-diffusion in cyclohexane are unusually high. This led to the conclusion that a co-operative diffusion process occurs in this crystal. It is considered that diffusion takes place by way of vacant lattice sites into which a number of adjacent molecules have relaxed. In the case of pivalic acid the pre-exponential factor and the activation energy indicate that diffusion occurs by a 'simple' vacancy mechanism with a much lesser degree of molecular relaxation than in cyclohexane.

Pivalic acid is a much harder plastic crystal than cyclohexane, probably as a result of hydrogen-bonding in the crystal. The hydrogen-bond might tend to create a more rigid lattice in pivalic acid, thereby reducing the degree of relaxation about vacancies in the crystal. It is thought likely, therefore, that hydrogen-bonding may be responsible for the apparent difference between the diffusion mechanisms in the two solids.

The activation energies obtained for self-diffusion in the two compounds studied are higher than the corresponding results calculated from nuclear magnetic resonance measurements. This fact, along with existing evidence, indicates that the nuclear magnetic resonance technique is of limited scope for studying diffusion in molecular solids.

This appears to be the only direct study of diffusion made in organic plastic crystals and is one of the few studies of self-diffusion in molecular crystals.

TRACER STUDIES ON THE SOLID STATE

A thesis submitted
for the degree of
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of the
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by
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ABSTRACT

A study of self-diffusion in 'plastic' crystals has been made using radioactive tracer techniques. Single crystals of cyclohexane and pivalic acid were used for the experiments.

Large single crystals of cyclohexane and pivalic acid have been grown from the melt, using methods based on the Bridgman technique. Radioactive forms of the two compounds were evaporated onto the end surfaces of cylindrical portions of their corresponding single crystals, and allowed to diffuse. The diffusion periods were, for cyclohexane, two to fifty hours in the temperature range -30°C to -60°C and, for pivalic acid, up to two hours in the range 8°C to 22°C. After the diffusion periods the crystals were sectioned parallel to the initial radioactive surface, using a calibrated microtome. The quantity of radioactive material which had diffused into each section was determined by scintillation counting.

The diffusion process in cyclohexane was also followed by measuring the rate at which the radioactivity on the surface of the crystal decreased, a thin end-windowed G.M. counter was used for the purpose.

It was found that the temperature dependence of the diffusion processes could be described by the equations

$$D = (6.31 \pm 3.80) \times 10^{6} \text{ EXP} - \left[\frac{16,500 \pm 300}{RT}\right] \text{cm}^{2}\text{sec}^{-1}$$

and $$D = (2.25 \pm 1.25)\ \mathrm{EXP} - \left[\frac{10,000 \pm 300}{RT}\right]\ \mathrm{cm^2 sec^{-1}}$$

for cyclohexane and pivalic acid respectively.

The high values of the pre-exponential factor and activation energy for the diffusion process in cyclohexane led to the conclusion that a co-operative diffusion mechanism occurs in this solid. Diffusion is thought to take place via vacant lattice sites associated with a region of molecular relaxation.

In the case of pivalic acid which is a much harder plastic crystal than cyclohexane, probably as a result of hydrogen bonding, the pre-exponential factor and activation energy for self-diffusion indicate that diffusion occurs by a 'simple' vacancy mechanism. The degree of molecular relaxation about a vacancy in pivalic acid is thought to be slight compared with the corresponding case for cyclohexane.

This appears to be the only direct study of self-diffusion to have been made in organic plastic crystals and is one of the few studies of diffusion in molecular crystals.

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to his supervisor, Dr. J.N. Sherwood, for his unflagging interest in this work and for his ready help, advice and encouragement throughout the period of this research.

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INTRODUCTION

There are two main reasons for studying diffusion in solids. One is that a knowledge of diffusion is fundamental to the understanding of high temperature processes which occur in solids. Thus it is essential for a person making a kinetic study of creep, oxidation, annealing etc., to be familiar with the basic concepts of diffusion.

The second reason for studying diffusion is to obtain information about transport mechanisms of atoms in solids.

The basic laws governing diffusion were first put forward in 1855 by Adolf Fick. The two familiar differential forms of Fick's laws of diffusion are

$$J = -D\frac{\partial c}{\partial x} \quad - \quad - \quad - \quad - \quad (1)$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \quad - \quad - \quad - \quad - \quad (2)$$

Equation one gives the rate of permeation, in the steady state of flow, through unit area of any medium, in terms of the concentration gradient across the medium and a constant, D, called the diffusion coefficient. The second equation refers to the accumulation of matter at a given point in a medium as a function of time. That is, it refers to a non-stationary state of flow.

Solutions of Fick's laws of diffusion have been developed, in order that practical measurements of diffusion coefficients can be carried out under standard conditions. (1)

The first kinetic measurement of diffusion in the solid-state was made in 1896 when Roberts-Austen measured the rate of diffusion of gold in lead (2). Following that initial work a vast number of diffusion measurements have been made in metallic systems and also in ionic crystals. More recently the field has been extended to include valence and molecular crystals.

The diffusion coefficients calculated from experimental results were found to vary with absolute temperature according to an Arrhenius type equation;

$$D = Do \exp \left[-\frac{E}{RT} \right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where D is the diffusion coefficient at a temperature T and R is the gas constant. Do and E are substantially constant for given systems. E is defined as the activation energy for the process and is related to the diffusion mechanism, since it will represent the energy required to move an atom from one equilibrium position in the solid to the next. It is also accepted that Do will be dependent on the diffusion mechanism.

Theoretical interpretations of the values of E obtained from diffusion experiments, have been made, in an attempt to determine probable diffusion mechanisms in particular cases. The commonly accepted diffusion mechanisms in solids, are by way of vacant lattice sites or interstices, or by direct interchange of neighbouring atoms, ions or molecules (3).

Much of the theory of diffusion in the solid state has been derived from diffusion studies in ionic crystals, in which the relation between diffusion and electrical conduction has been important. The relation, called the Nernst/Einstein (4, 5) equation, is

$$\frac{\sigma}{D} = \frac{Cq^2}{kT} \quad \ldots\ldots\ldots \quad (4)$$

where, σ is the conductivity of the ion
D is its diffusion coefficient
C is the concentration of the ion
and q is its electronic charge.

It was thus possible, using this relationship, to make indirect measurements of diffusion coefficients in ionic solids from conductivity data.

One outstanding advantage enjoyed by ionic crystals for such studies is that it is possible to generate known lattice defects and the effect of these on conduction and diffusion properties can be studied (6).

For example the addition of Ca^{++} ions to the NaCl lattice causes the generation of an equivalent number of cation vacancies in order to preserve electrical neutrality within the crystal (7).

Such studies have led to an understanding of diffusion mechanisms in ionic solids and have been indirectly responsible for the evolution of the theory of the defect solid-state (8, 9).

In addition to the work which has been devoted to ionic crystals many studies have been made of metallic systems. Theories of transport mechanisms in metals have been postulated (10) and calculations made, in an effort to forecast the most probable diffusion mechanism in a specific case (11).

As in the case of ionic solids it was possible to use the results of electrical conductivity measurements to obtain information concerning diffusion in metals, using quenching techniques. The latter involve the rapid cooling of specimens from high temperatures such that the high temperature equilibrium concentration of defects is 'frozen in' at the lower temperature. The conductivity of the metal is a function of the number of defects present and hence by quenching the metal from different equilibrium temperatures and measuring the subsequent conductivities, it has been possible to measure the heat of formation of defects in metals (12). The rate at which the defects anneal out at various temperatures has also been followed by conductivity measurements, which have provided a value for the heat of motion of these defects (13).

Initially all direct diffusion measurements in the solid state were concerned with impurity diffusion, in order that a chemical or physical analysis of the diffusing material could be carried out, to provide a concentration profile, from which the diffusion coefficient could be calculated. The increasing availability of radioactive isotopes and their use made it possible, however, to employ the sensitive methods of radiation detection for determining the concentration of a diffusing species.

The use of radioactive isotopes also opened up the possibility of making direct studies of self-diffusion, which is the translational motion of a component within its own lattice. Hitherto this had only been possible by indirect studies, such as those made in ionic crystals and metals, using relations between diffusion and electrical conductivity.

In the case of valence and molecular crystals one is limited to direct studies of diffusion using isotopic tracers and very few measurements have been made on these solids. The only measurements of diffusion in valence crystals have been made on germanium (14) and graphite (15, 16). The result obtained for self-diffusion in germanium agrees well with a theory of self-diffusion which has been developed for valence crystals (17).

Radioactive tracer studies of self-diffusion in molecular solids have been made on sulphur (18), α-white phosphorus (19) and anthracene (20) with widely diverging results. No theoretical treatment has been advanced, so far, which will explain the results available for self-diffusion in molecular crystals and further work in this field seems necessary, to clarify the situation.

The first determination of diffusion in a molecular solid was made by Cremer (21), from the result of a kinetic study of the ortho-para conversion of solid hydrogen. He calculated diffusion coefficients of the order of 10^{-20} cm^2/sec near the melting point, but the activation energy for the process was doubtful, due to the narrow temperature range studied and experimental scatter.

In their study of solid sulphur (18), Cuddeback and Drickamer grew O-rhombic crystals from a saturated solution of CS_2. The radio-active sulphur was coated on to a single (111) face of the crystal and the diffusion rates measured. They obtained two activation energies for the process over different temperature ranges, which they interpreted in terms of diffusion anisotropy. Nachtrieb and Handler followed with a study of self-diffusion in α-white phosphorus (19), because this was a cubic crystal and unlikely to exhibit diffusion anisotropy. The experiments were performed using polycrystalline compacts which were annealed near the melting point for 24 hours, prior to the diffusion experiments, to permit grain growth. The results showed the occurrence of two diffusion processes and the interpretation was that the low temperature process was normal vacancy diffusion, and that, at the higher temperature, was the result of some fairly large scale cooperative process, involving premelting.

Sherwood and Thomson (20) in their study of anthracene found evidence of two simultaneous diffusion processes. In this case radioactive anthracene was deposited on the 001 plane face of a single crystal. Their results showed the occurrence of a slow bulk-diffusion process accompanied by a minor rapid diffusion, which was considered to be the result of grain boundary diffusion.

Another experimental technique which has provided evidence of self-diffusion in molecular solids is that of nuclear magnetic resonance (N.M.R.) (22). In this method a spectrum of the magnetic interactions between neighbouring nuclei is obtained, from which information regarding molecular motions can be derived. A list of organic compounds which have been shown, by N.M.R., to exhibit self-diffusion has been compiled by Andrew (23). Since his list was published evidence has been obtained, using the N.M.R. technique, of self-diffusion in pivalic acid (24) and α-white phosphorus (25). An interesting characteristic of all the molecular solids which have been shown to exhibit self-diffusion by N.M.R., is that they are of the class of solid known as plastic crystals (26). Such solids have a low entropy of melting and the molecules comprising them are always roughly spherical in shape. They have at least one solid-state phase transition, and, in the phase stable immediately below the melting point (phase 1), they have a cubic structure and possess the ability to undergo molecular rotation (27). The latter phenomenom has been observed by dielectric studies (28) and N.M.R. work (29).

It has been noted that the occurrence of self-diffusion, as detected by N.M.R., sometimes does not set in until some degrees above the transition to phase I (the plastic phase), as in the case of cyclohexane (30), whereas with hexamethyldisilane (31), the N.M.R. line width narrows immediately at the II - I phase transition showing the onset of molecular self-diffusion at the transition to the plastic phase.

Evidence of translational molecular mobility in plastic crystals has been strengthened by the fact that they flow easily under low pressure (32) and that their X-ray diffraction patterns in the plastic phase become diffuse as the temperature of the sample is raised (33). More recently a technique involving irradiation of solids and observing the life times of free radicals formed, by electron spin-resonance, has indicated the occurrence of self-diffusion in some organic solids (34). In the plastic solids studied, which include cyclohexane, it has been found that the organic radicals produced at low temperatures exist until the II - I transition, i.e. until the transition to the plastic phase, at which point they rapidly disappear (34). In solids without phase transitions the radicals can exist right up to the melting point, in the case of benzene, however, they disappear 50°C below the melting point.

In spite of all the data now available illustrating the occurrence of self-diffusion in molecular crystals, the amount of detail regarding the diffusion process is slight. The difficulty of analysing N.M.R. spectra with a view to obtaining detailed information about self-diffusion, has limited the calculations, so far, to the evaluation of some activation energies for the diffusion process (35, 36, 37).

Since this work was commenced, Resing (25) has published a detailed analysis of self-diffusion in α-white phosphorus, from data obtained from an N.M.R. experiment. This appears to be the only publication of its kind so far attempted. In his paper Resing does not find agreement with the tracer results of Nachtrieb and Handler (19) and he finds that one diffusion process controls right up to the melting point. Resing has suggested that the high temperature range found by tracer studies (19), could have been caused by the melting out of grain boundaries, which would not affect the N.M.R. results.

From a comparison of diffusion results obtained by the N.M.R. technique and information available from other sources, there appear to be a number of discrepancies. Agreement between N.M.R. and tracer studies concerning self-diffusion has been found for sodium (38), but in the case of molecular solids existing reports are in conflict. The example of α-white phosphorus is a case in point.

N.M.R. studies made on anthracene (39) show no evidence of self-diffusion, but unfortunately, the temperature ranges covered by N.M.R. and tracer work (20) do not overlap, so a definite comparison is not possible. In benzene, however, N.M.R. studies right up to the melting point, do not reveal any evidence of self-diffusion (40), yet the evidence of an irradiation experiment (30) suggests the occurrence of self-diffusion as much as 50°C below the melting point. The latter result appears reasonable on the basis of tracer work on anthracene (20) and naphthalene (41).

The examples quoted above serve to indicate limitations of the N.M.R. technique with regard to the detection of self-diffusion. Both Powles (42) and Rushworth (43) have indicated that a jump frequency of 10^4c/s is required for self-diffusion before it will be detected by N.M.R. Tracer studies, which reveal the effect of an integrated series of atom movements, are not, however, subject to such limitations.

An empirical treatment of molecular self-diffusion has been suggested by Nachtrieb and Handler (19) on the basis of a theory postulated for cubic metals (44) and the validity of this treatment has been supported by some N.M.R. activation energies for self-diffusion (24, 31), but until supporting tracer data is available no satisfactory conclusion is possible.

Several methods are available for obtaining data regarding self-diffusion, utilising tracer techniques. These methods can be divided into two classes, those which involve a direct determination of the diffusion profile and those which give an overall picture of diffusion. An important technique of the latter class is the surface-decrease method which is based on the fact that the radiation from an active source is exponentially absorbed in the solid surrounding it. Hence if a layer of radioactive material is deposited on the surface of a specimen and allowed to diffuse into it, there will be a decrease in the count rate measured from the surface, which can be related to the rate of diffusion of the isotope.

The method whereby a direct determination of the concentration profile of the isotope is measured and from which the diffusion gradient is obtained, has the advantage of being able to reveal the presence of concurrent diffusion processes. A mathematical extension of Fick's laws of diffusion has been carried out such that diffusion coefficients may be readily determined using systems of standard geometry (1).

The system which has been most extensively employed is that in which an infinitely thin layer of an isotopic tracer is deposited on to an end surface of a right cylinder and allowed to diffuse inwards, until the tracer has reached a suitable depth, after which, the specimen is sectioned. The sections are taken parallel to the initial face and are of constant cross section. By measuring the isotope concentration in each section it is possible to construct a concentration versus depth of penetration, curve, from which a diffusion plot can be obtained and hence the diffusion coefficient for a given temperature.

One unfortunate consequence of the sectioning method is that it automatically involves destruction of the sample. This precludes the possibility of carrying out more than one diffusion experiment on each specimen, an advantage enjoyed by the indirect method employing conductivity measurements. In the case of the procedure described above, it is obviously desirable that each specimen of the same solid should be as similar as possible to the next, in order that conditions for diffusion within the samples are similar. One of the best ways of achieving this end is to use single crystal specimens grown from one batch of pure material under standard conditions. In this way side-effects which might arise from using compressed polycrystalline samples would be avoided. The latter specimens would be liable to provide short-circuiting paths for self-diffusion, as a result of the many grain-boundaries which they would contain, and this could seriously affect the measurement of bulk-diffusion.

In view of the very limited state of knowledge concerning self-diffusion processes in molecular solids, and because of the conflicting evidence which exists between results obtained from N.M.R. studies and those derived from other techniques, regarding molecular mobility, it seemed desirable that further tracer work in this field should be carried out. Since most of the evidence for self-diffusion in molecular crystals has been derived from N.M.R. studies of plastic crystals, it was decided to make a radio-tracer study of one or more of these solids. Such a study would be facilitated by the fact that in the plastic phase all these crystals have a cubic structure and hence the problem of diffusion anisotropy would not occur. The purpose of such a study would be as follows:-

1. To ascertain the occurrence of self-diffusion.
2. To determine the activation energy for the diffusion process.
3. To ascribe possible mechanisms to the self-diffusion process.
4. To compare the results obtained with existing N.M.R. results.

At the commencement of this work all the compounds which had been shown by N.M.R. to exhibit self-diffusion, had low melting points, and only a few activation energies were available for some of these solids. In an effort to avoid undue experimental difficulties it was decided to choose a compound with a relatively high melting point and one which was readily obtainable. Since the temperature range which was available for study lay between the melting point and the temperature of the II - I phase transition, it was desirable that this interval should be wide enough to permit a reasonable range of diffusion measurements to be made. Thus it was considered that the compound to be studied should fulfil the undernoted requirements.

1. The compound should exist in the plastic phase through a sufficiently wide temperature range.
2. There should be, in existence, an activation energy for self-diffusion, derived from N.M.R. data of the compound.
3. It should be possible to grow large single crystals of the compound.
4. It should be possible to obtain reasonable quantities of the compound in a very pure form.
5. There should be a ready synthesis of a radioactive form of the compound, or such a form should be commercially available.

Initially cyclohexane was chosen for study because it possessed most of the properties described above. Later, data became available for pivalic acid and a second study was made of this compound.

CHAPTER I

EXPERIMENTAL TECHNIQUES

.1.A. The growth of single crystals of cyclohexene.

(i) INTRODUCTION

The single crystals required for the diffusion experiments had to be very pure and of a reasonable size, dimensions of the order of centimetres being required. Such requirements limited the methods of crystal growth which could be employed.

The methods available for growth of organic crystals are: growth from a saturated solution, growth from the vapour phase and growth from the melt.

Growth of organic crystals from the vapour phase generally results in the formation of very thin crystals of limited dimensions (45, 46, 47). Due to the excessive solubility of cyclohexene in most solvents, the problem of obtaining a suitably saturated solution (48) from which to grow crystals could be complex. The latter method also presents the possibility of solvent inclusion in the crystal, which would render the growth of very pure crystals impossible. The final method, namely, growth from the melt, has been used with success for the growth of large single crystals of organic compounds (49) in the past, and is not subject to the disadvantages of the previous methods. It was decided, therefore, to adopt this latter technique.

Growth of crystals from the melt can be carried out in one of three general methods. These are the Kyropoulous (50) technique and the moving and stationary vessel techniques (51, 52).

In the first of these methods a cooled seed crystal is suspended into a melt and slowly withdrawn. Surface tension effects cause the adhesion of material from the melt to the seed, which grows, as it is raised from the hot region of the melt. If the rate of withdrawal is slow enough the crystal will grow epitaxially on to the lattice of the seed crystal forming a large single crystal. This method would be unlikely to succeed for organic crystals due to the high vapour pressure which such a melt would often have and also to the low surface tension of the liquid.

The remaining methods, in which the melt can be completely isolated during the growth process, have both been successfully employed for the growth of single crystals of organic compounds (53).

Both methods require a growth chamber in which a temperature gradient with horizontal isothermals can be maintained. The temperatures of the isothermals usually vary from about 30° above the melting point of the solid crystal to 30° below it. The methods differ in application of the temperature gradient to the melt. Fig. (1) represents the temperature gradient schematically, in which AB represents the melting point isothermal, Tm. The material is put in the tube (V) and allowed to melt in the upper part of the crystalliser, i.e. above AB.

For the moving vessel technique the temperature

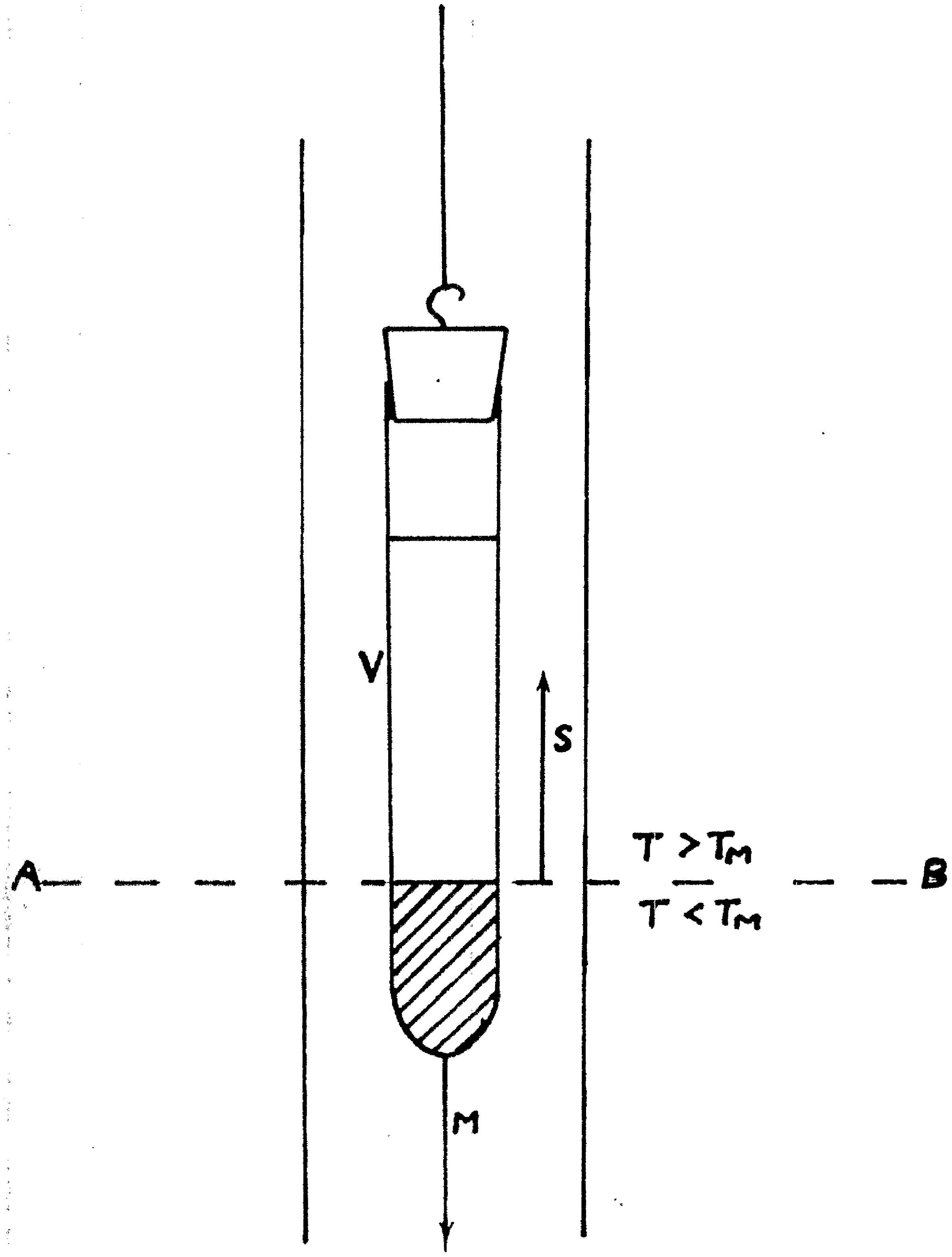


FIG. 1. TEMPERATURE GRADIENT

conditions in the crystalliser remain static and the tube, V, is slowly lowered down the gradient in the direction M, causing crystal growth to proceed up the tube, with the solid/melt interface always lying on AB.

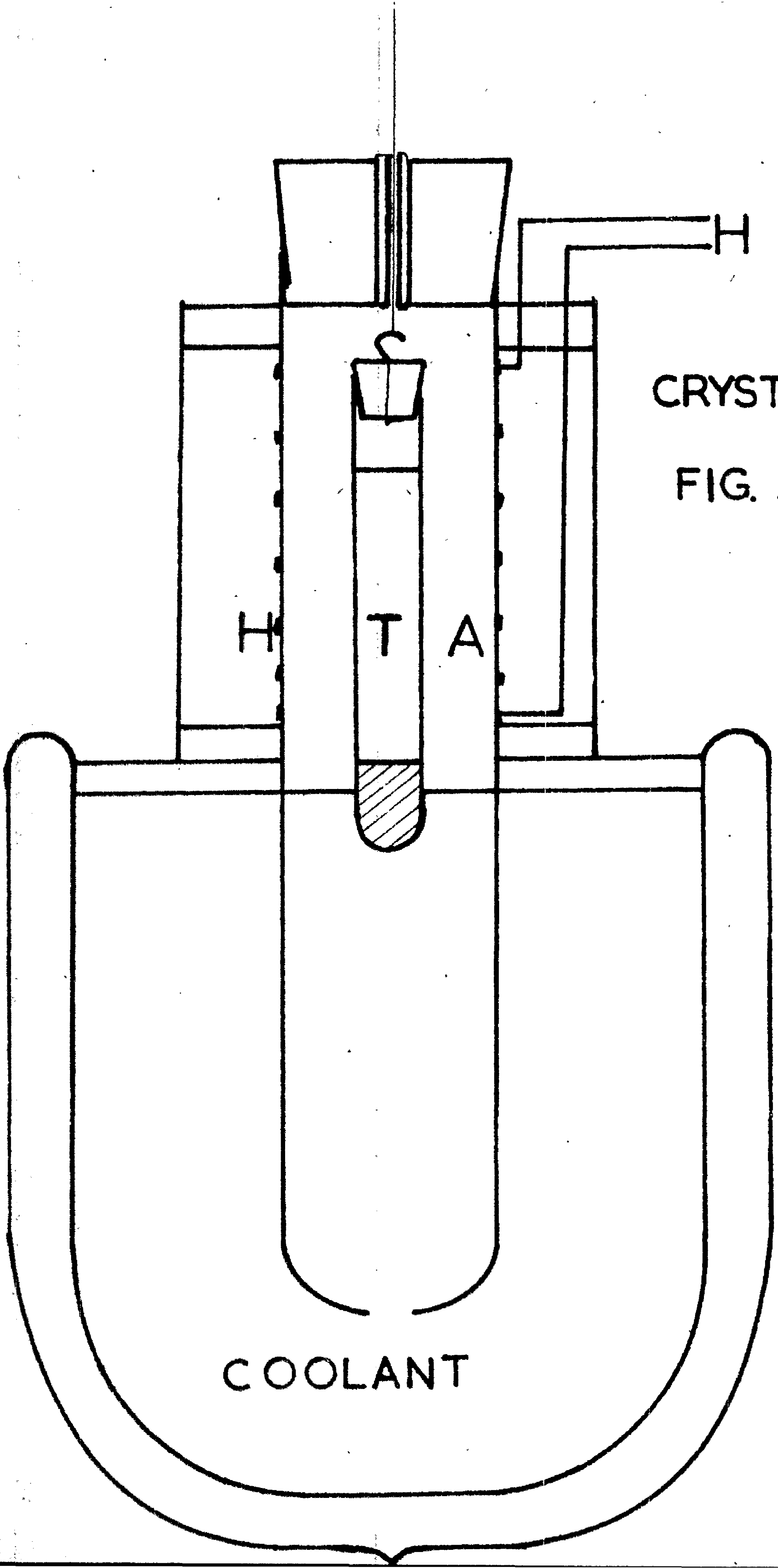
The stationary vessel technique differs from the above in that here the vessel containing the melt is held static, and the melting point isothermal AB is allowed to move upwards past the vessel, V, by lowering the heat input to the growth chamber, see arrows in fig. (1).

It was decided that the attainment of static temperature conditions and variation of the growth rate by mechanical means, as required by the moving vessel technique, would be more readily achieved, and hence that method was employed.

Since the melting point of cyclohexane is below room temperature [6.55°C, (54)], the establishment of a suitable temperature gradient required the use of a cooling mixture, or a refrigeration unit. The former was eventually found to be adequate.

(ii) THE ESTABLISHMENT OF A TEMPERATURE GRADIENT.

The formation of a temperature gradient was established inside a pyrex glass tube (A), 45 cms., long and 2.6 cms., in diameter, which was mounted in a vertical position. The upper half of the tube was warmed by a nichrome heating coil (H) of 90Ω resistance and insulated by a concentric glass sleeve, while



CRYSTALLISER

FIG. 2.

cooling of the lower half was achieved by suspending it in a suitable freezing mixture, [see fig. (2)]. The temperature gradient was varied by altering the voltage applied to the nichrome heater and by changing the coolant surrounding the lower half of A.

Prior to crystal growth the tube containing the cyclohexane was suspended in the upper half of A, until it had reached a temperature equilibrium with its surroundings. It was then slowly lowered down the temperature gradient by means of an electric clock motor fitted with a variable gear system, which allowed a wide range of growth rates to be studied.

The initial temperature conditions employed, were obtained by suspending the lower part of A in an ice/water mixture and varying the temperature of the top section from room temperature (16°C) to 50°C. In spite of the slow growth rates employed, often less than 1 mm. per hour, no evidence of single crystal growth was found. After several attempts at crystal growth using a variety of cooling mixtures, partial success was achieved using a very steep temperature gradient. The latter was obtained by dipping the lower half of A into a two litre Dewar flask filled with an acetone/Drikold slurry (-78°C). [Temperatures below -78°C were undesirable because cyclohexane undergoes a crystallographic phase transition at -86°C.] The upper half of the tube A was heated to a temperature of 40°C. With this arrangement and a growth rate of 1 mm. per hour, small clear

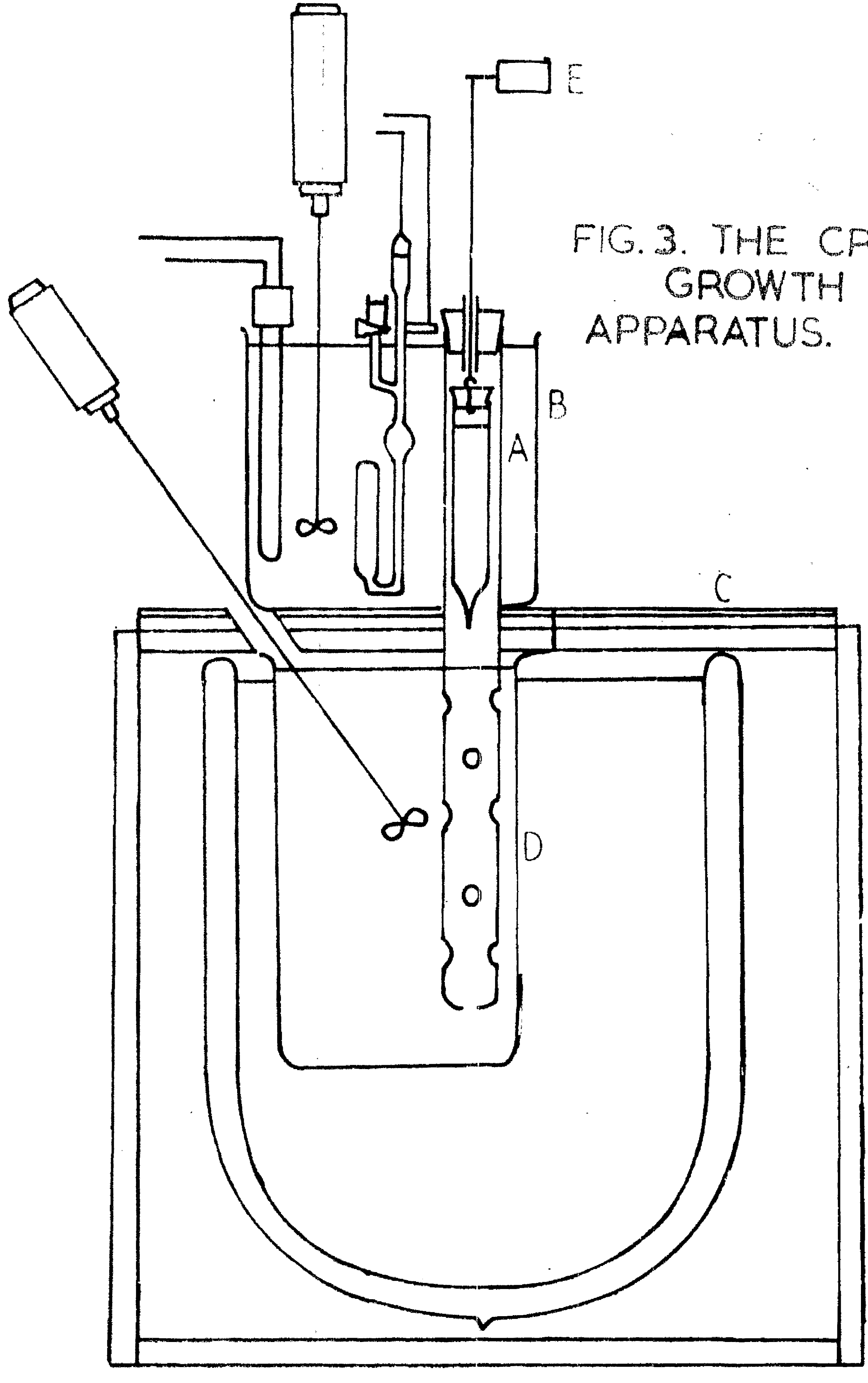


FIG. 3. THE CRYSTAL GROWTH APPARATUS.

pieces of crystal were formed at the base of the growth tube, the remainder being a white polycrystalline mass.

The base of the growth tube, which had been rounded, was now drawn out to form a tapering capillary which it was hoped would help to eliminate polycrystal growth. (55) It was found that lowering of the growth tube did now result in the formation, at the mouth of the capillary, of a single crystal portion which tended to grow into the main part of the tube. Although there had been an improvement of the crystal portion at the foot of the growth tube the quality of this crystal varied considerably and it was decided at this stage to try to improve the temperature stability of the apparatus.

The thermal capacity of the cooling section was increased with the aid of a fifteen litre Dewar flask, such that continual replenishment of the coolant during crystal growth was not required. The Dewar flask was housed in a large wooden box, the lid of which served as a support for A and a tall two litre beaker, (fig. 3) which was suspended in the acetone/Drikold slurry. The lower half of A dipped into the two litre beaker which was filled with acetone, the latter was stirred, and cooled by the surrounding slurry. This arrangement resulted in a more even temperature control of the cooling section and resulted in the production of better crystals, the quality of which, still varied somewhat. In order to stabilise the heating system, which

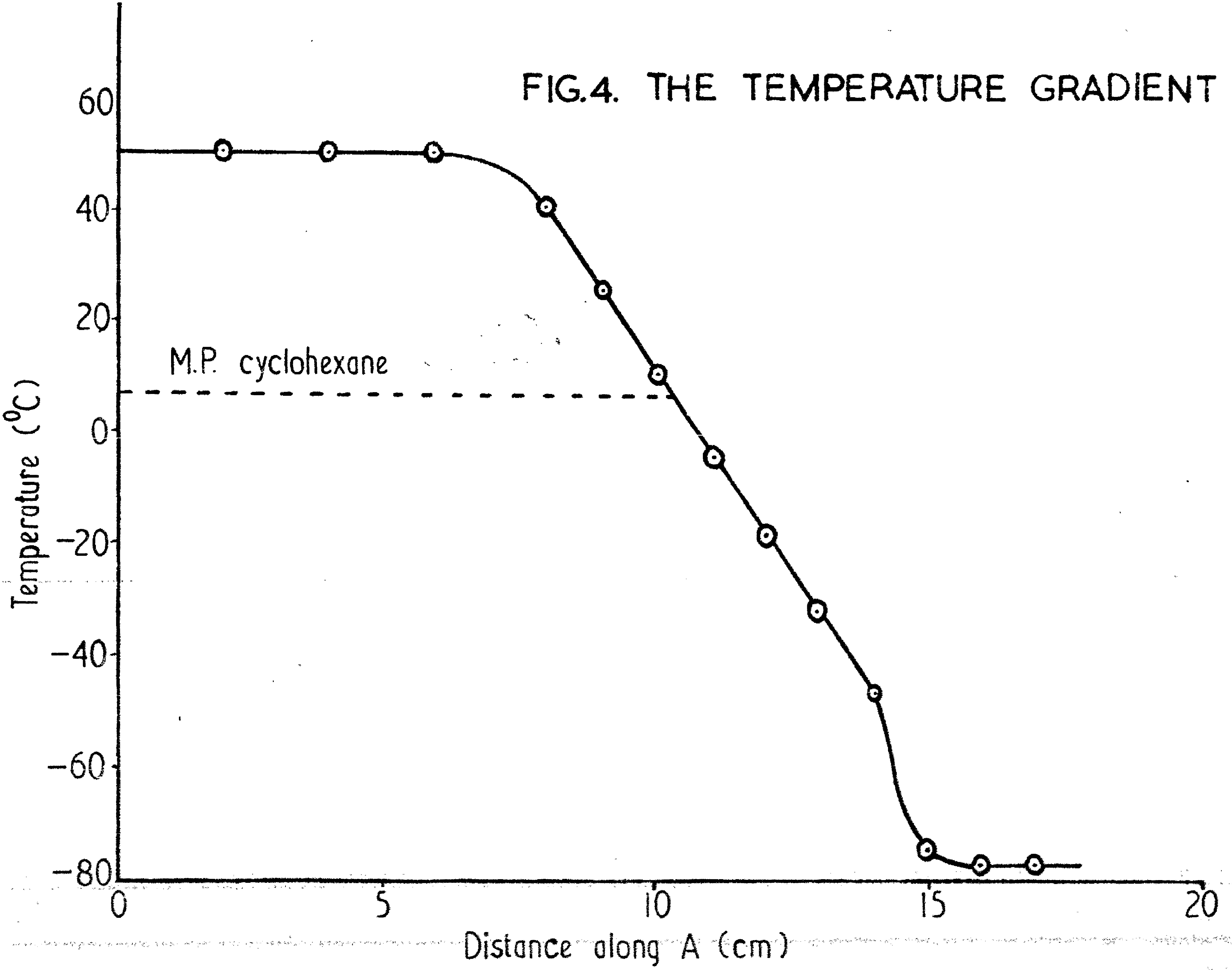


FIG.4. THE TEMPERATURE GRADIENT

was subject to fluctuations of room temperature and of the mains voltage to the heater transformer, another means of heating was employed.

The final design illustrated in fig., (3) incorporated what was essentially a water jacket heater for the upper section of A and a cooling unit for the lower half, as previously described. The pyrex tube A was sealed through the base of a two litre beaker B. The tube A was 45 cms. long and 2.6 cms. in diameter and the top of A was level with the rim of B which was 20 cms. high. The beaker (B) filled with water was heated with a 700W. immersion heater and the temperature of the water was controlled by a toluene regulator and associated electronic relay to ± .1°C.

The lower half of A protruded 25 cms. through the supporting board C, into the tall two litre pyrex beaker, D, which contained the cooled acetone.

The slope of the temperature gradient which proved most successful was obtained by heating the water in B to a temperature of 50°C. This gave rise to a temperature drop of 128C° between the hot and cold stages of the apparatus. The temperature gradient obtained is shown in fig., (4), and represents a slope of 15 deg C cm^{-1} at the melting point of cyclohexane.

(iii) PURIFICATION OF CYCLOHEXANE

Under the conditions good quality crystals were obtained in the lower portion of the growth tube which was about 15 cm., long, 2 cm., in diameter and had a tapering capillary tip of 3 cm., length. It appeared obvious that the reason for the deterioration of the crystal quality was the result of impurities being concentrated in the melt as crystallisation proceeded, until a point was reached when single crystal growth was no longer possible. (56) Melting point determinations on such a crystal showed that the impurity content in the single crystal portion was low, reaching a concentration of .46 mole % at the interface between single crystal and polycrystal sections. Since very pure crystals were required it was necessary to purify the starting material rigorously.

The starting material for the crystals had been McFarlans' "reagent grade" cyclohexane, melting point, 2.41°C, with an impurity content of 1.73 mole %. This was purified by recrystallising four litres of it slowly, in a deep freeze, and retaining the first solid fraction of two litres, melting at 4.1°C. This was melted and scrubbed with a 3 : 1 mixture of concentrated sulphuric and nitric acids at 10°C to remove unsaturated impurities. After separation from the acid layer the cyclohexane was washed with sodium hydroxide solution followed by distilled water. The cyclohexane was then distilled through a long packed column to yield 500 mls., of dry distillate (melting point, 5°C) which was stored over sodium wire. Further recrystallisations at this stage showed little improvement in the purity of the product; after four recrystallisations the cyclohexane melted at 5.4°C.

Because the single crystal pieces obtained from growth of the original starting material had shown such a marked refinement, it was decided to use this technique to purify further the cyclohexane melting at 5°C. It was felt that this would obviate the long and tedious series of recrystallisations which would otherwise be necessary to obtain the desired pure material. Using the purified material it was found that the crystals which were grown were almost completely clear, only a small fraction near the top of the growth tube was polycrystalline. It was decided to return the upper half of these crystals for repurification and retain the lower half which melted at 6.48°C (impurity content .03 mole %) for growth of the final specimens. The crystals grown from the latter material had a melting point of 6.53°C (impurity content .01 mole %).

It was never found necessary to degas the cyclohexane prior to crystal growth. The capillary tip of the growth tube was filled by gently boiling a small quantity of cyclohexane at the foot of the tube after which the remainder of the tube was charged. The tube was sealed off with a cork and suspended in the chamber, A, (figure 3) by means of a thread connected to the spindle of the lowering motor.

The final crystal specimens were completely clear and free of all visible defects. They were stored in a deep freeze at -25°C. The crystals were never observed to suffer thermal shock as a result of transfer from conditions at -78°C to -25°C.

The size of the crystals was from 8 to 10 cm., long and 2 cm., in diameter. They were removed from their growth tubes by warming the sides of the tube and sliding the crystals out. The solid cylindrical crystals were kept in a sealed storage jar in the deep freeze, until required.

Due to the size restrictions forced upon the growth tubes by the dimensions of the apparatus as originally constructed, and also because of the tendency of the seal between A and B to crack, an enlarged version of the apparatus described in fig., 3 was constructed. The beaker B was replaced by a copper can, 25 cm. high and 12 cms. in diameter, the pyrex tube, A, was replaced by a similar tube 50 cm. long and 5 cm. in diameter,which was sealed by Araldite into the base of the copper can. This enlarged version allowed growth of bigger crystals and enabled a more rapid purification of cyclohexane to be made. It was found, however, that with crystal growth tubes having an inside diameter in excess of approximately 3 cm. that the crystals tended to become polycrystalline. This could perhaps have been due to the inability of the crystallising melt to dissipate its heat rapidly enough to the solid crystal below it. The wider the crystal the slower will be its rate of heat transfer from the centre to the walls of the growth tube and hence there may be a critical diameter beyond which single crystal growth is not possible. The size of the growth tubes used for purifying the cyclohexane was usually about 20 cm. long by 3 cm. in diameter.

1.B. The Growth of Single Crystals of Pivalic Acid.

An apparatus similar to that already described for cyclohexane crystal growth was used, the main difference between the two crystallisers being the replacement of the acetone/drikold slush bath by a mains-water cooled bath. The latter consisted of a water filled, insulated glass thermostat tank, in which was immersed a long copper coiled-tube through which mains-water was constantly passed. It was found that the temperature of the water in this bath, when stirred, fluctuated little, and was sufficiently stable for the purpose required. The temperature of the cold section of A under these conditions was 12°C ± .2C°. Heat for the top section of the tube, A, was supplied from a thermostatted water bath as previously described, the temperature now being maintained at 60°C. The freezing isothermal for the molten pivalic acid (35.5°C) lay about 1 cm. above the surface of the cold water level in A.

Using these conditions and employing a growth rate of 1.2 mm/hour, as with the cyclohexane, it was found possible to grow good single crystals every time. The apparatus in which the pivalic acid crystals were grown was of all glass construction and it was possible to observe growth of the crystal in the crystalliser. The purification of pivalic acid was carried out by performing one single crystal growth on a sample of pivalic acid from Messrs. B.D.H., [reagent grade (m.p. 34.02°C)] retaining the lower half of the clear single crystal piece and growing the final specimens from this material (m.p. 34.94°C). The melting point of the pivalic acid in the final crystals was 35.38°C. (Impurity content .04 mole %)

The crystals of pivalic acid thus obtained were optically clear and appeared isotropic through the polarizing microscope, they were easy to cut at room temperature, but were not as soft as the cyclohexane crystals. No obvious cleavage planes were found to exist, but it was possible to fracture the crystals by dropping them onto a hard surface, the fractures occurred in a completely random fashion.

2A. The Preparation of Cyclohexane-1-C14 for Deposition.

The radioactive cyclohexane used for the tracer studies was obtained from the "Radiochemical Centre", Amersham. The cyclohexane was contained as a vapour in a breakseal tube, which contained .1 mc (millicuries) of cyclohexane-1-C14. The batch number of the sample was - P/N No., 014342 CFA 131.

In order to obtain a reasonable working concentration of the radioactive material which was supplied at a concentration of .1 mc/m mole, a theoretical estimate was made of the specific activity which would yield a good penetration of activity into a cyclohexane crystal from a thin surface deposit.

2A. 1. Calculation of the Desired Activity for the Radioactive Cyclohexane.

The calculation was based on the assumptions -

(1) That measurable diffusion would occur to a depth of 100 microns.

(2) That a self-diffusion coefficient of the order of 10^{-10} $cm^2/sec.$ would prevail.

(3) That the surface layer of the active cyclohexane would be 1 micron deep.

(4) That a count rate of 20d/s would be obtained from a slice 10 microns thick at a depth of 100 microns from the crystal surface.

(5) That the conditions would allow the valid application of a diffusion equation derived for an infinitely thin source diffusing from a right end face into a semi-infinite cylinder.

The supposition of a diffusion coefficient of 10^{-10} cm^2/sec. seemed reasonable on the basis of existing diffusion coefficients which have been published for molecular solids (18, 19, 20). Assumption number four was made in order that a reasonably accurate measurement of activity could be made in a fairly short time using an efficient counting system.

The estimate of the desired activity is based on an equation which relates the concentration of a diffusing species at a distance, X (cm), from the source after a given time, t (seconds), to the diffusion coefficient, D, of the species (1). The equation is:-

$$C = \frac{Q}{\sqrt{\pi Dt}} \exp \left[- \frac{X^2}{4Dt} \right] . \quad . \quad . \quad . \quad I.1.$$

in which Q is the initial activity of the source.

Considering a diffusion time of 48 hours and a diffusion coefficient of 10^{-10} cm^2/sec., the equation becomes:-

$$C = 100.Q. \exp - (X^2 \times 10^4).$$

If X is 100 microns:-

$$C = 100.Q. \exp - \left[(100)^2 \times 10^{-8} \times 10^4 \right]$$

$$\doteq 37Q.$$

Allowing for a count of 20d/s from the last slice 10μ thick, the volume of the slice is, $\pi r^2 h = 10 \times 10^{-4} \times 1$ (assuming a c. s. a. of 1 cm^2)

$$= 10^{-3} \text{ cm}^3,$$

and the number of counts from the slice = $C \times 10^{-3}$, the value of C becomes

$$C = 2 \times 10^4 \text{ (c/s)/cm}^3$$

This leads to an activity of 500c/s for Q, or .01μC.

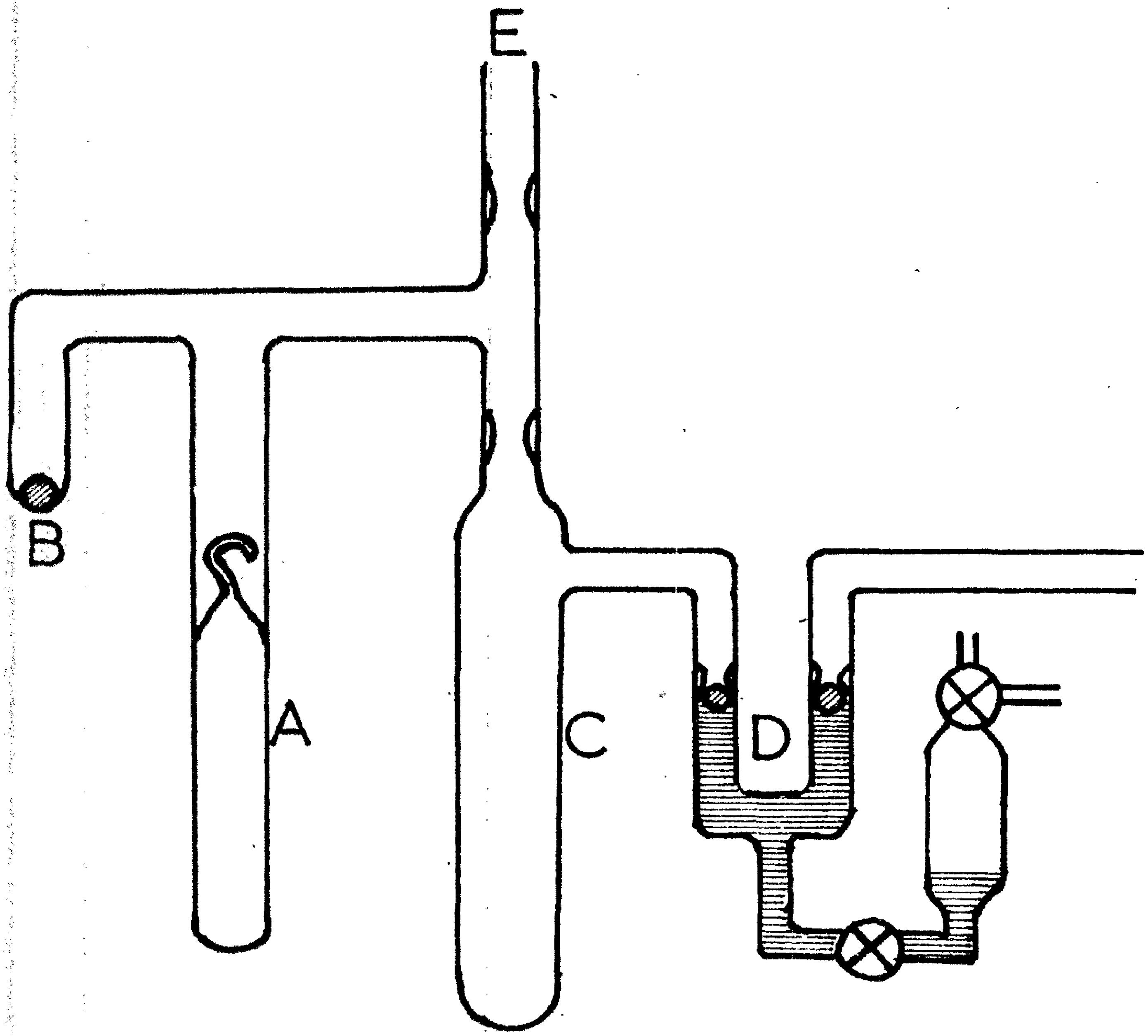


FIG.5. DILUTION OF C-14 CYCLOHEXANE

If the surface layer is 1 μ thick, then the concentration of the surface layer is $\frac{\text{activity}}{\text{volume}}$, (C/S)/cm^3, which gives:-

$$Cs = \frac{500}{1 \times 10^{-4}} (C/S)/cm^3$$
$$= 100 \quad C/cm^3$$

$$= .1 \ mC/cm^3$$

Hence a concentration of 100μC/cm^3 would provide sufficient activity for the surface layer to fulfil the conditions assumed. It was therefore decided to dilute the cyclohexane to this level for the experiments.

A. 2. Dilution of Cyclohexane-1-C14.

The apparatus used for the dilution of the cyclohexane-1-C14 is shown in figure 5. 1 ml. of pure cyclohexane (m.p. 6.53°C) was pipetted into the storage bulb (C), which was connected to a vacuum system used for the depositions of the radioactive cyclohexene, as in figure 8. The glass neck, E, (figure 5) used for entry of the pipette was then sealed off and the cyclohexane in C degased by cooling C with liquid nitrogen and pumping on the cyclohexane, closing off bulb C and allowing it to warm up, before recooling it and pumping again. This cycle was repeated several times until no further gas could be detected.

With the mercury seal closed the steel ball (B) was lifted over and dropped on to the breakseal of A, thus allowing the radioactive vapour to condense into C at liquid nitrogen temperature. The constriction at the top of C was sealed off leaving the radioactive

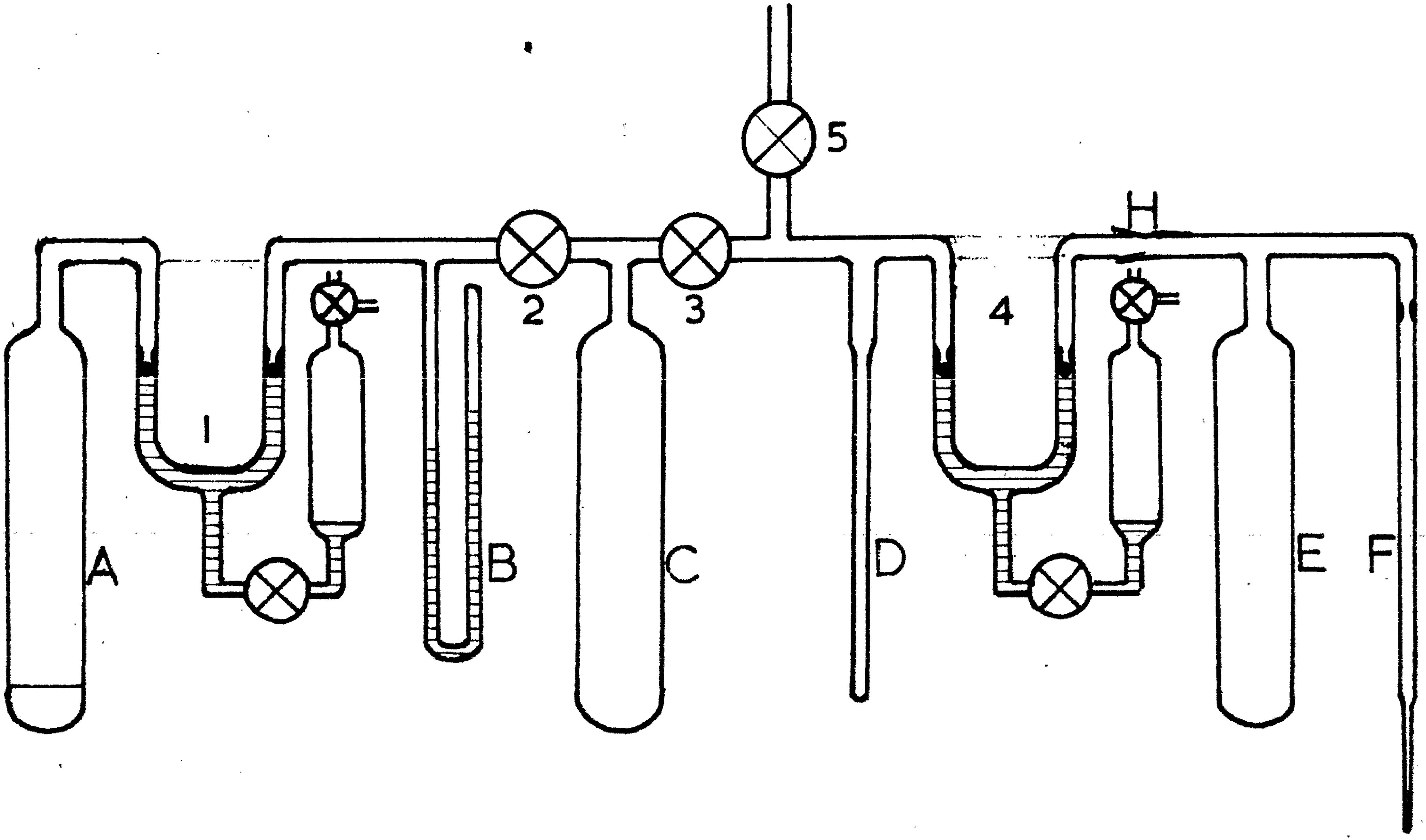


FIG. 6. TRITIATION APPARATUS

cyclohexane in C ready for use, when required. The radioactive strength of the cyclohexane in C was later checked and was, in fact, found to be .1 mC per ml.

.B. The Preparation of Radioactive Pivalic Acid.

The obvious method of preparation of radioactive pivalic acid was to make a C^{14} labelled form. However it had been shown that an organic acid labelled with H^3 showed similar diffusion rates to a carbon-14 labelled form (57). The electrical conductivity of solid pivalic acid in the plastic phase has been shown to be negligible and the absence of proton diffusion is inferred (58). It thus appeared that a tritium labelled form of pivalic acid would suffice for the self-diffusion studies intended.

The method of tritiation was simply to allow a specific quantity of tritiated water to undergo exchange with a known amount of pivalic acid in a suitable vessel. The apparatus used for the tritiation is shown in figure 6.

The source of the tritiated water was retained in bulb A and had a concentration of 1 curie per gram. It was cut off from the remainder of the apparatus by a mercury seal, 1. The transfer of tritiated water was carried out by allowing the vapour pressure of the water in A to saturate the evacuated volume of bulb C, with valves 1 and 2 open and 3 shut. The vapour pressure was recorded on the manometer, B, and hence the quantity of water in the known volume of C could be calculated. Taps 2, 4 and 5 were closed and the capillary, D, was cooled with acetone/Drikold., tap 3 was then opened and the vapour from C allowed to condense into D after which tap 3 was closed. The length of the water column in D provided a secondary means of measuring the water transferred from A. The water in D was used for tritiation in E by opening the mercury seal (4) and allowing the water to condense into E.

The tritiation of the pivalic acid was carried out as follows. A piece of 3 mm. bore tubing was drawn out at one end to form a sealed capillary tip and the other end of the tube (F) 10 cms long, was joined to a 1 cm. glass tube by means of a constriction. To this latter tubing was also joined the exchange bulb (E), 15 cms long by 2 cm. in diameter, and a B14 cone. A sample of pivalic acid (m.p. 35.3°C) and weighing approximately 1 gram, was put into bulb, E, and the side extension was joined to the vacuum line by the B14 cone and socket (M).

D and E were then cooled in liquid nitrogen and valves 4 and 5 opened to allow the evacuation of the extension, after which tap 5 was shut and D was warmed up, thereby allowing the contents of D to condense into E. The mercury seal (4) was closed and E brought to room temperature; on further warming of E the contents vapourised and condensed in a thin layer over the walls of E. The acid and water were left in contact for several hours with occasional warming of E to melt the acid. At the end of the exchange period the acid was all distilled into E by warming the rest of the extension.

Valve 4 was opened and the water vapour pumped off from E, by allowing that bulb to warm up until the acid started to condense on the tubing outwith E, at which point valve 4 was closed. The pivalic acid was then distilled into tube F, which was removed from the line by fusing the constriction above F forming a small hook at the top of F.

It was noted, as the pivalic acid warmed up inside the sealed tube, that it tended to clarify in the solid state. The tube was transferred to a crystal growing apparatus and a single crystal was grown from the acid therein. The crystal obtained was perfectly clear and melted at 35.3°C. Only the centre portion of the crystal was retained for use in tracer experiments. The specific activity of the acid thus obtained was .5μC/mg.

A. Deposition of a Thin Film of Cyclohexane-1-C14 on to a Single Crystal of Cyclohexane.

Two methods of depositing a thin film of cyclohexane on to a cyclohexane crystal, appeared possible. The first was to 'smear' a thin film of liquid cyclohexane on to the surface. This method suffers from two principal disadvantages one results from the high volatility of cyclohexane and the second from its very low heat of fusion. [.63 hcals/mole (54)]. The latter would probably cause pitting or dissolution of the crystal surface by the liquid, an occurrence which would almost certainly affect the results of a diffusion experiment. It was decided, therefore, to concentrate on the second method which was based on the condensation of cyclohexane vapour on to the cold surface of a crystal. This technique could utilise the high volatility of cyclohexane and would be more likely to produce an even surface film without the disadvantages of the first method.

Because solid cyclohexane exerts a considerable vapour pressure near its melting point, (6.55°C), it was necessary to cool the crystal to a low temperature, but not less than -86°C, at which point cyclohexane undergoes a crystallographic phase transition.

In initial experiments carried out at atmospheric pressure, cyclohexane was evaporated onto a crystal cooled with powdered Drikold. The crystal was mounted in a brass holder which was seated in a socket at the top of a glass tube containing some liquid

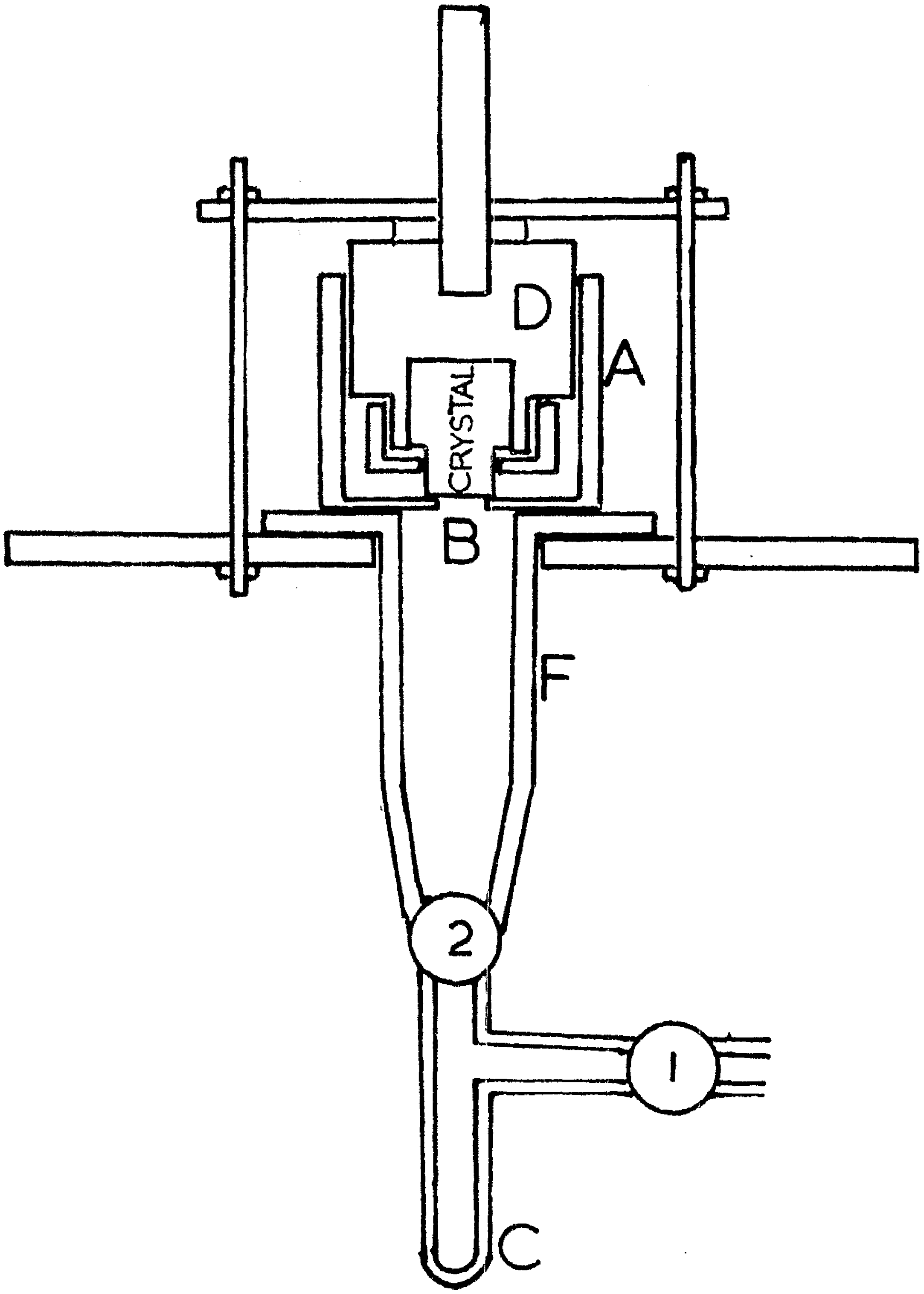


FIG. 7 EVAPORATOR NO. 2

cyclohexane, an aluminium tray fitted round the holder, was used to retain the Drikold. On warming the liquid cyclohexane it evaporated, but when the vapour reached the crystal the latter tended to melt with the heat from the condensing cyclohexane.

It was decided that deposition under vacuum would give better results since the heat required for evaporation of the cyclohexane could be reduced. An apparatus was constructed for this purpose (fig., 7,) and some improvement was noticed. An outer brass casing (A) was made for the crystal holder (D), such that only a well-defined area (B) of the crystal surface was exposed to the condensing vapour. The casing also served as a contact between the crystal holder and the flat glass flange (F) of the evaporation unit. Contact between the brass holder and the greased flange was secured by two thick-gauge aluminium plates held together by four retaining screws, the lower plate served as a holder for the Drikold coolant. When the crystal had been mounted and cooled, the liquid cyclohexane in C was frozen and the apparatus evacuated with taps 1 and 2 open, tap 1 was then closed and the cyclohexane in C, warmed up. Evaporation occurred, but it was found that the liquid in C tended to boil and spatter. Some cyclohexane was deposited on B, but sublimation had also taken place from the crystal during the evacuation, and the seal between A and D tended to leak. A more efficient system was obviously required, and the following conditions were now considered desirable for the deposition

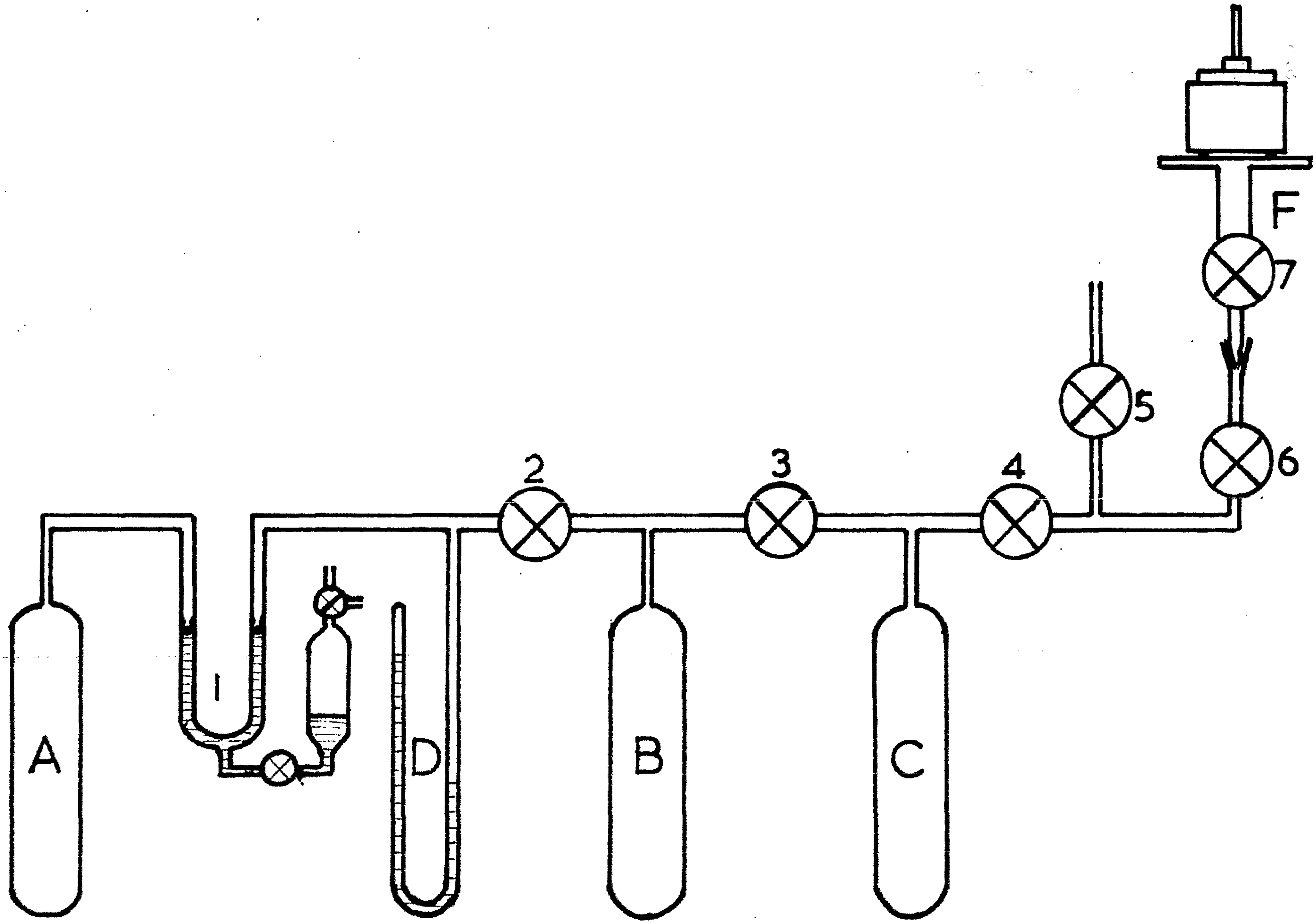


FIG.8. CYCLOHEXANE C14 DEPOSITION APPARARATUS

technique.

1. The evaporation should be carried out under vacuum.
2. The cyclohexane crystal should be cooled to a temperature of the order of -70°C, at which temperature its vapour pressure is .084 mm.
3. The cyclohexane should be stored as a vapour prior to deposition.

The last condition was possible because of the high vapour pressure which cyclohexane has at room temperature, 6.5 cms. at 15°C. An apparatus of the type illustrated in fig., 8 was constructed as a means of transferring desired amounts of cyclohexane from a source to the crystal surface.

The source was contained in bulb A and was sealed off from the remainder of the system by a mercury float valve, 1, which served to prevent contamination of the cyclohexane by stopcock grease and vice versa. When a sample of cyclohexane was required for deposition, taps 2, 3 and 4 were opened and 1 and 6 closed, tap 5 was then opened to allow evacuation of the system, after which taps 5 and 3 were closed and the cyclohexane in A cooled to liquid nitrogen temperature. The mercury seal (1) was then opened and the cyclohexane allowed to warm up until the vapour pressure registered on the manometer, D, reached a desired value, at which point tap 2 and the mercury seal were closed. Thus a quantity of cyclohexane vapour was sealed off in B

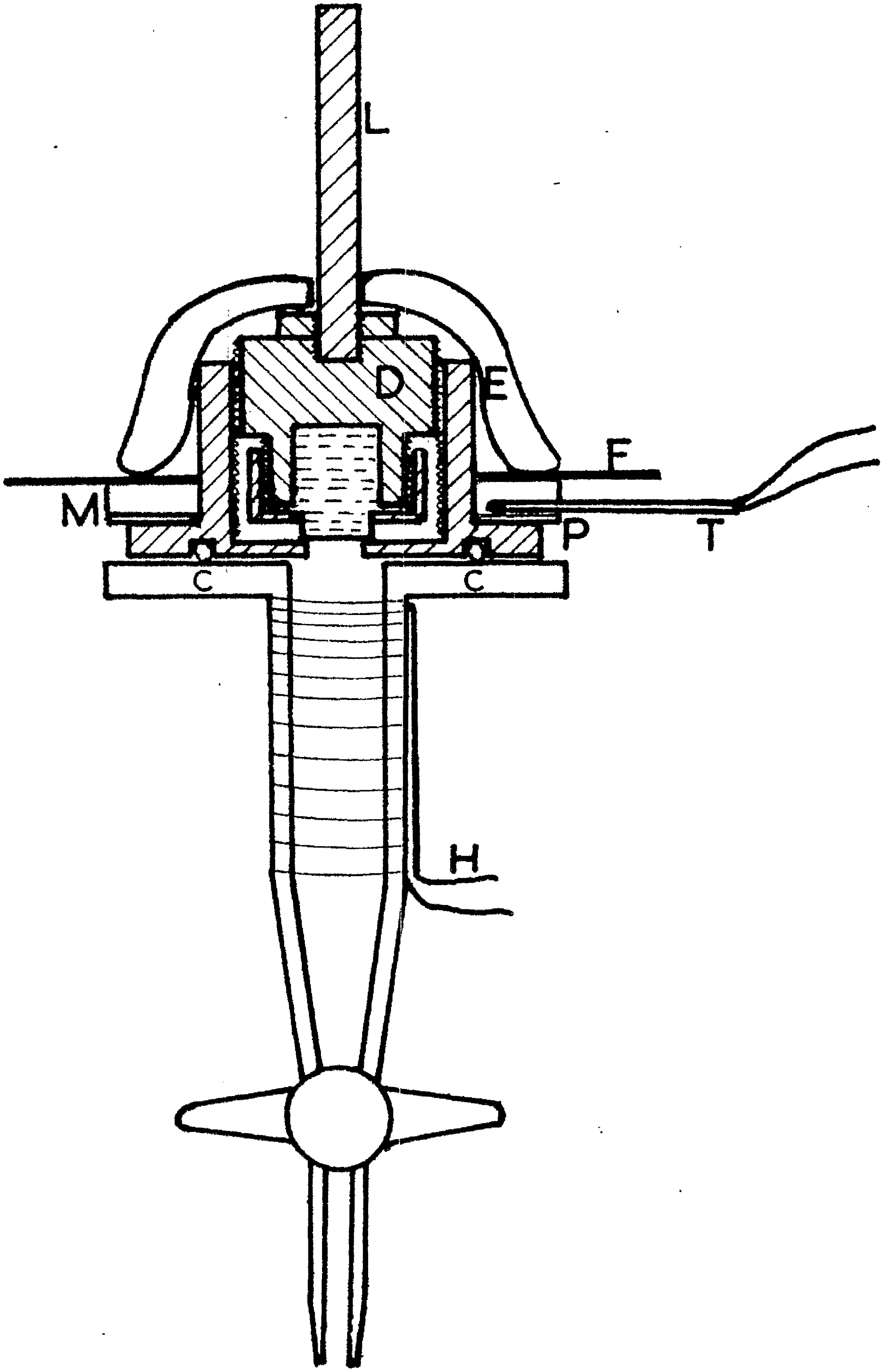


FIG. 9 THE DEPOSITION UNIT

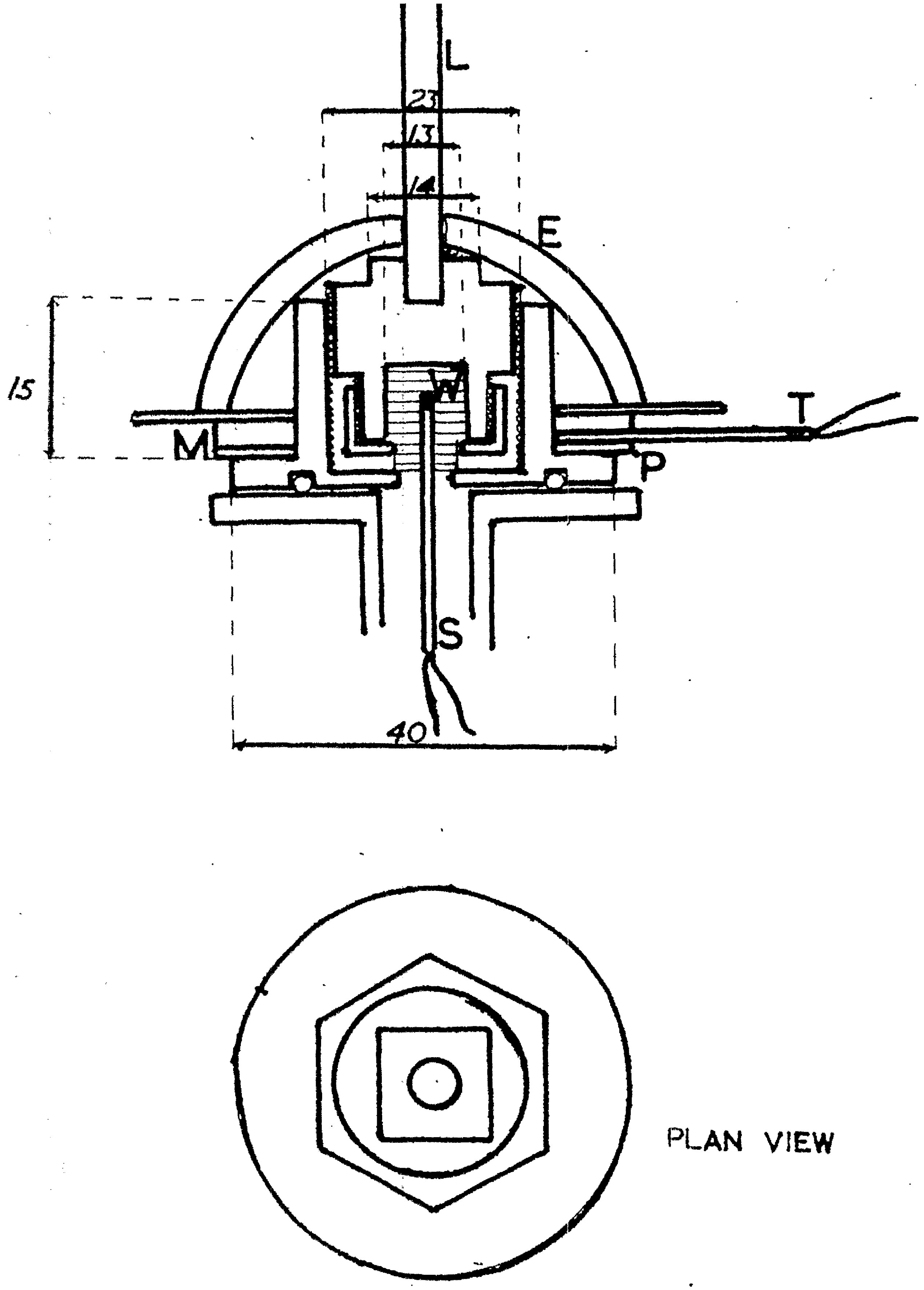
at a known temperature and pressure. Since the volume of the space between taps 2 and 3 was known, it was possible to estimate the amount of cyclohexane in B. Any desired amount of cyclohexane could be transferred from A at room temperature by trapping out a series of known quantities from B and storing these in bulb C.

Since the seal between the crystal holder and the glass flange as previously arranged had not proved very efficient, the cover of the holder was redesigned as in fig., 9. A hexagonal casing (A) welded to a flange (B) was made, with a recess in the face of the flange to take a Nygon V.R. 19, 'O' ring (C). The casing was shaped to allow it to be tightened onto the barrel of the crystal holder (D) with the aid of a spanner, the whole unit was constructed of brass. The thread between the casing and the barrel was greased with silicone grease, but it was found to leak under a high vacuum. This fault was remedied by winding 'Threadseal' tape round the crystal holder, thus tightening the join between the holder and casing and leading to a vacuum tight seal. The crystal holding unit was joined to the vacuum line by an 'O' ring seal between the flange of the crystal holder and an Edwards F.G. 15, flat glass flange. The latter was sealed to a B14 cone through a vacuum stopcock and could be removed from the vacuum system when desired. (see fig. 8)

With the arrangement as outlined above it was found possible to achieve a high vacuum seal between the crystal holder and the deposition apparatus without the use of fixing plates. This was only possible if the 'O' ring was properly greased with Edwards' High Vacuum silicone grease, the creation of the vacuum being sufficient to form a strong bond at the 'O' ring. The cooling of the crystal had not yet reached the desired level of efficiency, sublimation still occurred at high vacuum. The coolant used at this stage was an acetone/Drikold slurry which was contained in an aluminium tray fitted round the crystal holder.

It was then attempted to cool the crystal using a 'Cellosene' pad soaked in liquid nitrogen, the pad was laid over the top of the crystal holder and the nitrogen poured onto it. This cooled the crystal very rapidly, but led to 'overcooling' of the crystal, causing the occurrence of the phase transition at -86°C, which destroyed the single crystal character of the cyclohexane. Controlled cooling was obviously required and a method of determining the crystal temperature was evolved. The method involved the use of a calibrated thermistor and the arrangement is illustrated in figs. 9 and 10.

The top surface of the brass flange was covered with a cork mat (M) which fitted round the hexagonal casing, the base of the mat was stuck to a stiff polythene former (P) cut to the shape of the cork. Between the cork and P a hole was bored which allowed a thermistor (T) to be inserted as far as the brass casing. Above the cork was a thin polythene sheet (F) over



PLAN VIEW

FIG.10. DETAILED VIEW OF CRYSTAL HOLDER. [DIMENSIONS IN MM.]

which was placed a cellosene pad which was kept in place by the locating rod (L) of the crystal holder.

In order to calibrate the thermistor (T) to read the temperature of the crystal in the holder, a wax block (W) was mounted in the holder and a standard thermistor (S) was inserted in the wax (figure 10). The holder was mounted on top of a glass flange and some liquid nitrogen poured onto the pad (E). Resistance readings were taken from the two thermistors while the crystal was cooling and again as it warmed up. In this way it was possible to match the temperature of the block (W) with the resistance of the thermistor (T), located in the cork ring on the outside of the holder, see table I3A1 below. The resistance of T and S were measured by an ohmeter and a Wheatstone bridge circuit respectively.

Table I.3A.1.

Resistance of thermistor (T) (Ω)	Resistance of thermistor (S) (Ω)		Temp. °C
	Cooling	Warming	of crystal
1,000	1,100	1,200	- 30°C
2,000	3,400	3,600	- 52°C
3,000	4,300	5,500	- 58°C
5,000	11,000	12,000	- 71°C
6,000	12,400	13,000	- 74°C
7,000	18,000	20,000	- 81°C
10,000	25,000	26,000	(- 90)

The resistance of T, V the temperature of W, calibration, is an approximate one, e.g. at Rt = 5,000 ; TW = -72 ± .75°C and at Rt = 6,000 ; TW = -74 ± .5°C but it was felt that the accuracy was sufficient for the purpose required. The temperature of the crystal within the holder could now be determined, and it was found possible to carry out controlled cooling using liquid nitrogen. The resistance of the thermistor, T, was kept at a value between 5,000 and 6,000 ohms, corresponding to a crystal temperature of (-73°C), during the deposition period. The time required to cool the crystal to the desired temperature was very much reduced and handling made easier since the coolant was essentially a dry one.

The attainment of good surface deposits was now possible, but it was found that some of the cyclohexane tended to condense on the cold stem of the glass flange. A nichrome tape heater wound round the stem, see fig., 9, prevented this occurring, the resistance of the heater was 40 ohms and a current of .5 amps provided sufficient heat.

The remaining problem lay in providing a flat crystal surface on which to make the deposition and in preventing contamination of the remainder of the crystal, by the deposit.

Because the crystal was cubic there was no obvious need to make the deposition on any specific crystal face since isotropic diffusion was to be expected. It had been noted previously when microtoming crystal specimens, that a very smooth face was left on the crystal after removal of a number of slices, and it was decided to prepare a crystal face for deposition in that manner. The advantages of this method were, that a flat crystal face would be easy to prepare and that after the deposition of a radioactive layer and the subsequent diffusion anneal, it would be possible to realign the crystal with the microtome blade in a mechanical fashion.

With this end in view the locating rod of the crystal holder was shaped so that it could be returned to a fixed position in the brass mounting block. This was achieved by making a close fit between the rod and its seating in the block and machining a flat on to the rod so that the retaining screw in the block sat into the flat of the rod. The importance of accurate alignment of the crystal prior to sectioning after a diffusion experiment has been investigated by SHIRN ET ALIA (59) who calculated that for a misalignment of 1° an error of 8% could be introduced into the result of the diffusion experiment.

During any diffusion experiment the microtome and the brass block thereon were fixed in position by locking screws after the preparation of the crystal face, so that the crystal could be returned to exactly the same position, before sectioning.

In order to restrict the deposition area of the crystal face, the brass flange plate was screwed up as far as the face and to prevent excessive distortion of the latter, a minute rim was made on the inside of the flange round the central orifice, this sat onto the crystal face and prevented the spread of the radioactive deposit over the crystal. The crystal holder was clamped in a vice and a spanner used to screw the flange cover over the holder until the latter just touched the face of the crystal. During this operation condensation from the atmosphere tended to blanket the cold crystal surface, a piece of sellotape stuck across the opening of the flange prevented this occurring. After tightening the flange onto the holder the sellotape was easily removed before the crystal was mounted onto the precooled glass flange piece, which was then transferred to the vacuum line for the deposition.

The procedure thus evolved for making the radioactive deposition is summarised below.

1. The desired quantity of cyclohexane vapour was transferred to bulb B, (figure 8) from the source in A.
2. The barrel of the crystal holder was bound with 'threadseal' tape and a piece of transparent sellotape stuck across the orifice of the flange cover.
3. The crystal holder was clamped in an upright position on a small clampstand and the holder, the flange cover and the glass flange piece, were put into the deep freeze.
4. The O ring was placed on to the greased surface of the

glass flange and the top surface of the O ring covered with a layer of silicone grease.

5. A piece of cyclohexane crystal was shaped, placed in the holder and the retaining cap screwed on.

6. The crystal holder was fixed into the brass block of the microtome chuck and aligned so that the crystal and holder were almost perpendicular to the blade of the microtome. The crystal was then sliced until a smooth face was obtained, at which point the microtome was locked in position and the flange cover partially screwed on.

7. The holder and cover were removed from the block and cooled with powdered Drikold before being removed from the deep freeze to a vice, where the flange cover was screwed up to the face of the crystal.

8. The crystal holding unit was returned to the deep freeze, the sellotape removed, the unit mounted on to the flange piece and the parts for the liquid nitrogen cooler fitted on to the holder.

9. The whole device was then transferred to the vacuum line, the thermistor was inserted and the crystal cooled to -70°C. The flange heater was switched on and taps 4, 5, 6 and 7 (figure 8) opened to evacuate sections C and F. Tap 5 was quickly closed and tap 3 immediately opened to allow

the active vapour to pass to the crystal face. Approximately one minute was allowed for this, after which taps 6 and 7 were closed and section F and the crystal holder returned to the deep freeze, where the holder was removed by opening tap 7. A mica cover was clamped over the brass flange to seal off the crystal and its deposit.

A measure of the efficiency of the deposition could be obtained by a comparison of the pressure readings on the manometer, exerted by the cyclohexane vapour in bulb B, before and after the deposition. Any excess cyclohexane was always trapped out in B after a deposition.

A test carried out showed that approximately 50% of the available radioactivity was deposited on the crystal face and for a typical deposition of 1 mg., a surface layer 2 microns thick would be formed.

3. Deposition of a Thin Film of Radioactive Pivalic Acid on to a Single Crystal of Pivalic Acid.

Since the technique of vacuum deposition had proved successful with cyclohexane it was thought that a similar procedure should be used in the case of pivalic acid.

The design of the crystal holder and the means of connecting it to the vacuum line were identical with those previously described for cyclohexane. Because of its higher

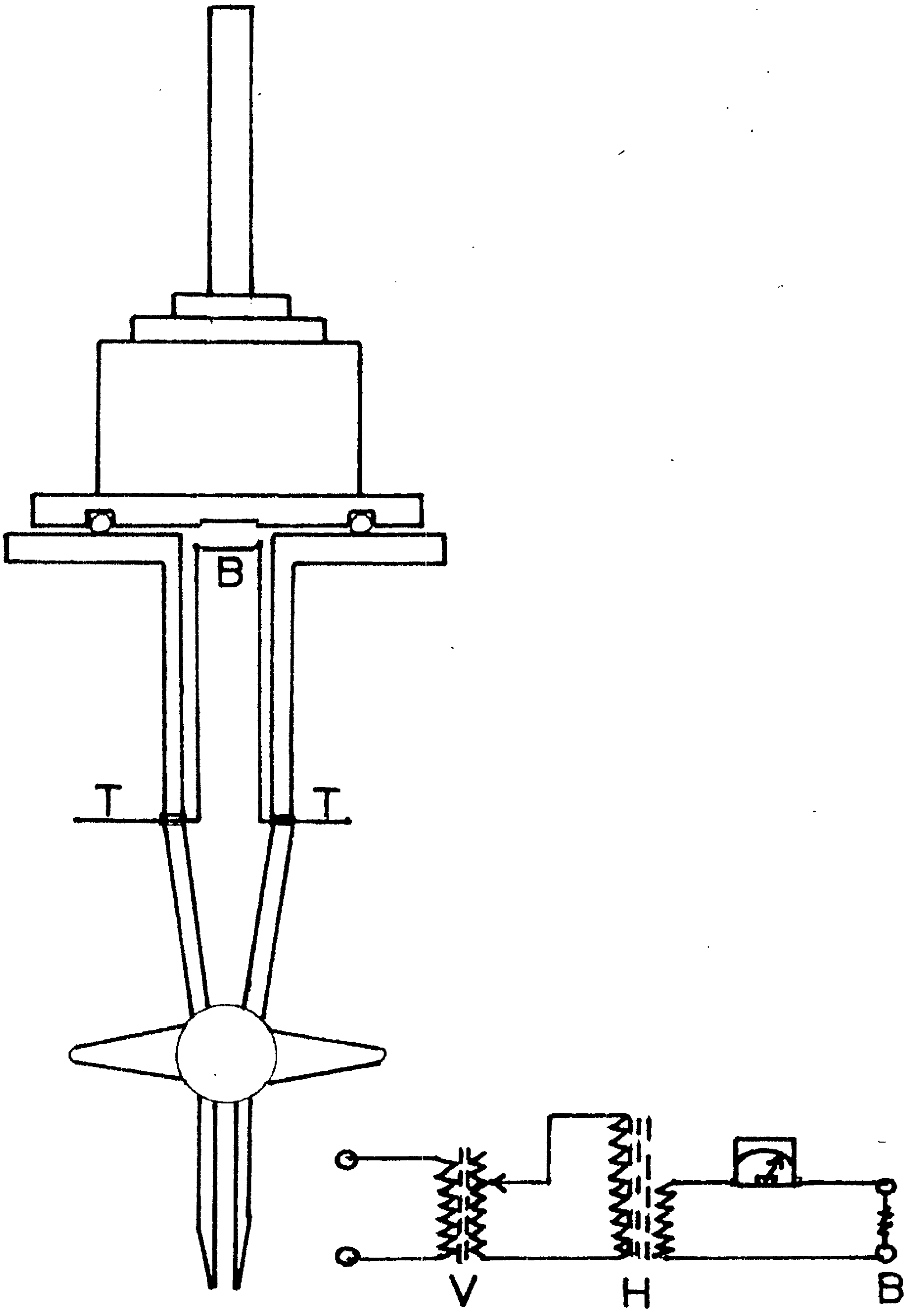


FIG. 11. PIVALIC ACID EVAPORATOR

melting point (35.5°C) and low vapour pressure at room temperature, it was not necessary to use a complex cooling system during the deposition on the pivalic acid crystals. The method of transfer of the radioactive pivalic acid from the source to the crystal was different from the case of cyclohexane because of its low vapour pressure at normal temperatures. The means of vapourization employed was a small platinum boat heater in which the sample to be evaporated was placed. The use of a heater of this type was thought to be advantageous because of its low heat capacity, which would mean a rapid temperature response to the applied voltage, and because of the simplicity with which such an evaporator could be designed. The evaporating system is shown in fig., 11, along with the electrical system which supplied the current for the heater.

The evaporator consisted of an F.G. 15 flat glass flange sealed to a B14 cone through a vacuum stopcock. Tungsten wires (T) bent at a suitable angle were sealed through the stem of the glass flange and a small piece of platinum in the shape of a boat (B) was silver-soldered to the top ends of the wires, such that the boat lay just beneath the surface of the flange. It was found that a piece of pivalic acid, placed in the boat, evaporated at atmospheric pressure, when the current through the heater was raised to 8 amps. The control of the current was carried out by adjusting the output of the variac transformer (V) to the heavy duty transformer (H), which supplied the heater. By sealing a glass plate across the flange and evaporating some pivalic acid from the heater under vacuum, an even film of pivalic acid was formed on the glass.

When carrying out a deposition the crystal was cooled slightly below room temperature, by allowing cold nitrogen gas to flow over it. The procedure was to prepare the crystal face as described for cyclohexane, but without the need for any low temperature arrangements. A small quantity of radioactive pivalic acid was placed in the boat, about 1 mg., and the crystal holder placed in position over the flange . The combination was then fitted to the vacuum line, the crystal cooled, the depositior evacuated and the connexion to the vacuum line shut off. The current was switched on to the heater and slowly raised to 9 amps over a period of approximately 1 minute and then switched off. The crystal and depositor were removed from the vacuum line and the crystal face sealed off by a piece of mica such that intimate contact was made between the mica and the flange face. With a successful deposition it was not possible to observe the deposition on the face of the crystal itself, but a trace of white film on the flange surrounding the crystal face was evidence of a good deposit.

THE DIFFUSION EXPERIMENTS

(A) CYCLOHEXANE

The main problems which arose during the diffusion experiments were a result of the low melting temperature of cyclohexane [6.55°C (54)], and its high vapour pressure at temperatures well below the melting point.

Because of the low melting point of cyclohexane, all handling of the material had to be carried out in a deep freeze, or with the aid of such coolants as solid carbon dioxide and liquid nitrogen. The condensation of water vapour from the air on samples of cyclohexane at these low temperatures, had also to be avoided. The vapour pressure of cyclohexane at -45°C is as high as 1 mm. and it rises to 40 mm. at the melting point. Thus evaporation at these temperatures under normal conditions could be a serious hazard, especially if it resulted in losses of radioactivity from the deposit during a diffusion run. Since it was hoped to carry out diffusion measurements within the temperature range quoted above, some means had to be found, whereby evaporation could be eliminated, or reduced.

The loss of radioactive cyclohexane from the surface could affect the experiment in two ways.

(1) If the initial surface deposit diminished at an appreciable rate, during the course of a diffusion experiment, due to evaporation, the results obtained would be meaningless,

since diffusion would be occurring under undefined conditions.

(2) Contamination of crystal faces other than the one on which the deposit was initially made, could occur by condensation of radioactive cyclohexane vapour on these surfaces. This could then cause false measurements of radioactive penetration due to a diffusion process, since one would be measuring activity due to diffusion and surface contamination.

It was necessary therefore, to take precautions to avoid errors arising from the aforementioned causes.

.A. 1. PRESERVATION OF THE CYCLOHEXANE DURING THE DIFFUSION EXPERIMENTS.

Since the technique developed for carrying out the deposition of radioactive cyclohexane required that the crystal be mounted in a vacuum-tight holder, and because the latter had been designed to prevent contamination of the crystal surfaces, as in figure (9), it was felt that a vapour tight seal across the opening of the flanged cover, would be sufficient to provide good protection for the crystal and its deposit during a diffusion experiment.

The sealing off, of the flange face, was carried out by clamping a flat glass plate, covered with a thin film of silicone grease, over the flange of the crystal holder after the deposition

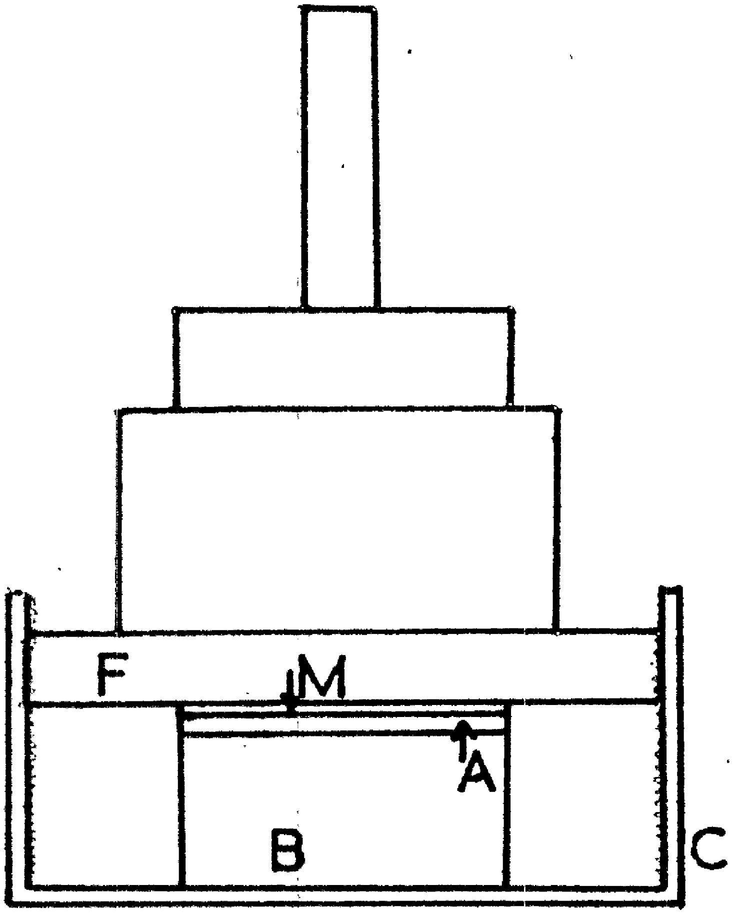


FIG. 12. SEAL FOR THE CRYSTAL HOLDER

had been carried out. The glass plate was mounted on a wooden base and held against the surface of the flange by a strong 'Quickfit' clip.

The crystal holder and cover were then put in a liquid tight can which was immersed in the thermostat bath for the duration of the diffusion run.

This method proved unsatisfactory for several reasons. The use of silicone grease to ensure a good seal between the glass and the brass flange sometimes led to contamination of the crystal surface, which rendered sectioning of the crystal unsatisfactory. The reason for the contamination was that the gap between the crystal face and the glass cover was so narrow (.5 mm), that any movement of the flange against the glass caused a build up of grease, which fouled the crystal surface. In addition, it was felt that absorption of radioactive cyclohexane by the layer of grease might occur, thus spoiling the conditions for the experiment. A final hazard of the method, was that the glass cover sometimes cracked during the sealing off process.

An alternative to glass was required, and one which would need no grease to provide intimate contact with the face of the flange. Mica was found to be an ideal substitute. A sheet of mica (M) fixed to an aluminium plate (A) on top of a cork base (B) mounted in a brass cover (C) was held tight against the flange (F) of the crystal holder, by screwing the brass cover on to the flange rim of the holder. The arrangement is shown in figure 12. The cork base served as a spring holding the mica to the flange face, forming a good seal to preserve the deposit and the crystal.

Since in this form the crystal in its holder was completely liquid tight, it was decided to dispense with the can and lower the crystal holder directly into the thermostat bath. This had the advantage that a very rapid temperature equilibrium would be established between the bath liquid and the crystal, so reducing any error which might be involved by a slow response of the crystal temperature to its surroundings.

An experiment was carried out to ensure that the crystal did, in fact, respond quickly to the temperature of the bath. A wax block was inserted in the crystal holder and a calibrated thermistor was embedded in the wax. A brass cover with a welded copper tube was screwed over the flange of the crystal holder, the tube serving as an outlet for the thermistor leads, which were incorporated in a Wheatstone bridge circuit. The crystal holder was cooled to about -80°C with liquid nitrogen, and then immersed in the thermostat bath at -40°C, the rate of temperature change of the wax block was followed by measuring the resistance change of the thermistor. The result of the trial is shown in table 1.

TABLE: I. 4. (1). Rate of response of crystal temperature to the temperature of its surroundings.

Time (Seconds)	0	30	60	90	120	150
Temperature of Wax Block (°C)	-72	-54	-43	-41	-40.4	-40.1
Bath Temperature (°C)	-40	-40	-40	-40	-40	-40

Because of the rapid attainment by the wax crystal of the bath temperature, it was decided that no appreciable error would be involved by assuming the crystal came to temperature immediately after its immersion in the thermostat. The slight delay on warming of the crystal would, theoretically, lower the observed value of the diffusion coefficient.

A. 2. CONTAMINATION BY RADIOACTIVE CYCLOHEXANE DURING A DIFFUSION EXPERIMENT.

It was found, using the technique previously described for mounting the cyclohexane crystals and for protecting the radioactive deposit, that satisfactory results could be obtained at temperatures up to -30°C without any apparent loss of cyclohexane. At temperatures greater than this, losses of cyclohexane from the crystal surface were experienced. That, in fact, at temperatures below -30°C, the conditions were satisfactory, was supported by the results of some end-window counts of the surface decrease of the crystal activity during a diffusion experiment, as shown in a later section.

In order to ensure that activity had not penetrated down the sides of the crystal during the deposition of the radioactive cyclohexane, a crystal was sectioned immediately after deposition. The result is shown in table 2.

TABLE I.4.2

DISTRIBUTION OF ACTIVITY ON THE CRYSTAL FOLLOWING DEPOSITION OF THE RADIOACTIVE FILM

Perpendicular Distance from the Crystal Surface (Microns)	0-15	15-30	30-45	45-60	60-75
Activity of Section (d/second)	874	14	0	0	0

The activity observed in the second slice was probably due to contamination of the knife blade, during the sectioning process, from the highly active first section. The remainder of the sections showed no sign of activity and it was therefore assumed that the method of deposition was satisfactory. A further proof of the absence of contamination of the sides of the crystal was obtained by removing the sides of a crystal, prior to sectioning, after a diffusion experiment (No. 5). The result obtained for self-diffusion in this crystal was similar to the value obtained for self-diffusion in another crystal at the same temperature, the sides of which had not been shaved (No. 4). This fact coupled with the evidence from table 2, showed that no

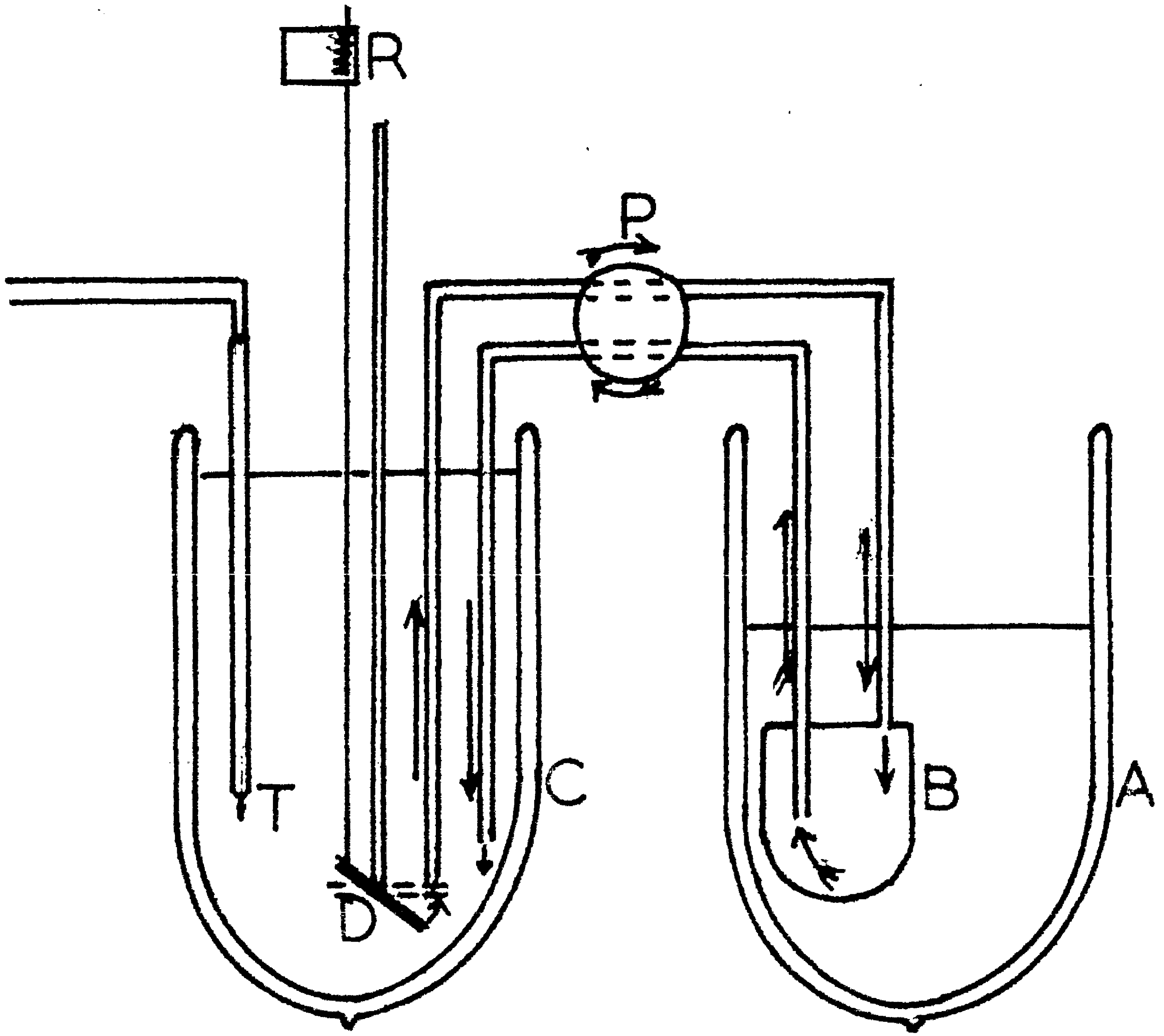


FIG. 13. THE LOW TEMPERATURE THERMOSTAT

significant contamination of the crystal by radioactive cyclohexane was occurring during the course of a diffusion experiment.

A.3. THE OPERATION OF THE LOW TEMPERATURE THERMOSTAT BATH.

The thermostat used for the diffusion runs was supplied by Messrs. Townson and Mercer under the trade name of 'The Minus 70 Thermostat Bath'. An illustration of the essentials of the bath is shown in figure 13.

Basically the thermostat consisted of two fifteen litre Dewar flasks connected by a liquid flow pump (P). The right hand Dewar vessel (A) contained a metal heat exchange chamber (B) which was surrounded by the cooling source, and the left hand Dewar vessel (C) held the bath liquid, which was cooled by pumping it through the closed heat exchanger (B). The pumping action was continuous but the flow could be shut off by a gate valve (D) which was activated by a relay (R) working in conjunction with a thermistor temperature control circuit. The control device allowed the temperature to be maintained over long periods within an accuracy of at least ± .1°C. Variation of the resistance of the thermistor, which was incorporated in a Wheatstone bridge circuit, served to actuate the relay and control the rate of heat exchange taking place in B, and hence the temperature of the liquid in C.

The bath was prepared for use by filling the Dewar vessel (C) with methylated spirits and charging the vessel (A), to two thirds of its capacity, with a slurry of methylated spirits and Drikold. Under these conditions and operating the thermostat at a bath temperature of -70°C, it was found that the supply of coolant would last for 48 hours without replenishment.

A.4. THE EXPERIMENTAL TECHNIQUE.

Prior to carrying out a diffusion run the thermostat was charged and the bath set to the desired temperature, by means of a potentiometer, which formed part of the thermistor control circuit. The temperature of the bath was measured by means of a calibrated thermistor (T) immersed in the bath liquid of C. The resistance of the thermistor was measured using a Wheatstone bridge circuit, which allowed the resistance to be measured to five significant figures.

The prepared crystal in its holder was lowered into C at the end of a long wire, such that the holder was suspended in the bath liquid adjacent to the thermistor (T). At the end of the diffusion time the holder was removed from the bath and the crystal mounted for sectioning in the deep freeze. Because the time which elapsed between the removal of the crystal from the thermostat and the commencement of sectioning of the crystal, was slight, usually less than two minutes, and since this delay would be compensated for by the short temperature adaption time when the crystal was put into the thermostat (Table I.4.1),

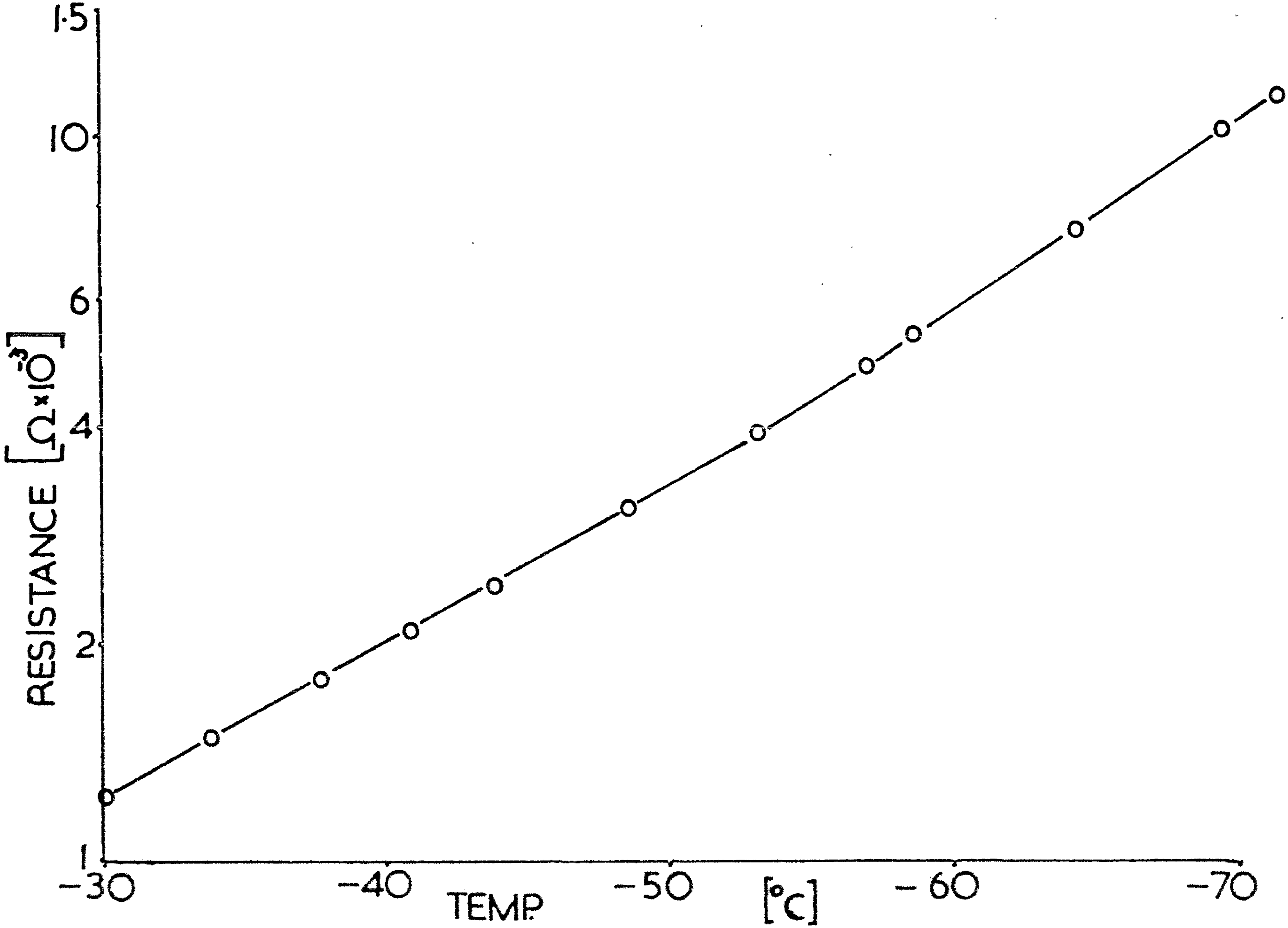


FIG.14. LOG OF THERMISTOR RESISTANCE V TEMPERATURE

it was considered that the time for diffusion would be given by the period during which the crystal was actually in the bath.

The temperature deviation which occurred during a typical experiment is shown in table 3, below. The thermistor used for measuring the temperature of the thermostat bath was a S.T.C., F.22, low temperature thermistor, which had been calibrated against an ammonia vapour pressure thermometer for the temperature range -30°C to -70°C. A graph of the resistance v temperature characteristics is shown in figure 14.

TABLE I.4.3.

THE TEMPERATURE VARIATION DURING EXPERIMENT No. 6

Time: Day 1	2.45 p.m.	3.30	4.30	5.00
Temperature:	-44.80	-44.70	-44.67	-44.70
Time: Day 2	9.00 a.m.	10.30	12 p.m.	2.30
Temperature	-44.67	-44.65	-44.70	-44.65

The maximum deviation of temperature during the run was .15°C which corresponds to a control accuracy of $\pm$ .075°C.

A. 5. THE PERIODS OF THE DIFFUSION PROCESS.

The temperatures and diffusion times for each experiment are shown below. Preliminary experiments were carried out at various temperatures and from these trials it was decided that diffusion times of the order of 24 hours would be required at

-60°C, decreasing to 2 or 3 hours at -30°C. The times were long enough to allow sufficient penetration of radioactive material into the bulk of the crystal, such that a reasonable measurement of diffused activity could be made.

TABLE I.4.4

THE DIFFUSION PERIODS AND TEMPERATURES FOR THE DIFFUSION EXPERIMENTS

Experiment Number	1	2	3	4	5
Temperature (°C)	-31.5	-37.5	-39.0	-44.8	-44.8
Diffusion Time (Minutes)	135	213	234	1350	450
Experiment Number	7	8	10	9	6
Temperature (°C)	-50.0	-57.5	-62.6	-57.5	-48.2
Diffusion Time (Minutes)	668	8570	2090	1440	728

B. PIVALIC ACID.

The experimental procedure with regard to the diffusion experiments on pivalic acid was very similar to that developed for cyclohexane.

There was in this case no need to employ any special methods for handling the crystals which melted at 35.5°C, and the vapour pressure of the solid was very much lower than that of cyclohexane. This meant the elimination of any handling difficulties and reduced the chance of error due to evaporation. The crystal was contained and sealed in the same way as the cyclohexane had been and the diffusion measurements were made in a thermostat bath which operated from 0°C to 40°C.

Temperature control of the bath was by means of a toluene regulator and Sunvic, N409, electronic relay, which allowed the temperature to be controlled to ± .05°C. The bath which was surrounded by an ice/water mixture at temperatures below 25°C, was heated by a 750 watt, metal immersion heater. The temperature of the bath was measured by a N. P. L. calibrated mercury thermometer.

The temperature range of the diffusion measurements on pivalic acid was limited by the phase transition temperature of 6°C and the melting point, 35.5°C. In fact the temperature range covered was from 7°C to 22°C and it was found that diffusion in this range was very rapid.

The latter property of pivalic acid meant that the time allowed for diffusion was comparatively short and all the measurements were made in periods of less than 2 hours.

As was the case with cyclohexane, measurements of contamination processes yielded negative results. The diffusion periods and temperatures for the diffusion measurements are shown in Table I. 4. 5.

TABLE I. 4. 5.

THE DIFFUSION PERIODS AND TEMPERATURES FOR THE DIFFUSION EXPERIMENTS

Experiment Number	1	2	3	4	5	6
Temperature (°C)	7.2	9.4	12.0	14.8	18.0	22.2
Diffusion Time (Minutes)	90	90	64	52	98	44

The crystals were removed from the thermostat at the end of each diffusion experiment and sectioned immediately.

THE SECTIONING OF THE CRYSTALS.

A. CYCLOHEXANE.

The amount of radioactive material which has diffused into the crystal during the diffusion period can be determined in two ways.

1. The decrease in radioactivity as measured at the surface of the crystal, due to penetration of activity into the crystal, can be measured.
2. The crystal can be sectioned parallel to the face on which the radioactive deposit was made and the concentration of activity in each section determined.

The former method makes use of the fact that radioactive radiations are absorbed in solids and hence as the radioactive material penetrates into the crystal, the radiations from it will no longer reach the surface and the activity as measured at the surface will be reduced. This method will reveal an overall picture of the diffusion process and it is discussed at a later stage, (I.7).

The technique involving sectioning of the crystals and measuring the diffused activity in each section has the advantage that it results in the direct determination of the diffusion profile of the radioactive material. This profile can often indicate whether one or more diffusion processes are occurring in the crystal and is likely to furnish more information about the diffusion process than the first technique.

It was decided to try to section the crystals with a microtome because they had proved very easy to cut with a sharp razor blade. The microtome operated by moving the crystal, mounted in a chuck, across the path of a knife blade situated to provide the correct depth of cut.

The low melting point of cyclohexane, 6.55°C, necessitated that all manipulation, including sectioning, of the crystals be carried out below that temperature. There appeared to be two ways in which the crystal could be cooled during the sectioning process, one was to mount the crystals on a cooling head and the other was to carry out the operation in a deep freeze. A head using the expansion of CO_2 gas as a cooling system, was employed, but it was found difficult to mount the crystal satisfactorily and the flow of gas tended to cause sublimation from the crystal surface. Sectioning in a deep freeze, however, was successful, a Beck microtome being used for the purpose.

.A(1) THE MOUNTING OF THE CYCLOHEXANE CRYSTALS.

In order to carry out satisfactory sectioning of the crystals it was necessary to have them securely mounted in the chuck of the microtome. The method by which the crystals were fixed to the microtome is illustrated in figure 15. A square brass block (B) with a hole ¾ inches deep drilled in one

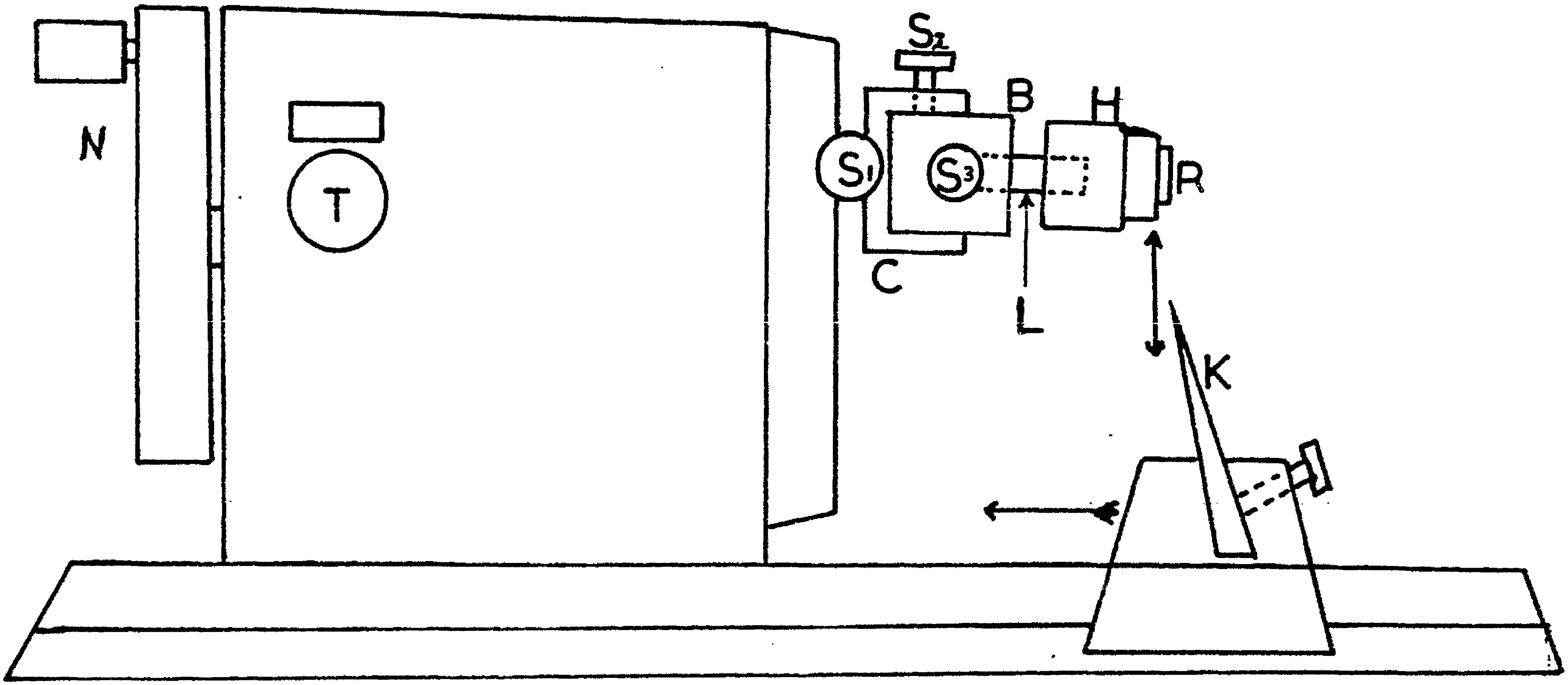


FIG.15. THE MICROTOME

face, was held in the jaws of the chuck (C) by a screw (S. 2.). The locating rod (L) of the crystal holder was machined to fit closely into the hole in the block and was secured in position by a screw (S. 3.). A flat had been machined at the end of L, onto which the screw (S. 3.) was tightened, thereby providing a means of locating the holder into the same position in B each time. The angle of the crystal holder with respect to the knife blade (K) was varied by loosening the screw (S. 1.) and moving the chuck, which was mounted on a ball bearing, into the desired position, in which it was clamped by tightening S. 1.

A. (2) THE OPERATION OF THE MICROTOME.

The microtome operated by moving the crystal vertically up and down in one plane, across the path of a travelling knife blade. One full revolution of the handle (N) served to move the crystal across the knife blade and also to position the blade for the next cut. The thickness of the slices could be varied between 1 and 15 microns, in steps of 1 micron, by turning the knob T, there being a click setting for each thickness, which was shown in a window above T.

It was found that the mechanism of the microtome tended to seize in the deep freeze, so all moving parts were relubricated with silicone grease, after which, no further trouble was experienced.

In order to ensure that the sectioning being carried out at the low temperature was accurate, a travelling microscope was mounted above the microtome in the deep freeze, the microscope was focussed on the knife blade and a series of cutting operations were performed, during which the travel on the microscope was compared with the theoretical travel of the knife blade. Because all sections, during the diffusion experiments, were taken with the microtome set to cut 15 micron slices, this was the setting used for the calibration. The result of the calibration is shown in table I. 5. 1.

TABLE I. 5. 1.

CALIBRATION OF THE MICROTOME MOVEMENT

Number of Sections Cut	25	25	50	25	25	50	
Travel of Microscope	.038	.038	.074	.037	.038	.076	(CM.)
Theoretical Travel of Knife	.0375	.0375	.075	.0375	.0375	.075	(CM.)
Thickness of Section	15	15	15	15	15	15	(CM. $\times 10^{-4}$)

From the results of the calibration it was clear that the microtome was operating correctly in the deep freeze.

The crystal face for the radioactive deposition was prepared by microtoming a specimen until a flat surface was obtained, and after the diffusion period, the crystal was remounted in the same position on the microtome for sectioning.

A.(3). THE COLLECTION OF SLICES DURING SECTIONING.

It was found that each slice adhered completely to the knife blade of the microtome after the cut had been made and that there was never any tendency for material to break off. The sections were in the form of minute rolls of soft wax and were removed from the microtome using cold flexible razor blades, which allowed the entire slice to be collected. The samples were washed off and dissolved from the razor blades with liquid scintillator, which was run into a counting vessel via a filter funnel. The counting vessels were sealed and later used for the determination of the radioactivity of the samples. A different razor blade was used to collect each slice and it was possible to prepare ten sections of a crystal in the above manner in less than five minutes. Because of the nature of the operation it was not feasible to weigh the slices prior to counting them. There were three main reasons for this.

1. The samples were liable to sublime rapidly.
2. Condensation of water vapour from the air was likely.
3. The slices were 'greasy' in nature and difficult to handle.

The first property resulted in complete vapourization of the samples when transferred to tubes for weighing and would almost certainly have resulted in loss of material before they could be prepared for counting. The second effect would have been to cause false weighings due to condensation on the sample or the container, or both. The third difficulty which arose was the result of the greasy nature of the samples and their readiness to melt or sublime, this made transfer of the material without loss almost impossible.

It was felt that the rapid method of sample collection outlined previously was justified from the experimental results. The supposition that the slices were collected at a constant weight, which was made in the case of cyclohexane, was supported by the results of slice weighings made later on specimens of pivalic acid, which was of a fairly similar physical nature to cyclohexane. These results showed the weight of each slice to be almost constant.

.B. PIVALIC ACID.

It was much easier to carry out sectioning in the case of pivalic acid due to three main factors.

1. Pivalic acid melts at 35.5°C.
2. The vapour pressure at room temperature of pivalic acid is low.
3. The sections obtained were not so 'greasy' as those of the cyclohexane.

The advantages obtained as a result of these factors were that the sectioning could be carried out at 'normal' room temperature conditions, that the slices were more readily transferable and that it was possible to weigh the sections before counting them.

The methods of mounting and sectioning were as previously described for cyclohexane, without the use of any low temperature devices. The method of slice collection was, however, different.

After the cut had been made with the microtome, the crystal slice remained on the microtome blade as before, but in this case there was less tendency for it to adhere to the blade and it was possible to remove the slice with a pair of tweezers. Occasionally the slices tended to break on removal from the blade, appearing to be somewhat brittle, but nearly always, it was possible to remove the entire slice.

The sections were put into preweighed ½ dram sample bottles, which were sealed off and later reweighed. The weighings in each case were to three decimal places of milligrams and the balance used was a Mettler balance. A typical series of sample weights is shown in table I. 5. 2. The slice thickness in each case was 30 microns, two 15 micron slices being used for each sample. A calibration of the microtome at room temperature using a travelling microscope, as for the low temperature check, showed the microtome to be functioning correctly.

TABLE I. 5. 2.

THE WEIGHTS OF PIVALIC ACID CRYSTAL SECTIONS FROM EXPERIMENT NUMBER 2

Number of Slice	3	4	5	8	9
Weight of Section	1.333	1.773	1.763	1.781	1.763
Number of Slice	10	11	12	14	
Weight of Section	1.727	1.392	1.728	1.776	

The loss of weight from slices 3 and 11 was due to breakage as the slices were being transferred from the microtome to the sample bottles, small fractions of the slices being lost in the process. Apart from these two slices, the weights of the remaining sections were constant to within 2%.

After weighing the slices, they were washed from the sample bottles with scintillator solution into scintillation counting vessels, from which the radioactivity of the sections was measured in a scintillation counter.

THE DETERMINATION OF THE RADIOACTIVITY IN THE CRYSTAL SECTIONS.

(A) CYCLOHEXANE-C14.

The radioactive isotope of carbon used in the experiments decays with the emission of a β particle, to form a stable isotope of nitrogen, of mass 14.

$$C_6^{14} \longrightarrow N_7^{14} + e \qquad (\text{E MAX.} = .156 \text{ M.E.V.})$$

The half-life of the carbon 14 isotope is 5600 years (60). Because of this long half-life and since the daughter product of the radioactive isotope is a stable one, there is no need to make any corrections for radioactive decay during the course of an experiment. These properties have resulted in the widespread use of the C14 isotope for many studies in which carbon is involved.

The low energy of the β radiation from C14, makes compounds labelled with it safe to handle, provided direct contact with the material is avoided.

The detection of the emissions from carbon-14 presents a problem because of their weakness. This means that methods of detection which are sensitive to weak β radiation must be used.

Solid-state samples containing the carbon-14 isotope can be counted, using thin-windowed G.M. counters, but the counting efficiency of this method is poor and it would not be very suitable for samples of low specific activity. The accuracy of the method is limited also by the large corrections which must be made for backscattering and self-absorption of the soft β radiations.

The most efficient methods of counting carbon-14 are by the scintillation and gas counting techniques. The latter method involves the conversion of the radioactive sample to a gas of suitable characteristics, for use in filling a G.M. tube. This gas is then transferred to a counting tube and counted internally. Since all the activity is inside a cylindrical cathode, conditions can be arranged such that almost 100% of the activity is detected.

The scintillation counting technique can also be adapted to yield very high counting efficiencies for carbon-14. Counting efficiencies of greater than 90% have been recorded (61). For scintillation counting the sample is dissolved in a suitable solvent containing an organic phosphor. The interaction of the radiation from the source, with the phosphor, results in the emission of light rays, which are detected by a photosensitive electrode on a photomultiplier tube, and the resulting energy pulse is recorded by a suitable electronic scaler. The advantages of the method of scintillation counting over gas counting techniques are that no radical alteration of the initial sample is required and that a greater number of samples can be counted in a shorter time.

It was decided therefore to use scintillation counting, as the means of detection of the cyclohexane-C-14 samples. One advantage which arises from the counting of cyclohexane-C-14 is that cyclohexane is very soluble in most organic solvents and so the dissolution of the samples in the scintillator solutions would present no problems. The scintillation counting of carbon 14 has been the subject of a number of publications in recent years (62, 63).

.A. 1. THE SCINTILLATION COUNTER.

The method used for the scintillation counting of carbon 14 is to dissolve the sample in a liquid scintillator contained in an optically clear glass vessel. The scintillations emitted are coupled up inside a light tight casing to the photosensitive cathode of a photomultiplier tube, which amplifies the initial electronic pulse to a level whence it can be detected by a scaler, which records each signal.

The scheme can be represented as follows:-

1. $C^{14}_{6} \longrightarrow N^{14}_{7} + \beta^{*}$
2. $\beta^{*} + S \longrightarrow S^{*} + \beta$
3. $S^{*} \longrightarrow S + hv$
4. $hv + P \longrightarrow e^{-}$

in which β^{*} is the energetic emission from carbon 14, S^{*} is the activated phosphor molecule and P represents the photocathode.

The scintillation counter used was supplied by Ecko

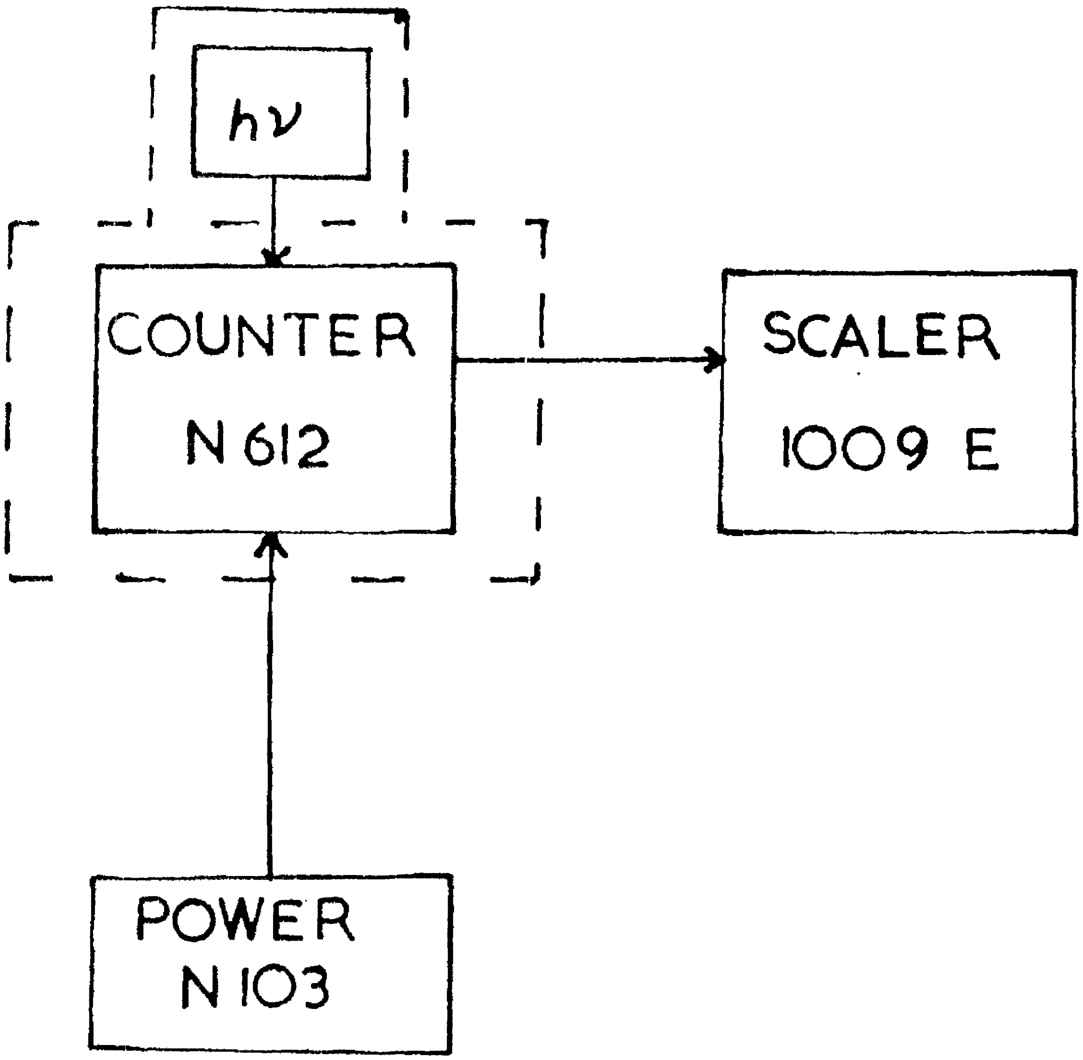


FIG.16 C-14 COUNTING CIRCUIT

Electronics and was the N612 counter. The high voltage required for the photomultiplier (P.M.) tube was supplied from a Dynatron N103 power pack and the scaling unit for counting the pulses from the counter was a Dynatron 1009.E., scaler, see figure 16.

A. 2. STABILISATION OF THE COUNTING RATE.

During initial experiments with the counter, it was found that steady count rates could not be obtained from a given sample during a day's counting using fixed counting conditions. It was originally suspected that this was due to faulty electronic apparatus, but investigation showed this was not the case. Since the photomultiplier tube is sensitive to its operating temperature it was decided to thermostat the counter in a deep-freeze. The reason for using a low temperature was that the background count rate falls with decreasing temperature, without affecting the sensitivity of the counter (64). This leads to increased counting efficiencies. The effect of the temperature on the background count rate is shown in table I. 6. 1.

TABLE I.6.1.

THE EFFECT OF TEMPERATURE ON THE BACKGROUND COUNT RATE OF THE N612 SCINTILLATION COUNTER.

Time	10 a.m.	10.20	11.10	2.10 p.m.
Background Count Rate (C/S)	22	25	31	56
Temperature	15°C	17°C	19°C	21°C

Time	2.50 p.m.	3.10	3.30	3.50	4.05
Background Count Rate (C/S)	44	33	19	11	9.7
Temperature	17°C	10°C	3°C	-7°C	-12°C

The background count rate rose steadily during the day and at 2.10 p.m. the counter was lifted into a deep-freeze and the cooling unit switched on., the count rate decreased very sharply. The following day by which time the counter had had a chance to come to equilibrium with its surroundings, a steady count rate was observed during a day's counting. The temperature in the deep freeze was -25°C and the background count rate readings were as follows:-

TABLE I.6.2.

BACKGROUND COUNT RATE OF N612 COUNTER AT -25°C.

Time	9 a.m.	10	10.30	2 p.m.	4.15
Background counts/second	6.43	6.36	6.39	6.39	6.48

The counter operating conditions were as for the previous tests at room temperature and the reduction of the background count rate, due to a decrease of 40°C in the ambient temperature, was approximately 75%. The advantages of operating the counter in the deep freeze were obvious, since it would lead to higher counting efficiencies and more stable conditions. The lower limit of temperature to which the counter could be taken depended on the solubilities of the solutes in the scintillator at low temperatures. Since -30°C was the lower limit recommended for scintillator solutions, it was decided not to operate the counter at a temperature lower than -25°C. Care was always taken to see that samples to be counted did not contain precipitates, prior to counting them.

.A.3. DETERMINATION OF THE OPTIMUM COUNTING CONDITIONS FOR CARBON-14.

Having stabilised the counting conditions it was now necessary to find the optimum operating conditions for counting

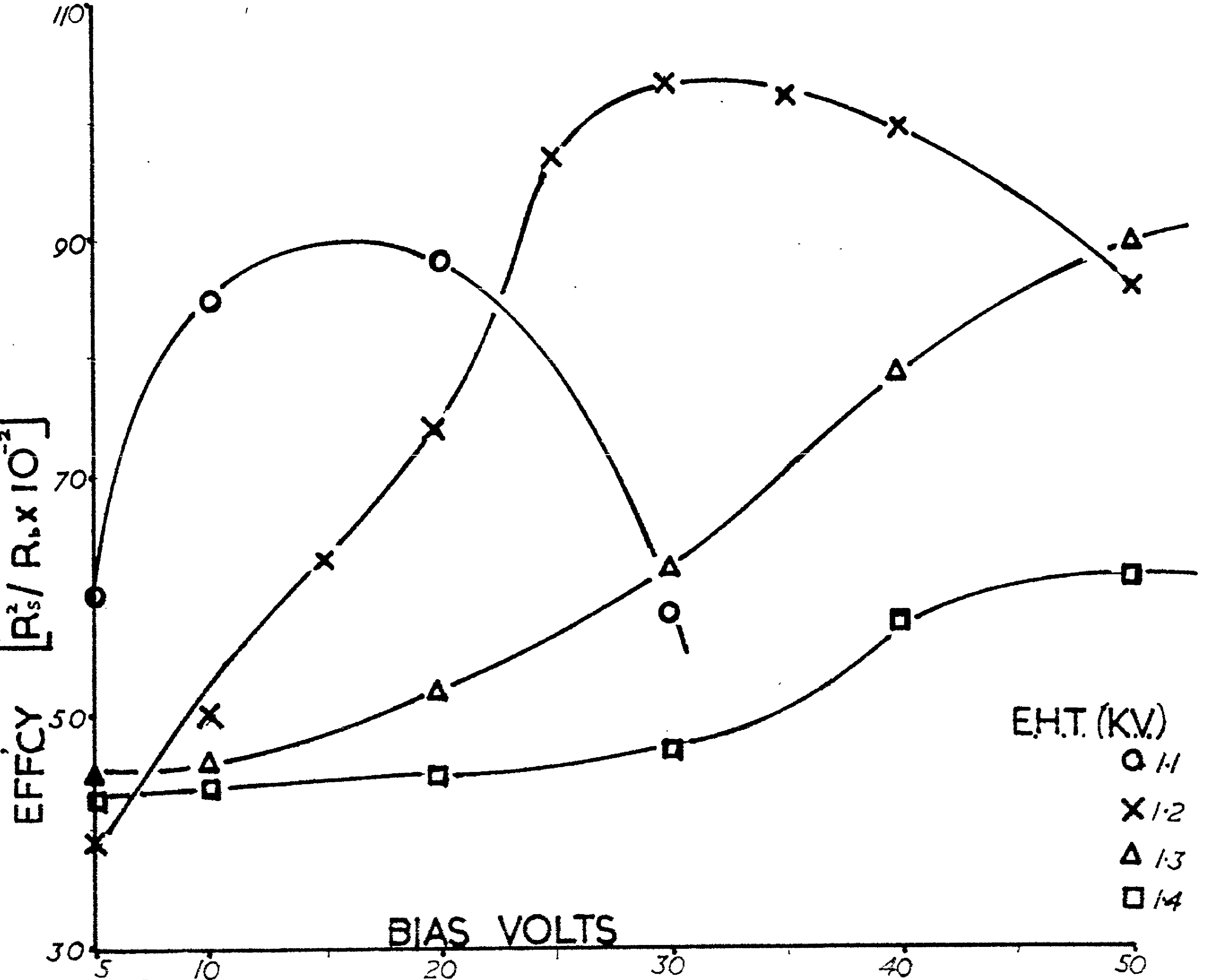


FIG.17. EFFICIENCY V DISCRIMINATOR BIAS VOLTAGE

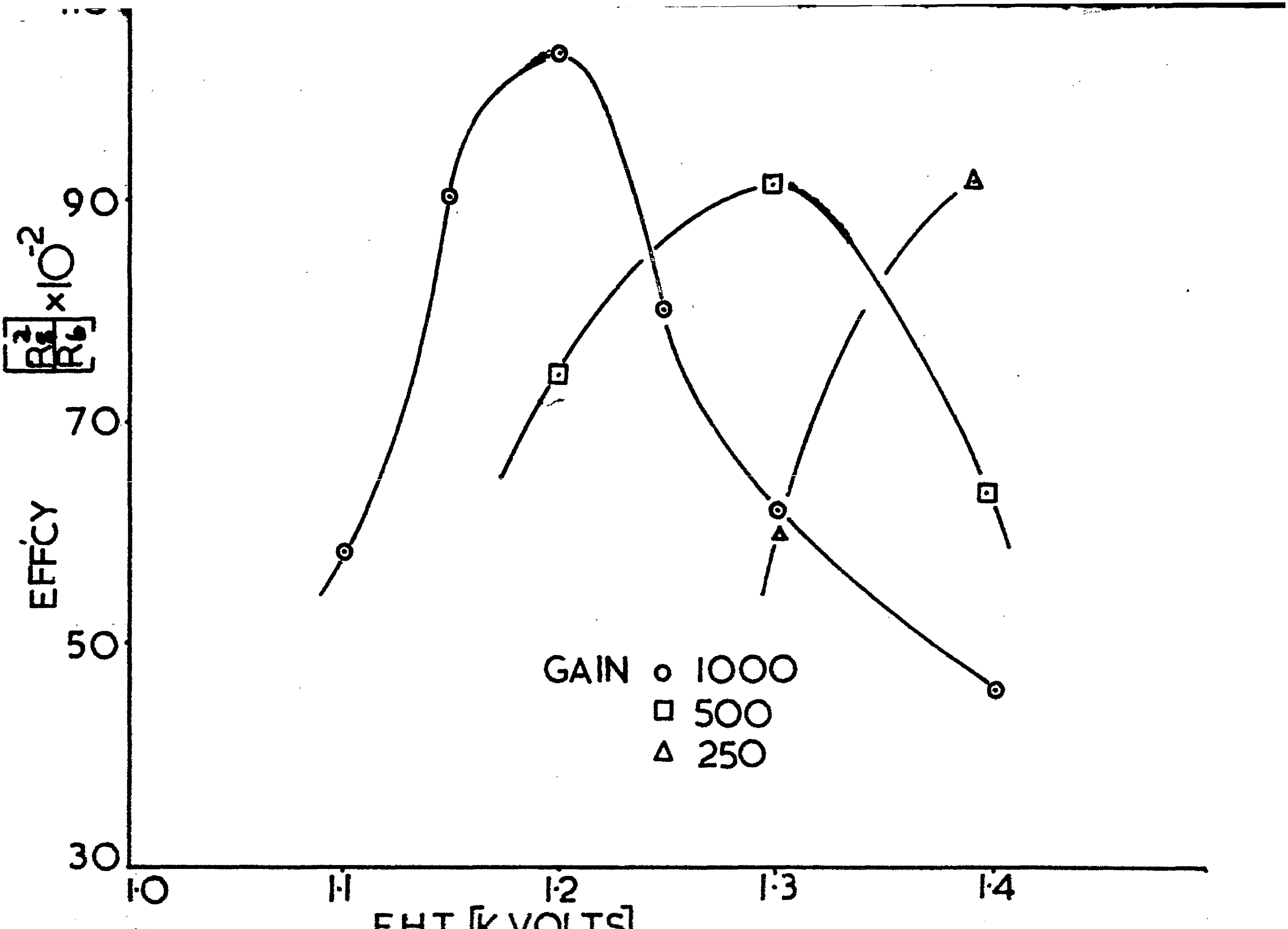


FIG.18. EFFICIENCY V. E.H.T. AT BIAS OF 30 VOLTS

carbon-14. With a scintillation counter the best counting conditions remain fixed for a given isotope, no matter the chemical form or the activity of the isotope. The most efficient counting rate is obtained when the value of Rs^2/Rb reaches a maximum (65, 66). Rs represents the count rate as derived from the source and Rb is the background count rate corresponding to the value of Rs.

In order to obtain the best counting conditions the most suitable values of three variable parameters had to be found. These variables were,

1. The high voltage applied to the photomultiplier tube.
2. The discriminator bias voltage of the scaling unit.
3. The gain of the amplifier following the P.M. tube.

By altering the variables one at a time, the most suitable values for counting carbon-14 were found. The sample used for determining the best conditions was made up of hexadecane-1-C.14 dissolved in 12 ml., of scintillator. The background was determined using a vessel containing 12 ml., of the same scintillator (N.E.213, supplied by Nuclear Enterprises Limited), but with no activity present. The results of the experiments are shown in figures 17, 18 and 19. From figure 17, it can be seen that for a gain of 1000, an H.T. of 1200V., coupled with a discriminator voltage of 30V, yields the highest efficiency. From figure 18 the effect of various gains is shown

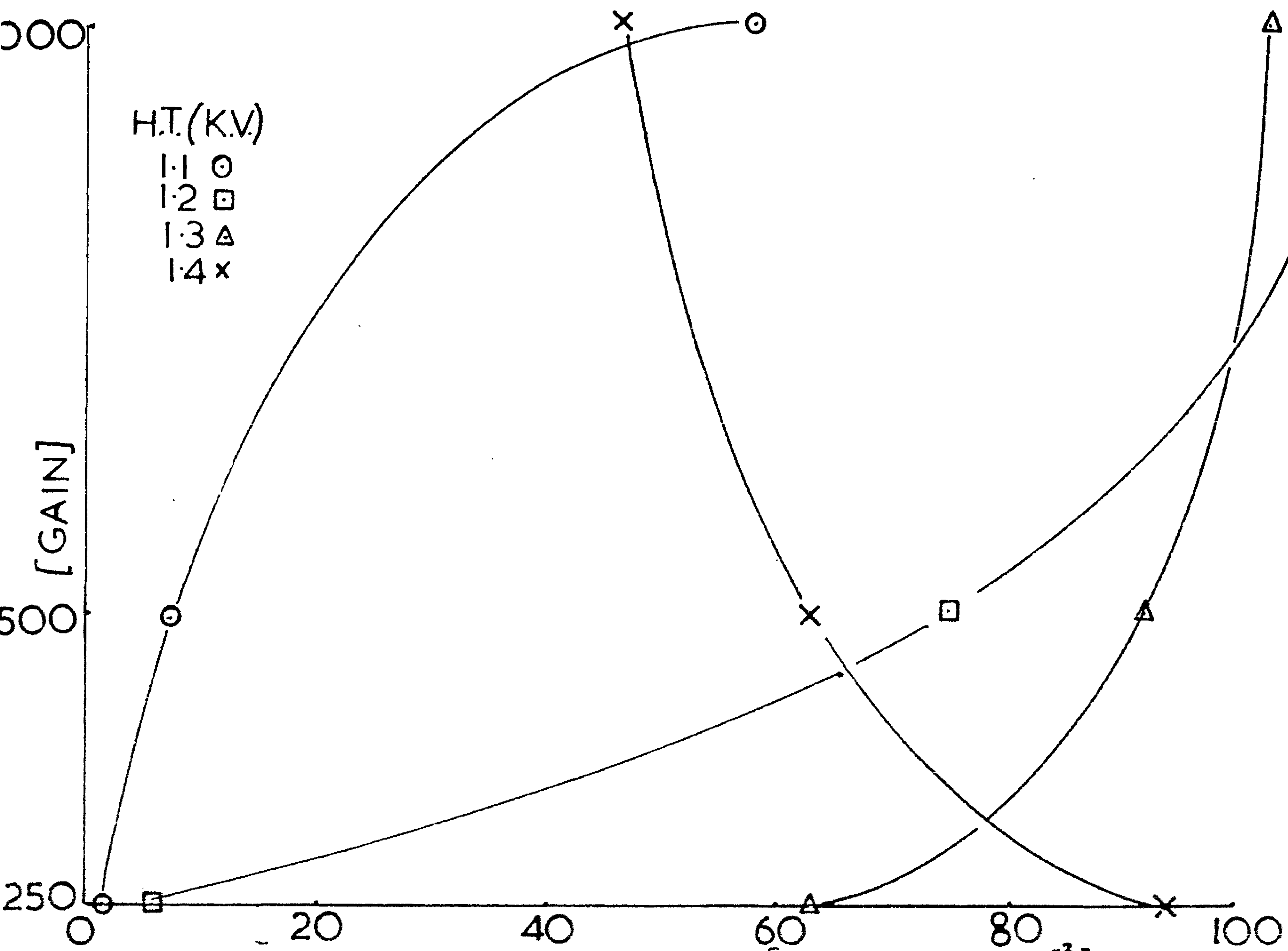


FIG.19. GAIN V. EFFICIENCY.

on the efficiency versus H.T. curves and figure 19 shows curves obtained for gain versus efficiency plots. From an analysis of the curves the best counting conditions for carbon 14 were found to be:-

(i) H.T. = 1200 Volts

(ii) Discriminator bias voltage = 30 Volts

(iii) Amplifier Gain = 1000.

Under the optimum conditions it was found that the actual counting efficiency for C14 was 62%. This figure was determined by counting a standard sample of hexadecane-1-C14 dissolved in N.E.213 scintillator. The background count rate at this efficiency level was about 5 counts per second. The conditions noted above were used throughout for the scintillation counting of carbon 14.

A.4. ADAPTATION OF SAMPLES FOR COUNTING AND THE QUENCHING EFFECT OF CYCLOHEXANE.

Occasionally it was noted when counting samples that a steady count rate was not initially observed. This effect was found to be mainly due to two factors. One was that the sample was not adapted to the temperature of the counter and the second was due to residual phosphorescence in the scintillator and the container. Both these effects were overcome by adapting the samples to darkness and temperature in the deep freeze for about 20 minutes prior to counting them. (67)

To determine what effect, if any, the volume of scintillator added to a sample, would have on the count rate, increasing amounts of scintillator were added to a sample of hexadecane-C14 and the count rate observed after each addition. The result is shown in table I. 6. 3.

TABLE I. 6. 3.

THE EFFECT OF ADDING INCREASING QUANTITIES OF SCINTILLATOR ON THE COUNT RATE OF A SAMPLE

Quantity of N. E. 213 added to the sample (M. L.)	2. 85	4. 90	8. 90	16. 90
Count rate of sample and background (counts/second)	140	144	145	144

With quantities in excess of 5 ML., the count rate was virtually unchanged up to the full capacity of the container used. In practice about 10 ML., of scintillator was used for dissolving samples to be counted.

It is known that certain types of chemical compounds tend to quench the count rate from radioactive scintillator solutions (61, 67) and it was important to know whether cyclohexane would have such an effect. A solution of hexadecane-C-14 was prepared with N. E. 213 liquid scintillator and its count rate determined. Successive amounts of cyclohexane were then

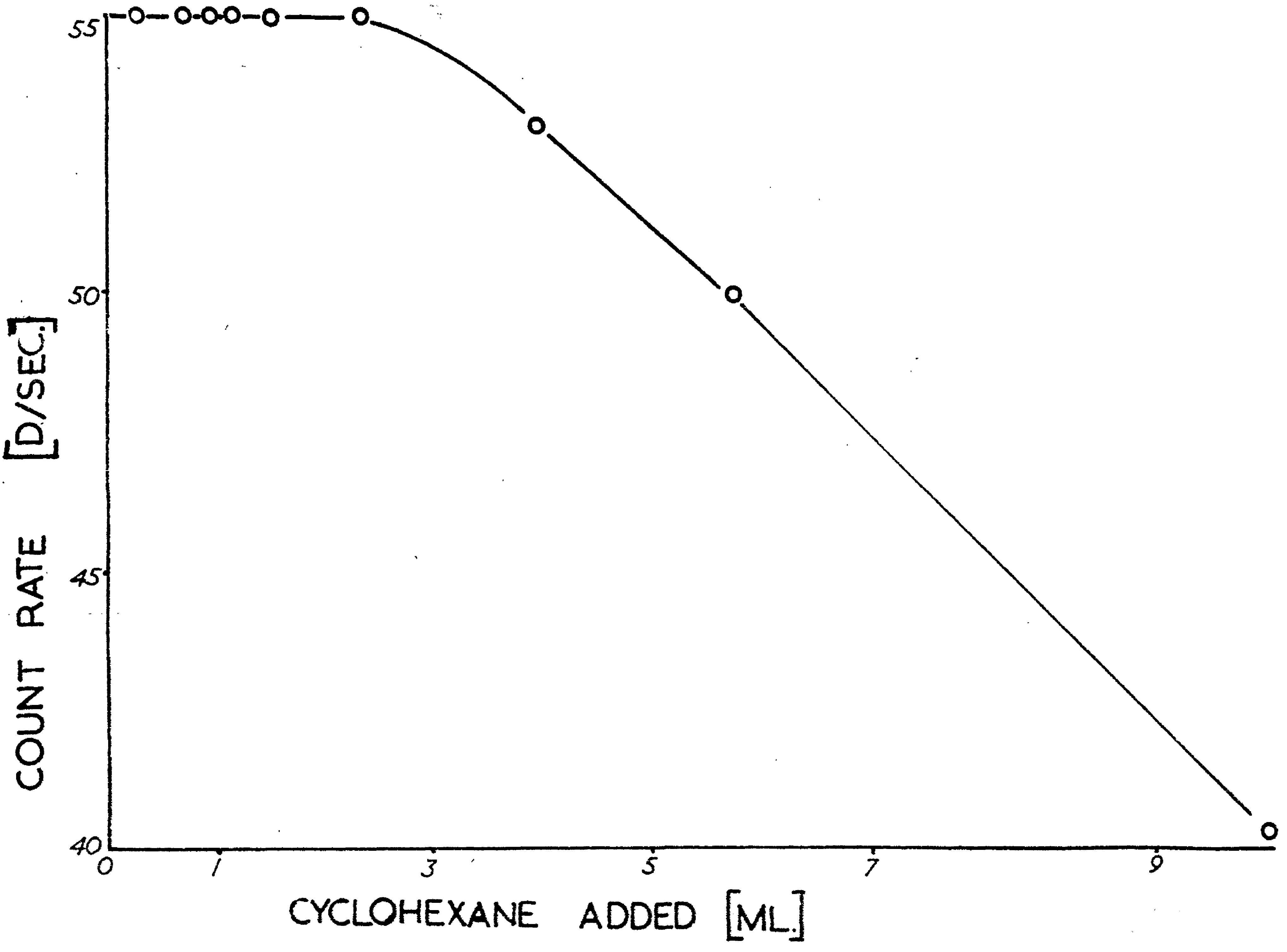


FIG.20. QUENCHING EFFECT OF CYCLOHEXANE

added to the solution and the count rate noted after each addition. It was found that no significant change in the count rate occurred until approximately 2 ml. of cyclohexane had been added to the sample. The result of this test is shown in figure 20. Since the quantities of cyclohexane to be counted were of the order of a few milligrams, the effect of quenching could be ignored.

A. 5. PREPARATION OF SCINTILLATOR.

Because large quantities of scintillator were liable to be required it was considered desirable to make up batches of scintillator in the laboratory. The preparation of liquid scintillators has been the subject of a number of written articles in the past (68, 69). The scintillator which was finally adopted was made up of 3 grams/litre of diphenyl-oxazole (P. P. O.) and .1 grams/litre of 1, 4-di-[2-(5-Phenyloxazolyl)] Benzene, (Popop). The former chemical acts as a phosphor while the latter serves to shift the spectrum of the emitted light to match the spectral response of the P. M. tube. The P. P. O. and P. O. P. O. P., were supplied as 'scintillation grade' chemicals by Nuclear Enterprises Ltd. The toluene solvent was 'analar grade' supplied by B. H. D. The counting efficiency for C14 under the optimum counting conditions and using the scintillator, as outlined above, was 60% which compared very favourably with the figure of 62% using the commercial

N.E. 213 scintillator.

All counting of cyclohexane-C14 samples was carried out using the lab-prepared scintillator and employing the optimum counting conditions for C14 as previously described. The samples were counted to an accuracy of at least 2% and, more generally, the figure was 1%.

B. TRITIATED PIVALIC ACID.

The energy of the β particle emitted from the decaying tritium atom is weaker than that from carbon 14. It is, in fact the weakest β particle emitter known and very sensitive method~~s~~ of analysis are required for its detection. Because of its soft radiation the use of tritium as a tracer has been widespread, especially in biological studies (67).

$$H_1^3 \longrightarrow He_2^3 + \beta^- \qquad (E_\beta \text{ max} = .02 \text{ MEV})$$

The method used for measuring the tritium activity was similar to that previously described for carbon-14, with several modifications.

Because of the weakness of the tritium radiation more sensitive counting conditions were required for its detection than had been the case with carbon-14. It was found, by increasing the sensitivity of the scintillation counter in the deep freeze, that very high background count rates were obtained and these rates were subject to fluctuation. The increase in sensitivity had been effected by increasing the high voltage

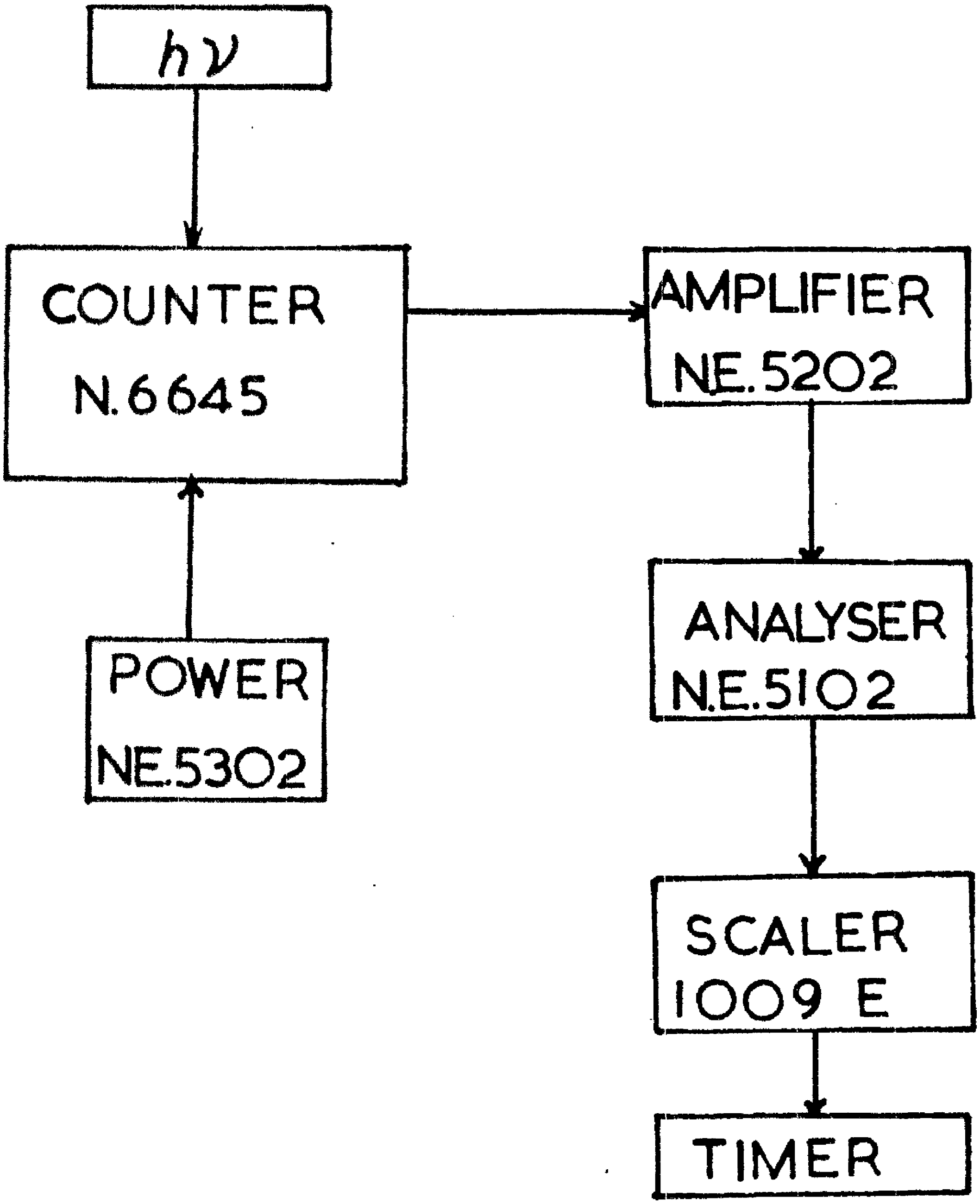


FIG.21. H-3 COUNTING CIRCUIT

applied to the P.M. tube and reducing the discriminator bias voltage. It was felt that if the response of the scaler could be controlled, such that it would only count pulses within a given energy range, that much of the background noise could be eliminated.

The reason for this conjecture was that the electronic signals amplified by the P.M. tube, vary in strength according to the origin of the signal. The pulses generated by scintillations due to radioactivity, are generally more energetic than the background pulses, most of which result from thermal noise of the P.M. tube. Thus if these weak signals could be eliminated, the background count rate would drop and the counting efficiency would rise. This effect was achieved by using a more complex counting circuit than that used previously, including a pulse height analyser.

A block-diagram of the circuit used for counting the tritium activity is shown in figure 21. It consisted of an Ecko scintillation counter (N. 664. B) followed by a Nuclear Enterprises linear amplifier (N.E. 5202) and pulse height analyser (N.E. 5102). The signals from the pulse height analyser were fed to a Dynatron 1009E scaler and automatic timing unit., power for the P.M. tube was from a Nuclear Enterprises power pack (N.E. 5302).

The scintillation counter, in this case, was operated at

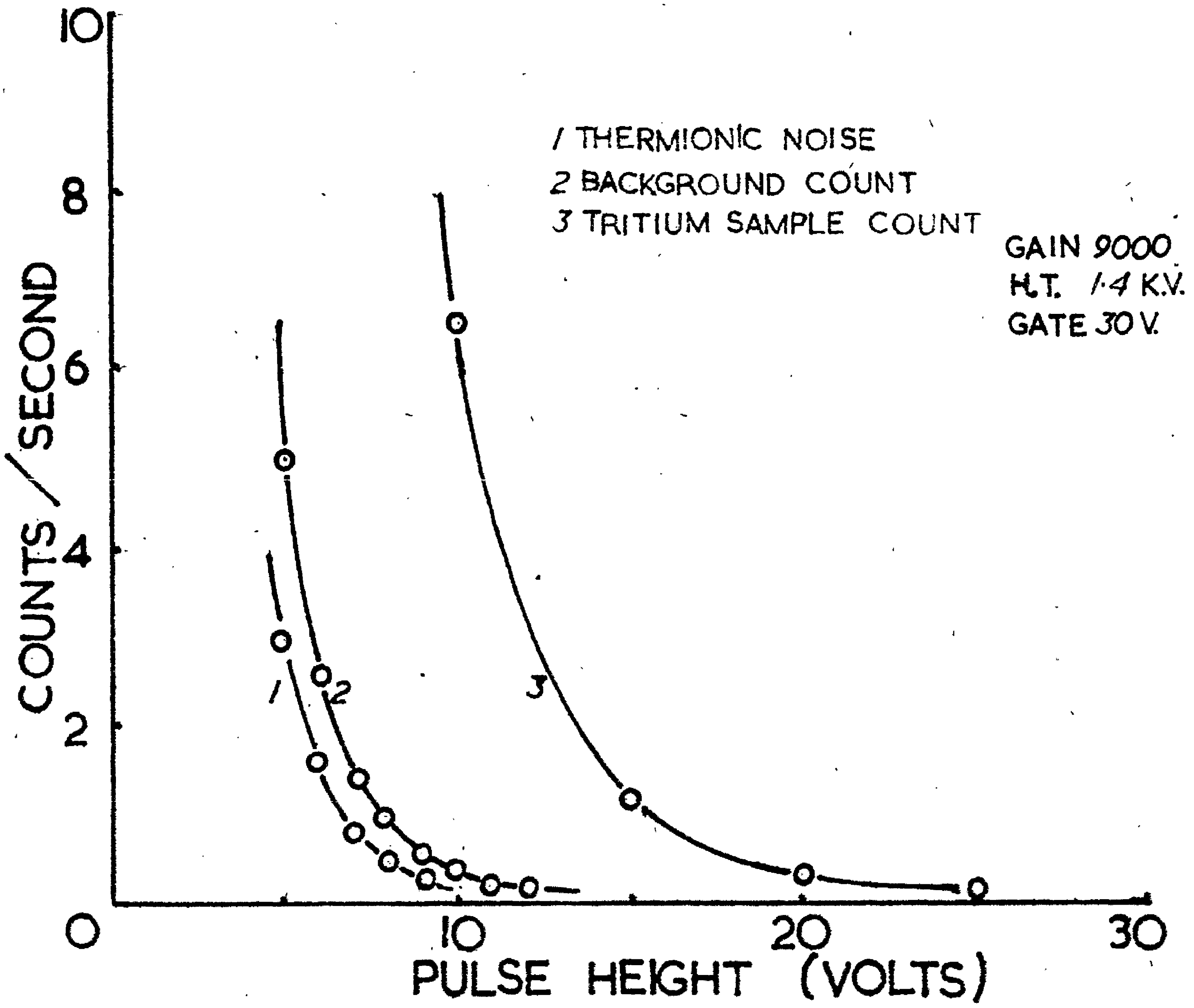


FIG.22. PULSE HEIGHT SEPARATION

room temperature and the P.M. tube was thermostatted by a water jacket through which mains-water was passed. The P.M. tube in the counter had been specially selected for its low thermal noise characteristics and the background level of counting at room temperature was lower than for the counter in the deep freeze. The incorporation of the linear amplifier allowed a greater range of amplification to be studied and led to a more stable output to the scaling circuit.

The signal from the amplifier was transferred to the pulse-height analyser and it was here that a separation of the source and background counts could be made. The effect is shown in figure 22. By suitable adjustment of the gate width, which was representative of the energy range which the analyser would pass on to the scaler, and the pulse height, which set the threshold of the energy spectrum, it was possible to cut out much of the background noise.

The conditions which were employed for counting the tritiated acid samples were as follows:-

(1)	Amplifier Gain	6400
(2)	Gate width	30 Volts
(3)	P.M. voltage	1400 volts
(4)	Pulse height	6 volts
(5)	Temperature	15°C

The background under these conditions was abaut 4 counts per second and the counter efficiency for a sample of tritiated water was 30%.

Because the light quenching effect of oxygen containing compounds is often severe, it was important to know if pivalic acid would have such an effect. It was found that the addition of up to 10 mg. of pivalic acid to a solution of tritiated hexadecane in scintillator, had no effect on the count rate. Since the weights of samples being measured were all of the order of 3 mg. it was considered that the quenching effect could be ignored.

When counting samples the background was measured twice a day and was found to be constant. All the pivalic acid samples were analysed for radioactivity to within an accuracy of 2% and more often 1%.

MEASUREMENT OF SELF-DIFFUSION IN CYCLOHEXANE BY THE SURFACE DECREASE METHOD.

As mentioned previously in section I.5. it is sometimes possible to measure the overall rate of diffusion of a radioactive material into a solid by studying the rate at which the radioactivity, as measured at the surface of the solid, decreases, due to diffusion of material from the surface into the solid (70).

The conditions required for diffusion are similar to those previously described for the sectioning method, in that an infinitely thin source is deposited onto a right-end-face of a semi-infinite cylinder and allowed to diffuse. An end-windowed G.M. counter, situated over the deposit, is used to measure the rate of decrease in activity of the latter. This method is very useful, when isotopes, having weak radioactive emissions, are being employed. The reason is that radiation from these isotopes is strongly absorbed by thin layers of solid and hence, even a very slow diffusion process can be readily detected by the method.

Although the weak radiation of an isotope can be useful for detecting a slow diffusion process, it also presents one of two main problems associated with the present study. The first of these is associated with the detection of the weak radiations from the carbon-14 form of cyclohexane and the second arises from the high vapour pressure of the latter in the solid state.

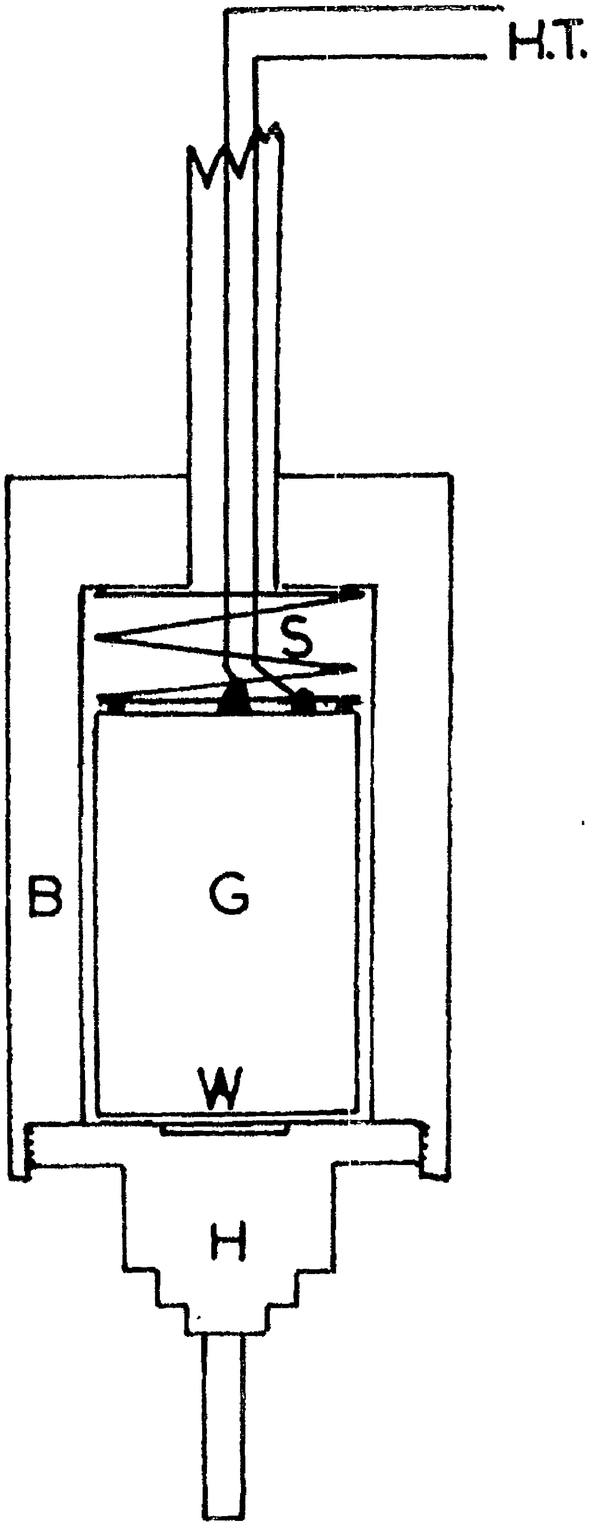


FIG.23. SURFACE DECREASE APPARATUS

Because of its high vapour pressure it was necessary to seal off the radioactive cyclohexane deposit completely from the atmosphere and the seal had to be very thin to allow passage of the radiation to the G.M. tube. Thin glass films were used but these invariably cracked when they were thin enough to transmit the radiations, a film thickness of approximately 2 mg. $cm.^{-2}$, was required. Mica was found to be more suitable for sealing off the deposit, but here also, small cracks tended to occur in the mica if it was too thin and in this case the count rate from the surface did not decrease, but increased, presumably because of escape of radioactive vapour into the space surrounding the G.M. tube. The counting efficiency obtained with a good mica film was about 3% of the surface activity.

1. THE SURFACE DECREASE APPARATUS.

An apparatus which would allow continuous measurement of the surface activity during a diffusion experiment was constructed and is outlined in figure 23. A cylindrical brass casing (B) was made to house the G.M. tube (G), which was an Ecko MX148 thin windowed counter. The window of the counter faced the surface of the cyclohexane crystal which was retained in a crystal holder (H) of the type shown in figure 10. The flange of the crystal holder screwed into the open end of H, the other end of which was brazed to a long copper tube through which the leads to the G.M. tube were passed. The copper tube also served as a support for the apparatus when it was lowered into the thermostat during a diffusion experiment. The whole device was liquid tight.

The mica window used to preserve the crystal and its deposit was sandwiched between two thin brass discs one of which had a protruding rim round a central orifice. The discs, which interlocked by means of three pins to avoid them turning against each other and crushing the mica film, set against the flange of the crystal holder, the rim of the lower one fitting closely inside the opening of the flange. The centres of both discs had been drilled out to a radius of 8 mm. to allow passage of radiation from the crystal surface to the G.M. counter through the mica window (W). The discs served to support the mica and limit the detectable radiation to a well defined area of the crystal surface. This was necessary because some radioactive cyclohexane always tended to condense on the flange of the crystal holder during the deposition and radiation from this source would have led to experimental errors. During an experiment close contact between the G.M. tube and the flange of the crystal holder was maintained by a plastic spring (S), which pushed the G.M. tube onto the flange.

The lower temperature limit for operating the apparatus was fixed by the G.M. tube, which could not be operated below -55°C. Between temperatures of +20°C and -50°C the counting efficiency of the tube was constant to within 1%, below -50°C the efficiency started to drop. The counting characteristics of the tube were studied and a plateau was found between applied voltages of 350 and 650 volts with a slope of 1% per 100 volts. All counting was carried out at an operating voltage of 450 volts and the background count was fairly consistent at 30 counts per minute.

2. THE EXPERIMENTAL PROCEDURE.

Prior to an experiment, the apparatus for the surface decrease was cooled to -30°C in the deep freeze. A crystal was mounted in a holder and a radioactive deposition carried out, as described in section I. 3. A. After the deposition, the mica window was fitted over the flange face of the crystal holder and the latter screwed tightly into its seating in the brass casing for the G.M. tube. The complete unit was then suspended in the low temperature thermostat bath being supported by the copper tube which held the leads for the G.M. tube. Immediately after immersing the counter into the thermostat the former was connected to a scaler via a probe unit. The scaler was a Dynatron 1009E, type, fitted to an automatic timing unit. A series of readings of the count rate were taken at frequent intervals from which the rate of decrease of the surface activity could be measured. The count rate was plotted as a fraction of the initial count rate at the start of the experiment. Background counts were taken before and after each experiment. In the experiments which were successful the time taken for the count rate to decrease significantly varied from 30 minutes at -30°C to 15 hours at -50°C.

It was not found practicable to section the crystals after the surface decrease experiments due to distortion of the crystal surface by the locating ring of the brass disc supporting the mica window.

A similar procedure was not employed with pivalic acid due to the weakness of the radiation from the tritiated tracer which could not be detected by the G.M. tube.

CHAPTER II

THE RESULTS OF THE DIFFUSION EXPERIMENTS AND THEIR INTERPRETATION

The results of the diffusion experiments.

The results of the successful diffusion experiments are given in the following tables. The results for self-diffusion in cyclohexane using the sectioning technique are shown in tables 2.A.1 to 2.A.10 and tables 2.AD.1 to 2.AD.4 show the results for cyclohexane obtained using the surface-decrease method. Tables 2.B.1 to 2.B.6 show the diffusion results for pivalic acid, using the sectioning technique.

Because of the cubic form of the crystal structure of cyclohexane and pivalic acid, both have face centred cubic structure, no particular crystallographic direction was preferred for any particular experiment. It was assumed that the nature of the diffusion, as had been found for all other diffusion studies on cubic solids, would be isotropic. In practice all the diffusion experiments were performed on single crystal sections, such that diffusion was measured along the length of the principal growth axis of the crystal.

Preliminary experiments were carried out for each of the three sets of diffusion experiments in order to determine suitable conditions.

In the case of the sectioning experiments on cyclohexane a vapour pressure of .5 cms. of mercury was developed in the storage bulb, B, fig. 8 and this was found suitable for making the deposition. The vapour corresponded to about .5 mg. of radioactive cyclohexane and yielded an initial surface activity of 800 counts per second. From initial experiments it was found that diffusion times of the order of 1 hour at -30°C and 50 hours at -60°C were required to produce measurable diffusion. The diffusion times for each experiment are shown in table I.4.4.

It was found that a much higher activity was required to produce a measurable record of the surface decrease of activity during these experiments on cyclohexane. The surface deposit required was of the order of 1 mg. and a vapour pressure in B of 2 cms. was used to produce this deposit. The diffusion times required to produce a reasonable decrease of the surface of activity corresponded fairly well with these required for the sectioning method at the same temperature. The diffusion periods for the surface decrease experiments are shown in tables 2.AD.1 to 2.AD.4.

The diffusion rates in pivalic acid over the temperature range examined were all found to be of the same order and diffusion times of about 1 hour provided sufficient penetration of diffused activity to enable the diffusion rates to be measured. The times for diffusion are shown in table I. The results of these diffusion experiments and of the other diffusion experiments are shown in the following tables and the interpretation of these results is developed in section II.2.

TABLE 2.A.1. Diffusion at -31.5°C

No. of Crystal Slice	Thickness of Slice CM x 10^3	Depth of Centre of Slice from the Surface (x) CM x 10^3	Depth (x) Squared $CM^2 \times 10^4$	Activity of Slice, Counts per Second	Log of Activity
		x	x^2	A	$\log_{10}A$
3	3.0	7.5	.592	10.9 ± .11	1.04
4	3.0	10.5	1.130	8.9 ± .10	.95
5	3.0	13.5	1.855	8.3 ± .10	.92
6	3.0	16.5	2.756	7.4 ± .09	.87
7	3.0	19.5	3.835	5.7 ± .09	.76
8	3.0	22.5	5.088	2.6 ± .07	.42
9	3.0	25.5	6.632	1.2 ± .07	.08
10	3.0	28.5	8.153	.7 ± .06	-.16

TABLE 2.A.2. Diffusion at -37.5°C

No. of Crystal Slice	Slice Thickness CM x 10^3	Depth of Slice from Surface (CM x 10^3)	Depth Squared (CM^2 x 10^4)	Activity of Slice in Counts/ Second	Log Activity
		x	x^2	A	$\log_{10}A$
1	1.5	.75	.00563	118 ± 1.25	2.07
2	3.0	3.0	.090	106 ± 1.14	2.02
3	3.0	6.0	.360	- -	-
4	3.0	9.0	.810	- -	-
5	1.5	11.25	1.265	39.9 ± .45	1.60
6	1.5	12.75	1.625	34.5 ± .42	1.53
7	1.5	14.25	2.030	20.6 ± .29	1.31

TABLE 2.A.3 Diffusion at -39°C

No. of Crystal Slice	Slice Thickness	Depth of Centre of Slice from Surface	Depth Squared	Activity of Slice Counts/ Second	Log Activity
	CM x 10^{+3}	X x 10^{+3}(cms)	X^2 x 10^{+4} cm^2	A	$\log_{10} A$
2	1.5	2.25	.0506	40.2 ± .44	1.60
3	1.5	3.75	.141	37.3 ± .41	1.57
4	1.5	5.25	.275	34.4 ± .38	1.53
5	1.5	6.75	.456	26.9 ± .30	1.43
6	1.5	8.25	.681	18.2 ± .22	1.26
7	1.5	9.75	.951	18.3 ± .22	1.26
8	1.5	11.25	1.266	13.3 ± .17	1.12
9	1.5	12.75	1.624	9.5 ± .13	.97
11	1.5	15.75	2.480	5.0 ± .09	.69

TABLE 2.A.4 Diffusion at -44.8°C

No. of Crystal Slice	Slice Thickness. cm x 10^3	Depth of Slice Centre from Face. cm x 10^3	Depth (X) Squared. $cm^2 \times 10^4$	Activity of Slice in Counts/ Second	Log Activity
		X	X^2	A	$\log_{10}A$
1	1.5	.75	.00563	66.8 ± .71	1.83
2	1.5	2.25	.0506	34.7 ± .44	1.54
3	1.5	3.75	.141	32.8 ± .42	1.52
4	1.5	5.25	.275	27.7 ± .37	1.44
5	1.5	6.75	.456	23.2 ± .33	1.37
7	1.5	9.75	.951	10.10 ± .20	1.00
11	1.5	15.75	2.480	3.4 ± .12	0.53
12	1.5	17.25	2.972	1.9 ± .11	0.28

TABLE 2.A.5. Diffusion at -44.8°C

No. of Crystal Slice	Slice Thickness cm x 10^3	Depth of Slice Centre from Surface cm x 10^3	Depth Squared cm x 10^4	Activity of Slice Counts/ Second	Log Activity
		X	X^2	A	$\log_{10}A$
1	1.5	.75	.00563	149 ± 1.5	2.17
2	1.5	2.25	.0506	85 ± .87	1.92
3	1.5	3.75	.141	93.7 ± .96	1.97
4	1.5	5.25	.275	54.8 ± .58	1.73
5	1.5	6.75	.456	28.9 ± .32	1.46
6	1.5	8.25	.681	17.3 ± .21	1.23
7	1.5	9.75	.951	9.5 ± .13	.96

TABLE 2.A.6 Diffusion at -48.2

No. of Crystal Slice	Slice Thickness cm x 10^3	Depth of Slice Centre from Face cm x 10^3	Depth (X) Squared $cm^2 \times 10^4$	Activity of Slice in Counts/ Second	Log Activity
		X	X^2	A	$\log_{10}A$
1	1.5	.75	.0056	32.5 ± .37	1.51
2	1.5	2.25	.0506	26.4 ± .31	1.42
4	1.5	5.25	.275	21.0 ± .26	1.32
5	1.5	6.75	.456	18.0 ± .24	1.25
6	1.5	8.25	.681	15.5 ± .21	1.19
7	1.5	9.75	.951	12.5 ± .18	1.09
9	1.5	12.75	1.624	6.4 ± .09	.80
10	1.5	14.25	2.030	4.8 ± .08	.68
12	1.5	17.25	2.975	2.2 ± .07	.34

TABLE 2.A.7 **Diffusion at -50.0°C**

No. of Crystal Slice	Slice Thickness cm x 10^3	Depth of Centre of Slice from Face (X) cm x 10^3	Depth (X) Squared cm^2 x 10^4	Activity of Slice in Counts/ Second	Log Activity
			X^2	A	$\log_{10}A$
1	1.5	.75	.00563	23.6 ± .28	1.37
3	1.5	3.75	.141	19.6 ± .24	1.29
4	1.5	5.25	.275	17.1 ± .22	1.23
5	1.5	6.75	.456	12.9 ± .17	1.11
6	1.5	8.25	.681	9.4 ± .14	.97
7	1.5	9.75	.951	5.9 ± .08	.77
8	1.5	11.25	1.266	4.5 ± .08	.65
9	1.5	12.75	1.624	2.7 ± .07	.43
10	1.5	14.25	2.030	1.4 ± .06	.14

TABLE 2.A.8 Diffusion at -57.5°C

No. of Crystal Slice	Slice Thickness cm x 10^3	Depth of Slice Centre from Face cm x 10^3 X	Depth (X) Squared $cm^2 \times 10^4$ X^2	Activity of Slice in Counts per Second A	Log Activity $\log_{10}A$
1	1.5	.75	.0056	136 ± 1.4	2.13
2	1.5	2.25	.0506	122 ± 1.3	2.09
3	1.5	3.75	.141	109 ± 1.1	2.04
4	1.5	5.25	.275	101 ± 1.0	2.00
6	1.5	8.25	.681	69.6 ± .73	1.84
8	1.5	11.25	1.266	42.5 ± .46	1.63
9	1.5	12.75	1.624	29.6 ± .33	1.47
10	1.5	14.25	2.030	21.6 ± .25	1.33
11	1.5	15.75	2.480	17.0 ± .20	1.23

TABLE 2.A.9 Diffusion at -57.5°C

No. of Crystal Slice	Slice Thickness cm x 10^3	Depth of Centre of Slice from Face (X) cm x 10^3 X	Depth (X) Squared cm^2 x 10^4 X^2	Activity of Slice in Counts/ Second A	Log of Activity $\log_{10}A$
1	1.5	.75	.00563	46.5 ± .57	1.67
2	1.5	2.25	.0506	15.7 ± .27	1.20
3	1.5	3.75	.141	14.6 ± .26	1.16
4	1.5	5.25	.275	11.7 ± .23	1.07
5	1.5	6.75	.456	6.8 ± .19	.83
6	1.5	8.25	.681	3.7 ± .13	.57
7	1.5	9.75	.951	1.4 ± .15	.08
8	1.5	11.25	1.266	.8 ± .1	-.10

TABLE 2.A.10 Diffusion at -62.6

No. of Crystal Slice	Slice Thickness cm x 10^3	Depth of Slice Centre from Face cm x 10^3 X	Depth (X) Squared cm^2 x 10^4 X^2	Activity of Slice Counts per Second A	Log Activity $\log_{10}A$
1	1.5	.75	.0056	222 ± 2.3	2.35
2	1.5	2.25	.0506	182 ± 1.9	2.26
3	1.5	3.75	.141	113 ± 1.2	2.05
4	1.5	5.25	.275	68 ± .72	1.83
5	1.5	6.75	.456	32 ± .36	1.50
6	1.5	8.25	.681	11.6 ± .16	1.06
7	1.5	9.75	.951	3.2 ± .08	.50

TABLE 2.A.D.1 Diffusion at -31.5°C

Diffusion Time (Minutes)	Surface Activity (Counts per Second)	Surface Activity / Initial Surface Activity $\left(\frac{A}{A_o}\right)$
0	30.32	1
5	23.67	.782
10	20.60	.680
13.5	17.87	.590
17.5	16.24	.536
21.5	15.27	.504
25	15.01	.496
29	13.60	.448
33	12.87	.427
38	12.17	.402
46	12.07	.398
79	11.00	.363

TABLE 2.A.D.2 Diffusion at -39.8°C

Diffusion Time (Minutes)	Surface Activity Counts per Second	Surface Activity / Initial Surface Activity $\left(\frac{A}{A_o}\right)$
0	8.65	1
15	7.75	.896
29	6.90	.798
40	6.68	.772
65	6.20	.718
81	5.98	.692
98	5.54	.640
130	5.31	.614
155	5.18	.600
190	5.20	.604
210	5.20	.604
1290	4.45	.398
1301	4.36	.390

TABLE 2.A.D.3 Diffusion at -44.5°C

Diffusion Time (Minutes)	Surface Activity (Counts per Second)	$\frac{\text{Surface Activity}}{\text{Initial Surface Activity}}$ $\left(\frac{A}{Ao}\right)$
2	9.35	
7	9.35	
19	10.45	1
31	9.95	.91
57	9.25	.88
111	7.50	.714
130	7.25	.690
233	7.42	.707
295	7.10	.686
450	6.89	.657
510	6.65	.633
1507	5.60	.533

TABLE 2.A.D.4 Diffusion at -50°C

Diffusion Time (Minutes)	Surface Activity (Counts per Second)	Surface Activity / Initial Surface Activity $\left(\frac{A}{A_o}\right)$
0	19.3	1
5	21.7	1
9	22.4	1
24	22.4	1
42	22.3	1
54	22.3	1
823	15.6	.695
868	15.8	.702
905	15.3	.680

TABLE 2.B.1. Diffusion at 7.2°C

No. of Crystal Slice	Thickness of Slice cm x 10^3	Depth of Centre of Slice from Face (X) cm x 10^3	Depth (X) Squared cm^2 x 10^4	Specific Activity of Slice in Counts/ Second/mg	Log Activity
		X	X^2	A	$\log_{10}A$
3	3.0	7.5	.562	13.9 ± .15	1.14
4	3.0	10.5	1.101	11.6 ± .12	1.06
5	3.0	13.5	1.822	10.6 ± .11	1.03
8	3.0	22.5	5.065	7.8 ± .09	.89
9	3.0	25.5	6.50	6.1 ± .07	.78
10	3.0	28.5	8.12	4.5 ± .06	.66
11	3.0	31.5	9.92	3.8 ± .05	.58
13	3.0	37.5	14.06	2.2 ± .04	.34
14	3.0	40.5	16.40	1.8 ± .03	.25
15	3.0	43.5	18.93	1.2 ± .02	.08

TABLE 2.B.2 Diffusion at 9.4°C

No. of Crystal Slice	Slice Thickness in cm x 10^3	Depth of Centre of Slice from Face in cm x 10^3	Depth (X) Squared in $cm^2 \times 10^4$	Specific Activity of Slice in Counts/ Second/mg	Log of Activity
		X	X^2	A	$\log_{10}A$
3	3.0	7.5	.562	41.6 ± .43	1.62
4	3.0	10.5	1.110	46.3 ± .47	1.67
5	3.0	13.5	1.822	36.6 ± .38	1.56
6	3.0	16.5	2.723	29.4 ± .31	1.47
9	3.0	25.5	6.500	28.0 ± .29	1.45
10	3.0	28.5	8.120	22.4 ± .23	1.35
14	3.0	40.5	16.40	8.3 ± .09	.92
15	3.0	43.5	18.93	5.8 ± .07	.76
16	3.0	46.5	21.62	4.5 ± .06	.65

TABLE 2.B.3. Diffusion at 12°C

No. of Crystal Slice	Thickness of Slice cm x 10^3	Depth of Centre of Slice from Face (X) cm x 10^3	Depth (X) Squared cm^2 x 10^4	Specific Activity of Slice, Counts per Second per mg.	Log Specific Activity
		X	X^2	A	$\log_{10}A$
3	3.0	7.5	.562	5.28 ± .09	.72
4	3.0	10.5	1.101	2.52 ± .05	.40
5	3.0	13.5	1.822	2.87 ± .06	.46
8	3.0	22.5	5.065	1.84 ± .04	.26
10	3.0	28.5	8.12	1.57 ± .05	.19
11	3.0	31.5	9.92	.96 ± .05	-.02
14	3.0	40.5	16.40	.46 ± .03	-.34

TABLE 2.B.4. Diffusion at 14.8°C

No. of Crystal Slice	Thickness of Slice cm x 10^3	Depth of Centre of Slice from Face cm x 10^3	Depth (X) Squared cm^2 x 10^4	Specific Activity of Slice in Counts/ Second/mg.	Log of Activity
		X	X^2	A	$\log_{10}A$
2	3.0	4.5	.203	17.11 ± .18	1.23
3	3.0	7.5	.562	18.66 ± .20	1.27
5	3.0	13.5	1.822	15.48 ± .16	1.19
6	3.0	16.5	2.723	10.36 ± .12	1.02
8	3.0	22.5	5.065	7.72 ± .08	.89
9	3.0	25.5	6.50	6.01 ± .07	.78
11	3.0	31.5	9.92	4.48 ± .05	.65
12	3.0	34.5	12.25	3.86 ± .04	.59
14	3.0	40.5	16.40	1.77 ± .03	.25
15	3.0	43.5	18.93	1.24 ± .02	.09

TABLE 2.B.5 Diffusion at 18°C

No. of Crystal Slice	Thickness of Slice cm x 10^3	Depth of Centre of Slice from Face cm x 10^3	Depth (X) Squared cm^2 x 10^4	Specific Activity of Slice Counts per Second per mg.	Log of Specific Activity
		X	X^2	A	$\log_{10}A$
3	3.0	7.5	.562	12.4 ± .12	1.09
5	3.0	13.5	1.822	11.6 ± .11	1.06
6	3.0	16.5	2.723	9.6 ± .10	.98
8	3.0	22.5	5.065	6.5 ± .08	.81
11	3.0	31.5	9.92	5.4 ± .07	.73
13	3.0	37.5	14.06	4.5 ± .07	.65
15	3.0	43.5	18.93	4.0 ± .06	.60

TABLE 2.B.6 Diffusion at 22.2°C

No. of Crystal Slice	Thickness of Slice cm x 10^3	Depth of Centre of Slice from Face (X) cm x 10^3	Depth (X) Squared cm^2 x 10^4	Specific Activity of Slice (Counts per Second per mg.)	Log of Specific Activity
		X	X^2	A	$\log_{10}A$
10	3.0	28.5	8.12	3.60 ± .11	.56
11	3.0	31.5	9.92	2.91 ± .64	.46
12	3.0	34.5	12.25	2.20 ± .04	.33
14	3.0	40.5	16.40	1.40 ± .06	.134
15	3.0	43.5	18.93	1.00 ± .05	.003

. Interpretation of the results.

.A. The interpretation of the diffusion results for cyclohexane obtained by the sectioning technique.

(i) The choice of a diffusion equation.

The conditions under which the diffusion studies have been carried out can be interpreted in terms of an infinitely thin source diffusing into an infinitely thick medium. This interpretation applies when the source thickness is negligible compared to the depth of diffusion, which in turn is less than the thickness of the diffusion medium.

The solution of the diffusion equation for an infinitely thin source diffusing from the right end face of a semi-infinite cylinder, which is the solution applicable to the present experiment, is (1, 3)

$$C = \frac{Q}{\sqrt{\pi D t}} \ \mathrm{EXP} \left[\frac{-X^2}{4\,Dt} \right] \quad . \quad . \quad . \quad \text{II. 1.}$$

Q is the total quantity of the diffusing source,

C is the concentration of the diffusing species at a perpendicular distance X from the source,

t is the time of the diffusion process

and D is the diffusion coefficient of the diffusing species.

The expression tends to zero for values of X approaching infinity when $t > 0$.

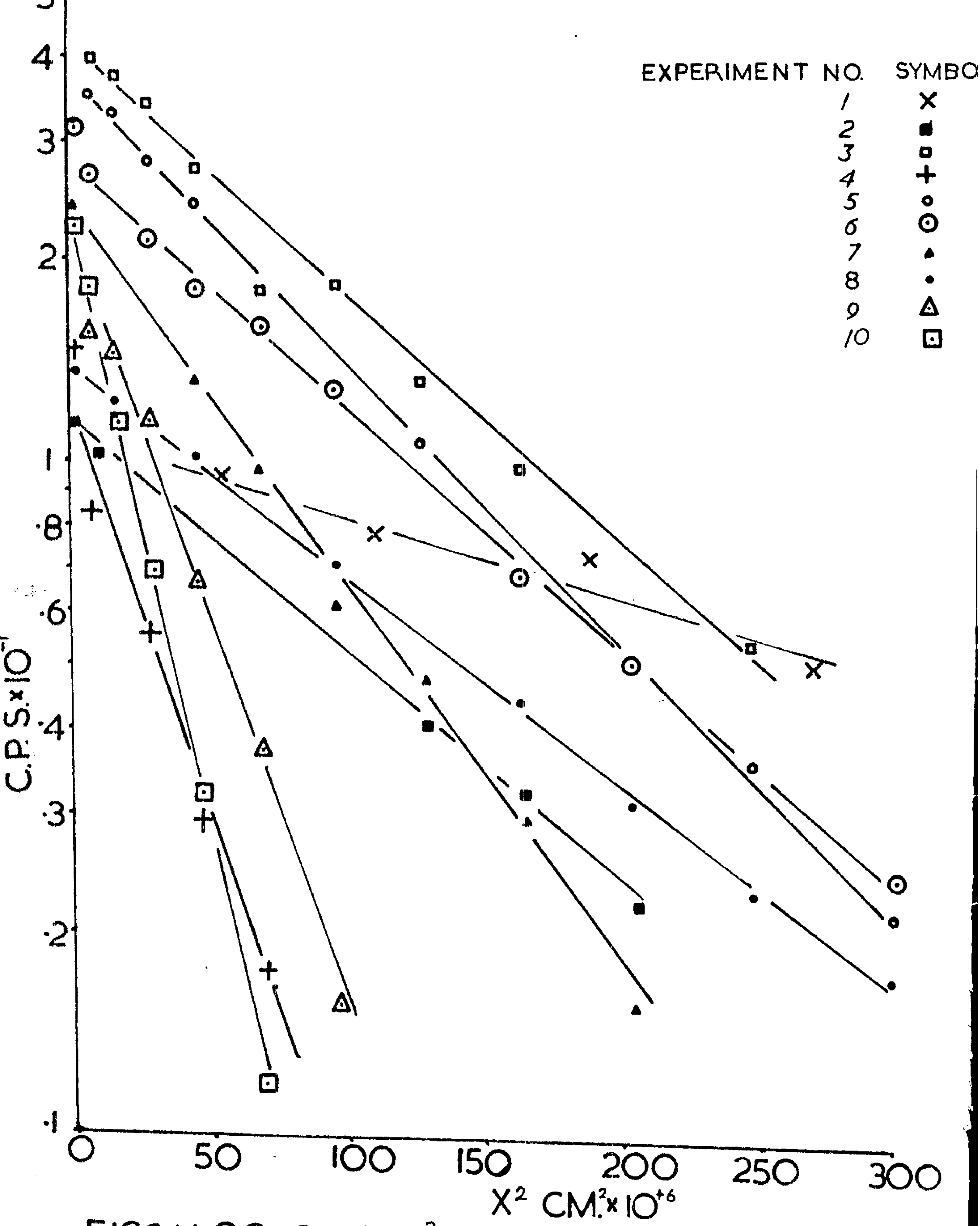


FIG24. LOG$_{10}$C V X^2

Taking logarithms of equation II. 1., we obtain:-

$$\log_e A = \log_e \frac{Q}{\sqrt{\pi D t}} - \frac{X^2}{4Dt} \quad . \quad . \quad . \quad . \quad \text{II. 2.}$$

in which A represents the concentration of radioactivity of the diffusing isotopic species and Q represents the total radioactivity of the source. If the above interpretation of the diffusion conditions is correct, then a plot of the logarithm of the concentration of radioactivity at a depth X, after a time t, versus the square of X, should yield a straight line of slope,

$$-\frac{1}{4Dt}$$

If logarithms are taken to the base 10, the slope of the straight line will become $-\frac{\log_{10} e}{4Dt}$. The diffusion period, t, is known from experiment and hence the diffusion coefficient can be calculated from the slope of this line.

Figure (24) shows a series of plots of $\log_{10} A$ versus X^2, made from the results of the diffusion experiments. The linearity of the plots suggests that the conditions for diffusion, as required by equation II. 1., are correct.

The diffusion conditions were such that the depth of diffusion was of the order of 100 times the thickness of the source and that the thickness of the crystal was 100 times greater than the diffusion distance. These figures were calculated on the basis that the source thickness was of the order of 1 micron [as indicated previously (section I. 3. A.)], that the diffusion depth was between 100 and 200 microns (as shown by experiment) and that the thickness of the crystal specimens was 1 cm.

2. A. (ii) Calculation of the diffusion equation for self-diffusion in solid cyclohexane.

The diffusion coefficients for self-diffusion in solid cyclohexane were evaluated from the slopes of the $\log_{10}A$ versus X^2 plots, shown in figure 24. The slopes in each case were calculated by the method of least mean squares from the experimental points. The results of the calculations are given in table II. 1.

TABLE II. 1.

SELF-DIFFUSION COEFFICIENTS FOR CYCLOHEXANE

Number	Diffusion Temperature T°C	T°K	$\frac{1}{T^\circ K} \times 10^3$	Diffusion Coefficient D. $CM^2\ SEC^{-1}$
1	-31.5	241.7	4.137	7.21×10^{-9}
2	-37.5	235.7	4.242	2.35×10^{-9}
3	-39.0	234.2	4.270	2.05×10^{-9}
4	-44.8	228.4	4.378	8.86×10^{-10}
5	-44.8	228.4	4.378	8.70×10^{-10}
6	-48.2	225.0	4.444	6.54×10^{-10}
7	-50.0	223.2	4.480	4.53×10^{-10}
8	-57.5	215.7	4.636	1.01×10^{-10}
9	-57.5	215.7	4.636	1.12×10^{-10}
10	-62.6	210.6	4.749	4.53×10^{-11}

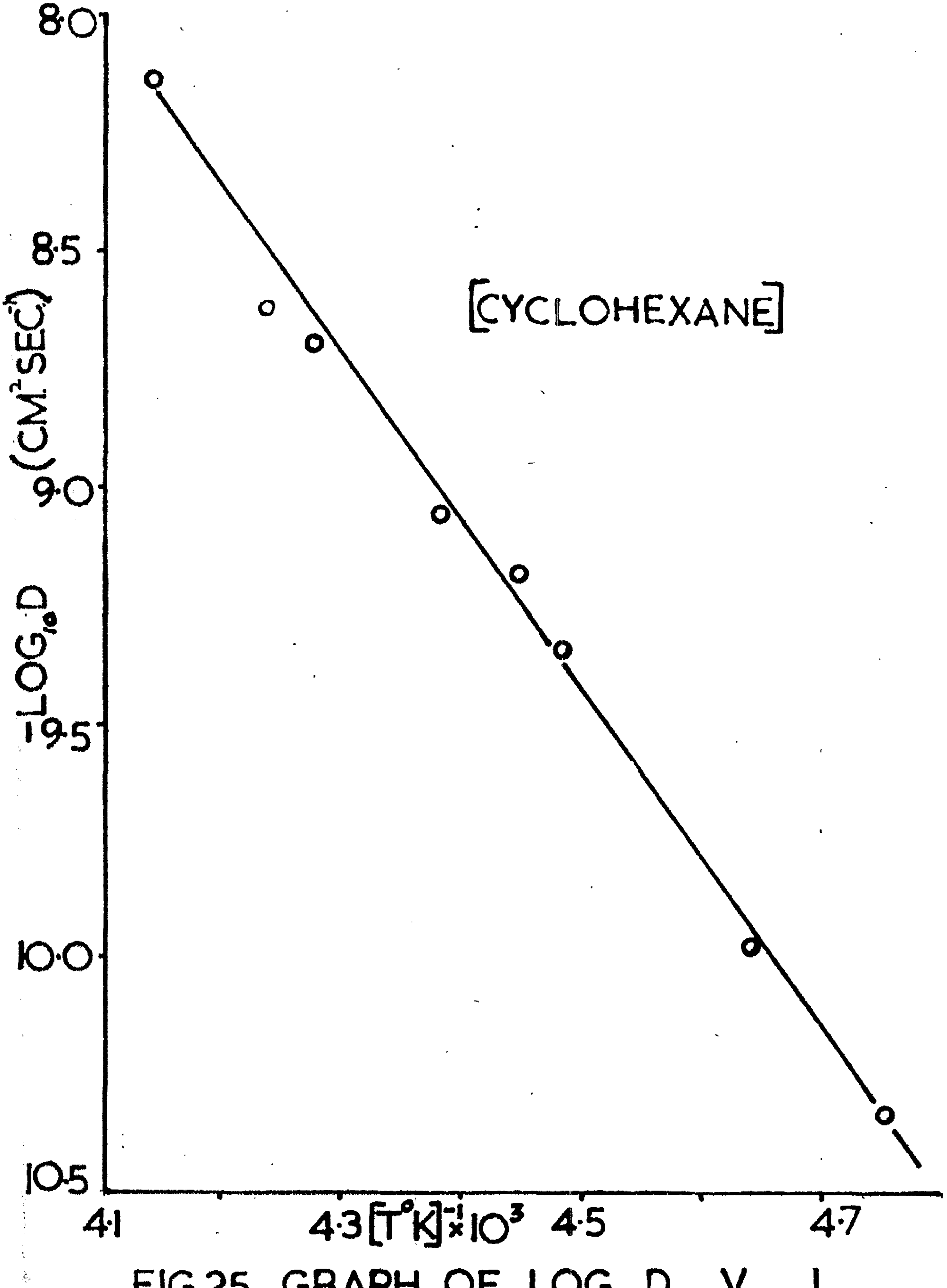


FIG.25. GRAPH OF $\mathrm{LOG}_{10}\, D$ V $\frac{1}{T}$

The temperature dependance of the diffusion process can be described in terms of an Arrhenius equation which gives (3):-

$$D = Do\ EXP\left(-\frac{E}{RT}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad II.3$$

Do and E are constants of the equation, E represents the activation energy for the diffusion process.

Taking logarithms of both sides of equation II. 3., gives

$$\log_{10}D = \log_{10}Do - \log_{10}e\left(\frac{E}{RT}\right) \quad . \quad . \quad . \quad II.4$$

A plot of $\log_{10}D$ versus $\frac{1}{T}$ should give a straight line of slope

$$-\log_{10}e \,.\, \left(\frac{E}{R}\right)$$

with an intercept of $\log_{10}Do$.

Figure 25 shows such a plot drawn from the values in table II. A. 1. The slope and intercept of the line were determined by a least mean squares calculation from the experimental points and from these values were derived the constants of equation II. 3.

The results obtained show that the self-diffusion coefficient in solid cyclohexane varies with the absolute temperature, according to the equation:-

$$D = [6.10 \pm 3.79] \times 10^{6}.\ EXP.\ -\left[\frac{16,500 \pm 300}{RT}\right]\ CM^{2}\ SEC^{-1}$$

The calculation of the above is shown in the appendix.

B. The interpretation of the diffusion results for pivalic acid.

The results for diffusion in pivalic acid were treated in the same manner as those for diffusion in cyclohexane since the

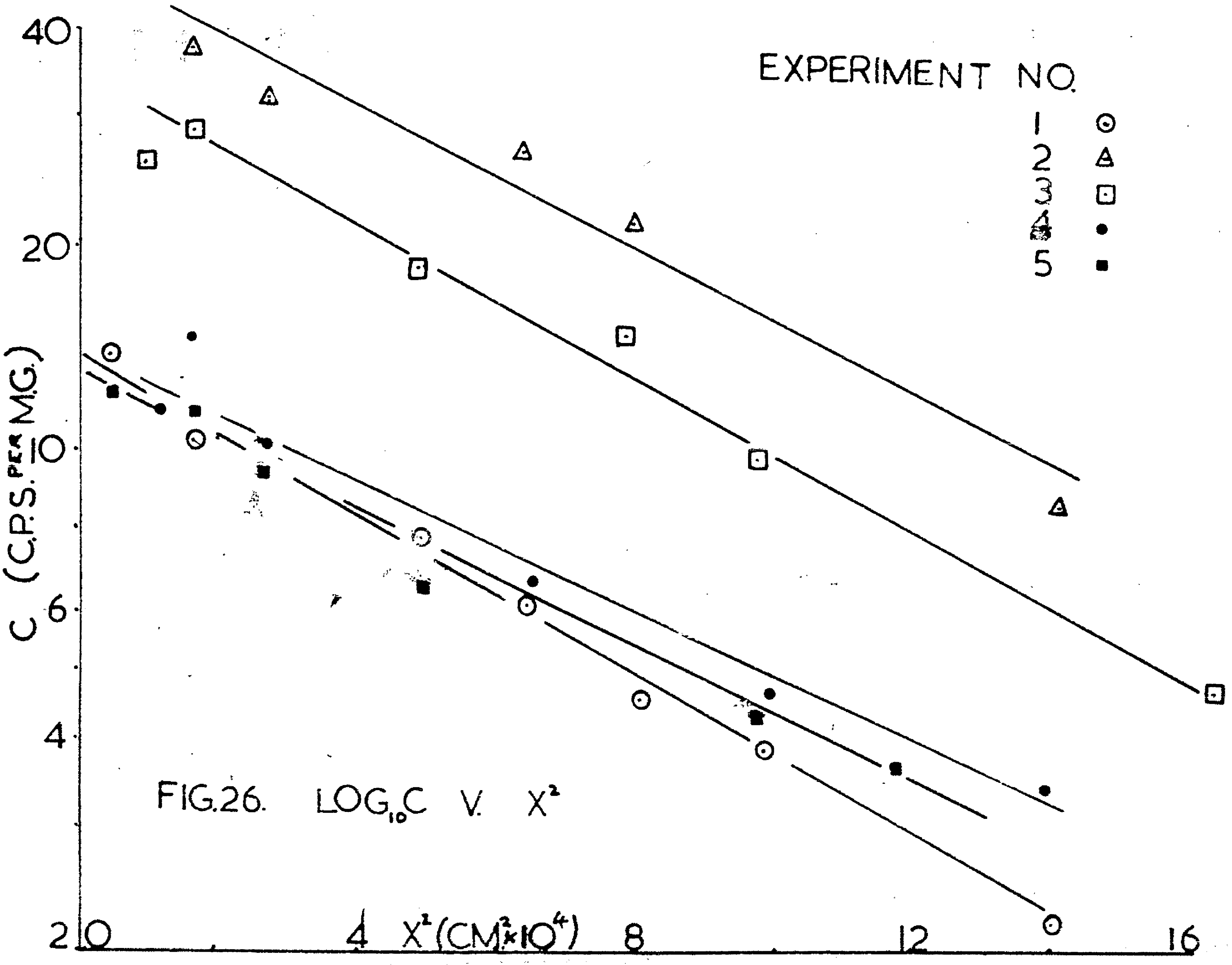


FIG.26. LOG$_{10}$C V. X^2

conditions for diffusion were similar in both cases.

Application of the diffusion equation II. 2. to the diffusion results led to a series of linear plots for $\log_{10}A$ versus X^2, as shown in figure 26. A least means squares calculation to find the best straight line for each set of experimental points led to the evaluation of the diffusion coefficients shown in table II. 2.

TABLE II. 2.

SELF-DIFFUSION COEFFICIENTS IN PIVALIC ACID

Number	Diffusion Temperature T °C	T °K	$\frac{1}{T\,^{o}K} \times 10^3$	Diffusion Coefficient D. $CM^2 SEC^{-1}$
1	7.2	280.4	3.565	3.54×10^{-8}
2	9.4	282.6	3.539	4.29×10^{-8}
3	12.0	285.2	3.507	4.92×10^{-8}
4	14.8	288.0	3.472	5.68×10^{-8}
5	18.0	291.2	3.438	6.53×10^{-8}
6	22.2	295.4	3.395	8.08×10^{-8}

The temperature dependance of the diffusion process is shown in the Arrhenius plot, figure 27, and from a least means squares calculation from the experimental points on the plot the constants of equation II. 3. were evaluated, (see appendix).

The results obtained show that the self-diffusion coefficient in solid pivalic acid varies with the absolute temperature according

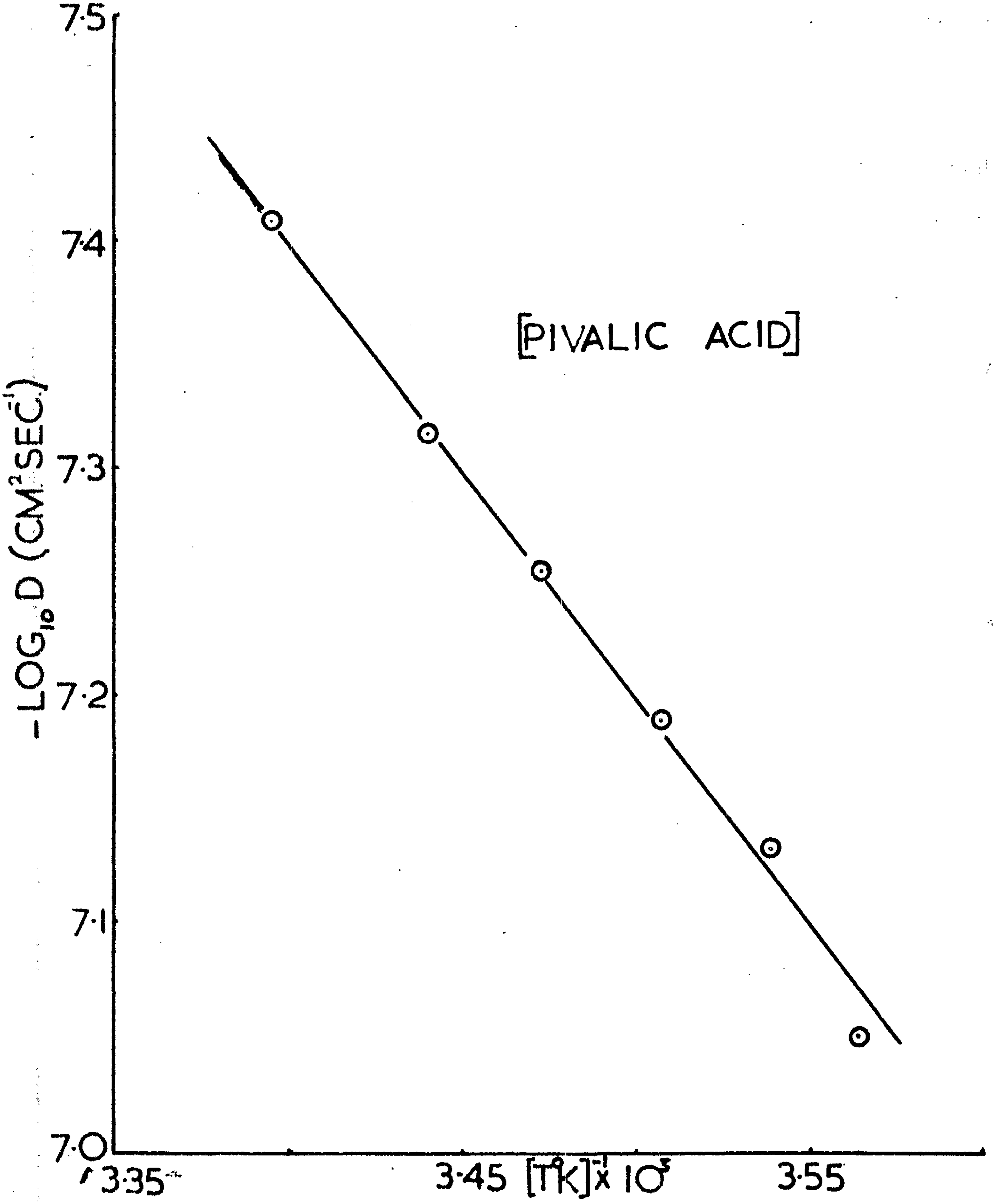


FIG. 27 GRAPH OF LOG_{10} D V 1/T

to the equation:-

$$D = (2.25 \pm 1.25).\mathrm{EXP} - \left(\frac{10,000 \pm 300}{RT}\right)\ \mathrm{CM}^2.\mathrm{SEC}^{-1}$$

.D. Interpretation of diffusion results obtained for cyclohexane by the surface decrease method.

The diffusion conditions for the surface decrease experiments were the same as for the previous experiments in which sectioning was employed. The equation II. 1. is therefore applicable:-

$$C = \frac{Q}{\sqrt{\pi Dt}}\ \mathrm{EXP}\left(-\frac{X^2}{4Dt}\right) \quad . \quad . \quad . \quad . \quad \mathrm{II.\ 1.}$$

Considering a section of crystal situated between the distances X and X + dX from the surface and supposing that the activity is exponentially absorbed, the contribution to the activity as measured at the surface will be dA (70):-

$$dA = K\frac{Q}{\sqrt{\pi Dt}}\ \mathrm{EXP}\left(-\frac{X^2}{4Dt}\right).\ \mathrm{EXP}(-\mu X)\ dx \quad . \quad . \quad \mathrm{II.\ 5}$$

is the linear absorption coefficient of the particles and K is a proportionality constant depending on the geometry of the counting.

The total activity at the surface is given, therefore, by:-

$$A = K\frac{Q}{\sqrt{\pi Dt}}\int_0^{\infty} \mathrm{EXP} - \left(\frac{X^2}{4\,Dt} + \mu X\right) dx \quad . \quad . \quad . \quad . \quad \mathrm{III.\ 6}$$

Changing the variable and substituting

$$\eta = \frac{X}{2\sqrt{Dt}} + \mu\sqrt{Dt}$$

it can be shown that

$$A = KQ\ \mathrm{EXP}(\mu^2 Dt)\left[1 - \mathrm{erf}(\mu\sqrt{Dt})\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad \mathrm{II.\ 7.}$$

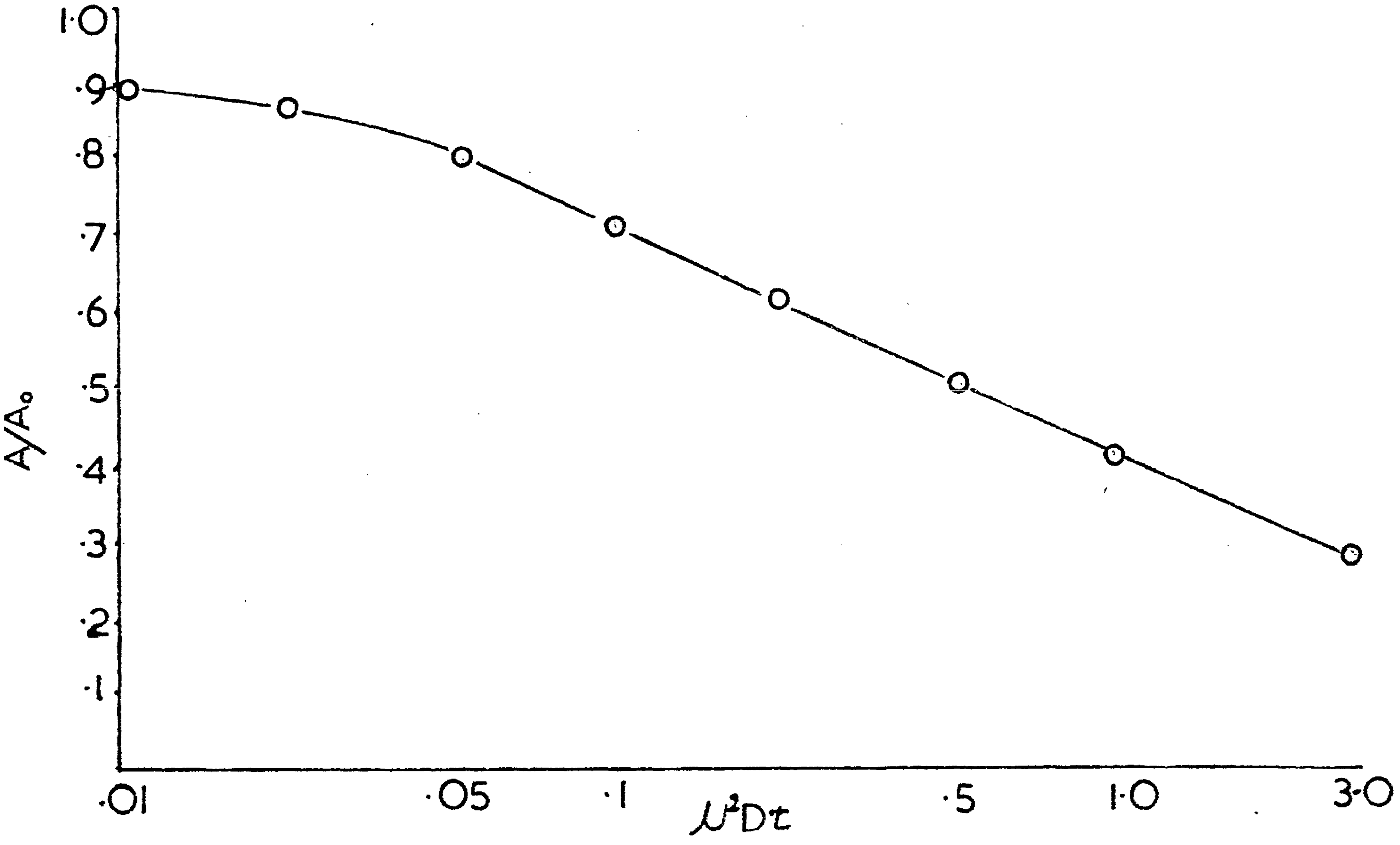


FIG. 28. VARIATION OF A/A_0 AS A FUNCTION OF $\mu^2 Dt$

The total surface activity prior to diffusion is measured as $Ao = KQ$, from which one can obtain:-

$$\frac{A}{Ao} = \mathrm{EXP}\,(\mu^2 Dt)\left[1 - \mathrm{erf}(\mu\sqrt{Dt})\right] \quad \ldots\ldots\ldots \quad \mathrm{II.8.}$$

It is then possible to draw a curve giving $\frac{A}{Ao}$ as a function of $\mu^2 Dt$ for values of $\frac{A}{Ao}$ less than 1, the values of $\mu^2 Dt$ are chosen to provide a suitable range for A/Ao and the corresponding values of $\mathrm{erf}\,\mu\sqrt{Dt}$ can be obtained from tables of the error function (71). The curve is shown in figure 28.

From the values of A/Ao given in tables II. AD. 1 to II. AD. 4, a series of figures can be obtained for $\mu^2 D$ for each diffusion experiment, and since both D and μ should be constant at a given temperature, the values of $\mu^2 D$ should likewise be constant.

The values of $\mu^2 D$ obtained from the figures of A/Ao and t for the surface decrease experiments are shown in table II. 3.

TABLE II. 3.

THE VALUES OF μ^2D OBTAINED FROM THE EXPERIMENTAL RESULTS IN TABLES II. AD. 1. TO II. AD. 4. AND THE CURVE IN FIGURE 28

Experiment Number	1	2	3	4
The Diffusion Temperature (^{o}C)	-31.5	-39.8	-44.5	-50.0
	$\mu^2D \times 10^{-4}$;	$\mu^2D \times 10^{-5}$;	$\mu^2D \times 10^{-6}$;	$\mu^2D \times 10^{-6}$
	2.11	1.11	5.38	3.04
	2.61	2.87	4.39	2.94
	4.55	2.92	16.50	2.96
	5.23	2.56	19.3	
	5.03	3.08	10.1	
	4.66	3.40	9.05	
	4.88	3.85	6.68	
	4.55	3.76	6.21	
	5.26	2.98	6.10	
	5.80	2.80		
	4.43	2.07		

The results show a marked deviation from constant values of μ^2D, the cause of which is somewhat uncertain. It is possible that leakage of activity through the mica window could have occurred, since small cracks in mica are not easy to detect, which could have given rise to errors. There is also the possibility that the absorption of the radiation from the cyclohexane did not follow an exponential form and that application of equation III. 8. might not be valid.

The results obtained, however, for experiments 1 and 2 are reasonably constant, if the first results in each case are rejected. The reason for the low values of μ^2D obtained for the initial results could perhaps be abscribed to time required to form equilibrium conditions when the apparatus was put in the thermostat. Such an explanation is not supported by results obtained previously which indicated that rapid thermal equilibrium was established very rapidly on immersion of the crystal specimen in the thermostat bath.

Accepting that the theoretical treatment of the results is valid and that the variation of μ^2D arises from experimental errors, the average values of μ^2D for each temperature were calculated, and hence D. The value of μ used for the calculation of D was determined from the absorption half-thickness of the carbon-14 (72) and the density of cyclohexane, using the formula:-

$$\mu_L = \mu_M \times \rho$$

where μ_L is the linear absorption coefficient and μ_M is the bulk absorption coefficient of the carbon-14 and ρ is the density of cyclohexane as determined from density (54) and crystallographic data (33).

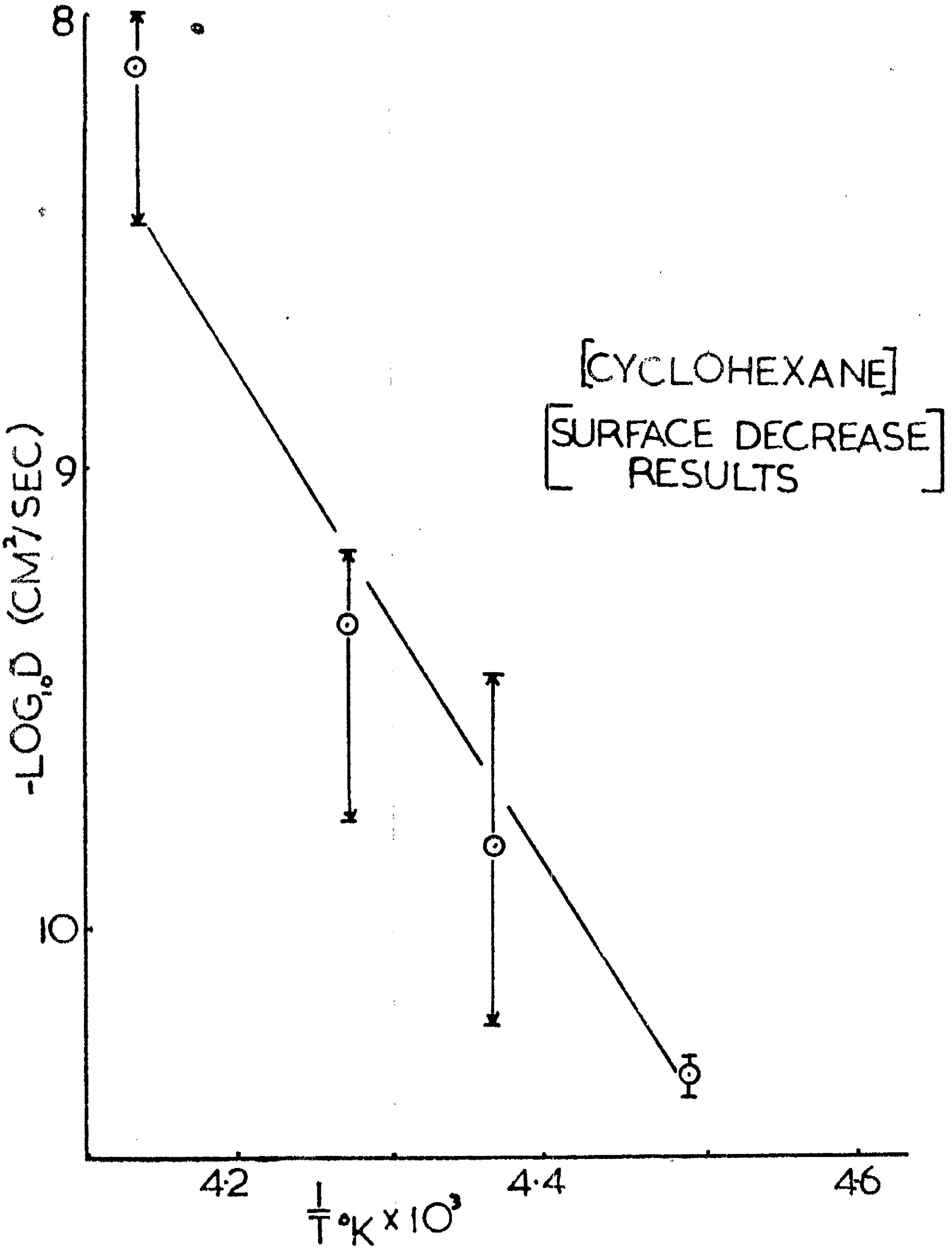


FIG. 29. GRAPH OF $LOG_{10}D$ V 1/T

$$= .285 \times .86 \times 10^{3}\ \text{cm}^{-1}$$

$$= 2.43 \times 10^{2}\ \text{cm}^{-1}$$

The average values of $\mu^2 D$ are shown below in table II.4. along with the corresponding values of D.

TABLE II.4.

SELF-DIFFUSION COEFFICIENTS DETERMINED BY SURFACE DECREASE EXPERIMENTS

Experiment Number	1	2	3	4
T, °K	241.7	233.4	228.7	223.0
$1/T \times 10^3$	4.141	4.280	4.368	4.489
$\mu^2 D$	4.46×10^{-4}	2.79×10^{-5}	9.08×10^{-6}	2.98×10^{-6}
D	7.6×10^{-9}	4.8×10^{-10}	1.6×10^{-10}	5.1×10^{-11}

The corresponding D values as determined by the sectioning technique are:-

$$7.2 \times 10^{-9};\ 2 \times 10^{-9};\ 9 \times 10^{-10};\ 4 \times 10^{-10}$$

Apart from agreement with experiment number 1, the values of D obtained by the sectioning method are all higher than those determined by the surface decrease method.

In view of the possible experimental errors and the uncertainty of the results obtained by the surface decrease method, it was decided not to pursue a further analysis of these figures. An activation energy was, however, determined and the Arrhenius plot is shown in figure 29 which indicates the degree of error associated with the results. The activation energy as determined from figure 29 was 23 K cals/mole, a much higher figure than that determined by the sectioning technique which is considered a more reliable method.

CHAPTER III

DISCUSSION OF THE RESULTS

Summary of previous work.

Results concerning diffusion in molecular solids have been obtained by three distinct techniques. These are:-

(a) the radioactive tracer method,

(b) the nuclear magnetic resonance (N.M.R.) technique

and (c) an energetic irradiation technique.

.1.(a) The diffusion results obtained by tracer studies of molecular solids.

Prior to the present work, only four direct measurements of diffusion in molecular solids had been made. These studies had been carried out on:-

(i) solid hydrogen (21),

(ii) ortho-rhombic sulphur (18),

(iii) α-white phosphorus (19)

and (iv) anthracene (20).

Because of the limited number of results in existence, it has not been possible, so far, to draw any general conclusions regarding diffusion in molecular solids. The lack of experimental results has forced previous workers in the field to make comparisons of their results with these in existence for ionic crystals and metals. This process has been of some interest, but much further work is required before any rules governing diffusion in molecular crystals can be established.

In 1938 Cremer (21) published the first determination of diffusion in a molecular solid. He assumed that the ortho-para conversion of solid hydrogen is bimolecular in character and becomes diffusion controlled at low concentrations of para-hydrogen. On this assumption, he calculated a diffusion equation for solid hydrogen at its melting point, which was:-

$$D = Do\ EXP\left(- \frac{790 \pm 130}{RT} \right) \quad . \quad . \quad . \quad . \quad . \qquad III. 1$$

The measurements were made over a very limited temperature range, 11 - 13 °C, and this, coupled with the experimental scatter, makes the result quite uncertain. Jost has proposed that the activation energy indicates bulk diffusion by means of a vacancy process (73).

It was not until 1951 that the next measurement of self-diffusion in a molecular solid was made, when Cuddeback and Drickamer measured self-diffusion in ortho-rhombic sulphur (18). Their technique was to deposit radioactive sulphur onto the (111) face of a single crystal of O-rhombic sulphur. They followed the diffusion process by microtoming the crystal after the diffusion period, and assaying each section for radioactivity. The radioactive sulphur was deposited by evaporation and by precipitation from a saturated solution. The latter technique was said to have provided a superior degree of contact, but the use of such a method might be criticised on the grounds that the solvent used could attack the surface on which the deposit was made.

The diffusion process in sulphur was found to have a dual character, in that at 30°C below the transition to the monoclinic phase the diffusion rate rose very rapidly, indicating the onset of a second diffusion process. The diffusion rate, prior to this rapid rise, was expressed by the equation:-

$$D = 8.32 \times 10^{-12} \, \mathrm{EXP} - \left(\frac{3080}{RT} \right) \mathrm{CM}^2 \, \mathrm{sec}^{-1} \quad . \quad . \quad \mathrm{III.2}$$

which was interpreted by the authors as representing diffusion perpendicular to the (111) plane. At temperatures approaching the transition point to monoclinic sulphur, they suggest that diffusion parallel to the (111) plane becomes important and presents a contribution to the overall rate of diffusion, thus accounting for the rapid rise in the diffusion rate. Analysis of this region leads to an expression for diffusion parallel to the (111) plane, given by:-

$$D = 1.78 \times 10^{36} \, \mathrm{EXP} - \left(\frac{78,000}{RT} \right) \mathrm{cm}^2 \, \mathrm{sec}^{-1} \quad . \quad . \quad . \quad \mathrm{III.3}$$

The increase in the activation energy is ascribed to the increased jump distance in the new direction.

The magnitude of the constants in the two equations are similar to those observed for bismuth (74), which has been reported as showing diffusion anisotropy.

In 1955 Nachtrieb and Handler (19) made a study of self-diffusion in α-white phosphorus. This material was chosen because it had a cubic structure, and would, therefore, be unlikely to exhibit diffusion anisotropy. In this case a tracer technique was again employed and evidence of two diffusion processes was found. One process occurred at temperatures below 35°C and a second became significant between 35°C and the melting point (44.1°C). The expression for the temperature dependance of the diffusion process was given by:-

$$D = 1.07 \times 10^{-3} \text{ EXP } \left(- \frac{9400}{RT} \right) + 2 \times 10^{46} \text{ EXP } - \left(\frac{80600}{RT} \right) \text{ CM}^2\text{SEC}^{-1} \qquad \text{III.4}$$

The second term of the expression becomes important at temperatures above 35°C.

The low temperature diffusion process has been interpreted in terms of the random walk of P_4 molecules via relaxed vacancies. This conclusion is arrived at by comparing the activation energy for diffusion at the lower temperatures, with a value predicted from the empirical equation:-

$$E = CL \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{III.5}$$

in which C is a constant equal to 16.5 and L is the latent heat of fusion. This latter equation was derived by Nachtrieb and Handler on the basis of results available for self-diffusion in cubic metals (75).

The activation energy predicted for self-diffusion by equation III.5 is 9920 cals/mole, which compares reasonably well with the value of 9400 cals/mole obtained for diffusion below 35°C. Above 35°C the authors propose that some large scale co-operative phenomenom is responsible for the high activation energy observed. They show that the entropy factor associated with the process is very large, indicating that a large number of molecules are involved in the process. Thus the more simple diffusion mechanisms, such as direct interchange and interstitial, have been ruled out. The proposed mechanism is based on a co-operative molecular motion involving premelted regions in the solid.

If such a consideration is realistic, then it might be expected that a gradual transition from diffusion in the solid state to that in the liquid state should occur. The only example of such a transition has been that reported for self-diffusion in solid indium, near its melting point (77).

Nachtrieb and Lawson (78) have shown that the rate of self-diffusion in α-white phosphorus is reduced by increasing the hydrostatic pressure and that lattice disordering, on a comparatively large scale, sets in well below the melting point. The pressure effect indicates that the diffusion process occurs by way of lattice defects, the concentration of which is reduced by application of increased pressure. This suggests that the diffusion is controlled by migration of molecules into vacant lattice sites.

The diffusion results of Nachtrieb and Handler (19) are subject to some doubt, in view of the fact that they used polycrystalline specimens for their diffusion experiments. These specimens would contain many grain boundaries which would provide short-circuiting paths for diffusion which would tend to enhance the observed diffusion rates.

The final direct measurement of self-diffusion in a molecular crystal, prior to this work, was made by Sherwood and Thomson (20). They studied self-diffusion in anthracene using a tracer technique. The tracer was evaporated onto a specific surface of a single crystal, which was sectioned after the diffusion period. The results indicated the occurrence of two simultaneous diffusion processes. The major one was assumed to represent bulk diffusion, while the other process, which accounted for a very small fraction of the diffused material, was thought to represent diffusion along lattice dislocations.

The bulk-diffusion process in anthracene which was measured perpendicular to the 001 plane was expressed as a function of temperature by the equation:-

$$D = 1.3 \times 10^{11} \text{ EXP} - \left(\frac{42000}{RT}\right) \text{ CM}^2 \text{ SEC}^{-1} \quad . \quad . \quad . \quad \text{III. 6}$$

An analysis of the rapid diffusion process was not made because of the limited accuracy of the experimental points associated with the process.

As was the case with the high temperature range of α-white phosphorus, Sherwood and Thomson found a high entropy factor was associated with the diffusion process (20). This fact, coupled with the high activation energy, led them to the conclusion that the diffusion process in anthracene was a co-operative phenomenon involving four to six molecules

Table III. 1 shows a summary of the results obtained for diffusion in molecular solids by tracer techniques.

TABLE III. 1

Molecule	Preexponential Factor (Do) (cm^2 sec^{-1})		Activation Energy (E) (k cals/mole)	Reference
hydrogen	10^{-7}		.8	(21)
sulphur	(8.3×10^{-12}	(A)	9.4	(18)
	(2×10^{36}	(B)	81	
α white phosphorus	(1.1×10^{-3}	(A)	3.1	(19)
	(2×10^{46}	(B)	78	
anthracene	1.3×10^{11}		42.4	(20)

A - low temperature diffusion

B - high temperature diffusion

The remaining results in existence, regarding diffusion in molecular solids, have been obtained from nuclear magnetic resonance (N.M.R.) measurements and irradiation techniques. A summary of the information available from these sources is shown later in table III. 2.

l. (B) (C) Diffusion results obtained from N.M.R. measurements and irradiation experiments.

Agreement between N.M.R. studies of self-diffusion and tracer work has been found in the cases of lithium and sodium (79), but in the case of molecular crystals, agreement has not as yet been found.

The information which has been obtained with regard to

self-diffusion in molecular crystals by N.M.R. has been limited,
with one exception, to the formulation of some activation energies for diffusion. The exception is the case of α-white phosphorus, where Resing has made a thorough study of self-diffusion, using the N.M.R. technique (25).

The diffusion equation which Resing calculated for α-white phosphorus is:-

$$D = 7.7 \times 10^{-2}\ \mathrm{EXP} - \left(\frac{12,200}{RT}\right)\ \mathrm{cm}^2\ \mathrm{sec}^{-1} \quad . \quad . \quad . \quad \mathrm{III.7}$$

which can be compared with the equation derived by Nachtrieb and Handler (19):-

$$D = 1.1 \times 10^{-3}\ \mathrm{EXP} - \left(\frac{9400}{RT}\right) + 2 \times 10^{46}\ \mathrm{EXP} - \left(\frac{80600}{RT}\right)\ \mathrm{cm}^2 \mathrm{sec}^{-1} \quad \mathrm{III.4}$$

Resing found that equation III.7 described the diffusion process in α-white phosphorus up to the melting point, and suggested that the high temperature process found by Nachtrieb and Handler could have been the result of grain-boundary premelting, in the polycrystalline specimens.

A comparison of equation III.7 with the first part of equation III.4, shows that there is a considerable discrepancy between the equations describing the low temperature process.

Other molecular solids which have been shown to exhibit self-diffusion by N.M.R. measurements, include methane, for which a diffusion equation has been calculated (80), it is:-

$$D = 7 \times 10^{-6}\ \mathrm{EXP} - \frac{1500}{RT}\ \mathrm{cm}^2\ \mathrm{sec}^{-1} \quad . \quad . \quad . \quad . \quad . \quad \mathrm{III.8}$$

More recently, however, Bloom (81) has calculated that the self-diffusion activation energy in solid methane is 3200 cals/mole, a value which is twice that shown in equation III. 8. Both results were obtained using the N.M.R. technique, which tends to throw some doubt on the value of the measurements.

Results of N.M.R. studies on solid hexamethyldisilane (31) and pivalic acid (24), have yielded values of 10 and 8 k. cals/mole respectively, for self-diffusion in these solids, but the authors have stated that the results represent only an order of magnitude. Activation energies of 6 (82) and 9.2 k. cals/mole (83) have been proposed from N.M.R. studies of solid neopentane, although the latter figure was obtained from a study made on an impure specimen.

Andrew and Eades (30) in an N.M.R. study of solid cyclohexane found evidence for self-diffusion. During their experiment, the N.M.R. line-width narrowed appreciably at 240 °K and they suggested that the degree of narrowing could best be explained on the basis of molecular self-diffusion. A calculation of the activation energy for self-diffusion was made, assuming the jump frequency of the molecules to be of the order of the N.M.R. line-width frequency, which was 10^4C/S. They also assumed that the jump frequency to a vacancy would be given by:-

$$V = f \, EXP - \left[\frac{\Omega}{RT} \right] \quad (84)$$

on the basis of a simple vacancy diffusion, and that the lattice frequency (f) would be 10^{12} C/S. A value of 8 k. cals/mole was derived for Q, which represents the activation energy for diffusion. This value of Q was, therefore, only an approximation, based on a series of assumptions.

More recently Resing (83) has indicated a value of 9.35 k. cals/mole for the activation energy for self-diffusion in cyclohexane, made from an Arrhenius plot of his N.M.R. results. Unfortunately, the sample used for the measurement was impure and so the result is suspect.

A review of the N.M.R. data for self-diffusion in molecular solids shows the wide variation of results which have been obtained. As mentioned previously (p. 10) the N.M.R. technique affords a limited means of studying self-diffusion processes. It has recently been stated that the technique can be sensitive to impurities, where the derivation of diffusion energies is concerned (82). Thus it is possible that the use of impure samples could account for the divergent diffusion results which have been proposed from different N.M.R. studies of the same compound.

Another contribution to diffusion data for molecular solids is supplied by the results of irradiation experiments carried out on some molecular solids. The solids are subjected to irradiation by or X-rays, and the lives of the free radicals so formed, are followed by an electron-spin-resonance technique.

In such a study of cyclohexane, Szwarc and Marx (85) irradiated solid cyclohexane with γ rays at 77 °K They found that the cyclohexane radicals so formed, did not recombine until a temperature in the region of 170 °K was reached. This is the region of the transition temperature of solid cyclohexane to the plastic phase. At the transition temperature the radicals recombine rapidly and the activation energy for recombination of the radicals was found to be 20 k. cals/mole. The authors could not reconcile such a high activation energy with any known diffusion mechanism. Their result, however, shows tolerable agreement with the present study, and may serve as another indication of the limits of N.M.R. as a means of detecting diffusion processes. Similar activation energies were found for radical recombination in cyclohexyl chloride and bromide (86).

A list of the diffusion data available from N.M.R. measurements and irradiation experiments is shown below in table III.2.

TABLE III.2.

Self-Diffusion Constants for Molecular Solids

Molecule	Pre-exponential Factor Do ($cm^2 sec^{-1}$)	Activation Energy E (k. cals/mole)	Reference
Cyclohexane (		8	(30)
(		9.4	(83)
(		20	(85)
Hexamethyldisilane		10	(31)
Neopentane (		6	(82)
(		9.2	(83)

Molecule	Pre-exponential Factor Do ($cm^2 sec^{-1}$)	Activation Energy E (k. cals/mole)	Reference
Methane	7×10^{-6}	1.5	(80)
		3.2	(81)
Pivalic Acid		8	(24)
t-butyl chloride		5	(82)
Xenon		5	(83)
α-white phosphorus	7.7×10^{-2}	12.2	(25)
2, 2 dichloropropane		6	(82)

With regard to plastic crystals (loc. cit. p.7) which constitute all the molecular solids in table III. 2, there is only one example (25) where results are available for comparison between N.M.R. and tracer studies. The discrepancy between these results has already been noted. Otherwise the only diffusion data in existence for diffusion in plastic crystals - the results of the present study will be discussed later - are a series of uncertain activation energies.

Considering molecular crystals as a whole, complete diffusion equations are available in only four cases, anthracene (20) α white phosphorus (19) (25), sulphur (18) and methane (80).

In analyses of the diffusion equation itself many theories have been postulated as to the meaning of the pre-exponential factor (Do) and its bearing on the diffusion process (87, 88). The value of the activation energy is also a guide to the type of diffusion process, since it represents the ease with which an atom or molecule can move through the lattice (3).

In the case of some metals values of Do and E for various diffusion mechanisms have been calculated, and these compared with experimental values in an attempt to determine the most probable diffusion mechanism in a particular case. This method has met with limited success in some cases, due probably to the approximate nature of the calculations. It has not been possible to make calculations of the above kind for molecular solids because of the lack of the necessary physical data for the solids studied.

The experimental pre-exponential factors for metals have been found to be in the range .1 to 10 (19). The corresponding range for molecular solids varies from 10^{-12} to 10^{11}, if one considers only the low temperature diffusion processes of sulphur and phosphorus. This is an enormous range compared to that found for metals and suggests, perhaps, that diffusion in the two systems should not be too closely compared.

In metallic systems several empirical rules have been advanced concerning self-diffusion. These rules relate the activation energy for diffusion to some physical property of the metal. Two of these rules correlate the diffusion energy with the latent heat of fusion (75) and the melting temperature (89) respectively. The former has been shown to hold for α white phosphorus (19) as well as for cubic metals, but later work (25) has thrown some doubt on that comparison.

Other correlations have been made concerning the activation energy and the latent heat of sublimation and these will be discussed later, with the cases of cyclohexane and pivalic acid.

2 The experimental expressions for self-diffusion in Cyclohexane and Pivalic Acid and a comparison of pre-exponential factors for self-diffusion in molecular solids.

The self-diffusion processes in cyclohexane and pivalic acid were found to vary with the absolute temperature, according to the equations:-

$$\text{(i)} \qquad D = (6.1 \pm 3.8) \times 10^{6}\ \mathrm{EXP} - \left(\frac{16500}{RT}\right)\ \mathrm{cm}^{2}\ \mathrm{sec}^{-1} \quad . \quad \text{III.9}$$

and

$$\text{(ii)} \qquad D = (2.5 \pm 1.25)\ \mathrm{EXP} - \left(\frac{10{,}000}{RT}\right)\ \mathrm{cm}^{2}\ \mathrm{sec}^{-1} \quad . \quad . \quad \text{III.10}$$

respectively.

Studies of diffusion in molecular solids have revealed the existence of two types of bulk diffusion processes, one involving diffusion via vacant lattice sites and the other a more complex diffusion process which occurs towards the melting point of the solid. The experimental values of Do from these studies are shown in table III. 1.

The values of Do for the low temperature ranges vary from 10^{-12} to 10^{11}, assuming that the diffusion process in anthracene is representative of normal bulk diffusion. The experimental values for the pre-exponential factors for cyclohexane and pivalic acid both lie within this range. The value of Do for cyclohexane ($10^{6}\mathrm{cm}^{2}\mathrm{sec}^{-1}$), is, like that of anthracene ($10^{11}\mathrm{cm}^{2}\mathrm{sec}^{-1}$), much higher than for the remaining results and suggests that the diffusion mechanism may not be a simple vacancy process.

The high temperature diffusion processes found in sulphur and phosphorus were characterised by very large Do values, 10^{36} and 10^{46} $cm^2 sec^{-1}$ respectively. These factors suggest a completely different diffusion process to the low temperature ranges. Two explanations have been advanced to explain the high temperature diffusion processes. The first is that diffusion anisotropy is responsible (18), but in the second, it is assumed that pre-transitional effects are responsible (19). The latter explanation involves the formation of premelted liquid-like clusters near the melting point with subsequent diffusion of these clusters.

Calculations of the pre-exponential factors for diffusion in metals and ionic crystals have been made (3), and it may be possible to obtain approximate figures for Do for molecular crystals by these methods.

Calculation of The Pre-exponential Factors for Diffusion.

A general approach based on classical rate theory has been made to the problem of diffusion in solids (90), and from this approach it is possible to calculate the pre-exponential factors for diffusion in cyclohexane and pivalic acid.

The equation which has been derived for diffusion in solids is:-

$$D = a^2 V \, \mathrm{EXP} \left(- \frac{E}{RT} \right) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \mathrm{III.11}$$

where a is the atom jump distance, V is the vibrational frequency of the atom in the direction of movement and E is the activation energy for diffusion. Comparing this equation with the Arrhenius equation for diffusion in solids, one obtains:-

$$Do = a^2V \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{III. 12}$$

Using this equation, the values of Do predicted for metals are of the order of 10^{-3} $cm^2 sec^{-1}$, whereas the experimental values of Do lie between 10^{-5} and 10 $cm^2 sec^{-1}$. It has been suggested that the disagreement is the result of over simplification in deriving the above equation.

The solid state structure of cyclohexane has been examined by X-ray methods (33, 91) and values of the intermolecular distances in the plastic phase have been evaluated. The structure of the plastic phase of pivalic acid has also been analysed by X-ray crystallography (92) and a value of the edge-length of the unit cell has been published. The structures of cyclohexane and pivalic acid were found to be face-centred cubic.

Using the published values of the lattice parameters and calculated values of θ, the Debye characteristic temperature, from which the lattice vibrational frequency can be obtained, the pre-exponential factors for diffusion in cyclohexane and pivalic acid were calculated.

The values of θ were calculated from the equation:-

$$\theta = 163 \left(\frac{Tm}{MV^{2/3}} \right)^{1/2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad \text{III. 13}$$

which has been shown to give good agreement between experiment and theory for argon, krypton and xenon (93). In equation III. 13, Tm is the melting temperature of the substance, V is its molar volume and M its molecular weight.

The value of the lattice vibrational frequency was calculated from the relation

$$V = \frac{k\,\theta}{h}$$

where k = Boltzmann's constant

h = Planck's constant

A For cyclohexane:

$$\theta = 59$$

$$V = \frac{1.38 \times 10^{-16}}{6.62 \times 10^{-27}} \times 59$$

and the lattice constant, $A_o = 8.6 \times 10^{-8}$ cms. (91).

Substituting these values in equation III. 12 gives:-

$$Do = \frac{1.38 \times 10^{-16}}{6.62 \times 10^{-27}} \times 59 \times (8.6)^2 \times 10^{-16}$$

or, $Do = .905 \times 10^{-2}\ cm^2 sec^{-1}$ . . . . III. 14

B For Pivalic Acid:

$$\theta = 50$$

$$V = \frac{1.38 \times 10^{-16}}{6.62 \times 10^{-27}} \times 50$$

and $A_o = 8.82 \times 10^{-8}$ cms. (92)

$$\therefore\ Do = \frac{1.38}{6.62} \times \frac{10^{-16}}{10^{-27}} \times 50 \times (8.82)^2 \times 10^{-16}$$

which gives $Do = .815 \times 10^{-2}\ cm^2 sec^{-1}$ . . . . . III. 15

These calculations, based on equation III. 12, do not take into account any limiting conditions to diffusion. The calculated value for the pre-exponential factor, therefore, represents the maximum value which that factor can have. Since the effect of considering any of the accepted diffusion mechanisms will be to constrain the diffusion process and hence reduce the calculated value of Do, it seems obvious that a combination of any of these mechanisms with the above theory for Do, will not account for the experimental results obtained.

A more precise determination of the diffusion equation has been made by Zener (76) and Le Claire (88). This involves a consideration of the free energy change associated with the diffusion process which effectively results in the replacement of E in equation III. 11 by ΔG, the free energy change involved in the diffusion process. Development of this equation leads to the incorporation of an entropy term in the expression for Do. Le Claire's treatment of the diffusion process is as follows:

If self-diffusion in a crystal occurs by a vacancy mechanism and if ΔGf is the free energy change associated with the formation of a vacancy, the concentration of vacancies in the crystal is:-

$$X = \mathrm{EXP} - (\Delta Gf/RT) \quad \ldots\ldots\ldots\ldots \quad \text{III. 16}$$

The diffusion coefficient can be given by:-

$$D = \frac{\alpha \lambda^2}{\tau} \quad \ldots\ldots\ldots\ldots \quad \text{III. 17}$$

where α is a geometric factor related to the lattice arrangement of atoms or molecules and τ is the average time between successive jumps of each molecule. In the cyclohexane crystal the probability that a molecule has a neighbouring vacant site will be 12X and if n is the jump rate into vacant sites, then:-

$$\frac{1}{\tau} = 12Xn \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad III.\,18$$

$$\text{and} \quad n = V \; EXP - (\Delta Gm/RT) \quad . \; . \; . \; . \quad III.\,19$$

where V is the molecular vibration frequency and ΔGm is the energy required to move a molecule from its equilibrium position to the top of the potential barrier separating it from a neighbouring equilibrium position. An appropriate combination of the above equations leads to the expression:-

$$D = A^2 V \; EXP - \frac{(\Delta Gf + \Delta Gm)}{RT} \quad . \; . \; . \; . \; . \; . \; . \quad III.\,20$$

$$\text{which gives,} \; D = A^2 V \; EXP \; \frac{(\Delta Sf + \Delta Sm)}{R} \; EXP \; \frac{(\Delta Hf + \Delta Hm)}{RT} \; . \quad III.\,21$$

$$\text{or } D = A^2 V \; EXP \; (\Delta S/R). \; EXP \; (\Delta H/RT) \quad . \; . \; . \quad III.\,22$$

Equation III. 22 contains the entropy and enthalpy terms associated with the diffusion equation, expressed as the composite terms ΔS and ΔH respectively.

Considering equation III. 22, we can identify Do of equation III. 16 with $A^2 V$ EXP (ΔS/R). The term $A^2 V$ has already been calculated for diffusion in cyclohexane and pivalic acid from equation III. 12, and so we can now calculate the entropy changes associated with the diffusion process in these solids.

4 The Calculation of The Entropy Factor Associated with Self-Diffusion in Cyclohexane and Pivalic Acid.

A Cyclohexane.

$$Do = A^2 V \text{ EXP } (\Delta S/R) \quad \ldots\ldots\ldots\ldots \quad \text{III. 23}$$

Substituting the experimental value of Do and inserting the calculated value of $A^2 V$, gives

$$6.1 \times 10^6 = .905 \times 10^{-2} \text{ EXP } (\Delta S/R)$$

$$\therefore \Delta S = 40.6 \text{ cals/mole. deg.}$$

B Pivalic Acid.

Substitution of the values of D and $A^2 V$ in the equation III. 23 gives

$$2.17 = .815 \times 10^{-2} \text{ EXP } (\Delta S/R)$$

$$\therefore \Delta S = 12.3 \text{ cals. /mole deg.}$$

The entropy factor for cyclohexane seems high for a simple vacancy mechanism when compared with entropy factors of 7 and 13 calculated for self-diffusion in solid sodium (44) and α- white phosphorus (94) by a vacancy mechanism. These factors were calculated on the basis of Zener's treatment (76) involving the elastic modulus of the solid. Zener's relation is:-

$$\Delta S = \frac{E.\beta}{Tm}$$

where ΔS and E are the entropy and enthalpy of activation for the diffusion process and β is a constant related to the temperature coefficient of the elastic modulus.

The experimental entropy factor for pivalic acid is very similar to that calculated by Lawson (94) for α-white phosphorus. This could indicate that self-diffusion occurs in pivalic acid by a vacancy process. The heats of sublimation and fusion of pivalic acid and α-white phosphorus are fairly similar and so a comparison of their diffusion characteristics seems not unreasonable.

Sherwood and Thomson (20) estimated the numbers of molecules involved in the diffusion process by dividing the activation entropy of diffusion by the latent heat of fusion of the solid. On this basis the numbers of molecules involved in the self-diffusion processes in cyclohexane and pivalic acid would be 19 and 7 respectively. The previous calculation was derived from a theory of Nachtrieb and Handler put forward to explain diffusion in α-white phosphorus (19). These authors suggested that the molecules around a vacancy relaxed into the volume of the vacancy forming a small region of liquid-like density and that diffusion took place by way of these relaxed vacancies. This theory had previously been advanced to explain diffusion in cubic metals (75) and was evolved from an empirical relation found between the activation energy for self-diffusion of some metals and their latent heats of fusion. A similar treatment may be of interest here.

The activation energies for self-diffusion in Cyclohexane and pivalic acid.

The activation energy for a diffusion process should give an indication of the ease with which the diffusion event can occur. In the case of metals the energy required for diffusion by the accepted mechanisms has been graded approximately as follows.

E direct interchange > E ring rotation > E vacancy > E interstitial

The above order was based on lattice strain considerations and it seems reasonable to suppose that a similar order might obtain in molecular crystals.

In the direct interchange mechanism for a face-centred cubic structure, the two adjacent molecules can only interchange by the co-operative relaxation of the eight nearest neighbours (76). The ring rotation mechanism involves the exchange of molecular sites by rotation of a planar ring involving four molecules in their lattice positions. Rotation of this ring would involve a smaller interaction between the lattice and the ring at the saddle point configuration, than for the interchange mechanism, with a subsequent reduction of the activation energy.

The interstitial mechanism can apply when the spaces between the molecules situated at lattice sites allow the inclusion of an extra molecule. Such a situation arises in the diffusion of gaseous atoms through metal lattices where the diffusing atoms are much smaller than the host atoms. This mechanism is not considered likely to apply in a close packed lattice where the molecules are all of a similar size, as would be the case for molecular self-diffusion.

Diffusion by a vacancy mechanism should require an energy approximately equal to the latent heat of sublimation (95), since this will be the energy required to form a vacancy in the solid. Thus for pivalic acid where the latent heat of sublimation is 10 k. cals/mole, calculated from Trouton's rule (96), a vacancy mechanism seems probable. This supposition is supported by the activation entropy value as already mentioned. In the case of cyclohexane, however, the energy of self-diffusion is twice the latent heat of sublimation [8.5 k. cals/mole (54)] Hence in cyclohexane the simple vacancy mechanism seems unlikely and one must consider the direct exchange machanism or some other alternative.

It has been shown in the case of sodium (44) that the activation entropy associated with the direct interchange diffusion mechanism is not very different from that resulting from a vacancy mechanism. On that basis, and from the entropies of activation calculated for phosphorus (94) and sodium (44) for self-diffusion by a vacancy mechanism, the direct interchange mechanism alone, will not account for the diffusion process in cyclohexane. A further objection to the direct interchange mechanism, arises from the close packing of the molecules in the cubic phase of cyclohexane. It has been shown (24) that the molecules have 15% less volume in the lattice than their maximum volumes of rotation. This indicates that direct interchange would not readily occur.

That the diffusion mechanisms in cyclohexane and pivalic acid should be different, is not perhaps surprising, in view of the physical differences between the solids. Pivalic acid, although a plastic crystal, is much harder than cyclohexane and is known to be hydrogen-bonded to some extent.

Kondo and Oda (58) have shown by means of dielectric studies and electrical conductivity measurements, that in the plastic phase pivalic acid should be composed of non-polar molecular units of disordered orientation. They have proposed that each molecule occupies a lattice point and associates with one of its twelve nearest neighbours to form a hydrogen-bonded dimer. They further add that rotation and migration of dimers rather than discrete molecules is possible, and in view of this it does seem likely that the diffusion process will be somewhat different from that in cyclohexane, where the lattice is not liable to be so rigid.

The correlation of activation energies for self-diffusion in molecular solids.

The energies for self-diffusion in metals have been related empirically to physico-chemical properties of the solid and the following correlations have been suggested:-

$H_A/T_m = 38$ (87) . . . . III. 24

$H_A = \frac{2}{3} \times$ lattice energy (87) . . . . III. 25

and $H_A = 16.5\ L_f$ (75) . . . . III. 26

where H_A is the activation energy for diffusion, L_f is the latent heat of fusion and T_m is the melting temperature of the solid.

TABLE III. 3

The relations between the activation energies for self-diffusion of some molecular solids and their physical properties.

Molecule	Activation Energy, E (k. cals/mole)	Latent Heat of Fusion, Lf (k. cals/mole)	Latent Heat of Sublimation, Ls (k. cals/mole)	Melting Temperature Tm (°K)	(I) $\frac{E}{Lf}$	(II) $\frac{E}{Ls}$	(III) $\frac{E}{Tm}$
Methane	3.2 (80) 1.5 (81)	.20 (54)	2.0 (54)	89 (54)	(16 (8	1.6 .8	36 17
Neopentane	9.2 (82) 6.0 (83)	.77 (23)	7.3	267 (54)	(12 (8	1.3 .8	34 22
Cyclohexane	16.5 (*) 9.4 (83)	.62 (54)	8.5 (54)	280 (54)	(26 (15	1.9 1.1	59 34
Hexamethyl-disilane	10 (31)	.72 (31)	9.6 (31)	288 (31)	14	1.0	35
Pivalic Acid	8 (24) 10 (*)	.48 (24)	10	308 (24)	(17 (21	.8 1.0	26 32
α-White Phosphorus	12.2 (25) 9.4 (19)	.61 (19)	14.0 (19)	317 (19)	(20 (15	.9 .7	39 30
Hydrogen	.8 (21)	.03 (97)	.22 (73)	14 (97)	27	3.6	57
Sulphur	3.1 (18)	.30 (98)	-	366 (97)	10	-	8
Anthracene	42.4 (20)	6.9 (54)	23.3 (20)	490 (54)	6	1.7	86

(I) (II) (III)

Values from the present study (*) Average values for metals 16.5 (19) 45 (97) 38 (97)

A similar table has been made for molecular solids (table III. 3), but the number of results available is very limited and many of these are of doubtful accuracy. From the table it can be seen that very little correlation exists at all and this is not perhaps surprising in view of the spread of results available. All the solids in table III. 3 are 'plastic' (26) with the exceptions of anthracene and sulphur. Because of this common property one might expect some correlation to exist between their diffusion activation energies and one of the physical properties mentioned in table III. 3.

In the case of pivalic acid the values of the ratios shown in table III. 3 as determined from the present study are similar to those determined for α-white phosphorus from Resing's results (25). This may indicate a similarity between the two diffusion processes. Since Resing's results were consistent with diffusion by a vacancy mechanism, such a mechanism is also likely for pivalic acid. The values shown for cyclohexane in columns I, II and III, of table III. 3 are consistently higher than those available for other plastic solids, apart from hydrogen, and probably indicate that the diffusion process is more complex. The high entropy factor obtained from the diffusion equation for cyclohexane supports the evidence of table III. 3 and indicates a co-operative diffusion mechanism involving a number of molecules is occurring.

The occurrence of co-operative molecular motions in plastic crystals have been mentioned previously by other authors. Dunning (27) has pointed out, that in plastic crystals, the volume available to the molecule in the lattice is usually less, by ~15%, than that required for free rotation. He has suggested that co-operative fluctuations are necessary to allow reorientation of molecules in a plastic crystal. That the molecules in plastic crystals do undergo reorientation, has been shown by N.M.R. (29) and dielectric studies (28). It has been found that polar molecular plastic crystals show a sharp increase in the dielectric constant on entering the plastic phase. The high entropy of transition to the plastic phase has been ascribed to the additional number of orientations available to the molecules and to their increased freedom of movement (97). In addition, Resing (25) has indicated that a co-operative rotational process is required to explain his N.M.R. results for the spin-lattice relaxation times in α- white phosphorus.

In view of the number of references which have been made to co-operative processes in plastic crystals, it does not seem unreasonable to suppose that diffusion in these solids should also be a co-operative phenomenom.

The energy of formation of vacancies in molecular crystals.

The energy of formation of a vacancy in a molecular crystal should be approximately equal to the latent heat of sublimation of the solid (95).

Pressure effects on diffusion processes in α- white phosphorus (78), sodium (100) and lead (101), show that there is a relaxation of atoms about a vacancy, such that the volume of the vacancy occupies about one half of the atomic or molecular volume. Calculations by Chihara and Morrison (102), based on specific heat data, suggest that in solid argon and krypton, the vacancy volumes are about ¼ of the atomic volumes.

Several authors have shown that the effect of relaxation of atoms about a vacancy, in metals, covalent solids and molecular crystals, is to reduce the energy of formation of the vacancy (75, 102, 103). A calculation based on a comparison of specific heat data with expansivity measurements, by Chihara and Morrison (102, suggests that in molecular crystals the energy of formation of a vacancy should be:-

$$H_v = .7 \times H_s \quad . \quad . \quad . \quad \text{III.27,} \; (H_s = \text{latent heat of sublimation})$$

The above authors also indicate that relaxation to about 25% of the molecular volume is to be expected round a vacancy. On this basis the energies of formation of vacancies in cyclohexane and pivalic acid would be 6 k.cals/mole and 7 k.cals/mole, respectively.

If these figures represent the energies of formation of the defects responsible for self-diffusion in cyclohexane and pivalic acid, then the energies of motion via these defects must be 10.5 and 3 k.cals/mole respectively. This indicates that the diffusion process in cyclohexane is more complex and probably involves the participation of a greater number of molecules than in the case of pivalic acid.

If the energies of motion are considered to be connected to the latent heats of fusion of the solids, in that the relaxed vacancy moves through the crystal lattice by the 'melting' and 'freezing' of molecules into, and out of, the vacancy, then the numbers of molecules connected with this motion could be obtained by dividing the energies of motion by the heats of fusion. This process yields 17 and 6 molecules for cyclohexane and pivalic acid respectively indicating a more co-operative diffusion process in the case of cyclohexane.

7 The nature of vacancies in pivalic acid.

It has been suggested that the number of vacancies to be expected in the lattice of a plastic crystal near the melting point should be of the order of 1% of the lattice sites (102, 104). A comparison of the observed and calculated densities of pivalic acid at 12.4°C (58) indicates that there are 2% vacant lattice sites at that temperature.

If these vacancies are relaxed to involve a number of molecules round the vacancy, then the number of molecules involved at vacant sites would be considerably more than 2%. A relaxation involving only 6 molecules would mean that 12% of molecules in the lattice were associated with vacancies. Such a high figure seems unrealistic, and if it were real then one would expect interaction between vacancies to occur, which would almost certainly lead to premelting.

The latter phenomenom was referred to by Frenkel (105) as a heterophase fluctuation, and he suggested that small elements of fluidity should exist in solids near their melting points. These elements were calculated to involve about 130 molecules and were expected to grow exponentially with temperature. Diffusion by way of these elements would, therefore, be expected to show a temperature dependence of the "constants" of the diffusion equation.

The results obtained for diffusion in pivalic acid indicate that 'normal' bulk-diffusion is occurring since both Do and ΔH are invariant over the temperature range studied.

Thus to account for the observed number of vacancies, three explanations appear possible. One is, that if the molecules in pivalic acid do exist as dimers (58), then the vacancy volume would be doubled and this would effectively lower the vacancy concentration by a half. A second explanation could be that relaxation about vacancies in pivalic acid is restricted, such that an appreciable number of molecules are not associated with each vacancy. This would be consistent with a diffusion mechanism on the lines of a simple vacancy model, a solution which is supported by the activation entropy and enthalpy for self-diffusion. The third possibility is that the density figures quoted are subject to error, since a very slight deviation would have a marked effect on the apparent number of vacancies in the solid. It is possible that all three solutions contribute to the solution in some degree.

It is unfortunate that comparative density figures are available at only one temperature otherwise it might have been possible to estimate the energy of vacancy formation. There are no similar density figures available for cyclohexane.

8 Conclusions.

The tracer method of studying self-diffusion in the solid-state shows that self-diffusion does occur in cyclohexane and pivalic acid.

In the temperature ranges studied the diffusion processes for cyclohexane and pivalic acid can be represented by the equations:-

$$D = (6.1 \pm 3.8) \times 10^{6} \, \mathrm{EXP} - \left(\frac{16500 \pm 300}{RT} \right) \mathrm{cm}^{2} \, \mathrm{sec}^{-1}$$

and

$$D = (2.25 \pm 1.25) \times \mathrm{EXP} - \left(\frac{10000 \pm 300}{RT} \right) \mathrm{cm}^{2} \, \mathrm{sec}^{-1}$$

respectively.

In the case of cyclohexane both the enthalpy and entropy factors associated with the diffusion process were found to be high. The conclusion is that diffusion occurs by a complex co-operative process. The diffusion mechanism is probably dependent on the formation of a vacancy associated with a region of molecular disorder as a result of relaxation into the vacancy. Diffusion is thought to occur by movement of molecules within the disordered region and of the disordered region itself, through the crystal.

The equation for self-diffusion in pivalic acid shows values for the enthalpy and entropy of activation which are in reasonable agreement with diffusion by a 'simple' vacancy process. It is thought likely that this mechanism is responsible for diffusion in pivalic acid.

The difference between the diffusion mechanisms for cyclohexane and pivalic acid probably arises from hydrogen bonding in the latter. This would tend to create a more rigid lattice which in turn would probably restrict relaxation about vacancies in the crystal, thereby limiting the need for a co-operative diffusion process in the crystal.

Finally, the activation energies for self-diffusion in cyclohexane and pivalic acid do not agree with the figures obtained, so far, from N.M.R. studies of these compounds. In both cases the N.M.R. values are less than the present figures, by 20% in the case of pivalic acid and about 40% for cyclohexane.

FUTURE WORK

An extension of diffusion measurements nearer to the melting point would be useful since the presence of any large scale premelting phenomena would almost certainly be revealed.

The effect of molecular rotation on diffusion rates would be of interest. Such an effect could perhaps be studied from the diffusion characteristics of a series of molecular solids graduating from a spherical shape to a straight chain molecule.

To determine whether the diffusion process in molecular solids is truly a co-operative phenomenon, a study of impurity diffusion could be made since impurities of a similar molecular size to the host lattice molecules could be expected to diffuse at a similar rate to the latter in a co-operative movement.

The effect of pressure could be used to indicate whether diffusion occurs in molecular solids by way of vacancies, since increasing the pressure would lower the equilibrium concentration of such defects and hence reduce the diffusion rate. An activation volume for diffusion could be obtained from such studies and this could be useful in elucidating the diffusion mechanism.

Plastic properties of molecular crystals, such as compressibility and plastic flow should be studied, to see if they bear any relation to the self-diffusion coefficients of the crystals.

Further tracer studies on molecular solids are desirable in order that any common trend for self-diffusion in these solids should become apparent.

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APPENDICES

APPENDIX I

Calculation of the constants for the Arrhenius Type Equations for self-diffusion in cyclohexane and pivalic acid.

The Arrhenius type equation is

$$D = Do \, EXP \left[- \frac{E}{RT} \right] . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad A.1.$$

from which the logarithmic form can be obtained:-

$$\log_{10}D = \log_{10}Do - \frac{E}{RT} \log_{10} e \quad . \quad . \quad . \quad . \quad A.2.$$

A plot of $\log_{10}D$ versus $\frac{1}{T}$ should be linear and this was found to be the case for cyclohexane and pivalic acid. The appendix shows the least mean squares calculations which were used to determine the best straight lines to fit the experimental points.

Where two values of D have been obtained for any temperature, an average of these values has been chosen for the temperatures concerned. The abbreviations used have their usual meaning (106). The values of $\frac{1}{T}$ and $\log_{10}D$ are represented as X and Y respectively.

<u>CYCLOHEXANE</u>

	Y	$X \times 10^3$	$X^2 \times 10^6$	XY
	-8.143	4.137	17.115	-33.686
	-8.629	4.242	17.995	-36.604
	-8.688	4.270	18.233	-37.099
	-9.058	4.378	19.167	-39.656
	-9.184	4.444	19.749	-40.816
	-9.344	4.480	20.070	-41.861
	-9.972	4.636	21.493	-46.227
	-10.344	4.749	22.553	-49.147
Σ =	-73.361	35.336	156.374	-325.095

N = 8

$$M = \frac{\Sigma X \Sigma Y - N \Sigma XY}{(\Sigma X)^2 - N \Sigma X^2}$$

$$= \frac{[35.336 \times 10^3 \times -73.361] - 8\,[-325.095 \times 10^{-3}]}{(35.336)^2 10^{-6} \qquad - 8 \times 156.374 \times 10^{-6}}$$

$$= -\frac{8.466}{2.360} \times 10^3$$

$$= -3.587 \times 10^3$$

$$C = \frac{\Sigma X \Sigma XY - \Sigma Y \Sigma X^2}{(\Sigma X)^2 - N \Sigma X^2}$$

$$= \frac{[35.336 \times 10^{-3} \times -325.095 \times 10^{-3}] - [-73.361 \times 156.374 \times 10^{-6}]}{-2.360 \times 10^{-6}}$$

$$= 6.679$$

Goodness of fit

Y	$X \times 10^3$	MX	MX + C	d = Y-(MX + C)	$d^2 \times 10^3$
-8.143	4.137	-14.841	-8.162	+.019	.361
-8.629	4.242	-15.218	-8.539	-.090	8.100
-8.688	4.270	-15.318	-8.639	-.048	2.304
-9.058	4.378	-15.706	-9.027	-.032	1.024
-9.184	4.444	-15.942	-9.263	+.079	6.241
-9.344	4.480	-16.072	-9.393	+.049	2.401
-9.971	4.636	-16.631	-9.952	-.019	.361
-10.344	4.749	-17.037	-10.358	+.014	.196
					=20.988

$$re = .6745 \left[\frac{d^2}{N-2} \right]^{1/2}$$

$$= .6745 \left[\frac{209.88}{6} \right]^{1/2} \times 10^{-2}$$

$$= .0388$$

$$D = N \Sigma X^2 - (\Sigma X)^2$$

$$= 2.36 \times 10^{-6}$$

error in M $= P_M$

$$= re \left[\frac{N}{D} \right]^{1/2}$$

$$= .0388 \left[\frac{6}{2.36} \right]^{1/2} \times 10^3$$

$$= .062 \times 10^3$$

$$\text{error in } C = \not{P}C$$

$$= re \left[\frac{\Sigma X^2}{D} \right]^{1/2}$$

$$= .0388 \left[\frac{156.374 \times 10^{-6}}{2.36 \times 10^{-6}} \right]^{1/2}$$

$$= .316$$

The equation of the line is:-

$$Y = -\left[3.587 \pm .062 \right] \times 10^{3} X + \left[6.679 \pm .316 \right]$$

Comparing this equation with A. 2 we have

$$\log_{10} Do = 6.679 \pm .316$$

$$\text{and } \frac{E}{R} \log_{10} = \left[3.587 \pm .062 \right] \times 10^{3}$$

$$Do = \left[6.10 \pm 3.79 \right] \times 10^{6} \text{ CM}^{2}.\text{SEC}^{-1}$$

$$\text{and } E = 16500 \pm 300 \text{ cals. mole}^{-1}$$

Therefore the Arrhenius equation for self-diffusion in cyclohexane is:-

$$D = \left[6.10 \pm 3.79 \right] \times 10^{6}.\ \text{EXP} - \left[\frac{16500 \pm 300}{RT} \right] \text{CM}^{2}.\text{SEC}^{-1}$$

PIVALIC ACID

Using the notations as before:-

Y	$X \times 10^3$	$X^2 \times 10^6$	XY
-7.451	3.565	12.709	-26.563
-7.368	3.539	12.525	-26.074
-7.308	3.507	12.299	-25.629
-7.246	3.472	12.055	-25.157
-7.185	3.438	11.820	-24.702
-7.093	3.395	11.526	-24.080
Σ = -43.650	20.916	72.933	-152.207

$$M = \frac{\Sigma X \Sigma Y - N \Sigma XY}{(\Sigma X)^2 - N\Sigma X^2}$$

$$M = \frac{\Sigma X \Sigma Y - N \Sigma XY}{(\Sigma X)^2 - N\Sigma X^2}$$

$$= \frac{20.916 \times 10^{-3} \times - 43.650 - 6 \times - 152.207 \times 10^{-3}}{[\,20.916 \times 10^{-3}\,]^2 - 6 \times 72.933 \times 10^{-6}}$$

$$= \frac{.2628}{-.1213} \times 10^3$$

$$= -2.167 \times 10^3$$

$$C = \frac{\Sigma X \Sigma XY - \Sigma Y \Sigma X^2}{(\Sigma X)^2 - N\Sigma X^2}$$

$$= \frac{20.916 \times 10^{-3} \times -152.207 \times 10^{-3} - [\,-43.650 \times 72.933 \times 10^{-6}\,]}{[\,20.916 \times 10^{-3}\,]^2 - 6 \times 72.933 \times 10^{-6}}$$

$$= \frac{.0333}{.1213}$$

$$= .275$$

Y	$X \times 10^3$	MX	MX + C	d = Y -(MX + C)	$d^2 \times 10^3$
-7.451	3.565	-7.725	-7.451	-.0002	0.000
-7.368	3.539	-7.669	-7.395	+.0270	0.729
-7.308	3.507	-7.599	-7.325	+.0172	.029
-7.246	3.472	-7.524	-7.249	+.0036	.013
-7.185	3.438	-7.450	-7.176	-.0094	.089
-7.093	3.395	-7.357	-7.083	-.0101	.102
					Σ = .962

$$re = .6745 \left[\frac{\leq d^2}{N - 2} \right]^{1/2}$$

$$= .6745 \left[\frac{.962}{4 \times 10^3} \right]^{1/2}$$

$$re = .011$$

$$D = N\Sigma X^2 - (\leq X)^2$$

$$= .1213 \times 10^{-6}$$

error in M = $\mathrm{P}M$

$$= re \left[\frac{N}{D} \right]^{1/2}$$

$$= .011 \left[\frac{4}{.1213} \right]^{1/2} \times 10^3$$

$$= .063 \times 10^3$$

error in C = $\mathrm{P}C$

$$= re \left[\frac{\leq X^2}{D} \right]^{1/2}$$

$$= .011 \left[\frac{72.933 \times 10^{-6}}{.1213 \times 10^{-6}} \right]^{1/2}$$

$$= .011 \times 24.5$$

$$= .2695$$

The equation of the line is

$$Y = -(2.167 \pm .063) \times 10^3 X + (.275 \pm .270)$$

Comparing this with equation A.2., we have,

$$\log_{10} Do = .275 \pm .270$$

and $\frac{E}{R} \log_{10} = (2.167 \pm .063) \times 10^3$

The Arrhenius equation for self-diffusion in pivalic acid is therefore:-

$$D = (2.25 \pm 1.25) \text{ EXP} - \left(\frac{10{,}000 \pm 300}{RT}\right) \text{CM}^2 . \text{ SEC}^{-1}$$

APPENDIX II

The Calculation of the Diffusion Coefficient

The logarithmic form of the equation which represents the process of diffusion in the present case is:-

$$\log_{10}C = \log_{10}\left[\frac{Q}{\sqrt{\pi D t}}\right] - \frac{X^2}{4Dt}\log_{10}e \quad ....A.3.$$

A plot of $\log_{10}C$ versus X^2 should be linear. This was the case for the experimental results obtained for diffusion in both cyclohexane and pivalic acid. The diffusion coefficient was calculated from the slope of the line of equation A. 3. which is

$$-\frac{\log_{10}e}{4Dt}$$

The following calculation is a typical one, the best straight line for a series of experimental points being calculated by the method of least mean squares. The calculation is for experiment number 3.

In the calculation the terms $\log_{10}A$ and X^2 are represented by X and Y respectively.

$X \times 10^4$	Y	$X^2 \times 10^{10}$	XY
.056	1.604	.317	0.090
.156	1.572	2.443	0.246
.281	1.537	7.913	0.432
.461	1.430	21.280	0.660
.687	1.260	47.128	0.865
.964	1.263	92.930	1.217
1.274	1.124	162.308	1.432
1.630	.978	265.690	1.594
2.486	.699	618.168	1.738
Σ = 7.996	11.466	1218.169	8.2733

$$M = \frac{\Sigma X \Sigma Y - N \Sigma XY}{(\Sigma X)^2 - N \Sigma X^2}$$

$$= \frac{7.996 \times 10^{-4} \times 11.466 - 9 \times 8.2733 \times 10^{-4}}{[7.996 \times 10^{-4}]^2 - 9\,[1218.169 \times 10^{-10}]}$$

$$= - \frac{17.2181}{45.699} \times 10^4$$

$$= -.3768 \times 10^4$$

$$= \frac{-\log_{10} e}{4Dt}$$

t in this case was 234 minutes

$$\therefore \; D = \frac{.4343}{4 \times 234 \times 60 \times .377 \times 10^{4}}$$

$$= 2.052 \times 10^{-9} \ \mathrm{CM.}^{2} \ \mathrm{SEC}^{-1}$$