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A STUDY OF THE DIFFUSION OF HELIUM IN METALS.

Thesis presented in candidature for the  
degree of Doctor of Philosophy in the  
University of Durham

by

R. Blackburn, B.Sc., A.R.I.C.,  
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ABSTRACT.

A greatly improved apparatus for the detection and measurement of micro-quantities of helium and neon was constructed and used to investigate the behaviour of helium in lithium/aluminium alloy, gold, beryllium and meteoritic iron.

The work described involved neutron transmutation techniques for the production of helium in lithium/aluminium alloy and beryllium, and took advantage of the fact that helium is produced in meteoritic iron when bombarded with cosmic rays. The work on gold utilised the alpha-decay scheme of radon as a source of helium.

The diffusion of helium in lithium/aluminium alloy appears to take place by a substitutional mechanism according to the equation

$$D = 42. \exp. \left( - \frac{49.7 \times 10^3}{R T} \right)$$

where D is the diffusion coefficient expressed in square centimetres per second. The conditions under which this equation is obeyed, however, are shown to be very restricted and highly dependent on the physical state of the metal and its previous annealing history. Accumulation of the gas into bubbles is believed to be the cause of the marked decrease in evolution of helium observed when annealing times longer than a few hours are used.

The values obtained for the diffusivity of helium in gold are believed to be invalid on account of the presence of voids along the line of the cold-weld used to sandwich helium-rich layers of this metal together. The validity of this particular technique for gas/metal systems is reviewed in some detail.

No values are presented for the diffusivity of helium in beryllium or meteoritic iron but the conclusion is that bubble-formation is a significant factor in diminishing the evolution of helium from these metals.



I N T R O D U C T I O N

INTRODUCTION.

The study of processes giving rise to diffusion of gases in solids (particularly in metals) is a subject of great academic interest since it can be made to yield much information on the structure of the solid, and in particular the various crystal defects which are now held to be chiefly responsible for diffusion. The classical theory of diffusion has been found to be inapplicable to certain systems and it seems very likely that the atoms concerned cannot be considered to be non-interacting particles influenced solely by their physical size. In some cases chemical effects have a profound influence on diffusion rates and the study of the inert gases in metals should enable these effects to be eliminated since these gases have no chemical affinities.

Technologically, the significance of gas diffusion studies has increased enormously in recent years with the development of the peaceful uses of atomic energy which has involved a great deal of research into the compatibility of materials to very high neutron fluxes. From thermodynamical considerations of the "Carnot cycle" type a nuclear reactor must be operated at a high temperature if useful power is to be efficiently produced, and it is very desirable to keep the equipment as compact as possible, i.e. to achieve a high power-density. This is especially the case in the new fast reactors where the volume of the fuel elements is very small. These con-

siderations lead to the release of energy in small volumes of material at high temperatures where the readier movement of atoms and crystal defects will be promoted. This ease of movement of atoms encourages the annealing out of normal fast neutron radiation damage (e.g. that due to "Wigner effect") and eliminates the need for the controlled release of stored energy such as is necessary in graphite moderated reactors operating at lower power levels. On the other hand, any gaseous products of nuclear reactions occurring in the solid reactor components — fuel elements, moderator, sheathing and structural materials — will possess a greater mobility on account of the higher temperature and it becomes necessary to know the possible results of such mobility.

The most acute form of the problem occurs in fuel elements since several fission product chains terminate with stable krypton and xenon isotopes, and in addition to these there is at least one long - lived inert gas fission product ( $\text{Kr}^{85}$ ) whose escape from the reactor could give rise to a serious contamination hazard. More immediately serious, however, is the effect of the accumulation of the fission gases, either homogeneously or in voids in the metal. This accumulation has a marked and rather unpredictable effect on the physical properties and dimensions of the fuel elements. Since helium is a product of a number of neutron-induced nuclear reactions, the problem is not restricted solely to fuel elements, but may occur in other

materials (particularly beryllium) which are subjected to the neutron flux. Moreover, with the increasing use of plutonium as a fuel the helium produced in this material by simple alpha-decay may well aggravate the problems already raised by the behaviour of the fission gases.

Less technological interest also attaches to the containment of inert gases in metals. Very few gas metal systems have been investigated from the point of view of diffusion, although much work has been directed towards permeation measurements. It has been stated (1,2) that a gas can only pass through a metal if it can react with it chemically, but this view has been modified by RHINES (3) who considers that solubility in the metal is a sufficient condition for permeation. Measurements on inert gas/metal systems would establish the validity or otherwise of these two statements since the inert gases cannot react chemically (unpairing of the 1s electrons in helium and the promotion of one of them to the 2s level would require an energy of 460 kilocalories per gram atom) nor can they dissolve to any appreciable extent.

Considerable confusion has arisen in the literature relating to gas movement in solids because of the synonymous use of the terms diffusion and permeation. There are in general two states of flow by diffusion, one stationary and the other non-stationary, the two differential forms of Fick's law for these states being respectively:-

$$P = -D \frac{\partial c}{\partial x}$$

$$\text{and } \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

In other words, from the first equation one can derive the permeability constant "P" (the quantity of matter transferred / unit time / unit area of unit thickness under a standard concentration gradient) in terms of a diffusion coefficient "D". The second equation, relating to the non-stationary state of flow, refers to the accumulation of material at a point in a medium as a function of time. "D" and "P" will be numerically the same if "P" is expressed as the quantity of gas diffusing in unit of time through unit area of the exit surface of a membrane when unit concentration exists at that surface. The two constants are, however, dimensionally different. Thus, while being closely related in theory, the mechanism by which each takes place is markedly different. Diffusion may be thought of as the movement of atoms through a lattice while the term permeation relates to the passage of material through a membrane.

In the case of the inert gases in metals the mechanism of permeation, assuming it to take place, could be broken down into the following steps.

1. Adsorption of the gas on the surface of the metal membrane, and its subsequent solution in the lattice.
2. Diffusion of the gas atoms through the metal lattice.

3. Transition of the atoms from the dissolved to the adsorbed state at the surface of exit.
4. Desorption of the atoms from the surface.

Each of these steps involves an energy term and the slowest of the stages will determine the overall rate of permeation. Should any of the above steps be energetically unfavourable permeation will not take place.

It therefore appears that the absence of permeation in a particular system need not imply an inability of the gas atoms to diffuse once they are in the crystal lattice of the medium. Diffusion is not dependent on boundary effects but is relatively simply influenced by the crystal structure, the size of the diffusing atom, and the nature and number of the defects present in the crystal lattice.

JOHNS (4) has shown that the quantity of argon absorbed by uranium at room temperature is less than 1 part in  $3 \times 10^5$  parts by weight, and less than 1 part in  $3 \times 10^4$  at a temperature of  $600^\circ\text{C}$ . Both these figures are of the magnitude of the uncertainty in the measurements, and the actual solubility may well be much less. In the cathodic 'clean-up' of gases in discharge tubes it has been found (5) that inert gas atoms can be projected into a metallic lattice and held there, but there is no suggestion that this represents any real equilibrium solubility. Similar work by SEELIGER et al. (6) gives further evidence of the insolubility of the inert gases in metals. In the case of the inert gases there is no well authenticated demonstration of permeation

through metals, and this is certainly a reflection of the non-solubility of these gases in solid metals. Most of the references to be found in the literature are shown in table 1. A result not included in the table is that of LOMBARD (7) who found that argon permeated in nickel as fast as nitrogen, and helium much faster. Since the solubility of nitrogen in nickel is negligible at temperatures less than 1200°C. (8) it is doubtful if permeation even of nitrogen could take place.

These results should therefore be treated with some reserve. LE CLAIRE and ROWE (9) have challenged the validity of RUSSELL's results (10) on the grounds that only a single experiment was made with helium and they suggest that the positive result obtained was due to hydrogen impurity, a likely source of error since the aluminium sample employed had just been used for a series of experiments with this gas. This explanation is the more likely since the method of detection used (McLeod gauge) was non-specific.

It would appear then that for most gases diffusion, rather than permeation, through metals is the more significant process; in the case of the inert gases it appears to be the only mechanism possible.

The case of helium diffusion is especially interesting since owing to the small size of the atom it might be expected to move by rather a different mechanism than that by which the heavier members of the group are thought to diffuse. The large atoms of argon, xenon and krypton are expected (11) to move in the lattice by a vacancy

mechanism only but it is possible that the smaller atom of helium may move interstitially. This would certainly be expected at low temperature where the concentration of vacancies will be small. Measurement of the activation energy of diffusion should be sufficient to decide between these two mechanisms since the energies characterising interstitial and vacancy movement are usually very different (12). Caution must be exercised, however, in that it is now generally accepted that lattice defect movements are not always characterised by a unique activation energy. If diffusion of gas takes place by a movement of defects then it might be expected that different effects come into operation at different temperatures. Such a phenomenon has certainly been observed in studies on the annealing of defects in metals (13,44).

Work carried out by BARNES et al. (14,15) suggests that even helium diffuses by a migration of vacancies towards the atom rather than an actual movement of the atom itself. However, the high temperature at which the experiments were conducted would lead to vacancy effects predominating over any interstitial mechanism which may have been operative.

The determination of the ages of iron meteorites depends principally on finding the helium content of the metal, and any loss of helium by diffusion should be allowed for. It should be noted in this connection that meteorites are supposed not to be unduly heated

during their flight through the atmosphere since the heat generated by friction causes the outer layers of the meteorite to melt, the molten layer being immediately lost by ablation. Thus the overall rate of temperature rise of the metal is small and the portion of the meteorite surviving the fall may be quite cool on impact (16). It may well be, however, that in certain cases warming does occur resulting in loss of helium by diffusion and a knowledge of the possible extent of such a loss becomes of importance.

Again, in experiments designed to measure the neutron cross-section of beryllium for helium production, HALL (17) has tentatively attributed some small discrepancies to loss of helium by diffusion. The temperature at which the irradiations were carried out was only slightly elevated and it seems likely that diffusion could cause little significant loss, but an investigation of this possibility would be desirable.

It may be seen therefore that a study of the diffusion of helium (or any inert gas) in metals is of some theoretical and technical consequence.

The incidental production of inert gases in metals (e.g. in nuclear reactors) has posed new problems which can no longer be adequately investigated by simple permeation techniques. The inert gases are no longer restricted by their inability to dissolve at a metal to gas interface since they are either created in the lattice by nuclear reactions or, in the case of alpha-particles, they can overcome

the boundary energy conditions by virtue of their high kinetic energy. The new problems, however, suggest techniques for their own solution and a few of the principal methods of introducing inert gases into metals are enumerated below.

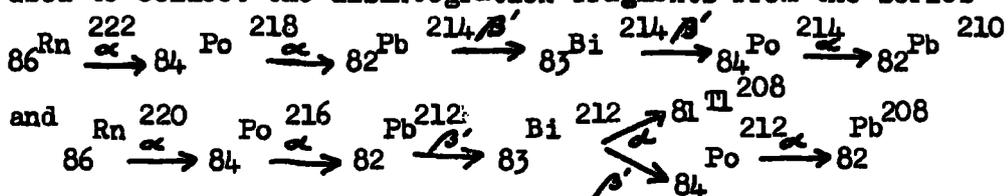
1. BOMBARDMENT BY CHARGED PARTICLES FROM SOURCES EXTERNAL TO THE METAL.

a. Sputtering methods.

LE CLAIRE and ROWE (9) have adapted the cathodic "clean-up" techniques of SEELIGER et al. (5,6) to the production of a gas impregnated layer sandwiched between two layers of metal. The method involves the use of a hollow cathode in a discharge tube containing the gas under consideration. On applying a voltage gradient, gas ions are driven into the surface of the cathode and remain trapped in the lattice. By collapsing the cathode and rolling the metal under pressure it is possible to cold-weld the surfaces in such a way as to produce a good metallurgical bond. In effect a metal specimen containing a central gas-rich layer is produced. The gas may be activated in a neutron flux so as to facilitate the measurement of the fraction evolved on annealing, or if no suitable active isotope exists mass-spectrometric methods may be used. This method has also been used by TOBIN (18,19).

b. Capture of disintegration fragments.

A cylinder of the desired metal containing radon or thoron may be used to collect the disintegration fragments from the series



The cylinder may then be rolled and cold-welded as in (a). The gold cylinders containing radon (gold "radon seeds") used in radio-therapy form a readily available source of helium-rich metal and advantage was taken of this in the present work.

#### c. Cyclotron methods.

A cyclotron may be used to bombard specimens with alpha-particles since these lodge in the metal lattice at depths dependent on their range in the material. This method (used by several workers (14,20) gives a very concentrated sandwich of gas-rich metal. It may be adapted (88) by using a variety of particle energies, to the production of a homogeneous solution of gas in the metal.

## 2. GAS PRODUCED BY NUCLEAR REACTIONS WITHIN THE MATERIAL.

### a. Fission fragment retention

Fission fragments have a very short range in solids and are consequently retained in the lattice of the metal undergoing fission. This method has been extensively used for the production of solutions of xenon and krypton in uranium, and of course may be extended to any other fissile material.

### b. Alpha-decay.

Radioactive decay by alpha-particle emission leads to the accumulation of helium in metals since the range of the particle is short.

### c. Cosmic-ray induced reactions

A natural source of helium-containing metal is produced by the

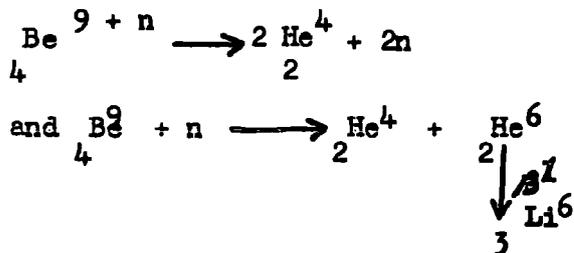
exposure of meteoritic iron to cosmic ray fluxes during their flight through space. This leads to the production of the isotopes  $\text{He}^3$  and  $\text{He}^4$ .

d. Tritium method.

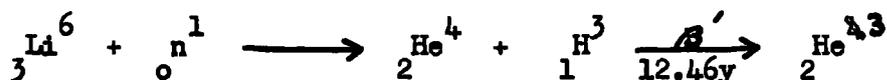
Any metal which is permeable to hydrogen may be saturated with tritium and this gas allowed to undergo the reaction  ${}^3_1\text{H} \xrightarrow[12.46\text{y.}]{\beta} {}^4_2\text{He}$ .

e. Neutron induced nuclear reactions.

If the metal in which it is desired to dissolve the inert gas is itself capable of undergoing a nuclear reaction with a neutron to produce helium or if it will form a homogeneous solid solution with a small amount of another metal which can undergo such a reaction, then helium may be produced in the metal or alloy by exposing it to a neutron flux. Examples of the first type of reaction are,



Aluminium does not have an appreciable cross-section for the production of helium but by alloying it with a small quantity of lithium advantage may be taken of the reaction



The lithium solid solution method was used in the present work on

aluminium but it is of limited application.

Methods in the first category suffer from non-uniformity of gas distribution. In the case of the cold-welded "sandwich" there is a possibility of the formation of voids along the line of the cold-weld which could have the effect of reducing the gas concentration available for diffusion since once liberated in a void the inert gases would not redissolve in the metal. More evidence on the nature of the cold-welded bond would be very desirable. Those methods in the second category suffer from the "end effects" inherent with energetic particles. These effects result in a depletion of surface gas concentrations since particles originating near the surface may have sufficient energy to escape. Recoil losses are especially important since they can have a disproportionate effect on the observed rate of diffusion especially where this is low. In these cases the gas evolved by an anneal of reasonable duration comes chiefly from the surface regions affected by recoil loss, and where the gas concentration is not representative of that in the main body of the specimen. Allowance should be made for this, or irradiations carried out in such a way that the effects are minimised (see present work on aluminium).

Table 1.

GAS.	METAL.	TEMP. °C.	AUTHORS.	REF.	PERMEABILITY.
He.	Pt Pd Fe	Red heat	Ramsay and Travers.	21	Nil
	Pd	" "	Paneth and Peters	22	"
	Pt	1000	Jacquerod and Ferrot	23	"
	Pt group metals	1600	Henning	24	"
	Cu Ni Fe Mo	-	Smithells and Ransley	25	At least $10^5$ times less than those gases which are known to permeate.
	Al	550	Russell	10	$2.6 \times 10^{-9}$ c.o./sec./cm. <sup>2</sup>
	Al	500	Gordon, Atherton, Kaufmann.	26	Nil
	Al	500	Non-ferrous metals Res.Ass.report.	28	$< 1 \times 10^{-10}$ c.o./sec./cm. <sup>2</sup>
	St. steel Inconel.	830 830	Wisohhusen "	27 "	Not detectable. " "
	Pt-Ir alloy	1420	Dorn.	29	Scarcely perceptible.
	Fe Bi	700	Urry	30	Nil
Ne	Fe	850	Seeliger & Lumpe.	5	Nil.
A	Steel.	1100	Ryder	31	Nil.
	Cu Ni Fe Mo	-	Smithells and Ransley.	25	At least $10^5$ times less than those gases which are known to permeate.
	St. steel Mild steel Al	1000 " 500	Non-ferrous metals Res.Ass.report. " "	28	$< 5 \times 10^{-11}$ c.o./sec./cm. <sup>2</sup> $< 1 \times 10^{-10}$ c.o./sec./cm. <sup>2</sup>

P A R T O N E

THE APPARATUS.

INTRODUCTION TO THE APPARATUS.

The mathematics of diffusion processes are exceedingly complex and solutions exist for only a few of the simpler cases (32). Modifications must be made to the general solutions depending on whether the gas is homogeneously distributed or restricted to a thin layer in the metal, the solutions required in the present work being dealt with fully in the section entitled "Mathematical treatment of experimental results." It suffices here to say that if the physical dimensions of a specimen of suitable shape are known, together with the fractional amount diffusing out in a given time at a known temperature, then the diffusion coefficient "D" at that temperature may be calculated.

The experimental techniques necessary, therefore, deal with the annealing of specimens at an accurately known temperature, the collection of the gas evolved during annealing, the isolation of helium from any other gases and its subsequent measurement, and the liberation and measurement of the amount in the specimen initially.

If a number of specimens have all been treated identically then three methods of determining the initial and evolved gas concentrations are available.

a.) The helium concentration of suitably sampled specimens may be measured and the assumption made that it is the same for all. Other specimens of the same batch may then be used for annealing experiments. This method suffers from the obvious drawback that

there may be chance variations in the helium content of different specimens but this need not be serious particularly if "end-effects" are allowed for.

- b.) The total quantity of gas evolved from a specimen during a series of anneals may be measured and this amount added to the residual quantity obtained by the melting or dissolution of the metal. The disadvantage of this method is that the total amount obtained is based on several determinations and will be subject to a cumulative error.
- c.) Calculation of the quantity of gas evolved may be made from a knowledge of the initial amount found as in (a) and the quantity remaining after annealing. This method is subject to the errors of (a) and, if the diffusion rate is not very high, involves the subtraction of one quantity from another not much greater.

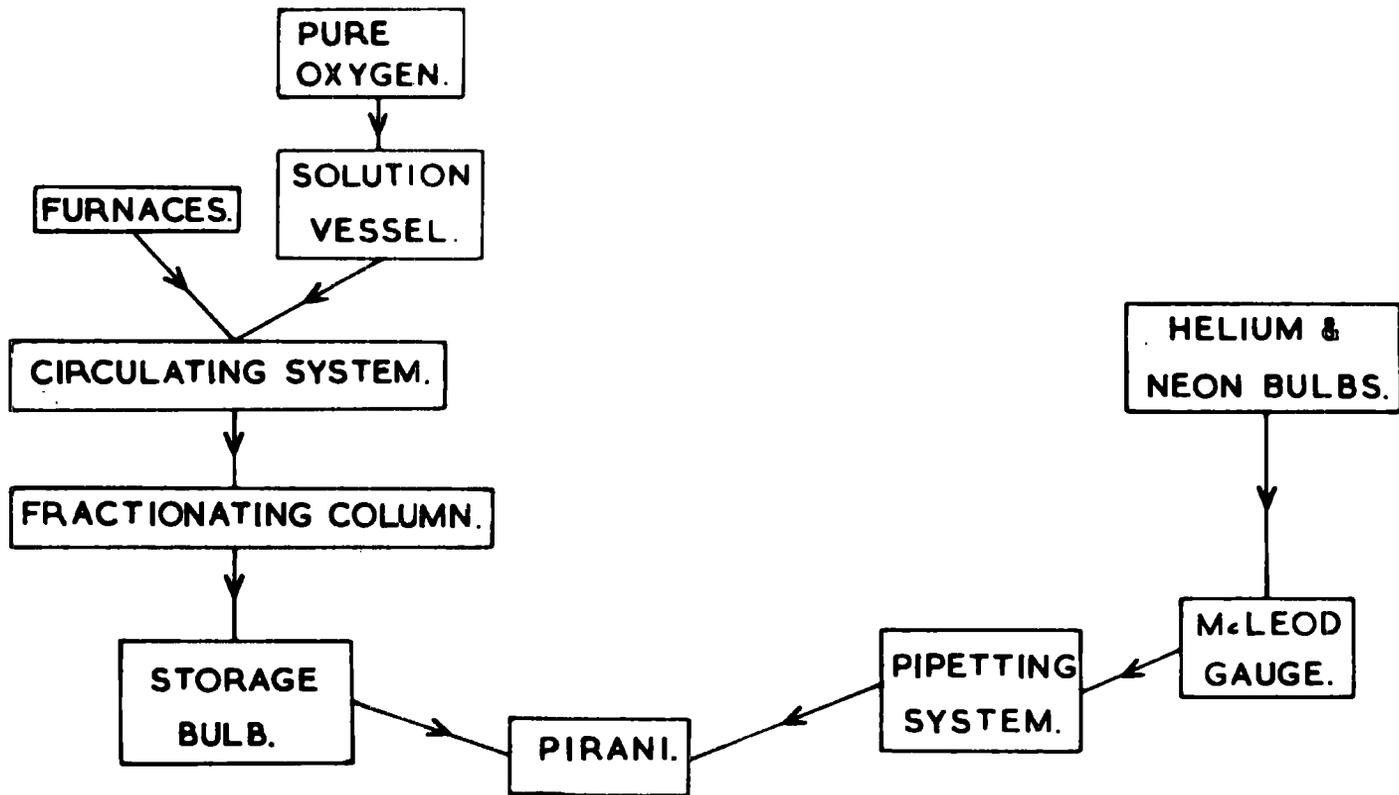
The heavier inert gases lend themselves to detection in that they possess suitably long-lived radio-active isotopes. In the case of helium and neon detection and measurement, however, it is necessary either to use methods specific to a particular isotope, such as mass-spectrometry, or to separate these gases from all other foreign gases present and measure the quantity recovered. This can be achieved by utilising the absence of chemical affinities in these gases and also the fact that they are the least strongly adsorbed of all gases on activated charcoal. Techniques for making such separations and measurements have been worked out by PANETH and his collaborators (33) and essentially these procedures have been used in the present work.

A diagrammatic summary of the apparatus is shown in fig.1, the sequence of operations being broadly as follows.

1. Dissolution of the metal in a suitable helium-free solvent, preferably with little or no hydrogen release.
2. The flushing of the liberated gases out of the dissolution vessel, the bulk of the associated water vapour being condensed out by means of a trap cooled in liquid air. Flushing is carried out with helium-free oxygen.
3. Collection of the gases in a circulating system where they are brought into contact with heated palladium, bringing about catalytic combination of the hydrogen and oxygen. The water vapour so produced is frozen out.
4. Transfer of the gases to a fractionating column, where the excess oxygen is adsorbed and the helium-free gas mixture is fractionated on wood charcoal at the temperature of liquid air.
5. The collection of the helium as it emerges from the fractionating column.
6. Compression of the helium into a Pirani gauge which is one of a pair located in adjacent arms of a Wheatstone bridge circuit. The off-balance current is measured with a sensitive moving coil galvanometer and compared with that produced by an accurately known quantity of pure helium.
7. The further operation of the column to collect the next fraction, neon. If this is present it can only have come from

Fig. 1.

A diagrammatic summary of the apparatus.



the atmosphere and is thus indicative of air leakage into the apparatus.

If it is desired to measure the helium evolved from a metal during an anneal the gases evolved by the specimen, together with the gases evolved from the walls of the furnace, are transferred directly to the circulating system by means of a Tüpler pump.

The apparatus is constructed in soda-glass, with the exception of the diffusion pumps, traps and Pirani gauges. This is to avoid error due to the appreciable permeation of helium through Pyrex glass. Since the atmosphere contains about  $5 \times 10^{-4}\%$  by volume of helium the whole apparatus must be evacuated to a high degree. The apparatus is divided into two halves, each half being evacuated by means of a mercury diffusion pump backed by a rotary pump.

All the taps used in the construction are of a special "all-soda" type. (Normally, so-called soda taps consist of a soda glass barrel with a Pyrex glass key.) The taps are carefully "ground-in" with fine grade "Sira" abrasive. Taps, together with the less permanent cone and socket fittings, are lubricated with "Apiezon N" grease except where they are likely to be exposed to heat. In such cases "Apiezon T" grease was used. The more permanent joints were effected with "Apiezon W" wax.

The delicacy of the Pirani gauge and its associated galvanometer renders the system very susceptible to vibration, hence the whole apparatus is mounted on a bench resting on a foundation independent of the foundation of the laboratory.

With one important exception the design of this apparatus is similar to that of previous workers (33), although several improvements of detail have been made. The fractionating column, however, while still operating on the same theoretical principle, has been completely re-designed. This has led to a considerable speeding up of the fractionation.

#### THE PREPARATION OF HELIUM-FREE OXYGEN.

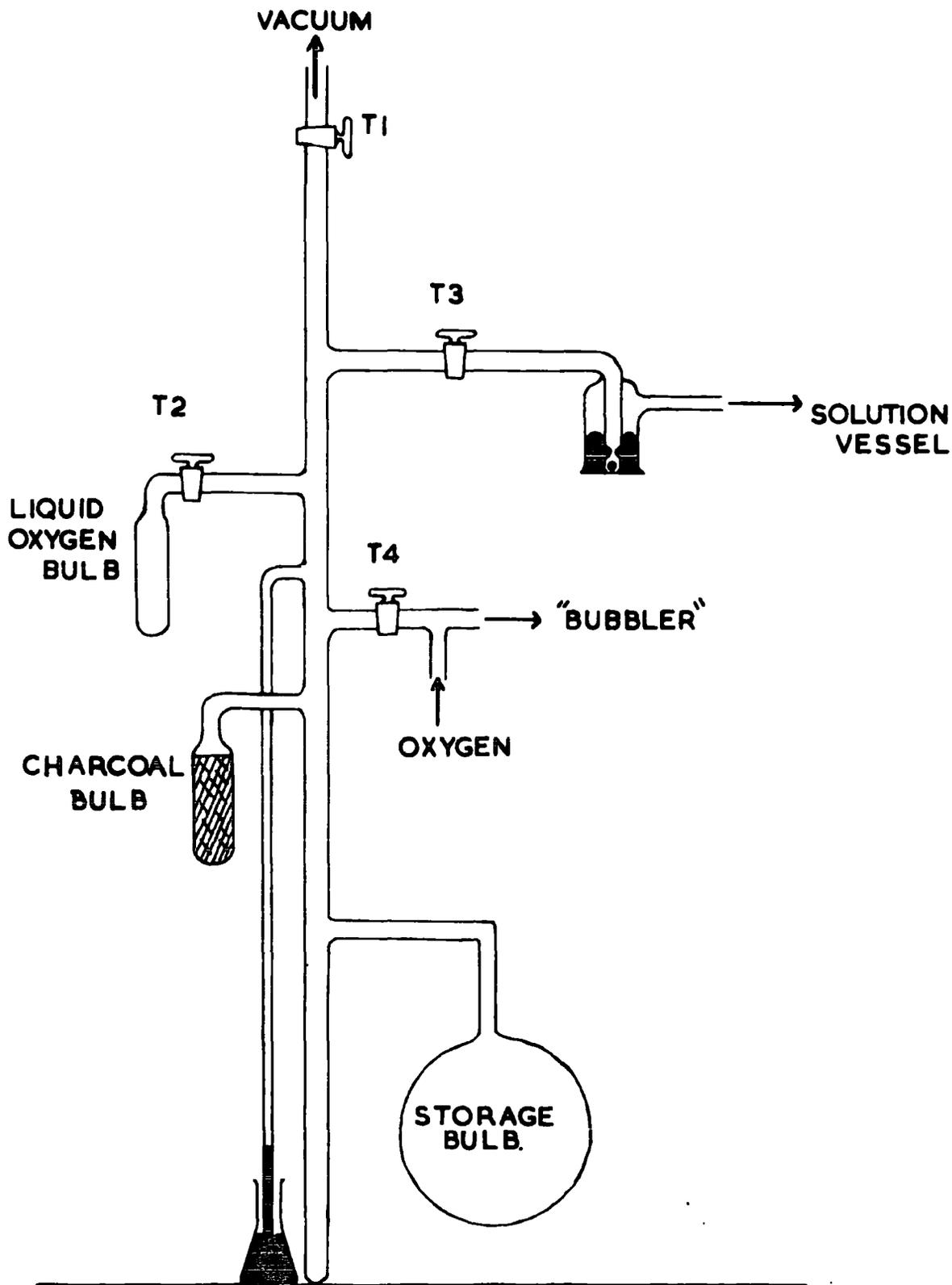
In the present work a relatively large quantity of pure helium-free oxygen was needed to act as a carrier gas for the small amounts of helium extracted from the metals under examination. In addition to acting as a carrier gas, the oxygen is required to remove the hydrogen which is almost always evolved in the techniques available for dissolving metals. If the amount of helium it is intended to measure is of the order of  $10^{-7}$  N.T.P.c.c.s, it is necessary to use oxygen with a minimum purity corresponding to one part of helium in  $10^{12}$  parts of oxygen, in order to achieve an accuracy of 0.1 per cent; this is assuming a hydrogen release of about  $2 \times 10^2$  c.c. at N.T.P., an amount not widely different from that usually obtained.

A very satisfactory method of purification uses (B. O. Co.) electrolytic oxygen supplied in cylinders. There is less chance of this containing helium impurity than the normal commercial oxygen obtained from the atmosphere. The apparatus used is shown in fig.2.

The whole apparatus is evacuated through tap T.1, the charcoal being baked out at  $250^{\circ}\text{C}$ . for several hours. When a high degree of vacuum has been achieved, the baking out is discontinued and tap T.1 is closed. Oxygen is bubbled past the outside of tap T.4 for several minutes in

fig. 2.

Oxygen apparatus.



order to flush out any air present in the tube, the waste oxygen bubbling away through a mercury non-return valve which prevents back diffusion of air from the atmosphere. Tap T.4 is then cautiously opened and the oxygen is allowed to enter the apparatus, the flow through the bubbler being maintained by opening the cylinder valve still further. When the oxygen storage bulb is full (the pressure being indicated by the manometer) tap T.4 is closed and the supply of oxygen cut off. The "liquid oxygen bulb" is surrounded with liquid air, the oxygen liquefying in the bulb till the pressure is that due to the vapour pressure of liquid oxygen at the temperature of liquid air (about 19cms. of mercury). Tap T.2 is now closed and the charcoal tube is immersed in liquid air, the pressure in the apparatus falling to a few m.m.s.. T.1 is then opened for about ten minutes and any helium present is pumped away. T.1 is then closed, T.2 opened, and the liquid air baths removed from the bulb and the charcoal, allowing the oxygen to vaporise and desorb. The process is repeated about six times till a sample of the gas, far in excess of that normally used in an analysis, shows no deflection when examined for helium in the normal way.

In this way about four litres of helium-free oxygen can be produced, the pressure being only slightly below atmospheric. In the present work it was found possible to keep the oxygen pure for several months, regular checks being made upon its purity. This agrees with the findings of most previous workers (34,35) but is contrary to the findings of WILSON (36). From figures (37) for the diffusion of helium through soda-glass, and for the outgassing of the helium already dissolved in the glass, it seems

unlikely that contamination due to these causes could be serious over a period of less than four or five months. However, the chief means of contamination is more likely to be leakage through the taps of the system, hence the necessity for frequent checks.

The purified oxygen may be tapped off through tap T.<sub>3</sub> via the non-return valve.

#### EQUIPMENT USED FOR THE ANNEALING OF SPECIMENS.

An important feature of the experiments was the annealing of the specimens. Since the annealing temperature occurs in the exponential term of expressions for diffusion it was evident that this quantity should be measured and controlled as accurately as possible. Each set of experiments demanded rather different conditions and it was necessary to use a selection of furnaces and control mechanisms.

The first requisite for the material of a furnace for this sort of measurement is that it is not permeable to helium and does not contain air (and therefore helium) in its crystal lattice. This immediately rules out the usual non-metallic refractory materials. Metals suffer from the disadvantage that they evolve considerable quantities of gas (mainly hydrogen) when heated. To minimise this effect the furnace tubes were outgassed for about twenty hours before they were used and by outgassing at a temperature higher than that actually required in an experiment it was possible to maintain quite a high vacuum in a furnace tube made of stainless steel, but not in a tube of mild steel or copper. A mild steel tube was therefore only used in those experiments where it was desired

to measure the residual gas, not that which had been evolved. In the case of the stainless steel tubes the evolved gases were analysed with regard to their helium content and the amount was found to be negligible, a not unexpected result in view of the insolubility of helium in solid metals (4,6).

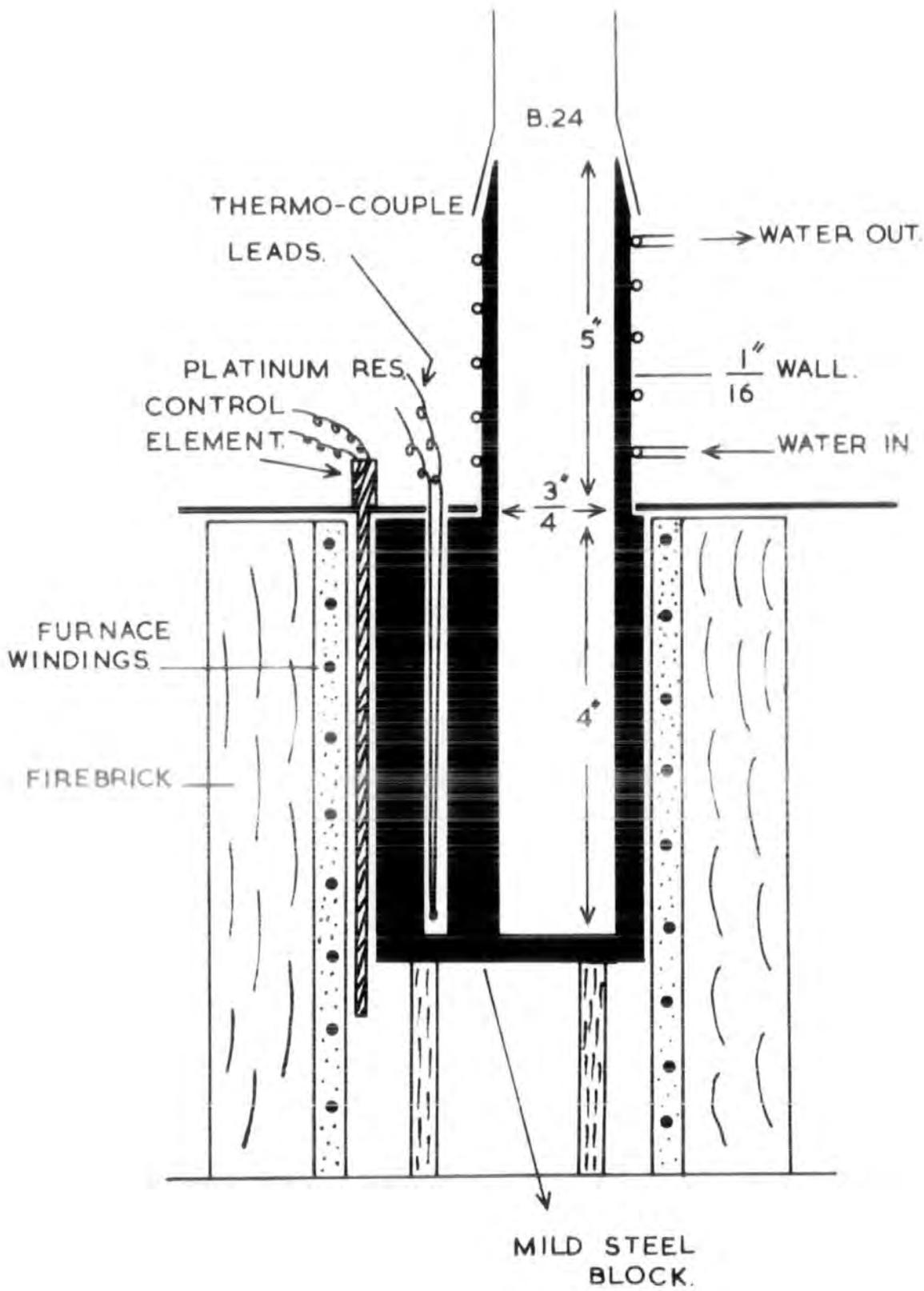
A disadvantage of metal furnace tubes is the joining of these, in a leak-proof manner, to the rest of the vacuum system. The stainless steel tubes had B/24 cones machined on their open ends but it was not found possible to effect a stainless steel to soda glass seal with "Apiezon W" wax. Although the joint would stand for several hours if allowed to cool slowly, subsequent changes of the ambient temperature led to cracking of the wax. It was curious that although both members of the joint were well heated to enable the wax to "bite" it invariably broke away from the glass. A similar difficulty in joining these two materials was experienced by WIBORG (38). The difficulty was finally resolved by machining the cones extremely accurately and greasing the joint with "Apiezon T" grease.

(a) Furnace used for long anneals in which evolved gas is not collected.

This is shown in fig.3. The material used was mild steel, this being satisfactory if the gases evolved were periodically pumped away. Temperature control was effected by means of a "Sunvio" platinum resistance thermometer controller operating in the circuit shown in fig. 4a. By continuous automatic variation from a maximum to a minimum value of the power supplied to the furnace it was easily possible to keep the temperature constant to within 1° C. The

Fig. 3.

Furnace used for long anneals during which the  
evolved gases were pumped away.



temperature was measured by means of a chromel-alumel thermocouple, the e.m.f. being indicated on a potentiometer unit. With this arrangement the temperature could be estimated to within  $1^{\circ}\text{C}$ . the thermocouple having been previously calibrated at the ice, steam and sulphur "fixed points".

(b) Furnaces used for short anneals and collection of evolved gas.

For this purpose two stainless steel tubes were used. Both were electrically heated in simple tube furnaces, the temperatures of which could be manually adjusted. Since the periods of heating were short such a method of temperature control was acceptable. A chromel-alumel thermocouple was again used for temperature measurement.

(c) Furnace for long anneals and collection of evolved gas.

A vacuum furnace for the collection of gas evolved over long periods was constructed but it was found impossible to keep this sufficiently helium-tight. The furnace is shown in fig. 34 and described in PART THREE under the title "Notes on some ideas tried but not adopted".

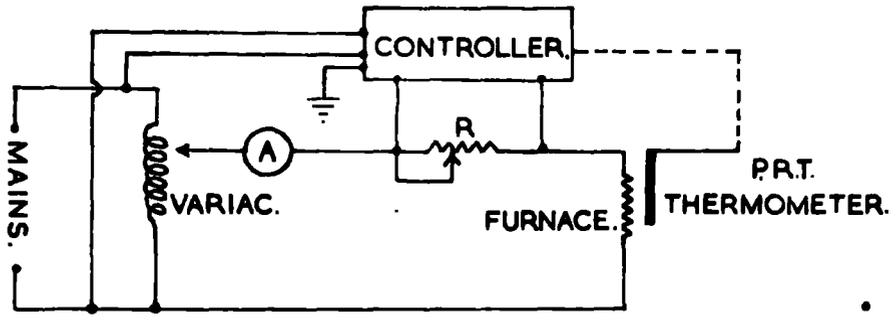
The specimens could be introduced into or withdrawn from the furnaces (a) and (b) by means of the device shown in fig. 4b. Usually it was possible to drill a very small hole in the specimen to provide a means of attaching the platinum wire but in some cases the metal was held in a platinum wire or molybdenum sheet "basket". Both the wire and the basket were thoroughly out-gassed before use, and no alloying problems were experienced with beryllium, gold, or aluminium specimens.

Fig. 4a.

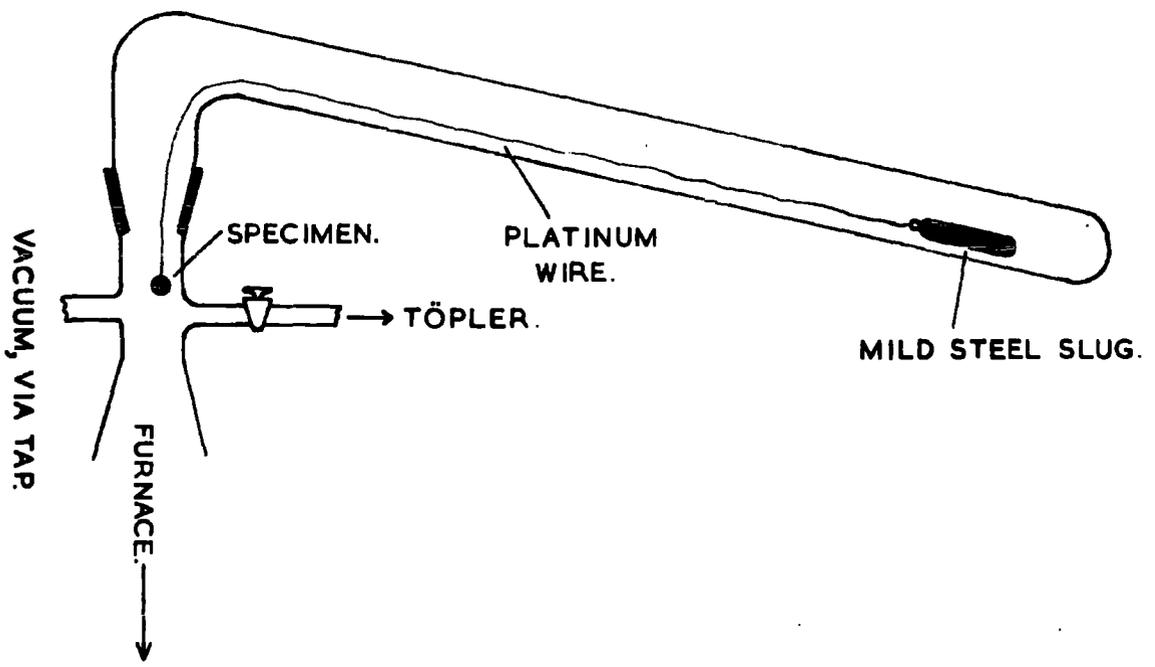
Temperature control mechanism for annealing  
furnaces.

Fig. 4b.

Device for introducing specimens into  
furnace.



R = INCREMENT RES..



THE RELEASE OF HELIUM FROM SPECIMENS TO DETERMINE THE INITIAL OR RESIDUAL CONCENTRATIONS.

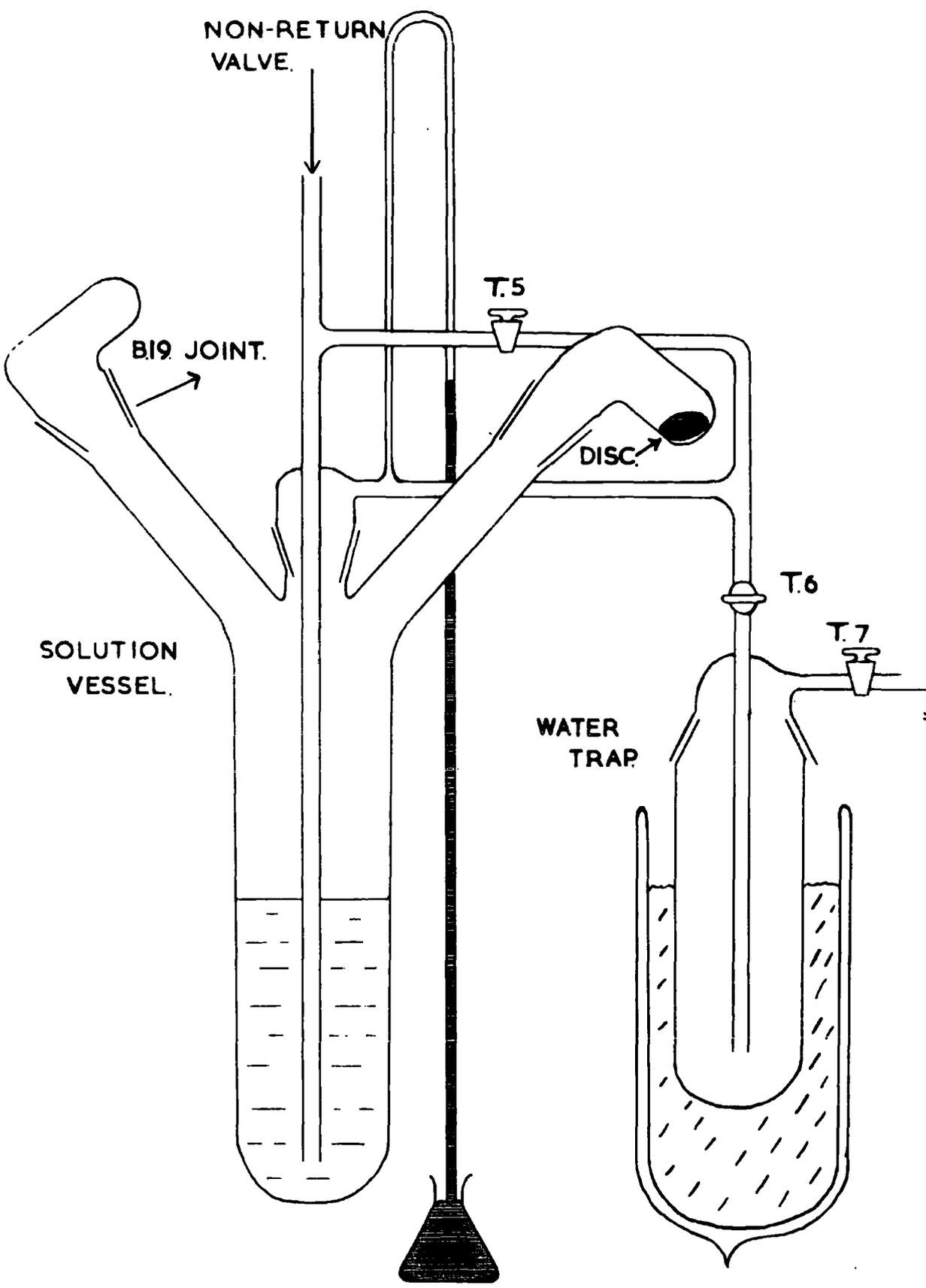
In order to release the helium contained in specimens it is necessary either to melt or dissolve them and to collect the gases evolved. The technique of vacuum melting is a difficult and expensive one and has rather special disadvantages in connection with the present work. Unless levitation melting is used it is impossible to melt the metal without the use of a containing vessel. Alloying effects may become a problem if this is made from metal, and the refractories normally used are quite unsatisfactory on account of their high air content.

The technique adopted in the present work was that of dissolution of the metal in a helium-free reagent, the subsequent flushing of the solution with helium-free oxygen, and the collection of the gas mixture. The apparatus used is shown in fig. 5.

The solution vessel is first evacuated (with T.5 open) to the vapour pressure of the solution, excessive amounts of water vapour being prevented from reaching the pumping system by means of a liquid-air cooled trap. Evacuation is carried out via taps T.6, T.7, and T.8, (fig.7), the mercury in the ventill "V" being raised to prevent contamination of the charcoal in the U-tube. When a suitable vacuum has been achieved, taps T.5 and T.6 are closed and helium-free oxygen is bubbled through the solution till the pressure in the solution vessel is about one centimetre of mercury. This gas is pumped away by opening T.6. After a few seconds T.6 is closed again, and the whole process is repeated seven or eight times, the interval between each evacuation being determined by the quality of the vacuum in the main pumping manifold.

Fig. 5.

Dissolution vessel.



Dissolution of the specimen is brought about by rotating the taper-joint in which it has been placed until the metal falls into the reagent.

Reagents used in the liberation of helium from specimens.

(1) For aluminium and beryllium.

The reagent used was a saturated solution of cupric potassium chloride. Hydrogen is briskly evolved and this causes the thin film of copper which is formed on the surface of the metal to break up, thus constantly exposing a fresh surface for the reaction which is complete in a few minutes. It is desirable to keep to a minimum the quantity of hydrogen evolved for reasons outlined in the next section, but the quantity of metal used in the present work did not involve the evolution of large amounts of this gas.

(2) For iron.

In the course of the work on meteoritic iron rather larger amounts of metal were involved but cupric potassium chloride dissolves this element with no evolution of hydrogen. Where the iron is in a massive form the reaction is slow, owing to the formation of a coherent protective layer of deposited copper, and it was found that a more satisfactory reagent could be produced by the addition of ten per cent by volume of a saturated solution of mercuric chloride. Using this mixed reagent one gram of iron can be dissolved in about an hour. Filings are readily dissolved in either reagent particularly if magnetic stirring is used. Acceleration of the reaction by warming the solution is undesirable because of the danger of driving occluded helium out of the walls of the vessel.

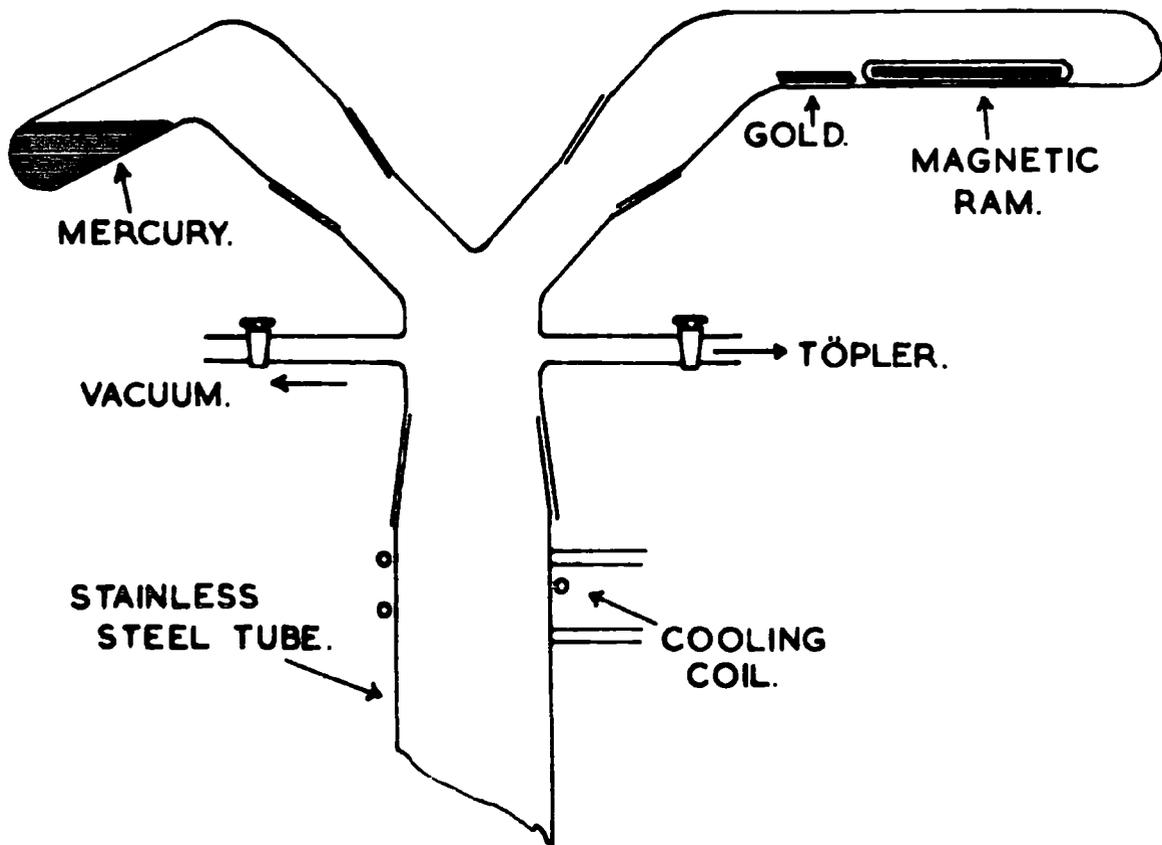
(3) For gold.

Considerable effort was expended in finding some means of bringing this metal quickly into solution without the necessity of excessive heating and the consequent risk of evolution of occluded helium. The usual alkaline cyanide solution method is too slow at acceptable temperatures and attack by mercury at room temperature has the same disadvantage. Since the stainless steel tubes used in the annealing of specimens were found to evolve as little as  $10^{-9}$  c.c. of helium in 120 minutes at  $815^{\circ}\text{C}$ . it was decided to release the helium from the gold by dissolving the latter in mercury contained in one of these tubes. In this way it was possible to raise the temperature of the gold till attack by the mercury was sufficiently rapid. An advantage of this method is that the mercury can be made to boil, and any helium is effectively flushed from the liquid phase and may be Töplered out of the furnace.

The apparatus used is that shown in fig.6. The furnace tube was outgassed at about  $700^{\circ}\text{C}$ . and the temperature was then reduced to about  $200^{\circ}\text{C}$ . Mercury from the side-arm was dropped into the stainless steel tube and any gases which may have been evolved were pumped away. The tap to the vacuum line was then closed and the gold specimen was pushed into the tube by a magnetically operated ram. The temperature was raised to  $250^{\circ}\text{C}$ . and after an hour the gases were Töplered into the circulating system.

Fig. 6.

Apparatus for the dissolution of gold.



No appreciable evolution of helium from the conditioned metal of the tube could have taken place at the relatively low temperatures involved and since the glass parts of the apparatus were not heated by the mercury vapour it is highly unlikely that any error was introduced in this way.

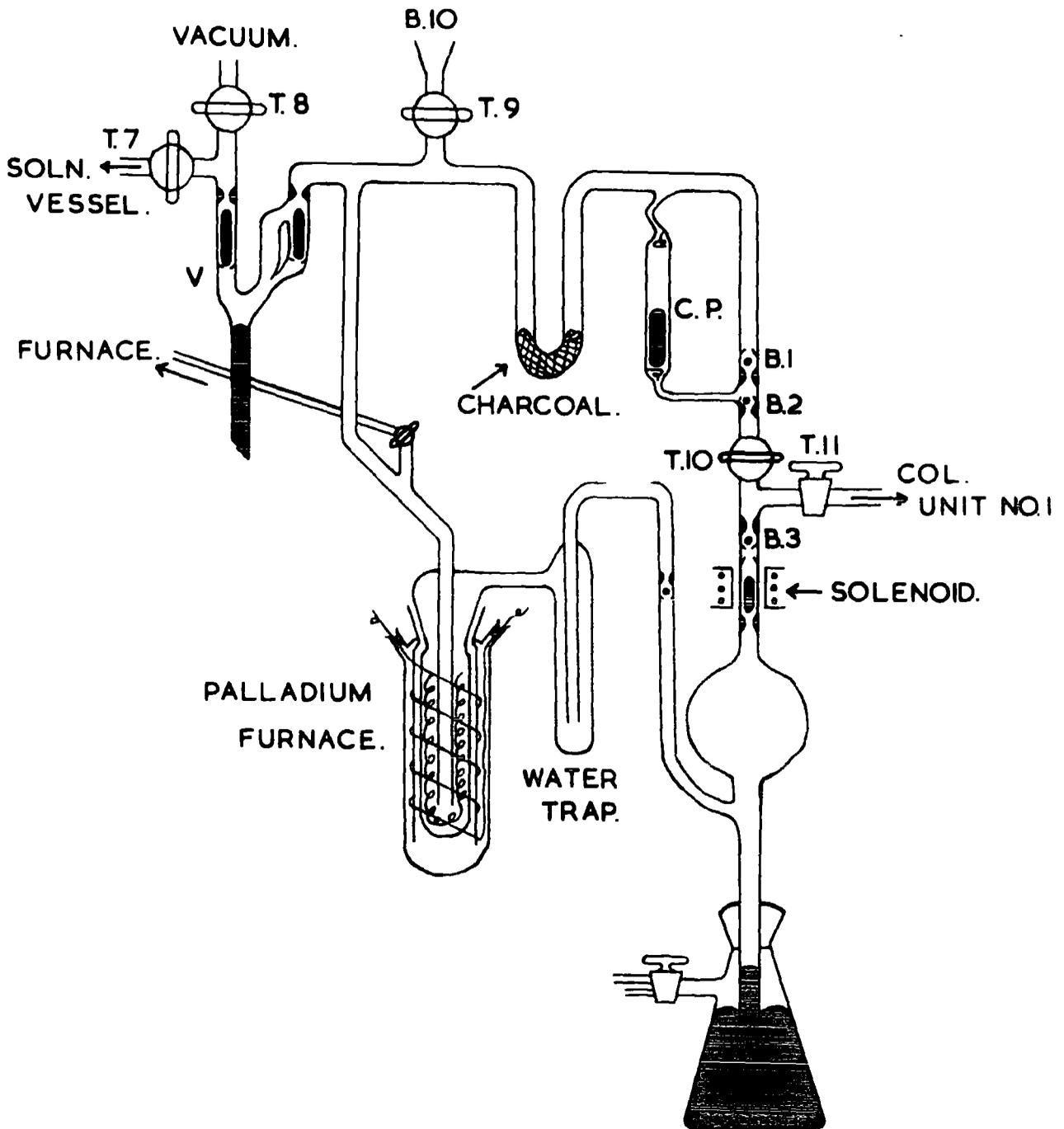
TRANSFER OF THE GAS MIXTURE TO THE CIRCULATING SYSTEM, AND THE REMOVAL OF HYDROGEN.

The gases present in the dissolving vessel from the dissolution of say, aluminium, are hydrogen, oxygen, helium, and water vapour, together with any other gas which may have been occluded in the metal. It is necessary to completely transfer these gases to the circulating system (after freezing out the water vapour) so that they can be prepared for fractionation on the column.

After the charcoal U-tube (see fig. 7) has been baked out at 300°C. and the whole apparatus evacuated, the procedure is as follows. Taps T.8, T.9, and T.11 are closed, T.10, and T.7 remaining open. The U-tube is immersed in liquid air and about ten minutes are allowed for temperature equilibration to take place. The two water traps are also immersed in liquid air. The mercury level in the vent "V" is then raised so that it just blocks the U-bend, acting as a non-return valve for gas bubbling through from the solution vessel, adsorption on the charcoal keeping the pressure in the circulating system almost at zero. The excess pressure in the solution vessel due to hydrogen evolution is relieved by opening tap T.6 for a few seconds. Pure oxygen is then bubbled slowly through the solution, flushing out any dissolved gases. The pressure of gas

Fig. 7.

Circulating system.



in the solution vessel is allowed to build up to about one centimetre of mercury and then the flow of pure oxygen is discontinued. Tap T.6 is then opened for about twenty seconds and the gases bubble past the mercury in the vent. This operation is repeated seven times, previous work having shown that this number of flushings is easily sufficient to effect a virtually 100% transfer of noble gas to the circulating system. The mercury in the vent "V" is then fully raised so that the solution vessel is completely separated from the circulating system.

The circulating system itself (fig. 7) consists of a circulating pump, a Töpler pump, a charcoal U-tube, and a palladium furnace. The circulating pump consists of a glass envelope enclosing an iron rod encased in soda-glass tubing. This makes a sliding fit with the envelope, and can be rapidly moved up and down by means of a solenoid energised by a "make and break" device. This motion, combined with the action of the two non-return ball valves B<sub>1</sub> and B<sub>2</sub>, causes the gas in the system to circulate. Two metal springs cushion the impact of the glass encased rod at both ends of its travel. The palladium furnace consists of a narrow soda-glass tube containing a spiral of palladium wire. This tube is encased in a Pyrex vacuum jacket and is surrounded by a glass former supporting a heating element which can be raised to dull red heat by a current of three amperes, the palladium being heated by radiation. Overheating of the apparatus as a whole is prevented by immersing the furnace in a beaker of cold water.

The procedure for circulating the gases involves the starting of the

pump and the removal of the liquid air bath from the U-tube. It is important to make sure that the pressure rise on desorption does not force gas into the secondary bulb of the Töpler pump and this is avoided by raising the mercury level in the pump before allowing the charcoal in the U-tube to warm up. The Töpler valve is kept open during the circulating operation. With the palladium furnace heating coil at red heat the hydrogen can be wholly removed in about twenty minutes, most of it being removed in the first few minutes. The water vapour so produced is frozen out in the cold trap.

Hydrogen is a highly undesirable impurity since, after helium and neon, it is the least adsorbed of all gases (39) and consequently comes through the fractionating column immediately after neon. The presence of hydrogen may therefore prevent a test for neon being made since even a small quantity of hydrogen would give a large deflection in the Pirani gauge system on account of its high thermal conductivity.

#### TRANSFER OF THE HYDROGEN-FREE GAS MIXTURE FROM THE CIRCULATING SYSTEM TO THE FRACTIONATING COLUMN.

Before transferring the gases from the circulating system to the fractionating column, the latter is evacuated, and the charcoal bulbs are outgassed at 250°C. for about two and a half hours. The charcoals are then allowed to cool and are immersed in liquid air. The mercury in the column is raised to the levels "E" and "D" (fig. 8) and a few experimental operations of the column are performed to check its correct mechanical operation. After ensuring that the column is functioning correctly, the mercury is held in the starting positions at "E" and "D".

Tap T.10 is shut, the ball-valves B.1 and B.2 are held open with a magnet, and the mercury in the Töpler is raised to about half-way up the bulb. The gas in the bulb is then adsorbed on the charcoal of the first unit by opening tap T.11, and raising the Töpler valve by means of the solenoid. Tap T.11, is then closed, and the mercury in the Töpler lowered to below the cut-off and then raised again, this time to just above the valve. T.11 is again opened. The solenoid is then de-energised, allowing the valve to fall back into its seating, and the mercury is lowered once more. The subsequent operations are then merely repetitions of the normal Töpler procedure. Care is exercised in the first few operations because, although the chief component of the gas mixture is oxygen and therefore readily adsorbable, an initial pressure may be built up in the first charcoal bulb if all the gas present in the circulating system were allowed to pass over at once. This would lead to a violent disturbance of the mercury in the first unit possibly resulting in an escape of gas into the second unit, or fracture of the column.

Eighteen Töpler operations are performed, the mercury being fully raised to the mercury-stop B.3 on the eighteenth operation, care being taken to ensure that no gas bubbles are trapped, especially near the Töpler valve. For a system of the type used about ten Töpler operations are theoretically sufficient to give virtually complete transfer, but in practice eighteen operations are performed to make absolutely sure that all the gas has been transferred to the column. Tap T.11 is left open during the operation of the fractionating column.

When all the gas has been transferred, a few minutes are allowed for temperature equilibration. The mercury level in limb-2 of the gas pipette "B" (fig.17) is raised till it is above the out-off, and tap T.15 (fig.16) is closed, T.16 being left open. The gas sampling bulb is kept filled with mercury when not actually in use. Thus, with T.12 open, the column can deliver the gas fractions only into the storage bulb. The "batch-wise" fractionation operations (see next section) are then begun.

At the end of the fourteenth operation the fractionation is stopped and the fractions in the storage bulb are examined for gas content. If no deflection is observed in the Pirani gauge system, the fractionation is continued till thirty-eight operations have been completed. The collected gas fractions are then measured in the gauge. If a deflection is obtained on measuring the first fourteen fractions, this is indicative of air leakage into the column or storage bulb, or inadequate baking-out of the charcoal bulbs. Usually the response of the gauge to the gas delivery of the first fourteen operations is negligibly small.

#### MECHANICAL OPERATION OF THE FRACTIONATING COLUMN.

The operation of the old-style column was effected by means of a synchronous motor governing solenoid valves which connected the mercury reservoirs of the column to the secondary pumping system or to the atmosphere. The fractionating column itself consisted of two identical rows of bulbs, only one row of which contributed to the separation described under "Theory of Fractionating Column". The other row, acting

simply as a set of non-return valves isolating each unit from the next, took the same time to empty and fill with mercury as did the actual "volume" bulbs. This arrangement led to very slow operation and it was therefore decided to adopt a new control mechanism, and to alter the design of the shut-off valves.

Two designs of valve were tried:-

- a. A magnetically operated non-return valve.
- b. A simple U-tube mercury cut-off.

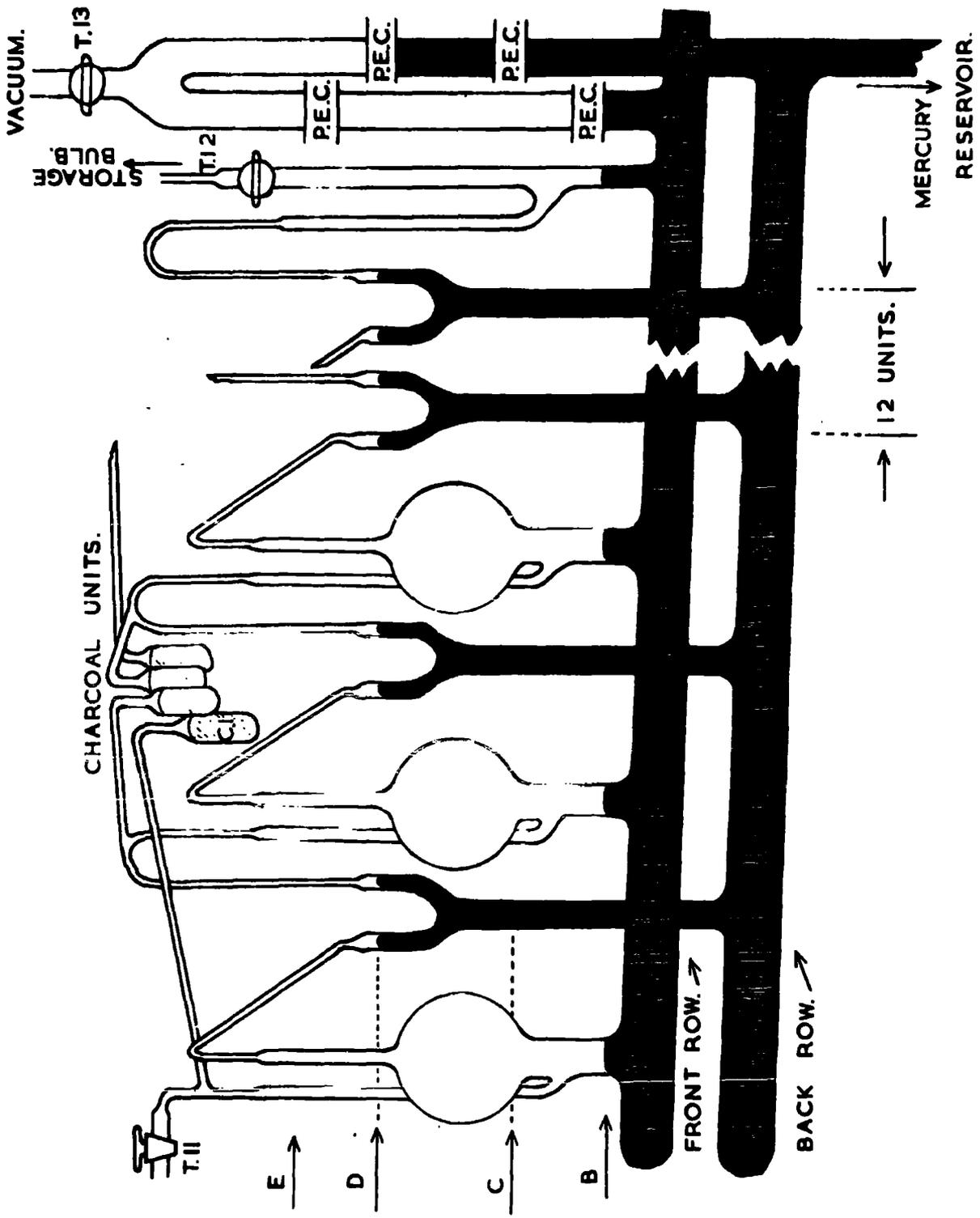
Initially experiments were made with an "a." type arrangement, but practical difficulties led to the eventual adoption of "b." (See Part three).

The method of control utilised the rise and fall of the mercury itself. Four control units, each consisting of a small lamp, a lens, and a germanium photo-diode are mounted on the column in such a way that the rise and fall of the mercury cuts the light-beam on and off. Suitably interconnected relays operated by the current from these photo-cells energise four solenoid valves which connect the mercury reservoirs of the row of bulbs and the row of non-return valves to the secondary vacuum line, or through capillary tubing to the atmosphere.

The column in its present form is shown in fig. 8. The starting position of the column is with the mercury levels at "E" and "D" when all the diodes are unenergised. The controlled circuit in this position is shown in fig. 11a. On switching on the column mechanism, the mercury level in the front (i.e. bulb) row falls to position "B" and the circuit

Fig. 8.

Fractionating column.



shown in fig. 11b. comes into operation causing the mercury to rise. In the normal way the mercury column would oscillate about the level "B" but this is prevented by applying a bias voltage through a second set of contacts (see figs. 12,13) in the relay governed by the control unit at "E". The mercury therefore continues to rise to position "E", when the circuit shown in fig. 11c. operates. This causes the mercury in the U-tube row to fall to "C", energising the photo-cell "C" and causing the circuit of fig. 11d. to come into operation. A bias is again required to prevent oscillation of the mercury about "C". When the mercury reaches "D" the whole cycle begins again, the number of complete cycles made by the column being recorded by a Post-office counter.

The time taken for each operation is sixty-five seconds as opposed to the four minutes required by the old apparatus. This saving of time is made good only on those parts of the cycle which do not involve gas-solid equilibration, or conduction of gas along the narrow-bore tubing of the column. The time allowed for the former process is the same as that allowed in the old design, and in any case there is substantial evidence that this sort of equilibration takes place extremely quickly (42). The time needed for the conduction of a typical amount of gas in tubing similar to that used was calculated and the time allowed was found to be sufficient.

THEORY OF THE FRACTIONATING COLUMN.

This column (in its original form) has been described many times, and the theory has been exhaustively described by GLÜCKAUF (40). For completeness a summary of the theory is given here. The work for which the column was originally designed was the analysis of air with respect to its inert gas content but since the present work is concerned only with helium estimation (the presence of neon being used solely as an indication of air leakage) it was necessary to modify the procedure with respect to the end-point of the fractionation. Otherwise the theory of operation is identical with that outlined by GLÜCKAUF.

Charcoal, at low temperatures, is a powerful adsorbent of gases, even the noble gases being adsorbed to some extent. The adsorption of these gases is due only to physical causes (i.e. Van der Waal's forces); chemisorption is not possible owing to their non-reactivity. Since no two gases could be expected to have identical adsorption characteristics, it should be possible to resolve a gas mixture by allowing it to equilibrate with an adsorbent. The usual way of doing this is to inject it into a stream of non-adsorbable carrier gas flowing through a long column of adsorbent material held on an inactive packing. The components of the mixture then pass out of the column in an order corresponding to their retention times. Unfortunately such a method is not possible for use with helium since this gas is itself the least adsorbable of all the gases. The process used must therefore be a discontinuous one and the method adopted is to allow the gas mixture (in this case helium and neon) to

equilibrate with a definite weight of charcoal at liquid air temperature. The gaseous phase becomes enriched in helium, this gas being less strongly adsorbed than neon, and then this enriched gas is allowed to equilibrate with a fresh batch of charcoal and the process of enrichment is repeated. The apparatus (fig.8) consists of fifteen bulbs of volume approximately 36ccs., and fifteen smaller bulbs each containing a definite weight of wood charcoal.

The starting position of the fractionating column is with the mercury levels at "E" and "D". The gas mixture from the circulating system is compressed into the space between tap T.10, and the ball valve B.3 (fig.7.) and since tap T.11 is open, the helium and neon are partially adsorbed on the first charcoal bulb, the oxygen being completely adsorbed. Lowering of the mercury to "B" then allows the gas mixture to equilibrate between the free space of the volume bulb and the charcoal in the charcoal bulb. The mercury is then raised to "E", compressing the helium enriched gas and movement of the mercury in the U-tube column from "D" to "C" and back again allows this gas to equilibrate with the charcoal of the second charcoal bulb. The whole process is repeated automatically.

The procedure is reminiscent of that used in fractional crystallisation, in which the precipitate from one operation is added to the mother-liquor of the next, resulting in an increasing yield of decreasing purity. As in fractional crystallisation we may select as many units and perform as many operations as is convenient.

The primary aim in this case is to isolate the helium in as pure a

form as possible, and in as great a yield as is consistent with purity. In order to estimate the optimum number of bulbs and cycles of operation, GLÜCKAUF (40) derived a number of quantitative expressions based initially on Langmuir's Isotherm. This is ordinarily written:-

$$C_s = \frac{K_1 C_v}{1 + K_2 C_v} \quad \text{EQU. 1.}$$

where  $C_s$  and  $C_v$  are the equilibrium concentrations in the solid and gaseous phases of a closed system. Only micro amounts are dealt with in this work and therefore the Isotherm may be written:-

$$C_s = \alpha C_v \quad \text{EQU. 2.}$$

since  $K_2 C_v$  is small compared with unity.

The adsorption coefficient,  $\alpha$ , is a constant independent of adsorbent pore-space, or tube dead-space, and relates simply to the particular gas-solid system. Suppose the initial quantity of gas "A" (helium) is  $A_0$ , and that it is allowed to equilibrate between a volume "V" and a definite weight "S" of adsorbent. The amount of gas left in the gaseous phase will be  $A_1$ , where

$$\begin{aligned} A_1 &= \frac{V \cdot C_v}{S C_s + V \cdot C_v} \cdot A_0 \\ &= \frac{1}{1 + \frac{S}{V} \cdot \frac{C_s}{C_v}} \cdot A_0 \\ &= \frac{1}{1 + \alpha \cdot \frac{S}{V}} A_0 \\ &= a \cdot A_0 \end{aligned} \quad \begin{array}{l} \text{EQU. 3.} \\ \text{EQU. 4.} \end{array}$$

The amount of gas "A" adsorbed will be

$$(1 - a) A_0.$$

For a second gas B (neon) these quantities become  $b \cdot B_0$  and  $(1 - b)B_0$ , respectively, where

$$b = \frac{1}{1 + \beta \cdot \frac{S}{V}}$$

$\alpha$  and  $\beta$  are functions of temperature, and the ratio  $\frac{\alpha}{\beta}$  differs increasingly from unity as the temperature decreases. A low temperature is therefore desirable, and is achieved in this case by the use of liquid air. Once the temperature has been fixed the degree of separation depends purely on the ratio  $\frac{S}{V}$ , and it is necessary to choose a value for this such that the separation of helium and neon is a maximum. Obviously if  $S$  is large the amount of neon in the gaseous phase will be very small and the purity of the helium in the gas phase will be great, although the amount will be too small to make this a practicable method of separation. For a given helium/neon ratio it would be expected that the best separation would occur when the distribution factors  $a$  and  $b$  differ as greatly as possible and GLUCKAUF has shown this to be indeed the case. Therefore the desired value of  $\frac{S}{V}$  is that which satisfies the expression:

$$\frac{d(a-b)}{d\left(\frac{S}{V}\right)} = 0$$

$$(a-b) = \frac{1}{1 + \alpha\left(\frac{S}{V}\right)} - \frac{1}{1 + \beta\left(\frac{S}{V}\right)}$$

$$\therefore \left(\frac{1}{a-b}\right) = \frac{1}{(\beta - \alpha)} \cdot \left[ \frac{V}{S} + (\alpha + \beta) + \alpha\beta\left(\frac{S}{V}\right) \right]$$

$$\therefore \frac{d\left(\frac{1}{a-b}\right)}{d\left(\frac{S}{V}\right)} = \frac{1}{(\beta - \alpha)} \left[ -\frac{V}{S^2} + \alpha\beta \right]$$

Therefore, for a maximum (a - b),

$$\frac{V}{S} = \sqrt{\alpha \beta}$$

Work done by GLÜCKAUF suggests the values

$$\alpha = 10.6 \quad (\text{Helium}).$$

$$\beta = 110.72 \quad (\text{Neon})$$

Since the volume V was chosen to be about 36 mls., the weight of charcoal used for each unit was approximately 1.1g. The charcoal bulb on the first unit, however, contains 1.2g. of charcoal, the extra 0.1g. offsetting the slightly larger dead-space of this unit.

In the construction of the fractionating column narrow bore (1 m.m.) tubing was used as much as possible in order to keep the dead-space small. This is important if an efficient transfer of gas from one unit to the next is to be achieved. Where the tubing comes into contact with the mercury at some part of the cycle a slightly larger (3 m.m.) bore was used so that blockage would not be caused by the retention of small pellets of mercury.

Having derived the optimum value of the volume/solid ratio it is necessary to obtain expressions for the number of units and the number of operations which would give the best separation. Suppose there are "m" units in the column, and "n" operations have been performed:-

The amount of gas A in the gas phase of the unit "m" may be shown to be  $A_n^m$

where

$$A_n^m = A_0 \cdot \frac{(n-1)!}{(m-1)!(n-m)!} \cdot a^m \cdot (1-a)^{n-m}$$

EQU. 5.

The amount of gas "A" adsorbed on the solid of the same unit is

$$A_0 \frac{(n-1)!}{(m-1)!(n-m)!} \cdot a^{(m-1)} \cdot (1-a)^{n-m+1} \quad \text{EQU. 6.}$$

The ratio of the amounts of gas delivered from the last (mth) unit by two successive operations (n) and (n + 1) is

$$\frac{A_{n+1}^m}{A_n^m} = \frac{n}{n-m+1} \cdot (1-a) \quad \text{EQU. 7.}$$

The value of (a), which is effectively the slope of the delivery curve, may be calculated and used to determine the "helium only" curve for those operations where the helium and neon are delivered together. Thus the degree of neon contamination of the helium may be determined and allowed for.

No gas can be delivered to the storage bulb till the (m-1)th. operation has been completed. The gas then delivered is stored in the bulb where an amount  $A_B$ , accumulates.

$$A_S = A_m^m + A_{m+1}^m \dots \dots A_n^m .$$

The amount of gas "A" remaining on the column will be:

$$A_R = A_{n+1}^m + A_{n+2}^m \dots \dots A_{\infty}^m .$$

Corresponding expressions may also be derived for the gas "B". Thus the gas in the storage bulb will consist of a mixture of gases "A" and "B", and after (x) fractionations the relation

$$F_x = A_x^m + B_x^m \quad \text{EQU. 8.}$$

will hold.

$A^m$  and  $B^m$  both rise to a maximum and then decrease again, so the best separation will be achieved when  $A^m$  has decreased to a low value but  $B^m$  has not increased to a significant value. In air analyses it is good practice to adjust the number of operations of the column in such a way that at the "end-point" the amount of gas  $A$  remaining on the column is just compensated for by the quantity of contamination  $B_s$ . (This is strictly a volume compensation, since the Pirani gauges have different sensitivities for the two gases.) However, in the present work any neon in the gas mixture is due only to accidental causes, so the fractionation was discontinued at a rather earlier stage than would be the case for an air analysis. This ensures a high purity of the helium, and minimises the uncertainty of the compensation by the neon; allowance was made for the small part (0.65%) of the helium retained on the column at this point.

GLUCKAUF showed that a column of twelve units would give an efficient separation, but to increase the resolving power a 15-unit column is used in practice. It was also shown that the number of operations required is about twice the number of units.

Since it is not possible to blow identical bulbs, or achieve a zero dead-space, the column needs to be calibrated with helium, neon, and air, the above theoretical results being used solely as a guide to the conditions to be expected. From the viewpoint of the column, air acts solely as a mixture of neon and helium, the other gases being completely adsorbed on the wood charcoal at low temperatures.

As well as estimating the helium content of a gas mixture it is desirable to test for the presence of neon, since this is an indication of any leakage of air into the apparatus. After the helium fraction has been collected continued operation of the column yields the neon. At liquid air temperature neon is fractionated only very slowly and it is desirable to accelerate the process by removing the Dewar flasks from the last fourteen charcoal units. The first charcoal unit is lower than the others and it is possible to keep this immersed so as to retain strongly adsorbed gases such as oxygen. The flasks may be removed from the units as soon as the last helium fraction has passed through the last unit of a particular cluster of charcoals. If it is merely required to test for the presence of neon it is useful to pump away the gases delivered by operations 39 to 42 inclusive since these fractions still contain a small amount of helium. Subsequent operation of the column delivers virtually pure neon, about twenty operations being sufficient to give a measurable quantity if it is present.

Fig. 9.

Calibration curve for fractionating  
column.

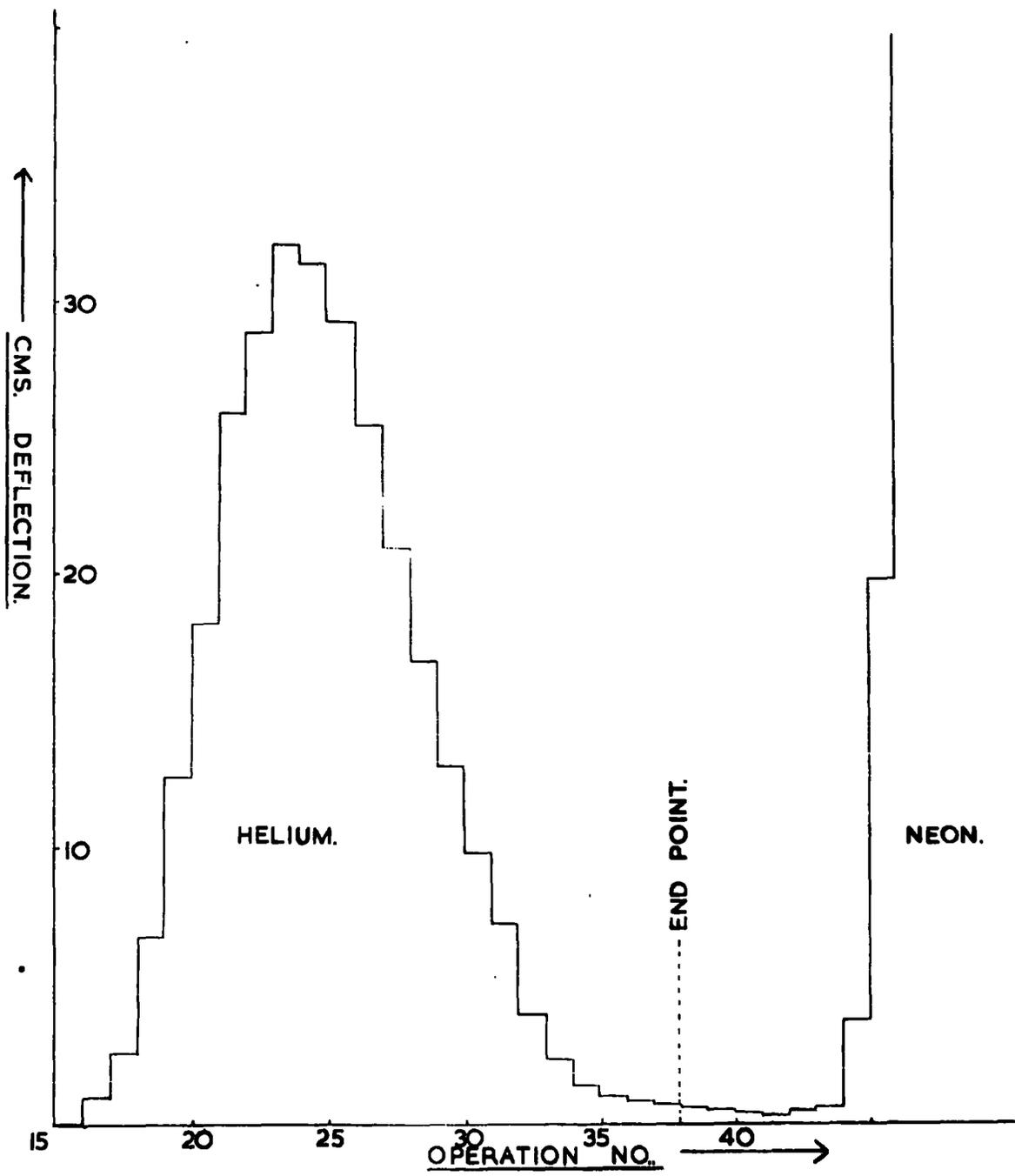


Fig. 10.

Air-pipette.

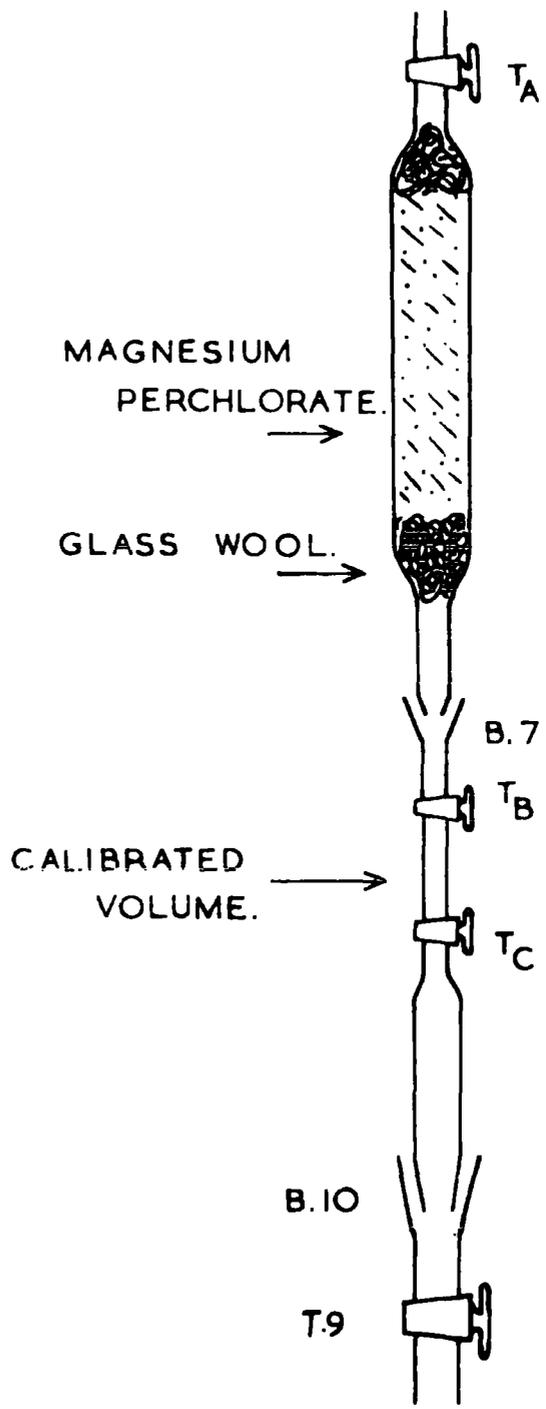


Fig. 11a.

Fig. 11b.

Fig. 11c.

Fig. 11d.

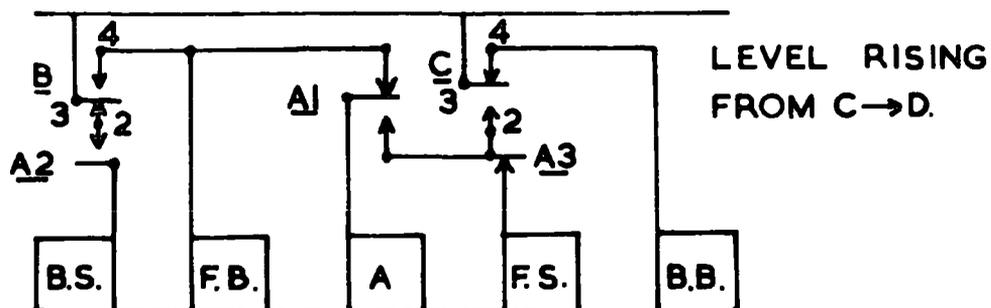
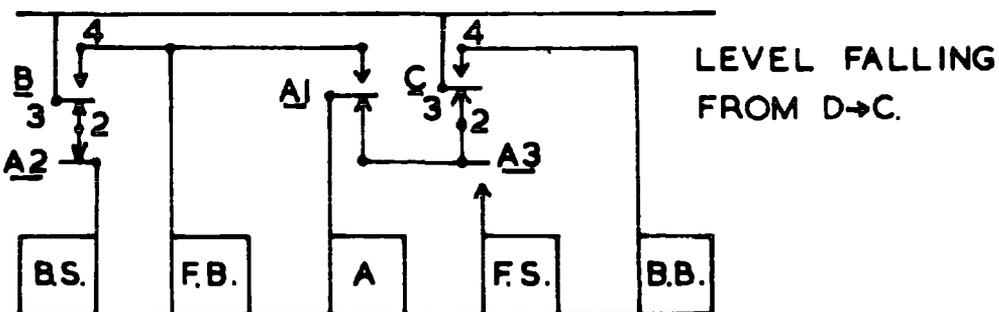
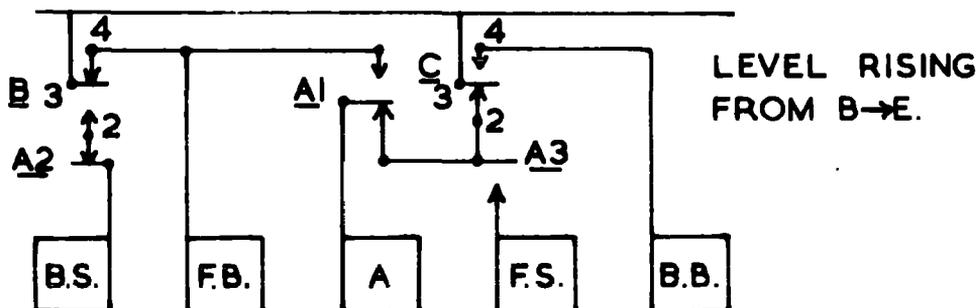
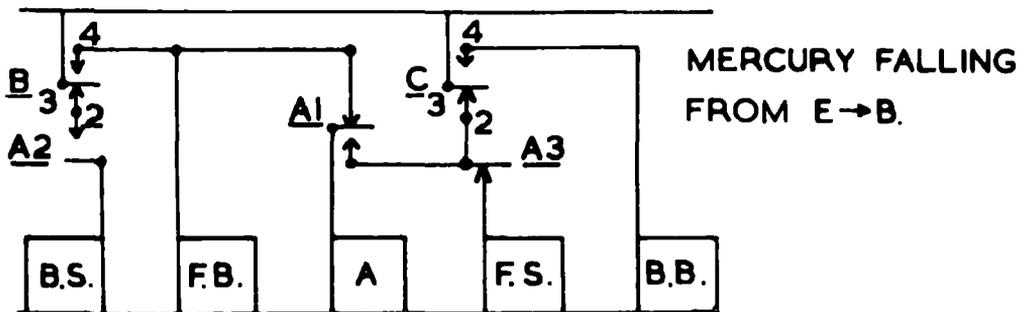


Fig. 12.

Controlling circuit for fractionating

column.

EACH RELAY CONTAINS TWO SETS OF  
SWITCH TERMINALS 2,3,4 & 5,6,7.

Q = BIAS RES.  
R = 100Ω.  
S = 4700Ω.

-VE. 3-4,5-6 ARE CLOSED WHEN PEC IS EXPOSED.

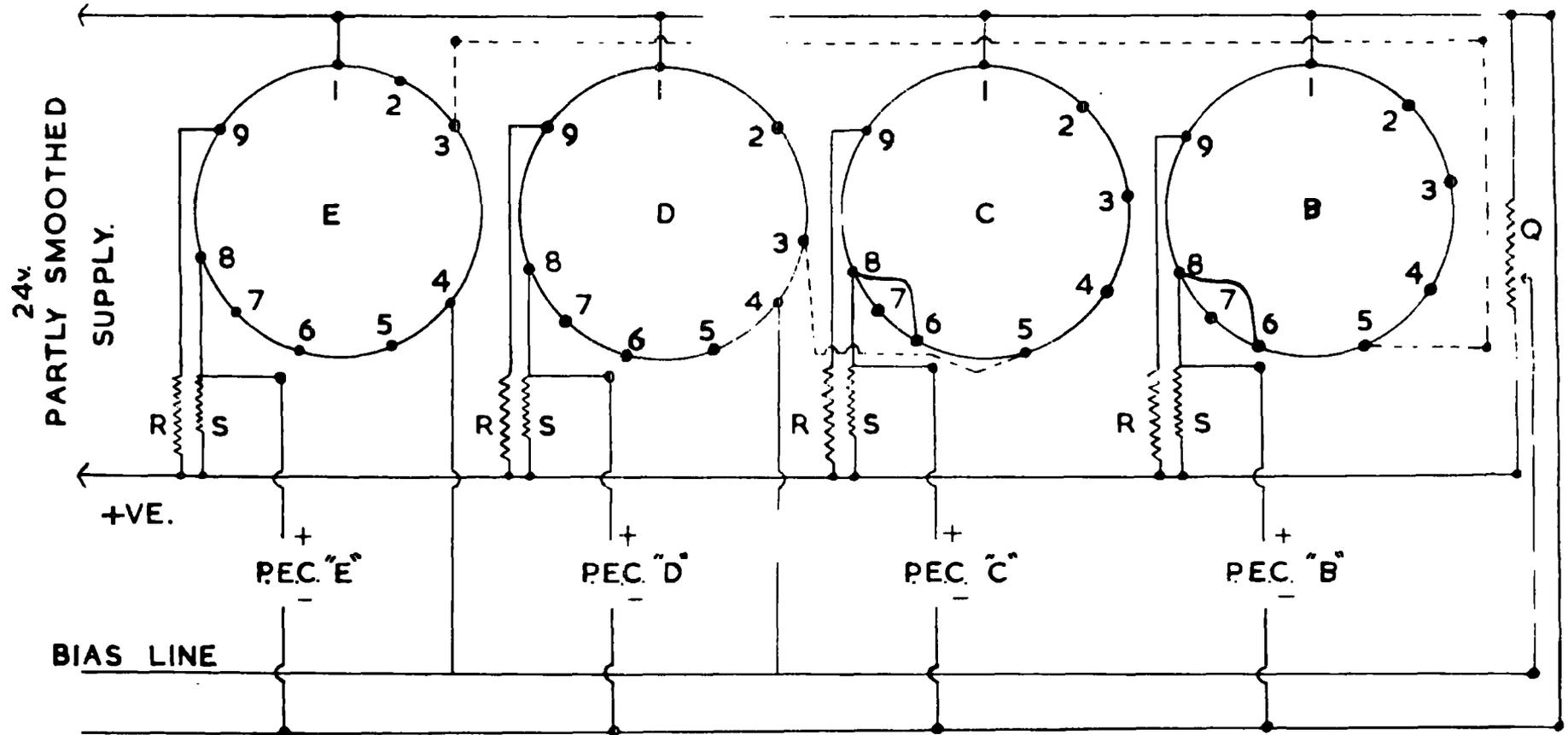
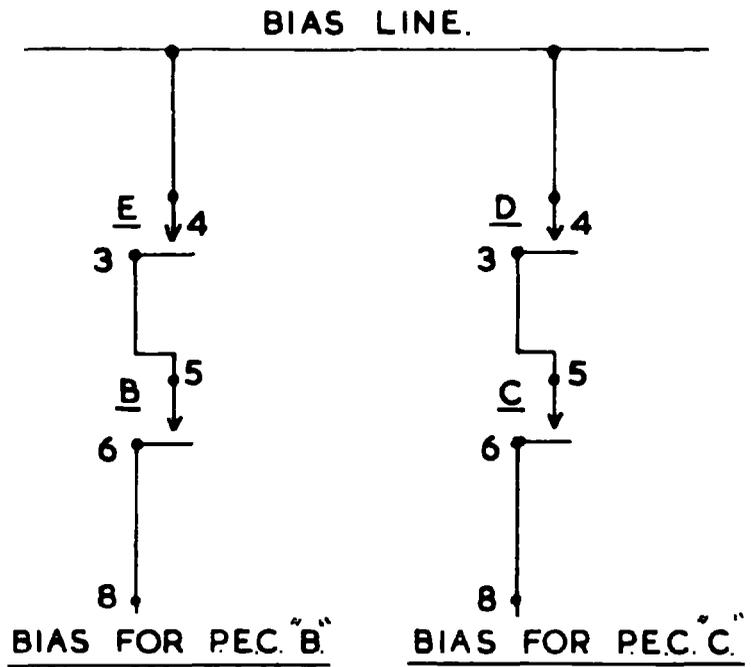
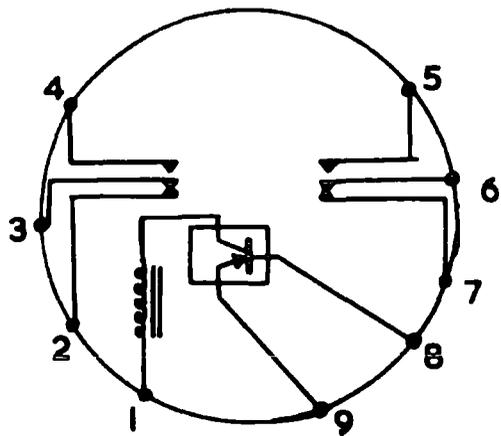


Fig. 13.

Bias-line for controlling circuit, and  
internal connections of photo-cell relays.



CIRCUIT SHOWN IS THAT  
FOR MERCURY LEVELS AT E & D.



INTERNAL RELAY CIRCUIT.

CALIBRATION OF THE FRACTIONATING COLUMN.

In order to completely determine the characteristics of the fractionating column it is necessary to carry out two separate experiments:-

Expt.A. This involves the fractionation of a suitable quantity of dry air (the amount used need not be known exactly) and the measurement of the gas delivered to the storage bulb by each successive operation. This enables the position of the minimum to be found in the curve expressing gas delivery as a function of the number of operations performed. Such a minimum is inherent in Equn.8. and corresponds to the maximum delivery of helium with minimum contamination by neon. By making use of Equn.7 it is possible to estimate the degree of overlap of the two parts of the curve, and to calculate the resultant contamination of the helium by neon. The final result is shown in fig. 9 and it may be seen from this that by stopping the fractionation at Op. No. 38, a pure and nearly quantitative sample of helium may be obtained.

Expt. B. It is necessary to measure the percentage recovery of the helium from the column since it is obvious that by stopping the fractionation after thirty-eight operations not all the helium will have been collected. A convenient quantity of pure helium (again the amount need not be known exactly) is fractionated and the amounts delivered by successive operations of the column are measured, the operations being continued till a negligible quantity of gas is issuing from the column. It may then be assumed that 100% of the

helium has been recovered. The amount of gas delivered by any number of operations may then be readily compared with that delivered by what is effectively an infinite number of operations. In the present case it was found that thirty-eight operations gave a recovery of 99.35 per cent.

Since the origin of the charcoal used in the present work was not known, and since a previous worker (34) in this laboratory had encountered trouble due to the irreversible adsorption (at liquid air temperature) of a large fraction of the helium, it was thought necessary to test the fractionating column for completeness of recovery of the helium introduced into it. This was done by measuring the deflection of the Pirani gauge for a small quantity of helium, and then Töplering this into a small tube fitted with a stop-cock by means of the gas sampling bulb, fig. 16. By raising the mercury level as far as the tap, closing this, and transferring the tube to the B.10 socket on the circulating system, it is possible to Töpler the whole of the gas into the column. After fractionation it was found that the gas collected in thirty-eight operations (after allowance for the known retention described in B.) gave virtually the same deflection as had been obtained before fractionation. Thus it may be concluded that there is no significant retention by the charcoal.

Throughout the whole series of experiments checks were regularly made on the correct functioning of the column by means of air analyses, the results of which were compared with the generally accepted values of (41).

These analyses were carried out by fractionation of samples of air dried and measured in the air-pipette shown in fig. 10. This pipette was calibrated by the mercury weighing method described in the section on the MacLeod gauge and gas-pipetting system.

#### PIRANI GAUGES AND THEIR CALIBRATION.

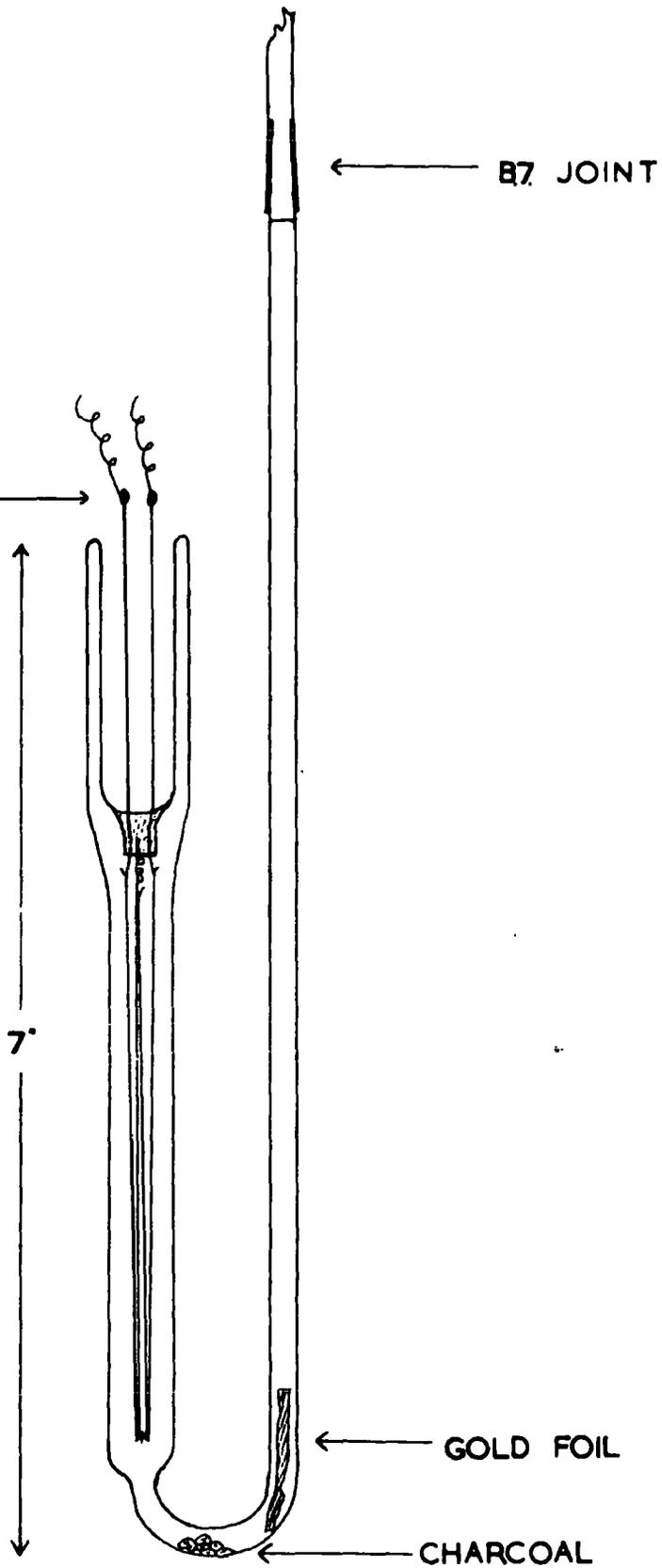
This type of pressure gauge has been found to give very satisfactory results in this field (33). Many variations in design have been made, and the instruments used in the present work embody most of the improvements (chiefly aimed at reducing zero drift) suggested by previous workers.

The design of the present gauge is shown in fig. 14. Initially the gauge is constructed in two sections, these being joined later by a ring seal. The gauge is made from Pyrex glass, through which are sealed three tungsten leads (0.3m.m. diam.) two of which are fashioned into hooks, the third consisting of a helical spring with a hook at one end. Over the tungsten hooks, and the hooks on a glass stem, is stretched a fine (0.003m.m. x 0.05m.m.) nickel tape. The ends of the tape are soft-soldered to the tungsten hooks, these having been copper-plated and tinned beforehand to make this possible. Before soldering the tape, a five gram weight is hung from each end so that the filament is under a tension of ten grams. This prevents undue drifting or other irregularities due to microsonic effects which would affect a slack filament. The filament is "W" shaped, of length about 27 cms. Kinking or twisting of the tape causes serious instability of the gauge, so these are stringently avoided. Nickel tape is used since this metal, in this geometrical form, has a

Fig. 14.

Pirani gauge.

HARD  
SOLDER



B7 JOINT

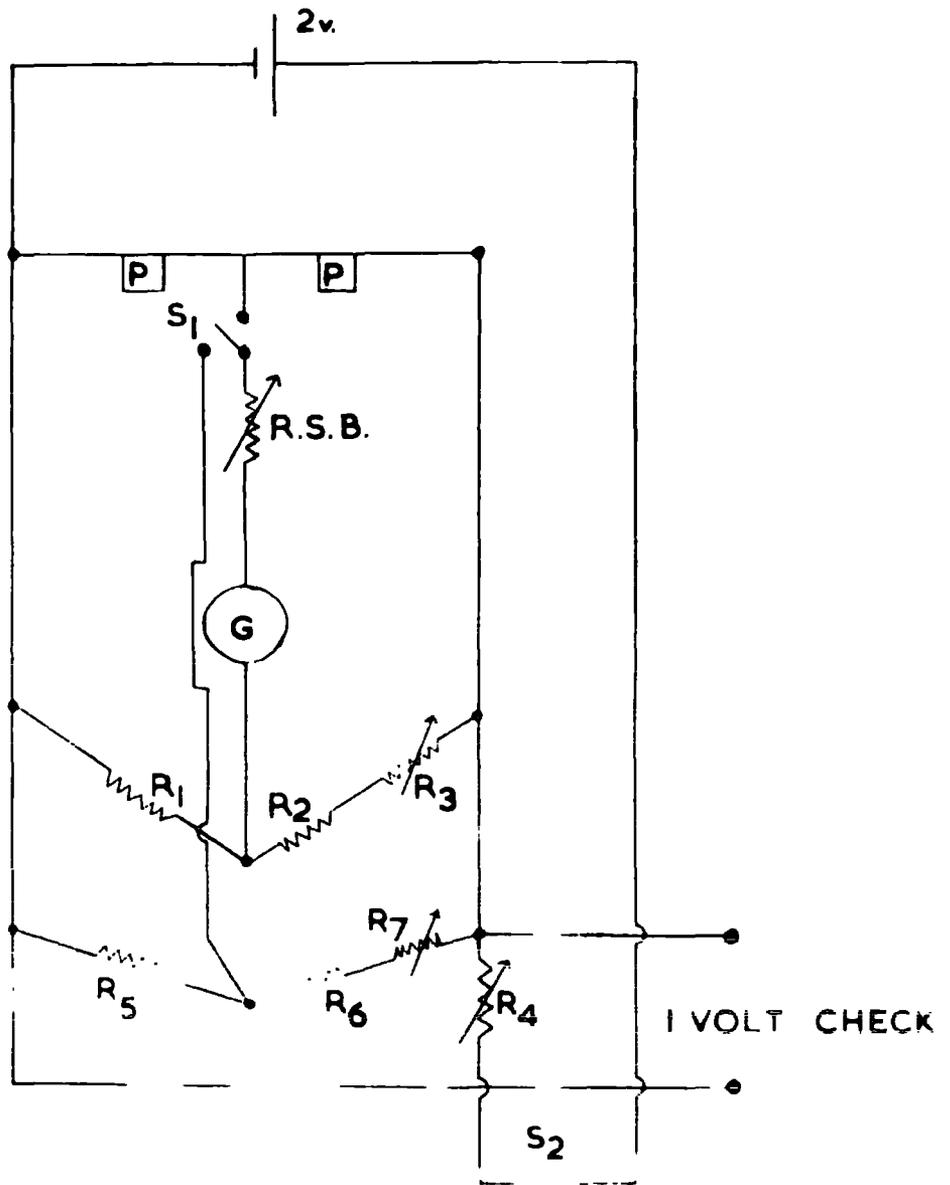
7'

GOLD FOIL

CHARCOAL

Fig. 15.

Circuit for Pirani gauges.



R. S. B. = RANGE SELECTION BOX. 0 → 66.5K.

$R_1, R_5 = 150 \Omega$  HIGH STABILITY RES..

$R_2, R_6 = 50 \Omega$  .. .. .

$R_3 R_7 = 10 \Omega$  VAR. RES..

$R_4 = 100 \Omega$  .. .. .

theoretical superiority over other systems (99).

In practice two gauges are used, one being the compensating arm in a Wheatstone bridge circuit. (fig.15). The gauges are connected in adjacent arms of the circuit, a potential of one volt being applied across the bridge. The bridge is balanced by means of resistance R.3, the galvanometer spot being brought to a convenient place on its scale, and the degree of unbalance caused by admission of gas to one of the gauges is measured by the deflection of the spot. A resistance box enables a choice of galvanometer sensitivities to be made.

The heat transfer from filament to envelope due to the gas is given by the relation:-

$$E = \frac{4}{3} \frac{\alpha}{2 - \alpha} \lambda_M \frac{P}{\sqrt{\frac{273.2}{T_0}}} \cdot (T_1 - T_0) \text{ watts/cm}^2$$

where  $\alpha$  = accommodation coefficient for the system helium-nickel.  
 $\lambda_M$  = molecular heat conductivity (watts/cm<sup>2</sup>) at 0°C.  
 $T_1$  = filament temperature.  
 $T_0$  = envelope temperature. (43).

It can be seen that the sensitivity of the gauge will be increased by keeping the envelope at a constant low temperature. This condition is provided by completely immersing the gauge in a bath of liquid air, hence the construction of the gauges in Pyrex glass. Attempts have been made to use soda glass instruments (17) but these have not been able to withstand the thermal shock on immersion. The potential across the filament is sufficient to maintain this at about room temperature, and this prevents undue contraction of the filament on cooling the gauge.

Since mercury vapour is present in the system, a small piece of gold foil is placed in each gauge to protect the soft-soldered joints. Indium may also be used, but this is not so satisfactory since it is difficult to see when it is saturated with mercury, there being no colour change on amalgamation. Moreover, the low melting point of indium carries with it the risk of fusion, and consequent blockage of the gauge inlet, when the small quantity of wood-charcoal enclosed in each gauge is baked out. This charcoal serves to adsorb any gases released from the tap grease due to the turning of the taps of the gauge system.

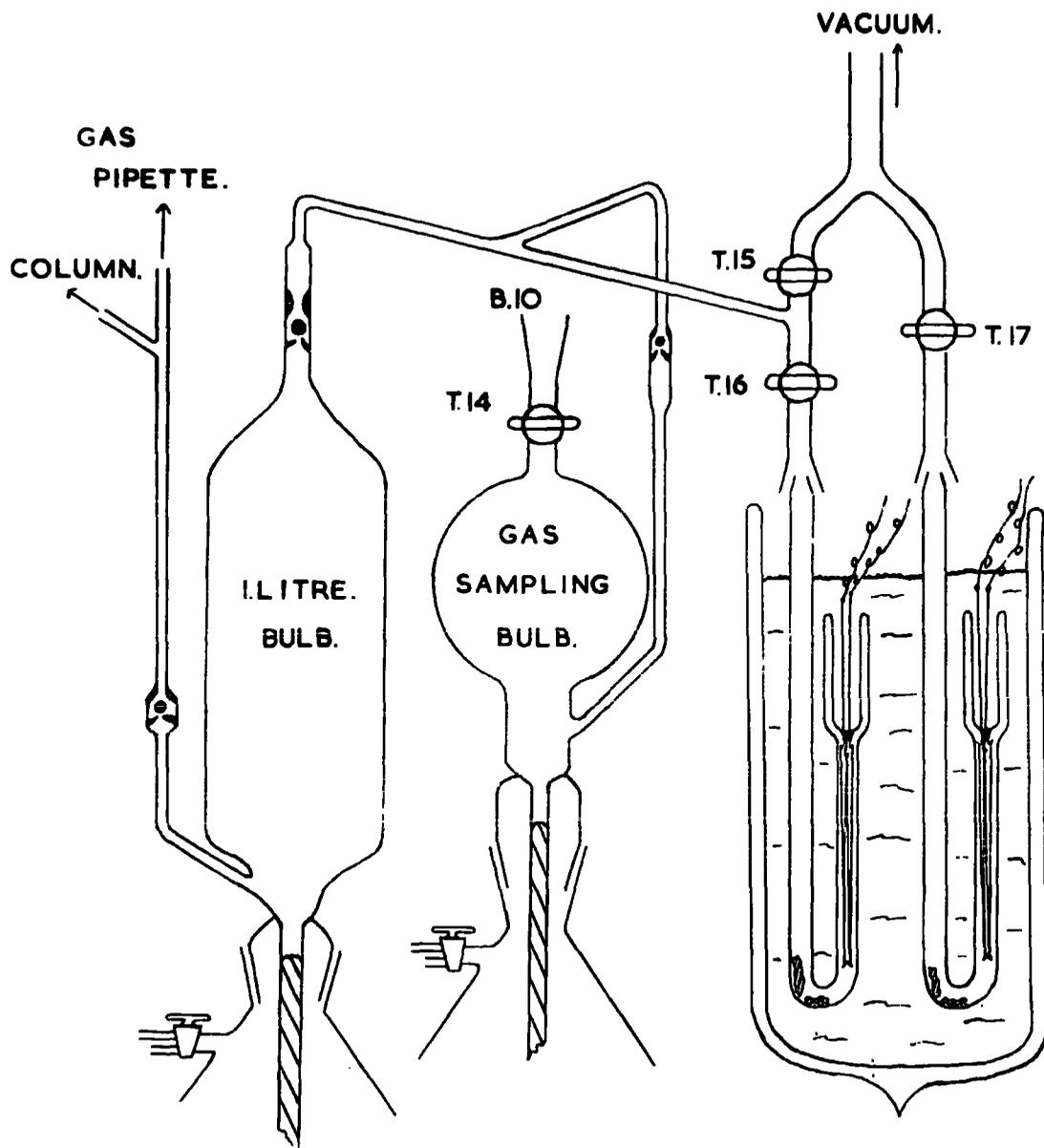
Electrical connection of the tungsten leads of the gauge to the bridge circuit is made by copper leads enclosed in a single sheath, thus eliminating spurious effects due to variations in the temperature of the leads. The copper wire is hard-soldered to the tungsten, care being taken when using the gauges to ensure that the soldered joints are kept fully immersed in the liquid air bath. If this is not the case, marked irregularities occur due to thermal e.m.f.s..

Since the gauges are of Pyrex glass the question of the permeability of this glass to helium immediately arises. From published values of the permeability (37) it may be calculated that the accumulation of helium in the gauges would amount to approximately  $10^{-9}$  c.c. over a period of two hours at  $0^{\circ}\text{C}$ . Since the gauge is at a much lower temperature than this, and since the permeability decreases sharply with decreasing temperature, it may well be assumed that helium accumulation is negligible. In practice no accumulation has ever been observed.

Fig. 16.

Storage-bulb, gas sampling bulb, and Pirani

gauge system.



Connection of the Pyrex instruments to the soda-glass apparatus is made by a black-waxed B.7, cone and socket arrangement.

PROCEDURE.

In an actual analysis the gauges are evacuated with the taps T.15, T.16, and T.17, open (fig.16), the charcoal being outgassed with a very small flame. When a "hard" vacuum has been attained the current in the bridge circuit is switched on and the gauges are immediately immersed in the liquid air bath. The initial rate of drift of the gauges is very high, but after about three hours it amounts to only a fraction of a millimetre per minute on the most sensitive range of the galvanometer system.

When the gauges have reached equilibrium, taps T.15, and T.17, are closed, the gas sampling bulb is completely filled with mercury, and the gas from the column is collected in the storage bulb. When collection of the gas is complete, tap T.16, is closed and the mercury level in the storage bulb is raised, compressing the gas. T.16, is then opened and the deflection of the galvanometer spot on the scale is recorded at minute intervals. The deflection is directly proportional to the "off-balance" current in the bridge, which in turn is directly proportional to the gas pressure in the Pirani gauge. A typical deflection takes about five minutes, to reach a steady value, after which time the spot has a tendency to drift slightly. The value attained after five minutes is usually accepted as the true deflection, any uncertainty being resolved by graphical methods if necessary. Tap T.16, is then closed and the

mercury in the storage bulb is lowered to a fixed reference mark. When the galvanometer spot has become steady at a suitable part of the scale, tap T.16, is again opened and the deflection in the reverse direction is measured. Readings may be taken as many times as is necessary to obtain good statistical accuracy, those readings differing by more than about half of one per cent being rejected. Usually about six or eight readings are sufficient.

A correction is necessary for the fact that the scale should strictly be part of the circumference of a circle at the centre of which is the galvanometer mirror. This is not a practicable arrangement, however, and a straight scale is used instead. The readings at either end of the scale will be larger than at the centre, but a series of readings of the same small deflection at all parts of the scale enables a graphical correction to be applied to any given readings. By limiting the deflections to about thirty centimetres, and by taking readings only in the mid-part of the scale, the magnitude of the corrections is much diminished, and by suitably measuring the amount of gas for calibration it is possible to obtain an almost identical deflection over the same part of the scale, virtually eliminating the scale correction.

The gas used for calibration is measured in an absolutely calibrated McLeod gauge and a small fraction is introduced into the Pirani gauge by means of the gas pipetting system shown in fig. 17 and measured in the usual way. The deflection produced by the unknown amount of gas is then compared with that produced by the measured quantity, and the

unknown amount found by simple proportion. In effect the gauges are calibrated after each determination since, being very sensitive instruments, they cannot be permanently calibrated. On the most sensitive range of the galvanometer system it is possible to measure a quantity of helium of the order  $10^{-8}$  N.T.P.c.c.s. to an accuracy of about 1%.

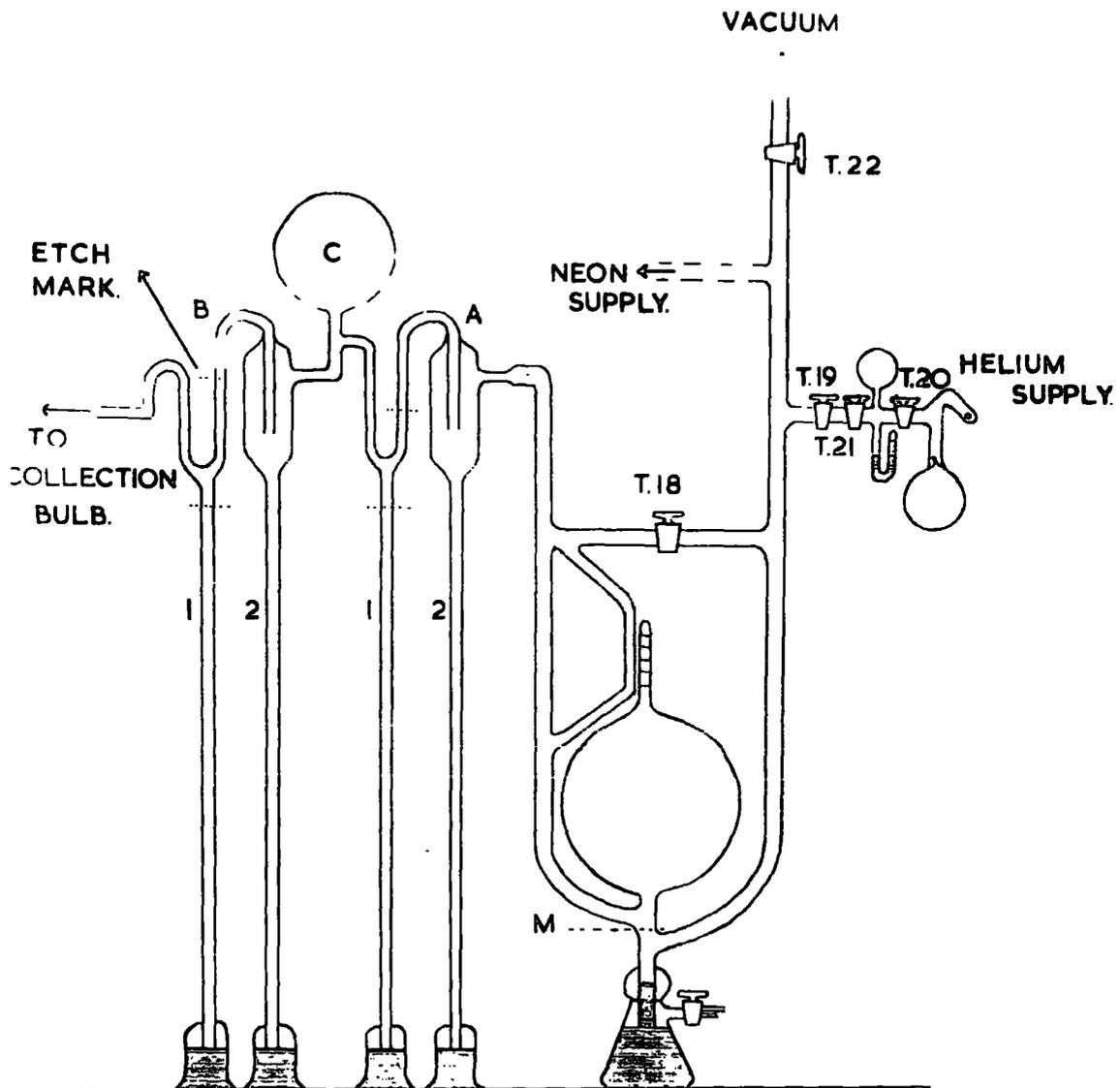
Since the gauges are so sensitive to vibration, care is taken while opening and closing tap T.16, during the course of measurements. The gauges are also sensitive to light, and all readings are taken in a darkened room to eliminate chance variations in light intensity. High-frequency electric fields have a completely unsettling effect upon the gauges, and "leak-testing" may not be carried out before or during an experiment anywhere in the laboratory.

The measurement of small quantities of helium for calibration of the Pirani gauges.

Since Pirani gauges are not "absolute" instruments the deflection produced by the unknown quantity of helium must be compared with that produced by an accurately known quantity of pure helium which has been measured absolutely. In the present work a Mo.Leod Gauge was used to measure a volume of helium about  $10^4$  times greater than the amount under test. This volume was reduced to the appropriate magnitude by means of the gas pipetting system shown in fig. 17, and the final known fraction was admitted to the Pirani gauge in order to measure the deflection.

Fig. 17.

Gas-pipetting system.



MEASUREMENT AND PIPETTING OF THE GASES.

The whole apparatus is first evacuated through tap T.22, taps T.19, T.20, T.18, and T.21 being open. Taps T.19, and T.20 are then closed and the small ball above the break-off seal of the ampoule is manipulated so as to smash the tip of the seal. Tap T.20 is then cautiously opened so as to admit a few centimetres pressure of gas into the small bulb between T.20 and T.21, this bulb acting as a subsidiary reservoir. During an actual experiment the mercury in the pipetting system is raised to the upper etch mark in limb-1 of "A" and to the upper mark of limb-1 of "B". The levels of the mercury in the second limbs of "A" and "B" are just below the out-offs in these pipettes. Tap T.22, is closed, then T.21 is closed and T.19 opened, allowing a small fraction of the reservoir gas to enter the McLeod gauge. This small amount is compressed in the gauge, the mercury level being raised to one of the etch marks on the measuring tube, and the pressure difference and meniscus heights are measured by means of a travelling microscope. The McLeod side-arm is then evacuated for a few minutes through T.22. T.18 is then closed and the mercury is lowered to the mark "M" allowing the known quantity of gas to expand into the measured volume of the McLeod gauge bulb and side-arm. By raising the level in limb-2 of pipette "A" till the mercury is just above the out-off, then lowering the level in limb-1 to the lower etch mark and repeating the operations with pipette "B", final known fractions may be collected in the expansion bulb.

Occasionally it is necessary to take more than one pipette "B" of

gas and in this case a Boyle's law correction must be applied to compensate for the drop in pressure of the gas in the bulb "C". In order to complete the measurement of the gas volume the temperature of a thermometer in contact with the McLeod gauge is taken as affording the true temperature of the gas inside the gauge.

A factor of the greatest importance in determining the accuracy of the calibration is, of course, the purity of the helium used. In the present work B.O.Co. spectrally pure samples were employed, and at intervals the purity was checked by passing a known amount of gas through the fractionating column, the deflection produced by this gas being measured on the Pirani gauges. The deflection of an amount of helium direct from the reservoir was then measured. No appreciable degree of contamination was ever observed.

#### Calibration of the McLeod gauge and gas pipetting system.

##### A. Calibration of the McLeod gauge.

The calibrated measuring tube of the McLeod gauge consisted initially of a length of constant-bore soda-glass (5m.m.) tubing with etch marks at approximately centimetre intervals. One end of this tube was ground flat and waxed to a microscope slide; clean dry mercury was then poured into the tube till the bottom of the meniscus corresponded to the lowest etch mark. The correspondence of level was checked by means of a microscope and the whole tube and its contents were weighed, the tube having been previously weighed empty. This procedure was adopted for

each of the etch marks and hence the volume between each mark could be found, the density of the mercury (corrected for temperature) being known. The end of the tube was then rounded off in a gentle flame. It only remained to find the volume between the last etch mark and the rounded-off end. This was measured by completely filling the tube with mercury, "wiping-off" the meniscus at the ground-glass end with a microscope slide, and weighing the residual mercury. The difference in weight between the tube filled to the last mark and the completely filled tube corresponds to the volume between the last etch mark and the rounded-off end.

The volumes between the marks were plotted against the distance from the lowest etch-mark and the points were found to lie accurately on a straight line. This would only be expected if constant bore tubing was used and, since this was the case, it is a good indication that the calibration was sufficiently accurate. The advantage of calibrating the tube in this way is that it is calibrated in the position in which it is used.

It was also necessary to find the volume of the McLeod bulb, between the tap T.18, the mark "M", and the cut-off in limb- 2 of the pipette "A" (fig.17). This was done by cutting the connecting tube near the pipette "A" and filling the bulb and corked side-arm with water up to the mark "M"; the volume of the water was then measured. This operation was performed

three times the agreement between the readings being better than 0.01 per cent. The side-arm was then connected to the calibrated gas-pipette "A" with the minimum of volume change. Any error resulting from this operation must be relatively small because of the large volume of the bulb and side-arm.

B. Calibration of the gas pipettes "A" and "B".

The pipettes "A" and "B" and the small bulb "C" were joined together in one unit. The volume from the cut-off in limb-2 of "A" to the upper etch mark in limb-1 of "A" was found by a mercury weighing method, correction being made for the fact that the menisci at both points were inverted during calibration. The volume from the cut-off in limb 2 of "B" to the upper etch mark in limb 1 of "B" was similarly measured. The dead space in "A" actually constitutes part of the volume of the side-arm of the McLeod gauge and its volume was also found by the mercury method. ~~The volume bounded by the cut-off in "A", the lower etch mark in limb 1 of "A", and the upper etch mark of "B", was measured by a~~ weight of water method, the mean of several readings being:-

Vol. of pipette "A" = 4.610 c.c.  
 " " " " "B" = 4.494 c.c.  
 " " "A" + "B" + "C" = 179.5 c.c.

These volumes were checked by a gas expansion method and the values were found to agree to within 0.4%. Most of this discrepancy must arise in the several meniscous corrections necessary in the gas expansion method and in actual calculations the results obtained by the weighing methods were used as ~~is~~ this was considered to be a more reliable technique.



P A R T T W O

RESULTS.

MATHEMATICAL TREATMENT OF EXPERIMENTAL RESULTS.1.) Homogeneous distribution of helium.

In the present work most of the specimens were in the form of discs, or slightly irregular pieces of large area and thin uniform section, and consequently could be treated as semi-infinite solids. Provided the gas is homogeneously distributed the diffusion equations (assuming "D" is constant) for such cases is

$$\bar{c} = \frac{8c_0}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp. \left[ - \left( \frac{(2n+1)\pi}{h} \right)^2 Dt \right] \quad (67) \quad \text{EQU. 9.}$$

$\bar{c}$  = amount of gas left in sample after time (t).

$C_0$  = amount present initially.

h = sample thickness.

D = diffusion coefficient.

If (c) is the amount diffusing out in time (t) (i.e.  $c = c_0 - \bar{c}$ )

then for (t) sufficiently large the first term in the series gives the good approximation,

$$\frac{\bar{c}}{c_0} = \frac{8}{\pi^2} \cdot \exp. \left[ - \frac{t}{\tau} \right] \text{ where } \tau = \frac{h^2}{\pi^2 D} \quad \text{EQU. 10}$$

$$\text{i.e. } 1 - \frac{c}{c_0} = \frac{8}{\pi^2} \cdot \exp. \left[ - \frac{t}{\tau} \right] \quad \text{EQU. 11}$$

The series expressed in Equation 10 is shown graphically in fig.18 and it may be seen that the approximate form of the series holds only when the curve has become asymptotic to the straight line whose

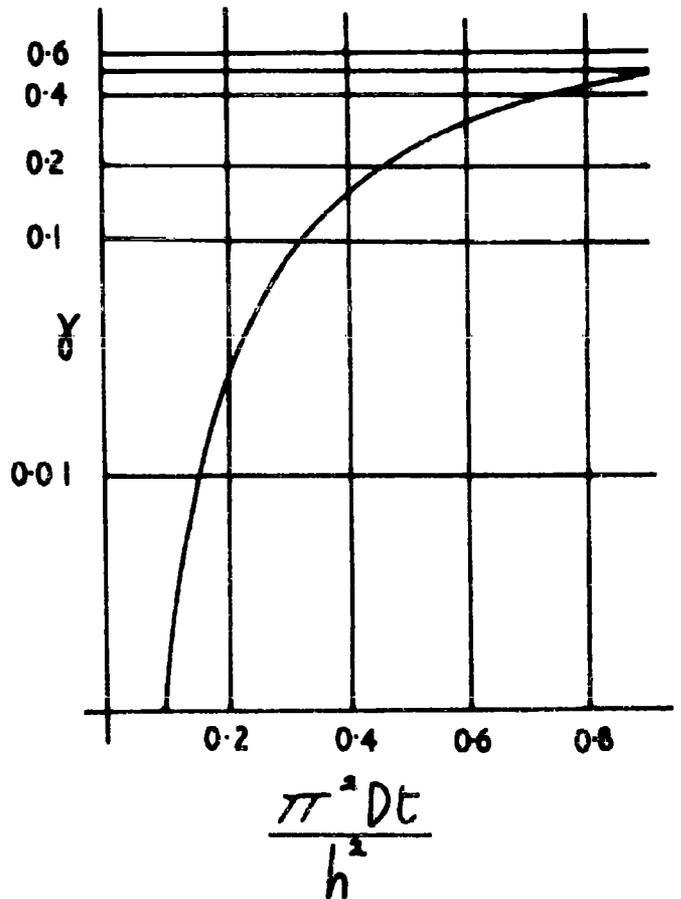
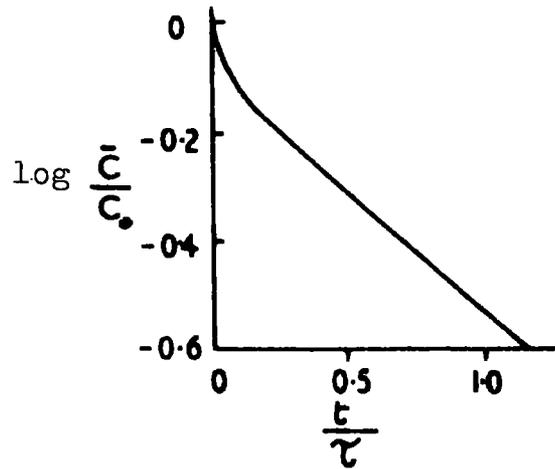
Fig. 18.

Equation 10.

Fig. 19.

Equation 15.

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equation is

$$\log \left( 1 - \frac{c}{c_0} \right) = \log \frac{8}{\pi^2} - \frac{t}{\tau}$$

EQU. 12

Thus "D" may be obtained from the slope.

If "D" is small then  $\frac{c}{c_0}$  will be small unless (t) is compensatingly large. In the present case the value of "D" was about  $10^{-10}$  cm.<sup>2</sup>/min. and with typical anneals of only  $\sim 10^3$  minutes total duration the asymptotic relation was never achieved. The value of the diffusion coefficient must therefore be obtained from some other series relating "D" and (t) with (c) and (c<sub>0</sub>)

The series shown in Equation 9 converges rather slowly for small (t) and a more rapidly converging error - function series has been developed by LIEBHAFSKY (66).

Equation 9 can be rearranged in the form

$$1 - \frac{c}{c_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp. \left[ -(2n+1)^2 y \right]$$

EQU. 13

$$\text{where } y = \frac{\pi^2 Dt}{h^2}$$

If (y) is less than 0.2, this simplifies to

$$\frac{c}{c_0} = \frac{4}{h} \left( \frac{Dt}{\pi} \right)^{\frac{1}{2}}$$

EQU. 14

and thus if  $\frac{c}{c_0}$ , the fractional loss of gas, is plotted against  $\sqrt{t}$

the result should be a straight line. The slope of this line readily yields "D".

The curves obtained in practice are shown and discussed in the appropriate sections.

2.) Inhomogeneous distribution of helium; sandwich case.

Mathematically this is a rather more complex case, the complete solution having been worked out by LE CLAIRE and ROWE and used in their investigation of the diffusion of argon in silver (9). Briefly, if the central layer of helium is very thin the fraction of gas evolved from the surfaces of the sandwich is  $\gamma$  where

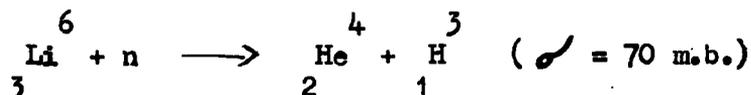
$$\gamma = 1 - \frac{4}{\pi} \sum_{1}^{\infty} \frac{(-1)^{v+1}}{(2v-1)} \cdot \exp\left[-\left(\frac{2v-1}{h}\right)^2 \pi^2 Dt\right] \quad \text{EQU. 15}$$

Knowing the thickness (h) and the time of annealing (t) it is possible to deduce "D" from experimentally determined quantities.

Equation 15 is expressed graphically in fig. 19.

ALUMINIUM.

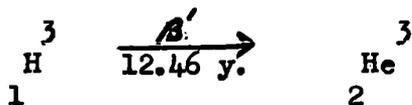
Strictly, the metal investigated was not aluminium but a solid solution of lithium in aluminium. The lithium was present as a source of helium from the reaction



the neutron flux being provided by the BEPO reactor at A.E.R.E. Harwell. Since, however, the amount of lithium is small and this element does not cause significant expansion of the aluminium lattice (68) the diffusion characteristics should not differ too widely from those of pure aluminium.

Two different alloy samples were used containing 160 and 1120 p.p.m. of lithium respectively. The alloy was cold-rolled into the form of sheets 0.5m.m. thick from which discs of about 1.1 cms. diameter were punched. The size of the discs was chosen so that

- a. slow neutron self-screening was less than 0.5%, and
- b. loss of recoil alpha-particles was limited effectively to the discs at the end of each irradiated stack. These end discs were discarded. Since the samples were used within a relatively short time of each other no trouble was experienced from accumulation of helium from the reaction



It may be expected then that the specimens contain a uniform concentration of helium in a metal matrix consisting essentially of

pure aluminium.

Before irradiation the discs were given a light surface etch with a reagent consisting of 2% concentrated hydrofluoric acid and 10% nitric acid in order to remove minor blemishes and give, as far as possible, the same surface characteristics to every disc. Some of the samples were annealed before irradiation in order to test the effect of crystal size on the amount of helium diffusing from the discs. The reactor BEPO was used for this irradiation since it has a relatively low fast neutron flux and the samples thus sustained the minimum of damage due to the "Wigner-effect".

Several of the discs, both irradiated and unirradiated, showed slight blistering and "pitting" on annealing. These blemishes were about the same size and it was thought that they may have been due to part of the lithium distilling out of the metal. However, it was suggested by KAY (69) that a more probable cause was the distilling out of water trapped during the rolling process. To rule out any possibility of inhomogeneity of the lithium content some of the irradiated discs were autoradiographed before annealing. Any undue concentration of lithium should then be manifested by a "hot-spot" of beta- activity due to tritium. The samples were placed on a strip of Kodak "Kodirex" X-ray film and left for four days before developing. Several regions of high activity were observed but it was concluded that they were not due to tritium betas since when the experiment was repeated using an aluminium absorber (10mg./cm<sup>2</sup>) the intensity of blackening was only slightly re-

Surface before annealing.

Fig.20.

Surfaces of aluminium discs before and after  
annealing. (Mag. X 42)

Surface after annealing.

Fig.20 continued overleaf.

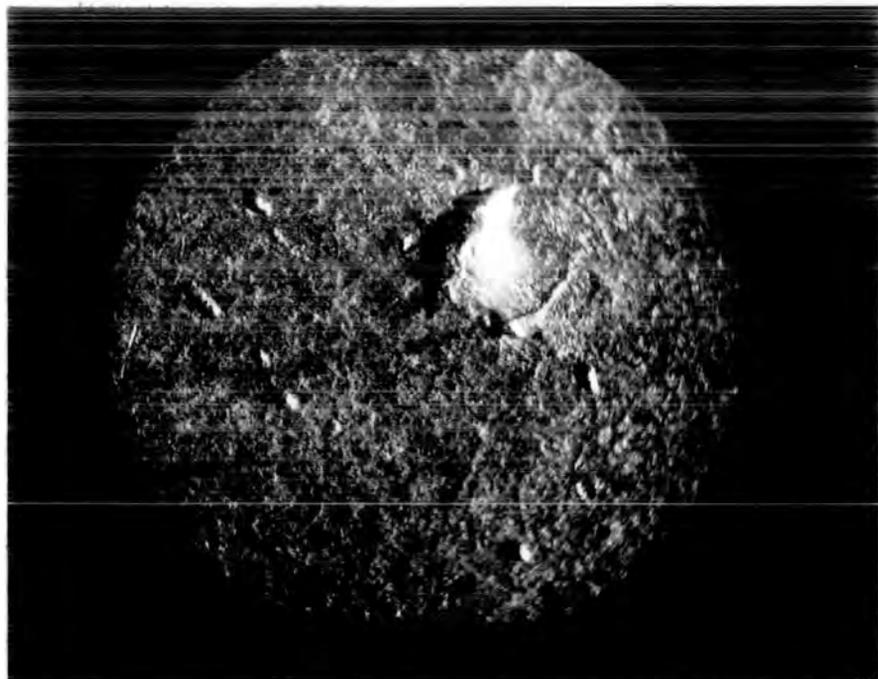
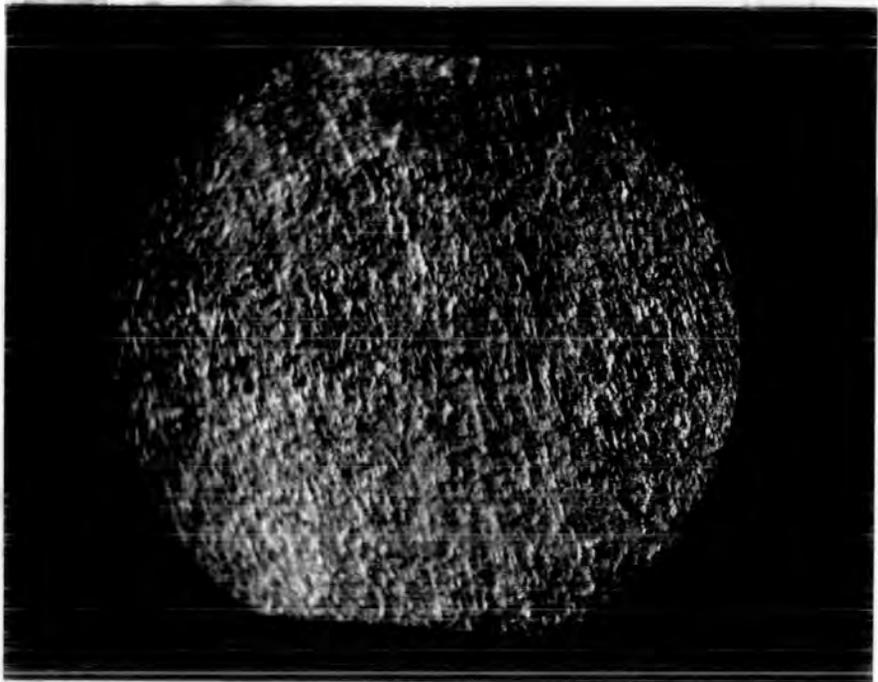


Fig. 20 cont. from  
previous page.

Surface layer of metal removed.

Fig. 20 (cont.).

Autoradiographs of the disc AlO with and without  
the removal of the surface layer. (Mag. X 4)

Disc without any treatment.



duced. Since the spots were confined to the surface and edges of the discs and could be completely removed by lightly rubbing with fine emery-paper it appears likely that the activity is due to impurities introduced during the rolling or punching-out processes. Apart from these spots the autoradiograph showed a uniform field of blackening. Some of the autoradiographed discs were then annealed and microscopically examined for blemishes, but no correlation was found between these and the hot-spots of the autoradiographs. It may therefore be concluded that the lithium concentration is uniform, the hot-spots being an irrelevant phenomenon. Where possible specimens showing gross defects were not used in the present work, but in any case effects due to these will be small since they are few and cover only a very small fraction of the surface.

Photo-micrographs of the defects, and enlarged pictures of the autoradiographs are shown in fig. 20.

The results obtained for the diffusion of helium in aluminium are derived from four batches of samples which are designated (A), (B), (C), and (D). The irradiation data and percentage lithium content of all the discs are shown in table 2.

As may be seen from fig. 21 and tables 3, 4, 5, 6, the results indicate that:-

1. The total amount of helium evolved is very small even after very long anneals.
2. The (C) and (D) discs have markedly different initial rates of evolution, although at the same temperature they eventually tend to the same limit of  $\frac{a}{\infty} \sim 0.03$ .

3. The results are remarkably self-consistent with the exception of D<sub>4</sub>. This is attributable to an inconsistency in the Pirani gauges during the earlier stages of annealing and since the slope of the straight part in fig. 22 is not affected by this it has been used for the calculation of the diffusion coefficient for D<sub>4</sub>.

At the time the (B) discs were investigated it had not yet been possible to obtain a really helium-tight furnace and it was deemed better to measure the helium remaining in the discs after a long anneal than to try to collect and measure the small amount evolved. The latter quantity was calculated by subtraction of the residual amount from the amount of gas obtained from another unheated disc which had the same history as the annealed one. Some of the errors inherent in this method have already been discussed and it may be seen that the spread in the results obtained under identical conditions is quite large. It is apparent, however, that the total amount of helium evolved is small even after very long periods at high temperatures. In fact the total amount evolved after 400 hours is not much more than that evolved in 30 minutes and this seems to indicate that the expected linear relationship between the amount evolved and the square root of the time is not obeyed for annealing times of this magnitude. The more accurate and detailed experiments carried out on the (A), (C) and (D) discs also support this conclusion.

The curves expressing  $\frac{Q}{\sqrt{t}}$  as a function of the square root of the time are not wholly linear except at the lowest temperatures

Table 2.

DISC DATA.

Batch.	Li (p.p.m.)	App. thermal flux, (n./cm. <sup>2</sup> /sec.)	Duration of irradiation. (days.)	App. fast flux. (n./cm. <sup>2</sup> /sec.)	Irradiation temperature.	Pre-irradiation treatment.
A	160	$10^{12}$	28	$1.6 \times 10^{11}$	52° C.	Light surface etch with (2% HF, 10% HNO <sub>3</sub> ) reagent.
B	1120	$10^{11}$	28	$0.03 \times 10^{11}$	23° C.	Light surface etch with (2% HF, 10% HNO <sub>3</sub> ) reagent.
C	1120	$10^{12}$	28	$1.6 \times 10^{11}$	52° C.	Light surface etch with (2% HF, 10% HNO <sub>3</sub> ) reagent.
D	1120	$10^{12}$	28	$1.6 \times 10^{11}$	52° C.	Light etching as above and annealing, in vacuo, at 615° C. for 1 hr.

Integrated fast neutron dose for (A), (C), (D) discs is  $3.73 \times 10^{17}$  n./cm.<sup>2</sup>

Integrated fast neutron dose for (B) discs is  $7.0 \times 10^{15}$  n./cm.<sup>2</sup>

Table 3.

(B) DISCS.

Disc and Anneal.	Total time (hrs.)	T° C.	$\frac{a}{\infty} \times 10^2$	$\sqrt{t(\text{mins})}$	Mass. (gms).	Thickness (h) (cms.) $\times 10^2$
B1	168.6	472	2.53	100.6	0.1279	4.790
B2	115.5	472	6.19	83.25	0.1298	4.854
B3	217.3	472	0.72	114.19	0.1262	4.803
B4	219.4	574	10.20	114.72	0.1306	4.892
B5	154.4	574	7.55	96.25	0.1234	4.624
B6	100.0	574	8.20	77.46	0.1353	5.070
B9	642.0	613	3.50	62.07	0.1290	4.834
B10	190.3	613	9.40	106.86	0.1292	4.839
B12	341.0	613	2.60	143.04	0.1286	4.823
B13	421.5	637	7.30	159.03	0.1318	4.939
B15	406.5	637	12.30	156.07	0.1231	4.701

Table 4.

(A) DISCS.

Disc and Anneal.	Total time. (mins.)	T° C.	$\frac{g}{cc} \times 10^2$	$\sqrt{t(\text{mins.})}$	Mass. (gms.)	Thickness (h) (cms.) $\times 10^2$
A11 1	15	538	0.62	3.87	0.1217	4.560
A12 1	15	615	2.35	3.87	0.1266	4.744
2	45	613	2.82	6.71	"	"
A13 1	15	494	0.396	3.87	0.1238	4.654
A14 1	15	575	1.61	3.87	0.1143	4.280
A10 1	25	610	2.39	5.00	0.1326	4.965
2	100	610	2.60	10.00	"	"
3	180	610	2.67	13.42	"	"
A10 <sup>re</sup> 1	+20	611	+0.66	-	0.1168	4.374
A8 1	75	610	4.69	8.66	0.1224	4.579
2	165	615	5.32	12.85	"	"
3	260	604	5.32	16.13	"	"
A2 1	22680	648	9.80	150.59	0.1306	4.894
A3 1	22680	648	12.70	150.59	0.1116	4.182

\* A 10 was reannealed for 20 minutes after grinding off a thin surface layer (~ 6% off each side).

Table 5.

---

(C) DISCS.

Disc and Anneal.	Total time. (mins).	T° C.	$\frac{a}{\infty} \times 10^2$	$\sqrt{t}$ (mins)	Mass. (gms.)	Thickness (h) (cms.) $\times 10^2$
G2 1	15	614	1.49	3.873	0.1389	5.127
2	45	610	1.78	6.710	0.1389	5.127
3	85	613	1.84	9.22	0.1389	5.127
G4 1	15	535	1.09	3.873	0.1402	5.175
2	45	535	1.31	6.710	0.1402	5.175
3	75	612	1.77	8.66	0.1402	5.175
G7 1	10	614	1.345	3.16	0.1390	5.130
2	25	614	1.553	5.00	0.1390	5.130
3	45	614	1.694	6.71	0.1390	5.130
4	75	614	1.850	8.66	0.1390	5.130
5	130	614	2.054	11.40	0.1390	5.130
6	215	614	2.247	14.70	0.1390	5.130
7	300	614	2.352	17.30	0.1390	5.130
8	400	614	2.434	20.00	0.1390	5.130
9	580	614	2.516	24.10	0.1390	5.130
G13 1	10	580	1.303	3.16	0.1378	5.087
2	25	580	1.487	5.00	0.1378	5.087
3	50	580	1.630	7.07	0.1378	5.087
4	100	580	1.807	10.00	0.1378	5.087
5	200	580	2.000	14.14	0.1378	5.087
6	324	580	2.147	18.00	0.1378	5.087

Table 6.

(D) DISCS.

Disc and Anneal.	Total time (mins.)	T <sup>o</sup> C.	$\frac{c}{co} \times 10^2$	$\sqrt{t}$ (mins.)	Mass. (gms.)	Thickness (h) (cms.) $\times 10^2$
D4 1	15	614	0.510	3.87	0.1382	5.121
2	35	"	0.595	5.92	"	"
3	55	"	0.711	7.42	"	"
4	75	"	0.883	8.66	"	"
5	110	"	1.12	10.50	"	"
6	170	"	1.54	13.00	"	"
7	270	"	1.71	16.40	"	"
8	370	"	1.88	19.20	"	"
9	490	"	2.01	22.10	"	"
10	640	"	2.16	25.30	"	"
D7 1	10	614	0.521	3.16	0.1366	5.065
2	25	"	0.715	5.00	"	"
3	46	"	1.01	6.78	"	"
4	100	"	1.53	10.00	"	"
5	205	"	1.94	14.32	"	"
6	305	"	2.08	17.50	"	"
7	455	"	2.22	21.33	"	"
8	650	"	2.33	25.50	"	"
9	850	"	2.40	29.15	"	"
10	1240	"	2.49	35.21	"	"

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Disc and Anneal.	Total time. (mins.)	T <sup>o</sup> C.	$\frac{c}{co} \times 10^2$	$\sqrt{t(\text{mins.})}$	Mass. (gms.)	Thiickness (h) (cms.) x 10 <sup>2</sup>
D8 1	10	614	0.539	3.16	0.1403	5.202
2	26	"	0.687	5.10	"	"
3	60	"	1.132	7.75	"	"
4	120	"	1.522	10.95'	"	"
5	240	"	2.150	15.49	"	"
6	360	"	2.330	18.97	"	"
7	510	"	2.460	22.58	"	"
8	810	"	2.603	28.46	"	"
9	1125	"	2.677	33.54	"	"

About equal amounts were ground-off each side of D8, reducing the mass to 0.1138 gms.. After etching, the disc was reannealed as D8<sup>1</sup>.

D8 <sup>1</sup> 1	11	614	0.121	3.32	0.1138	4.219
2	35	"	0.149	5.92	"	"
3	85	"	0.1597	9.22	"	"
4	185	"	0.1597	13.60	"	"
D13 1	10	580	0.424	3.16	0.1400	5.191
2	26	"	0.517	5.10	"	"
3	55	"	0.649	7.42	"	"
4	95	"	0.908	9.75	"	"
5	195	"	1.396	13.96	"	"
6	299	"	1.732	17.29	"	"
7	431	"	1.958	20.76	"	"
8	576	"	2.070	24.00	"	"

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Disc and Anneal.	Total time. (mins.)	T° C.	$\frac{c}{c_0} \times 10^2$	$\sqrt{t(\text{mins.})}$	Mass. (gms.)	Thickness (h) (cms.) $\times 10^2$
D16 1	10	580	0.5835	3.16	0.1344	4.946
2	25	"	0.6731	5.00		
3	52	"	0.7872	7.21		
4	90	"	0.9805	9.49		
5	144	"	1.275	12.00		
6	249	"	1.692	15.78		
7	380	"	1.973	19.49		
8	625	"	2.182	25.00		
D6 1	15	556	0.5155	3.87	0.1289	4.779
2	35	"	0.5990	5.92	"	"
3	75	"	0.6720	8.66	"	"
4	145	"	0.8110	12.04	"	"
5	245	"	0.9640	15.65	"	"
6	365	"	1.190	19.10	"	"
7	485	"	1.330	22.00	"	"
8	<u>615</u>	"	<u>1.450</u>	<u>24.80</u>	"	"
9	630	<u>614</u>	1.530	25.10	"	"
10	670	"	1.640	25.88	"	"
11	790	"	1.955	28.11	"	"
12	955	"	2.196	30.90	"	"
13	<u>1280</u>	"	<u>2.450</u>	<u>35.78</u>	"	"
14	1310	640	2.496	36.20	"	"
15	1567	"	2.555	39.60	"	"

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Disc and Anneal.	Total time. (mins.)	T° C.	$\frac{a}{\infty} \times 10^2$	$\sqrt{t(\text{mins.})}$	Mass. (gms.)	Thickness (h) (cms.) $\times 10^2$
D14 1	10	550	0.400	3.16	0.1354	5.020
2	25	"	0.434	5.00	"	"
3	60	"	0.508	7.75	"	"
4	120	"	0.618	10.95	"	"
5	240	"	0.838	15.49	"	"
6	360	"	1.057	18.97	"	"
7	500	"	1.240	22.36	"	"
8	620	"	1.350	24.49	"	"
D17 1	10	464	0.342	3.16	0.1358	5.035
2	25	"	0.366	5.00	"	"
3	145	"	0.411	12.04	"	"
4	291	"	0.462	17.06	"	"
5	484	"	0.511	22.00	"	"
6	664	"	0.544	25.77	"	"
7	961	"	0.580	31.00	"	"
D11 1	10	464	0.323	3.16	0.1340	4.968
2	25	"	0.354	5.00	"	"
3	55	"	0.374	7.42	"	"
D9 1	10	350	0.154	3.16	0.1346	4.991
2	25	"	0.197	5.00	"	"
D10 1	10	265	0.126	3.16	0.1347	4.994

Fig. 21.

The percentage of helium evolved from  
aluminium as a function of time.

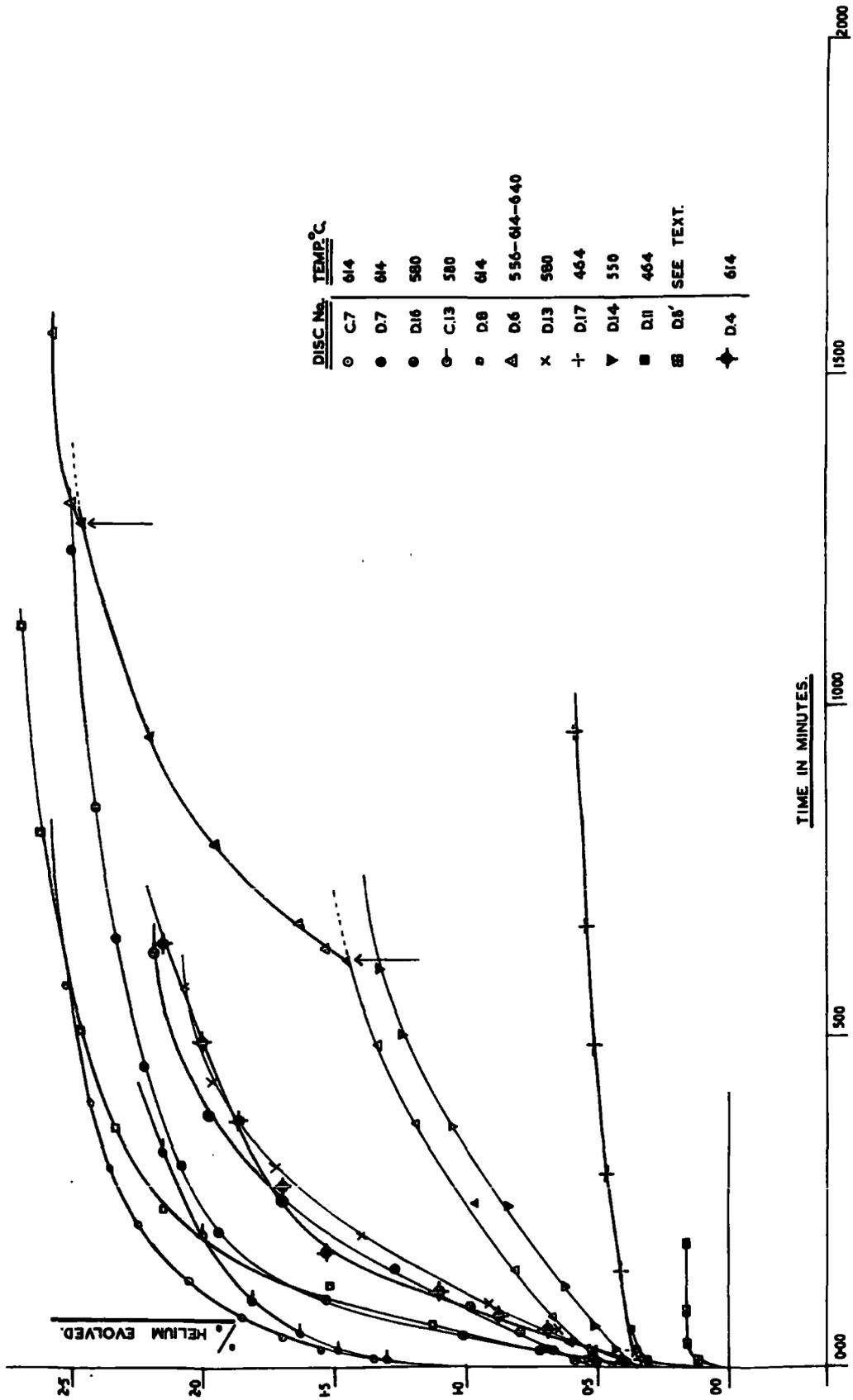
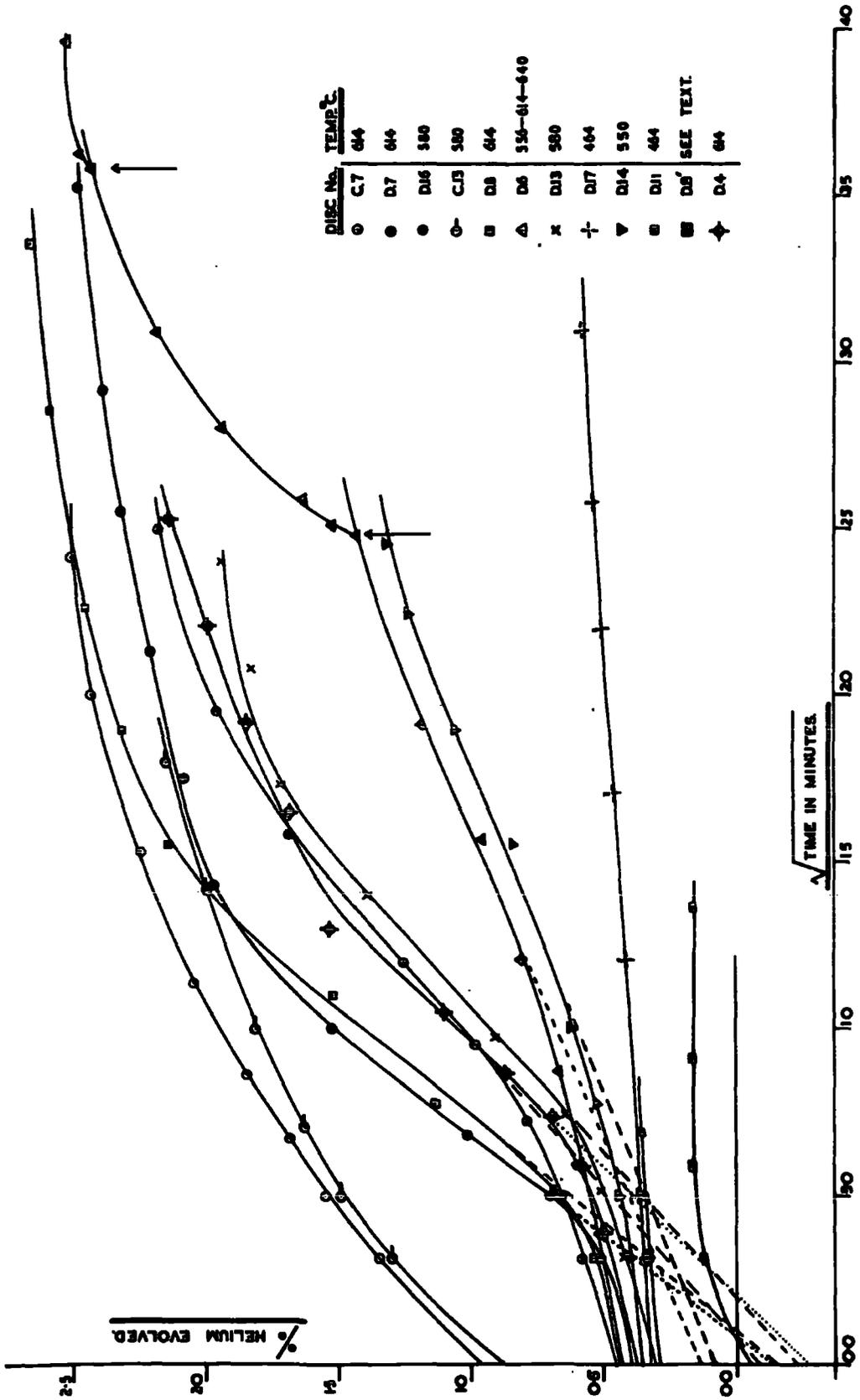


Fig. 22.

The percentage of helium evolved from aluminium  
as a function of the square root of time.



investigated, the curves for the higher temperatures showing three distinct regions which may be designated as:-

A. initial 'burst',

B. linear release,

and

C. 'fall-off' of helium evolution with time.

(A) Initial 'burst'.

The initial high rate of release could be due to a number of factors.

1. It was thought possible that atmospheric helium was loosely adsorbed on the surface of the discs and that this was readily released on annealing. This hypothesis was tested by measuring the quantity of helium evolved from some of the unirradiated alloy. Since this was found to be negligibly small there can be no question of helium adsorption from the air. This would be expected on the basis of EHRlich's (70) adsorption and JOHNS's (71) solubility measurements.

2. It is possible that the lithium/aluminium alloy may not be in a single phase, and that free lithium exists in the metal. The work of NOWAK (72) suggests that the solubility of lithium in aluminium at 300°C is only 0.3% and falls off rapidly as the temperature decreases. If this is correct then the percentage of lithium in the (B), (C) and (D) discs (0.1%) may be too high to admit of all the lithium being in true solution. NOWAK's

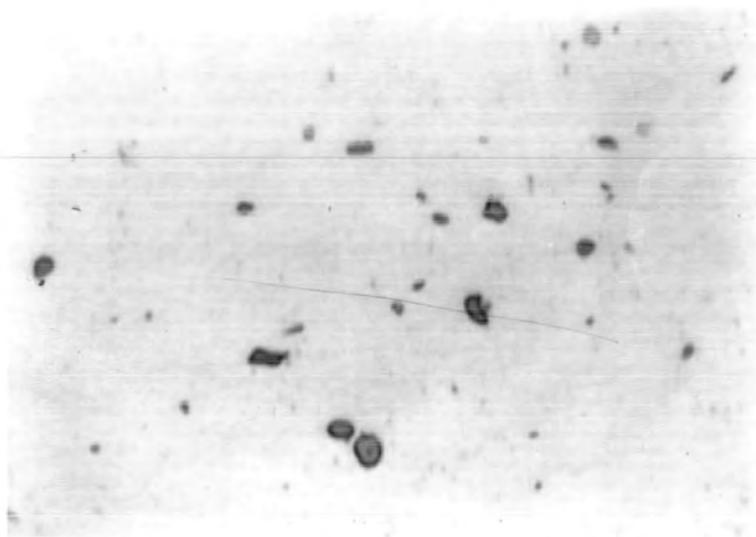
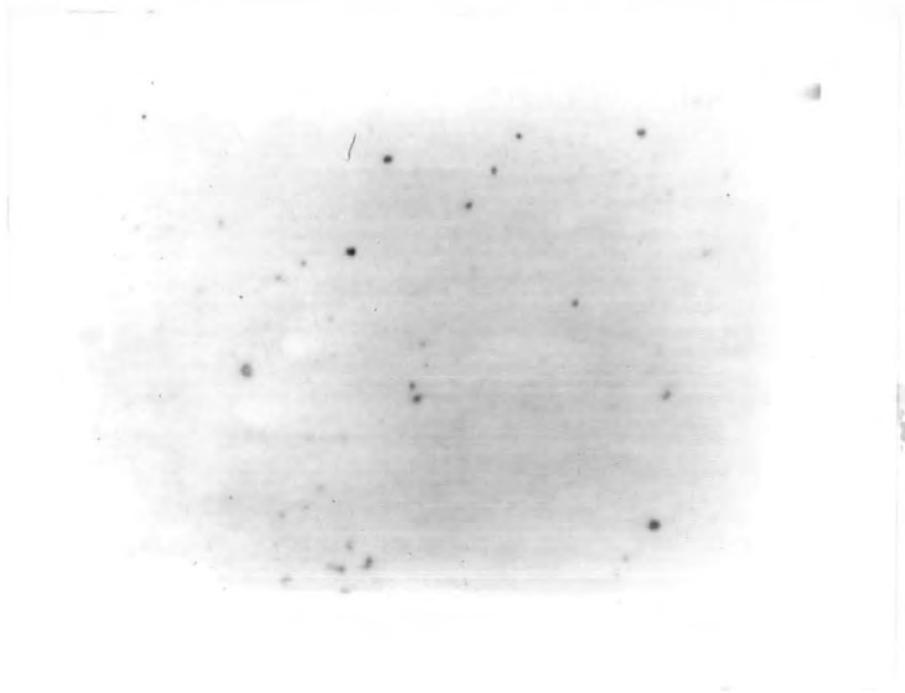
results, however, although probably the most accurate available, differ substantially from those of other workers (73, 74). Although the spread of data is fairly great a typical result is that of VOSSKÜHLER(68) who suggests a value of 1.15% for the solubility at room temperature. Owing to the lack of precise data it was decided to examine the alloy metallographically (microanalyser techniques are useless with an element of such a low atomic number). This investigation showed that there was no evidence of the formation of intermetallic compounds and only very minor inclusions of foreign material, probably oxide (see fig. 23). As already mentioned, autoradiographic examination suggests that there are no gross accumulations of lithium-rich phase and it would therefore appear that all the lithium is indeed in true solution. Even if this is not entirely true, if the lithium-rich phase were sufficiently dispersed throughout the alloy then the alpha-particles originating in this phase would still be trapped in the aluminium lattice. It seems unlikely therefore that any separation of lithium-rich phase is responsible for the initial 'burst' of helium.

3. At the pile factors used for irradiation there is a considerable flux ( $\sim 10^{14}$  n./cm<sup>2</sup>/sec.) of fast neutrons in the neutron spectrum and it may be that sufficient radiation damage was caused by these neutrons to allow a fraction of this damage to persist. Since

Surface of unetched aluminium alloy (disc D12)  
after mechanical polishing. (Mag. X 1000).  
Note the very small amount of non-metallic  
oxide impurity.

Fig. 23.

Surface of unetched "commercially pure"  
aluminium after identical treatment. (Mag. X 1000).



radiation damage would lead to a higher than normal concentration of vacancies and interstitials this could speed up diffusion in the metal to a considerable degree. Damage due to electron irradiation, of course, would anneal out extremely quickly and could not possibly persist for very long after the end of the irradiation. The persistence of fast neutron damage appears to vary quite considerably from metal to metal, although much of it is known (75,76) to anneal out very readily even at very low temperatures. Some damage, however, sometimes remains at room temperature and usually manifests itself as an increase in the critical shear stress of the metal.

In aluminium almost all the irradiation damage appears to anneal out at quite low temperatures. Mc REYNOLDS et al. (77,78) have shown that the radiation induced electrical resistivity and increase in yield strength both anneal out below  $-20^{\circ}\text{C}$ . Their irradiation was carried out at liquid nitrogen temperature and the total dose was  $10^{19}$  n./cm.<sup>2</sup> The absence of effect on the critical shear stress is highly indicative of an absence of persisting defects since these are extremely effective in modifying this property (79). These results are confirmed by (75,76). STEELE and WALLACE (80), however, state that aluminium irradiated with  $10^{20}$  n/cm.<sup>2</sup> at  $65^{\circ}\text{C}$ . retains its hardness at room temperature. Since these conditions (apart from the considerably greater total fast neutron flux) correspond more closely to the conditions used in the present experiments it is not possible to completely rule out radiation damage

as a cause of the helium evolution. Moreover, the virtually identical behaviour of the (A) and (B) discs after irradiation at different pile factors cannot be said to eliminate radiation damage as a factor in the release of helium since the fluxes were only slightly different and the radiation damage density varies only as the square root of the neutron flux (81). Any variation of the helium release which was due to damage would therefore be well within the experimental error. It is apparent, however, that at least one other factor must be operative besides that of radiation damage since the (C) and (D) discs show different initial release effects.

4. One very striking result is the difference between the initial amount of helium evolved in the case of the (C) and (D) discs which were both irradiated to the same extent. The (C) discs, which were not annealed before irradiation, evolve almost twice as much helium in the first ten minutes or so of annealing. Since the (C) discs show considerable cold work (fig.24), and since the (D) discs have had this cold work annealed out, it is quite possible that the extra evolution in the former case is due to the cold work which is known (82) to produce vacancies, often in strings. Vacancies produced in this way cannot be responsible for all the initial evolution, however, since the (D) discs also show this effect, and it may well be that the pre-irradiation annealing or non-annealing of the discs has the effect which is described in (5).

5. Micrographic examination (see fig. 24) of annealed and unannealed discs shows that grain growth of the metal is virtually complete in about fifteen minutes. Thus the larger initial burst of the (C) discs could be due to the "sweeping out" of some helium as the grain boundaries move outwards. Such an effect would be limited to the first ten minutes or so but should be confined only to the (C) discs and this is not the case. Moreover, recent work by BOKSHEIN et al. (83) suggests that atoms on grain boundaries are not disturbed to any great extent by the movement of the grain boundary across them and this makes the "sweeping out" effect of rather doubtful significance.

6. Closely linked to (5) is the case of grain boundary diffusion. This should be characterised by a relatively low energy of activation for diffusion and as may be seen in fig. 26. this is the case if a "square law" evolution can be assumed for the first few minutes of annealing. There is, however, no experimental evidence for this assumption in the present case. This mechanism, however, would explain the difference in the initial rates of evolution from the (C) and (D) discs since the latter having much bigger grains must have a correspondingly smaller total grain boundary surface. The fact that the linear part of the  $\frac{Q}{\infty} \sqrt{t}$  curve can be extrapolated approximately to the origin suggests that the helium released initially (at least from the (D) discs) is different in kind from that represented by the linear part of the curve and it seems reasonable to suppose that it is present as loosely trapped

Specimen C14 showing highly cold-worked structure of the un-annealed metal. Note the absence of grain boundaries.

(Anodised+non-polarised light. Mag.X200).

Fig. 24.

Unirradiated aluminium after five minutes annealing at 614°C. Note recrystallisation.

(Anodised+non-polarised light. Mag. X 200).

cont. overleaf.

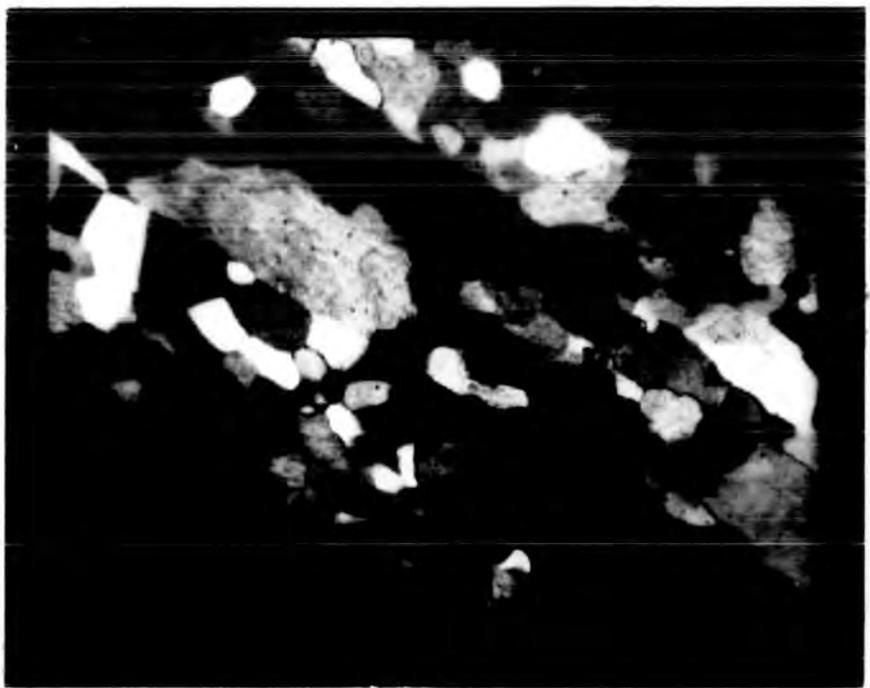
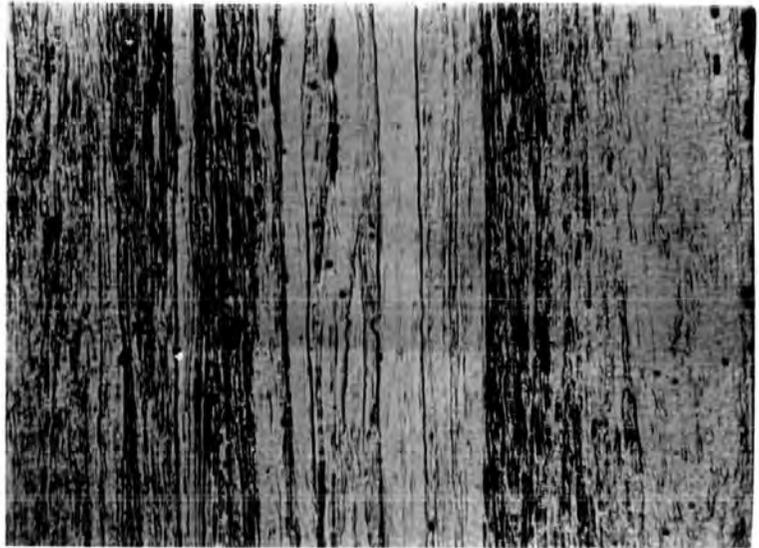


Fig. 24 cont.

Grain size of unirradiated metal after ten minutes annealing at 614°C.

(Anodised+polarised light. Mag. X 200)

Note that recrystallisation is almost complete.

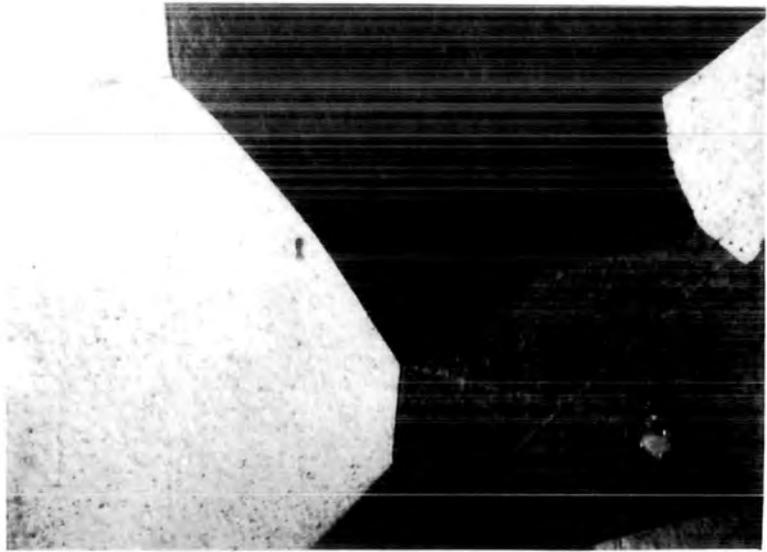
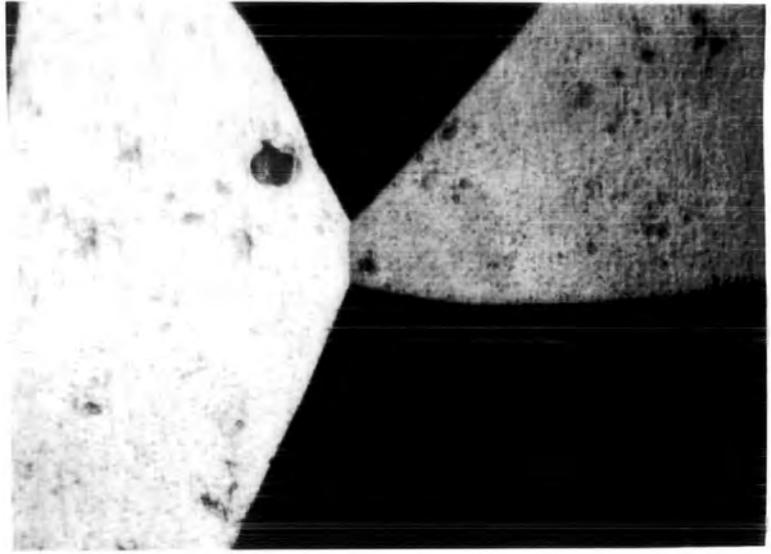
(cf. below.)

Fig. 24(cont.)

Grain size of D12 after sixty minutes at 614°C.

(Anodised+polarised light. Mag. X 200).

Note that recrystallisation has gone little further than the stage shown in the previous photograph.



gas on the surfaces of grains. A secondary effect of grain size is due to the fact that the grain boundaries can supply vacancies for diffusion (14,15,20).

7. Interstitial movement of the helium is possible since although the energy of formation of an interstitial atom is large (at least in copper) (11) it can easily move once it has been formed. The helium atoms, by virtue of the method of their introduction, must be already in interstitial positions and the energy of formation of an interstitial no longer has to be surmounted. Thus a small rise in temperature should produce a large increase in the movement of the gas. As the temperature rises a vacancy mechanism must predominate (11) but until a sufficient concentration of thermal vacancies has been produced an interstitial mechanism might be expected to be operative.

Experiments with material of stabilised grain size would obviously afford much evidence concerning (5) and (6) and enable the relative importance of grain size and growth to be ascertained. Two batches of discs, each of different grain size and stabilised against further growth, were supplied by A.W.R.E. but experiments have not yet been undertaken with these.

#### (B) Linear release.

The linear part of the curve  $\frac{Q}{\infty} / \sqrt{t}$  has a slope which exhibits temperature dependence. On plotting the logarithms of the diffusion coefficients obtained from this slope against the inverse absolute temperature an energy of activation of 2.15 ev. (49.7k. cals./mole) is obtained for the diffusion process. This value is of the same

Table 7.

$E_F$  and  $E_M$  are, respectively, the energies of formation and movement of a vacancy in the metal.

$E_D$  is the energy of activation for self-diffusion.

ENERGY CHARACTERISTICS OF LATTICE DEFECTS IN SOME METALS.

Metal.	$E_F$ (ev.)	$E_M$ (ev.)	$E_F + E_M$ (ev.)	$E_D$ (ev.)	$T^0$ K.	Reference.
Au	~1.30	0.40	~1.7	-	300	(45)
	0.79	0.52	1.31	-	370	(46)
	1.28	0.68	1.96	-	300	(47)
	1.02	0.66	1.68	-	300	(48)
	0.95	0.68	1.63	-	370	(49)
	0.70	0.50	1.20	-	-	(46)
	0.60	-	-	-	-	(50)
				1.71		(51)
				1.81		(52)
				1.86		(52)A
Fe				1.96		(53)
				2.6	-	(100)
				2.60		<del>(54)</del>
Ag	1.1	-	-	-		(55)
	-	-	-	1.77		(56)
Al	0.76	0.44	1.20	-	300	(57)
	1.00	-	-	-	300	(58)
	-	-	-	~0.90	-	(59)
	-	-	-	~1.40	-	(60)
Cu	1.0→1.2	0.9→1.0	~2.0	-	-	(61)(62)(63)(50)
	-	-	-	2.07	-	(64)

~ Measured indirectly.

Table 8.

COMPARISON OF PRESENT WORK WITH THAT OF

MURRAY AND PINCUS.

Reference and method.	Sample.	E(ev).	Dom. <sup>2</sup> /sec.	% At. Li.	T° C.
Present work.	D4	2.15	$1.93 \times 10^{-11}$	0.44	614
	D7	"	$2.22 \times 10^{-11}$	"	614
	D8	"	$1.87 \times 10^{-11}$	"	614
<u>Li/Al alloy.</u>	D13	"	$1.21 \times 10^{-11}$	"	580
	D16	"	$1.05 \times 10^{-11}$	"	580
	D14	"	$2.50 \times 10^{-12}$	"	550
	D6	"	$2.39 \times 10^{-12}$	"	556
	D17	"	$7.17 \times 10^{-13}$	"	464
	Murray and Pincus. (91)	-	-	$3.4 \times 10^{-11}$	~ 10
<u>Li/Al alloy.</u>					
Murray and Pincus. (91)	-	0.65	$8 \times 10^{-10}$	-	400
<u>Sandwich.</u>					
Murray and Pincus. (92)	-	-	$2.4 \times 10^{-10}$	0.02	575
<u>Li/Al alloy.</u>					

Fig. 25.

Log<sub>e</sub> D (D=diffusivity of helium in aluminium in cm.<sup>2</sup>/min. units) as a function of the inverse absolute temperature.

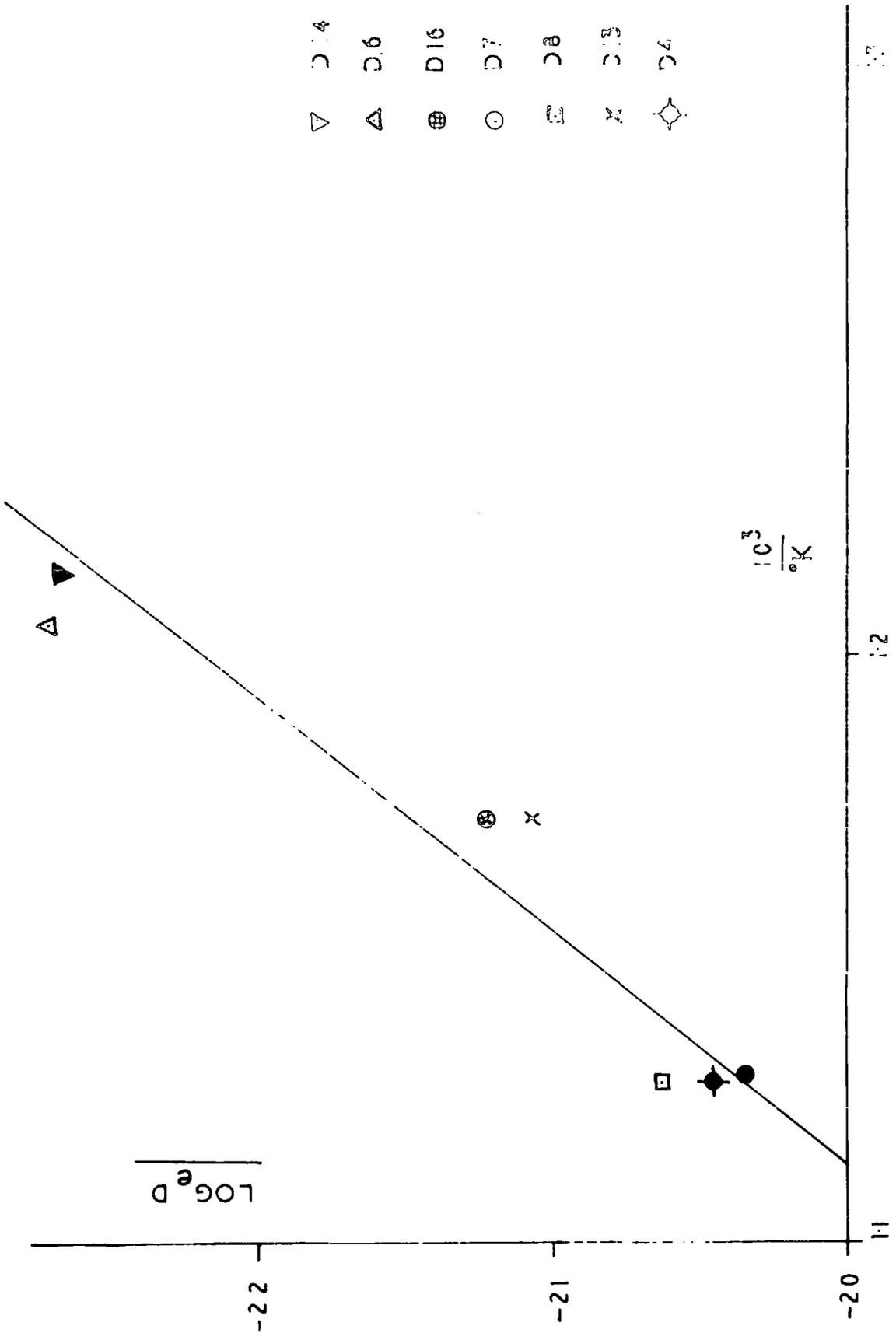
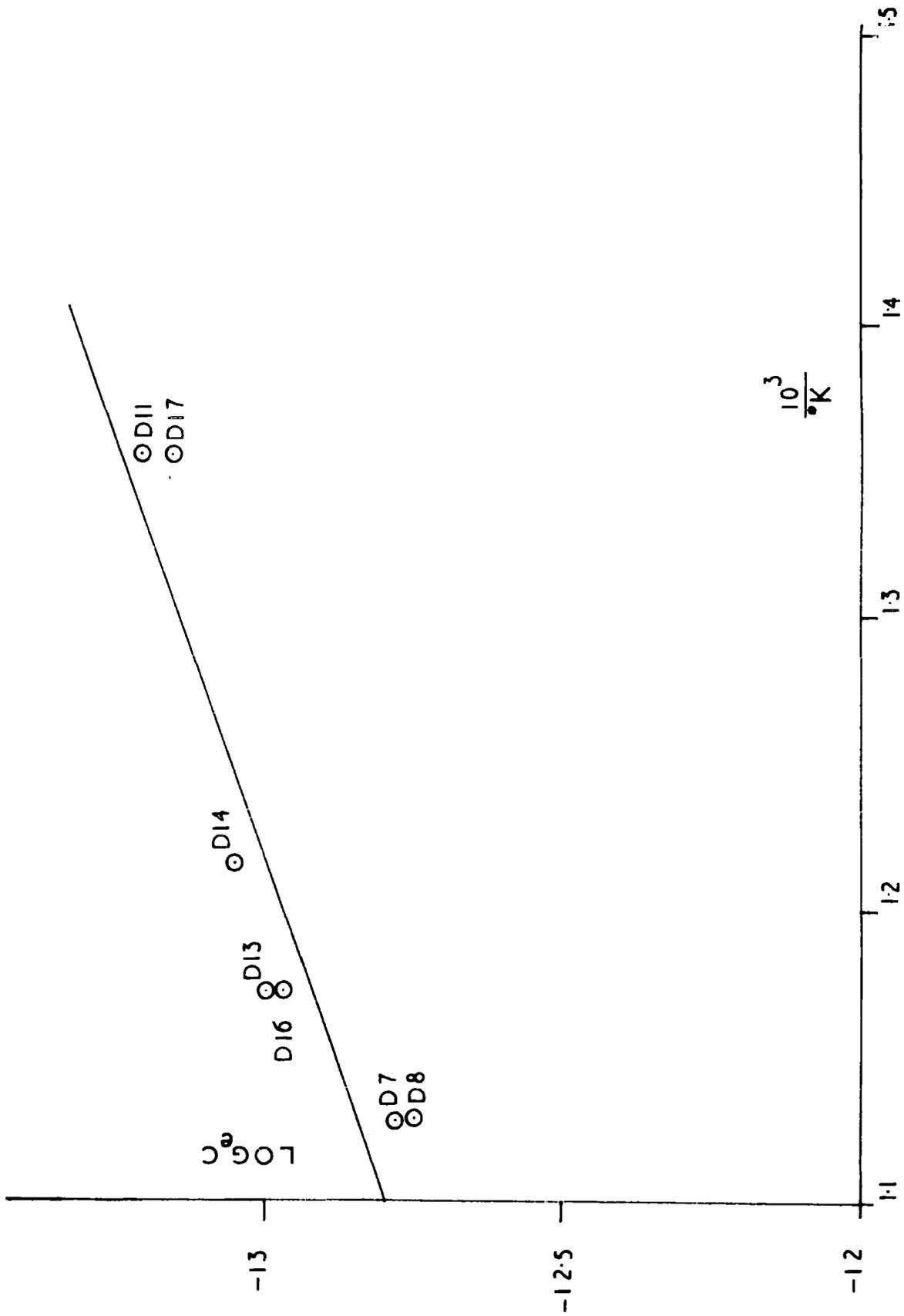


Fig. 26.

Log (c) ( where c=amount of gas evolved in the first ten minutes of heating) as a function of the inverse absolute temperature. The slope of the line is a measure of "E", the activation energy. Since the relation between (c) and "D", the diffusion coefficient, is not known for the initial stages of the annealing it is therefore impossible to deduce a value for "E" from the curve, but it would appear that the activation energy is relatively small unless the diffusion coefficient in this region is proportional to a very high power of (c).



order as the energies of activation for self diffusion in many metals (table 7) and since this process is believed to take place by a substitutional mechanism it is probable that helium moves in aluminium in the same fashion. However, the energies of formation and movement of vacancies in aluminium, and the energy of activation for self diffusion in aluminium, are listed in table 7, and it may be seen that these suggest a rather lower value for "E" than that obtained. Since no tracer method is readily available for measurements of self diffusion in aluminium, however, less accurate indirect methods are necessary and the spread of results is high. Therefore, in the absence of any evidence to the contrary, it appears reasonable to attribute a substitutional mechanism to the movement of helium in aluminium.

The diffusion coefficients at various temperatures together with the energy of activation for diffusion (see fig. 25) calculated from these are shown in table 8. ~~All these quantities are based on this~~ section of the curve.

(C) Fall-off of evolution with time.

As may be seen from fig. 22, the  $\frac{c}{\infty} / \sqrt{t}$  curves cease to be linear after a time depending on the temperature of annealing. The higher the temperature the earlier does the fall-off of gas evolution begin and only in the case of the anneals conducted at relatively low temperatures was no evidence of "tail-off" forthcoming even after several hours heating. At the higher temperatures, however, the total

fraction of helium evolved tended to a limiting value of about 3%. The admittedly less accurate results obtained on the (B) discs suggest that less than 10% is evolved even after several hundred hours heating. Theoretically there is no reason why such a phenomenon should be observed especially since the metal is by no means exhausted of gas and it therefore seems that some mechanism is at work restricting the free movement of the helium. At first it was thought that the free surfaces of the metal, acting as sources of vacancies, gave rise to a high concentration of these near the surface, the concentration decreasing towards the centre of the disc on account of capture by impurities or dislocations. By this means the helium atoms near the surface would be afforded relatively easy movement while those nearer the centre would be less mobile. After a few hours annealing the helium concentration in the vacancy-rich regions near the surfaces (for the purposes of this discussion grain boundaries are included in this term) would become depleted, and a fall-off in the rate of evolution might be expected. It was decided to test this hypothesis by exposing fresh surfaces on a "spent" disc, D8, by grinding off about 10% of the total thickness from each surface. After etching with the same solution as had been used in the original preparation the specimen was reannealed at the same temperature as before, no significant evolution of gas being observed. This leads to the conclusion that more than about 90% of the helium is very effectively trapped in what can only be conceived

as voids or bubbles. Such a phenomenon has frequently been observed with fission product gases in uranium and thorium (85, 86, 87, 88, 89) and also with helium in copper (14,11) and beryllium (65,93,98). In these cases, however, a much greater local concentration of gas was involved.

The bubble mechanism is further substantiated by the relatively small increase in the quantity of gas evolved when a spent disc, D6, was heated to rather higher temperatures than that at which the original anneal was conducted (see fig. 21). Moreover, the fact that the falling-off in the rate of evolution occurs at a later stage in the case of the lower temperature anneals agrees with the work of BARNES et al. (14,93,98) who found that the rate of bubble formation, due to vacancy accumulation, was a steep function of temperature.

#### BERYLLIUM.

A few pieces of neutron-irradiated vacuum-cast beryllium containing  $6.9 \times 10^{-5}$  c.c./gm. were available (the gas being produced by the reactions  $\text{Be}^9(n,2n)\text{Be}^8$  and  $\text{Be}^9(n,\alpha)\text{He}^6$ ), and probing experiments were carried out on these. No attempt was made to draw rigorous quantitative conclusions from these experiments since the pieces of metal were irregular in shape and microscopic examination showed them to contain a number of cracks (fig. 27) which made it impossible to estimate the true thickness of the specimens. Indeed, when sample (Be2) was withdrawn from the furnace it was found to have split into one large piece and two smaller pieces and a large part of the helium released in this

Beryllium Results.

BERYLLIUM.

Specimen.	Total time (mins.)	° T C.	° (c.c./gm. x 10 <sup>6</sup> )	$\frac{\sigma_1}{\sigma_0} \times 10^2$	Mass. (gms.)	Thickness (cms.)
Be 1	30	620	0.901	1.306	0.09935	~ 0.38
	90	622	1.053	1.528	"	"
Be <sup>#</sup> 2	30	960	16.11	23.37	0.1014	"
	90	960	17.60	25.54	"	"
Be 3	30	808	2.467	3.580	0.0785	"

# Be 2 split into one large and two small pieces during annealing  
and the high rate of release could be partly due to this.

case could probably be attributed to this.

The release of helium was found to be temperature dependent but, as the curve in fig. 28 shows, it does not obey the expected relation with time. The initial quantity of gas released is large, subsequent release being much diminished. This effect may be due to micro-crack or grain boundary evolution of helium initially, or bubble-formation at a later stage, or to a combination of both these mechanisms. This last possibility seems by far the most likely taking into consideration the cracked state of the metal and also the tendency for helium to form bubbles in beryllium (93,65).

Further work on beryllium was planned but has not yet been executed.

#### IRON/NICKEL ALLOY FROM METEORITES.

A naturally available source of helium-containing metal is meteoritic iron. The isotopes  $\text{He}^3$  and  $\text{He}^4$  are produced in the metal lattice by cosmic ray bombardment and, since the flux is only slightly attenuated by the iron, the gas may be considered to be homogeneously distributed if the specimens are small.

Samples of two meteorites, BETHANY (Harvard) and TOCOPILA (Cerros del Buei Muerto), were available and were examined for helium content to ascertain their suitability for diffusion measurements. BETHANY was found to contain a quantity of helium too small to be of any use, but TOCOPILA contained a somewhat larger amount. Unfortunately the

few available samples of this meteorite were irregularly shaped and small in size, thus making it difficult to estimate their physical thickness.

Annealing was carried out, in vacuo, in a stainless steel tube at 960°C., the evolved gases being transferred directly on to the fractionating column and measured in the usual way. The results of the experiments on both meteorites are given in table 9.

Owing to the very restricted number of specimens it was not possible to conduct experiments at several different temperatures to obtain an activation energy for the diffusion process. Moreover, the quantity of gas evolved would not have permitted measurements of any accuracy at temperatures much lower than about 960°C. Although the results obtained are few, their distribution (fig. 29) allows some idea of the shape of the evolution/time curve to be obtained. This curve suggests that the initial rate of gas release is high but falls off very rapidly. Such a conclusion is in agreement with the work of PANETH (94) and PANETH and URRY (95). These workers suggest that only the helium near the surface of a meteorite is readily evolved on heating, the total quantity evolved being less than about 6% even after several hours at temperatures in the region 1000°C. Unfortunately the results of these workers are presented in a form unsuitable for making any further comparison with the present work, and they do not allow the estimation of any diffusion characteristics.

It seems highly probable that once again bubble formation takes place in the metal and prevents further release of helium. This is in general agreement with PANETH's conclusions since the surface atoms will be the least susceptible to trapping by this mechanism.

Although meteoritic helium contains a substantial proportion of  $\text{He}^3$  (in the case of TOCOPILA 16% (96) ) the effect introduced by the slightly greater diffusion coefficient expected for this isotope would be far too small to account for the rapid initial release of helium.

Fig. 27.

Photo-micrographs of cracking in beryllium

specimens after annealing.

(Mag. X86)

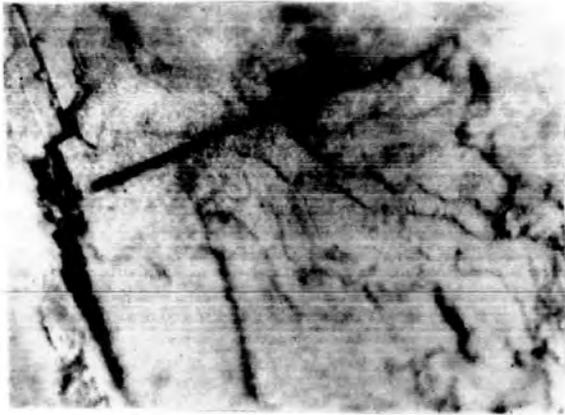
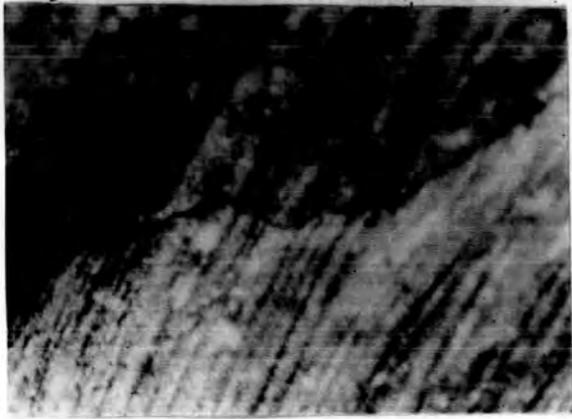


Fig. 28.

The evolution of helium from beryllium expressed as  
a function of time.

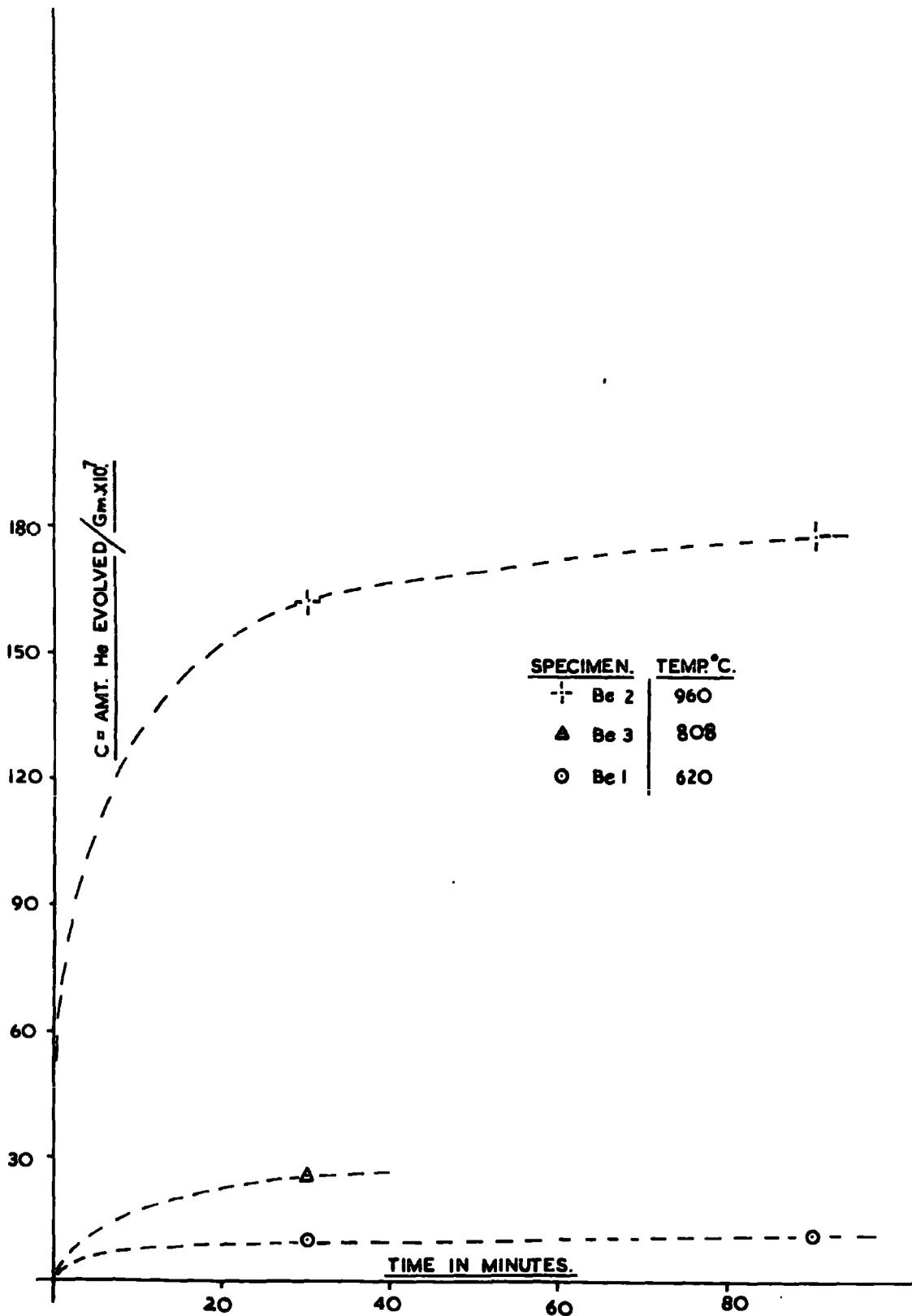


Fig. 29.

The evolution of helium from meteoritic iron/nickel  
alloy expressed as a function of time.

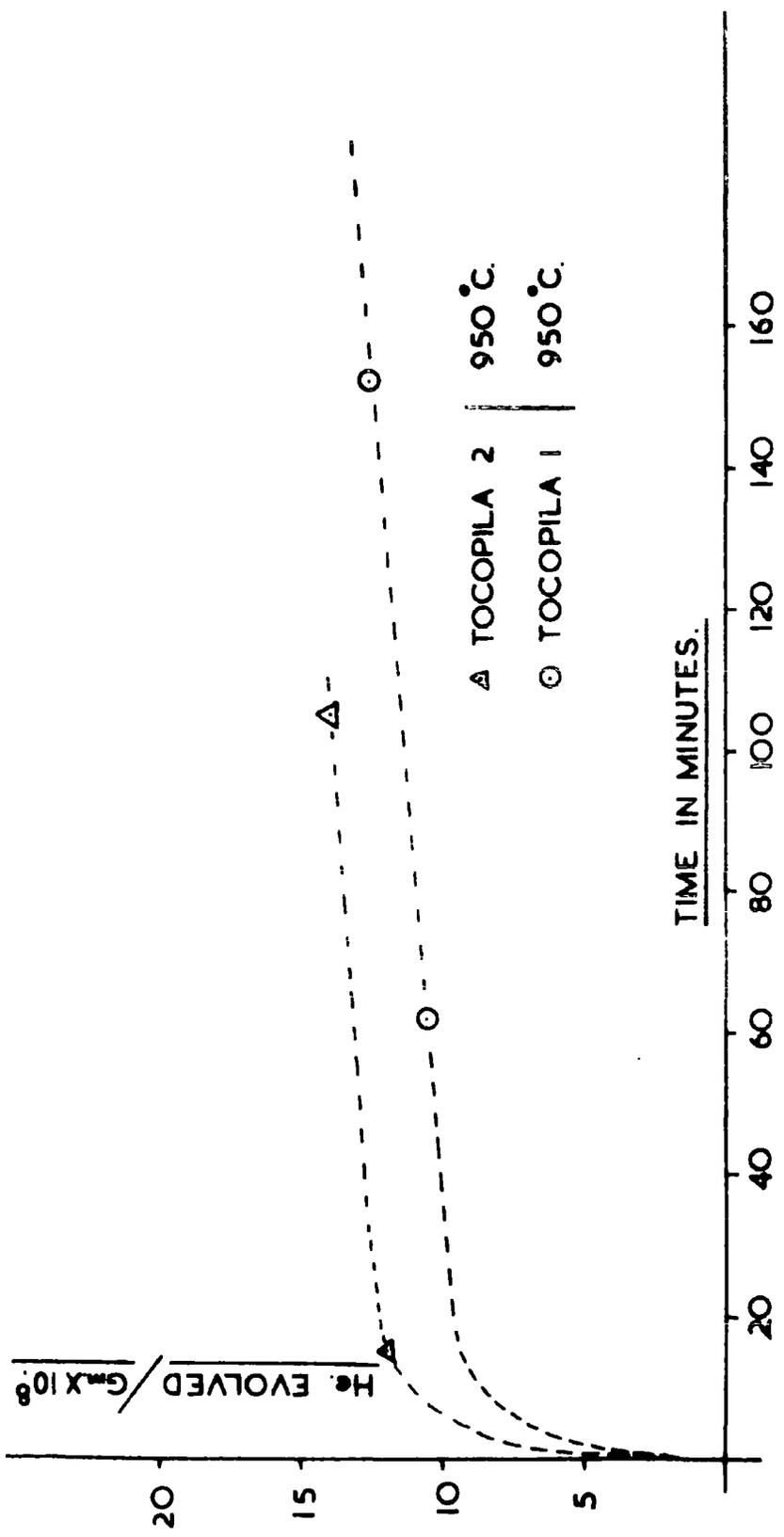


Table 9.

TOCOPIIA.

Specimen.	Total time (mins).	T° C.	(C) (c.c./gm. x 10 <sup>6</sup> )	$\frac{g}{cc} \times 10^2$	Mass. (gms.)	Thickness (cms.)
TOC. 1.	62	952	0.105	2.62	0.3591	0.2
	152	945	0.125	3.12	0.3591	0.2
TOC. 2.	15	955	0.119	2.97	0.3356	0.1
	103	950	0.139	3.47	0.3356	0.1

% Ni = 5.43 (101)

% Fe = 93.75

$C_o = 4.01 \times 10^{-6}$  c.c./gm.

BETHANY. (Harvard).

<u>Description of sample.</u>	<u>Mass. (gms.)</u>	<u>He content. c.c./gm.</u>
Unheated turnings.	1.2691	Nil
Unheated turnings.	1.0603	$2 \times 10^{-8}$
Unheated turnings.	1.1724	$< 2 \times 10^{-8}$
Unheated turnings.	1.2305	$2.2 \times 10^{-8}$
Solid slab.	1.4101	$< 2 \times 10^{-8}$

The values for the helium content of BETHANY are considered to be upper limits.

Table 10.

Summary of published inert-gas/metal  
diffusion data.

Author	System	T°C.	D(cm <sup>2</sup> /sec.)	D <sub>0</sub> (cm <sup>2</sup> /sec)	E(ev)	Method of gas introduction and remarks.
Le Claire, Rowe (9)	I/Ag	600 700 800	5 X 10 <sup>-10</sup> 3 X 10 <sup>-9</sup> 1 X 10 <sup>-8</sup>	0.12 " "	1.46 " "	"Sandwich" method. If several anneals were made on the same sample a progressive fall-off in "D" was observed. This was tentatively ascribed to thermally-produced voids trapping the gas.
Tobin (18)	Kr/Ag	700 800	2.2 X 10 <sup>-8</sup> 1.2 X 10 <sup>-7</sup>	1.05 "	1.52 "	"Sandwich" method. Very little experimental data given but the fact that no fall-off in the value of "D" was observed in successive anneals is specifically mentioned.
Tobin (19)	Xe/Ag	-	-	0.036	1.63	As above
Zimen, Schmeling (84)	Xe/U (Alpha-phase) (only)	400 570	2 X 10 <sup>-16</sup> 1.9 X 10 <sup>-15</sup>	- -	0.43 "	Gas obtained by fission. The extremely low "E" points to micro-crack diffusion.
Zimen, Dahl. (85)	Xe/U	1000	1.8 X 10 <sup>-10</sup>	2.40	2.6	Gas obtained by fission. The value of "D" is regarded as an upper limit due to grain size considerations. No change in "D" was observed in passing from alpha to beta to gamma phases.
Spedding (86)	Xe/U	1000	1.4 X 10 <sup>-10</sup>	-	-	Gas obtained by fission. The value of "D" quoted here was obtained by Zimen and Dahl from results quoted by Spedding.
Reynolds (87)	Kr/U	Up to 1000	-	-	-	Gas obtained by fission. No gas evolution observed below 1000°C. Above that temperature gas was evolved in an irregular fashion.
Andrew, Davidson, Glasgow. (88)	He/U He/Th	Up to 1040 900 1200	- 1.06 X 10 <sup>-13</sup> 5.13 X 10 <sup>-10</sup>	- 3 X 10 <sup>-4</sup> "	- 1.3 "	Negligible gas evolution in the case of uranium. In the case of both uranium and thorium foils the gas was introduced by means of alpha-particle bombardment in a cyclotron.
Hates, Clark. (89)	Xe/U	700 900	3.5 x 10 <sup>-15</sup> 8.0 X 10 <sup>-14</sup>	- -	- -	Fission xenon was utilised. There is a wide spread in the results which is attributed to oxidation of specimens. "D" thus represents an upper limit.
Walker (90)	Kr/U	607 650	1.7 X 10 <sup>-16</sup> 3.0 X 10 <sup>-15</sup>	- -	- -	Fission gas used. The conclusion is that bubble formation might explain some of the low temperature results but it is not considered to be a major factor in diminishing the diffusion coefficient. The evolution $\sqrt{t}$ curve is almost linear but falls off a little too rapidly.
Murray,* Pincus. (91)	He/Al	400 400	8 X 10 <sup>-10</sup> (sandwich) 3.4 X 10 <sup>-11</sup> (alloy)	- -	0.65 -	Used both "sandwich" and lithium alloy method. The former method gave higher values for "D" than the latter and micro-crack diffusion from the cold weld was suggested. A high percentage of lithium was used in the alloy and may be the cause of inconsistent results.
Murray,* Pincus. (92)	He/Al	575	2.4 X 10 <sup>-10</sup> (alloy)	-	-	Further work on a low percentage lithium alloy suggests results very similar to those obtained in the present work.

\* See text and table 8.

GOLD.

The sandwich method previously used for studying the diffusion of one metal in another has been adapted by LE CLAIRE and ROWE to the study of the movement of argon in silver. The extension of the method to gases is not altogether justified in that it is easier with a metal to eliminate void formation at the interfaces. With gases in metals it is very easy for the two phases to separate, and in the particular case of the inert gases the effect of separation is enhanced by the fact that the gas cannot redissolve. It is therefore particularly necessary to make sure that the cold-weld (for obvious reasons heat treatment of any sort cannot be used) is a good one and that there are no voids or microcracks along the line of the join. For this reason the method is restricted to those metals which readily undergo the phenomenon of cold welding and in the present work the malleable metal gold was used. Gold radon-filled tubes, used in radiotherapeutic work, may be adapted to producing a helium rich sandwich between two layers of pure metal (see Introduction). Three such specimens were made by opening the ends of these tubes (to allow any gases present to escape) and then cold-rolling the metal. Since the inside of the tubes are impregnated with helium from the alpha-decay of radon a helium sandwich is thereby formed.

The specimens produced in this way were rather irregular in outline, although of uniform thickness, and their dimensions were found by projecting an enlarged image of the metal on to a piece of squared paper. From a knowledge of the degree of enlargement of the image and the weight and

density of the specimens the area and thickness were then calculated by the method of counting squares. The area/thickness ratio of the specimens is sufficiently large to allow their being treated as semi-infinite plane sheets.

The thickness of the helium layer is governed by the range of the alpha-particles in the radon decay scheme and since the most energetic alpha has a range in gold of only  $\sim 1.1 \times 10^{-3}$  cms. the mathematical treatment of LE CLAIRE and ROWE may be used.

One of these specimens, (Au.A), was annealed in vacuo in five successive stages at  $815^{\circ}\text{C}$  and one stage at  $900^{\circ}\text{C}$  and the gas evolved from each anneal was collected. It may be seen from table 11 (where data for all the three gold specimens examined are given) that the quantity of gas evolved was very small and consequently difficult to measure. The deflections obtained during control anneals of the furnace were of the same magnitude as the smaller deflections produced by the gas evolved from the specimen and it is thus possible to state with certainty only that the amount of helium evolved from the gold was not greater than  $8.8 \times 10^{-8}$  ccs. per gram after 965 minutes annealing at  $815^{\circ}\text{C}$ . A considerable fraction of this gas could certainly have been produced by sources other than the specimen (e.g. the metal of the furnace and the glass apparatus) and the value calculated from these figures for the diffusion coefficient for helium in gold at this temperature must be taken as being very much an upper limit.

After annealing the specimen at 815°C a final 120 minute anneal was conducted at 900°C the quantity of gas evolved corresponding to less than  $1.05 \times 10^{-8}$  ccs. per gram. The amount of helium actually evolved from about 0.2 grams of gold was therefore approximately  $2.1 \times 10^{-9}$  ccs. and this is the amount normally evolved during a 120 minute control anneal of the furnace at the same temperature. Thus virtually no helium was evolved from the gold even after two hours annealing at 900°C. The residual gas in the specimen was then liberated by dissolving the gold in mercury and measured in order to find the initial helium concentration ( $c_0$ ). The value obtained,  $7.69 \times 10^{-5}$  ccs. per gram, agrees very well with that expected from the activity of the radon originally present in the gold tubes. Two similar experiments were carried out and the results of both substantiate the results of the first anneal. The variations in the initial concentration ( $c_0$ ) may be attributed to the variations in the quantity of gold and radon used in the fabrication of the tubes, and do not represent errors of estimation of the helium content.

Using the solution of the diffusion equation for the sandwich case (9) a value of  $4.36 \times 10^{-10}$  cm.<sup>2</sup>/sec. was obtained for the diffusion coefficient for (Au.A) at 815°C. This is almost certainly too high, since even if the helium from the walls of the furnace did not make an appreciable contribution to the total measured amount there is no reason why such a small quantity of gas cannot have escaped from the edges of the cold weld by way of microcracks or flaws rather than from the lattice by a volume diffusion mechanism. It would appear then either that the

diffusion of helium in gold is a very slow process, supposing it to take place at all, or that there is some mechanism involving rapid local diffusion of the helium to positions within the specimen where it is released from solution in the metal lattice and thus effectively trapped. Such a situation could arise in a number of ways:-

- (i) The helium is within a very short distance of the line of the cold weld (since the range in gold of the most energetic alpha particles in the radon decay scheme is only about  $1.1 \times 10^{-3}$  cms.) and any imperfections along the line of the cold weld must therefore exert a very significant effect on the movement of helium. It is difficult to assess the degree of perfection of the weld but it might be expected that a large fraction of the metal boundary would be effectively welded together and that a corresponding fraction of helium would be available for diffusion. After annealing (Au.B) and (Au.C) a discontinuous line of blisters were observed along the length of the specimens. This may well be due to gas which had been trapped during the fabrication of the tubes or during the rolling process. Again it is possible that during the filling of the tubes with radon a little mercury from the gas handling apparatus may have become entrained and, by vaporisation or amalgamation with the gold, this could cause bubbles to be formed in the region of the weld.

- (ii) It may be that relatively gross voids exist in the main body of the gold, not necessarily just along the cold weld junction, and that these trap helium. Here again it would not be expected that the capture of helium would be very significant without assuming an improbably high void concentration.
- (iii) A third possibility is the formation of voids throughout the metal by aggregation of vacancies. As already mentioned this effect has been observed in a number of metals and might possibly be more significant in gold on account of the rather lower energy (about 0.6 ev.) necessary to form a vacancy in gold.

The most likely possibility appeared to be the first one and it was decided to carry out a metallographic examination of pieces taken from the specimens (Au B) and (Au C) both before and after annealing. The examination was carried out at A.W.R.E. Aldermaston and the conclusions reached were that, of the four specimens examined, three showed gross laminations of a discontinuous nature. The fourth specimen (B2) is known to have the same defect but in this case it was not possible to photograph it since the defect was less severe. Enlarged photographs of the sections taken are shown in fig. 30.

Scratches produced on polishing appear to originate from the laminations and the suggestion is that the failure to cold-weld properly may have been due to the presence of gritty material. Although metallo-

graphic evidence is not conclusive, there is no evidence of amalgam formation anywhere in the specimen and it seems unlikely that mercury contamination has anything to do with the effects observed.

It would therefore appear that the cause of the negligible gas evolution observed in the case of the gold specimens could well be due to the migration of the helium to voids along the line of the weld. The helium remains in these voids in the gas phase and is unable to re-enter the lattice on account of its low solubility in solid gold. The presence of these voids thus makes it impossible to draw any very definite conclusions from this series of experiments. The effects observed, however, do serve to underline the weaknesses of the sandwich method as applied to gases, in particular the inert gases, and demonstrate the need for proper metallographic examination of the cold-weld.

Fig. 30.

Photomicrographs of sections across the gold  
"sandwiches" showing incomplete cold-welding. The  
sections, which were taken both before and after  
annealing, were mounted in the ends of split gold  
rods and polished and etched by an electro-mechanical  
technique. The electrolyte used was an aqueous  
solution of 10% KCN + 0.5% AuCl<sub>3</sub>.

(AuB)1 before annealing. (Mag. X 45)

Note the heavily cold-worked structure with centre-line lamination.

(AuB)1 before annealing. (Mag. X 400)

This photograph shows the ragged and discontinuous nature of the lamination.

(AuB)2 after annealing. (Mag. X 45)

No gross defect is visible in the field of view but lamination was observed during polishing.



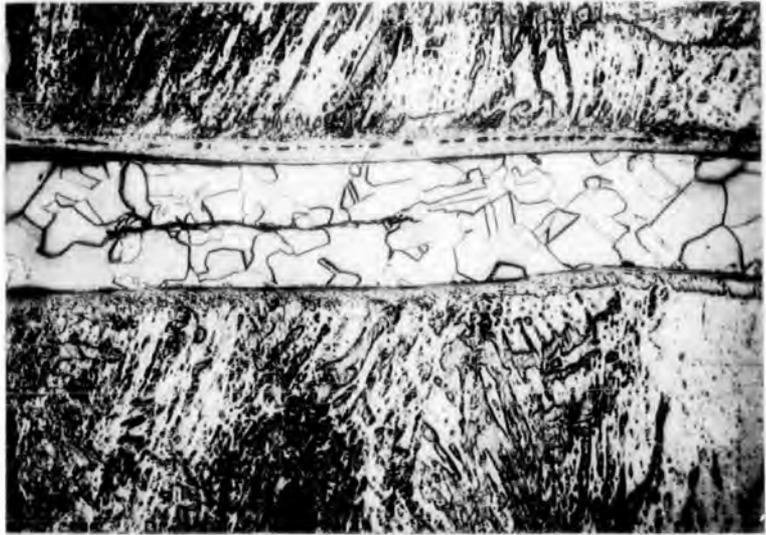


Table 11.

GOLD.

Specimen.	Wt. (gms)	Thickness after rolling. (m.m.)	Thickness after rolling. Total thickness before rolling.	He content initially. c.c./gm. ( $\alpha_0$ )	He evolved c.c./gm. ( $\alpha$ )	$\frac{\alpha}{\alpha_0} \times 10^4$ ( $\delta$ )	T° C.	t (mins)
(AuA)	0.19345	0.4868	~ 0.6	$7.697 \times 10^{-5}$	$0.35 \times 10^{-8}$	0.455	815	15
					$1.86 \times 10^{-8}$	2.42	815	+60
					$2.74 \times 10^{-8}$	3.56	815	+190
					$2.76 \times 10^{-8}$	3.56	815	+310
					$1.06 \times 10^{-8}$	1.38	815	+390
					$1.05 \times 10^{-8}$	1.36	900	+120
⊠ (AuB)	0.1748	0.2014	~ 0.25	$9.275 \times 10^{-5}$	$1.406 \times 10^{-8}$	1.52	814	257
⊠ (AuC)	0.16465	0.3041	~ 0.4	Not determined	$2.73 \times 10^{-8}$	-	815	15
					$3.04 \times 10^{-9}$	-	815	+50
					0.00	-	815	+125
					$1.21 \times 10^{-8}$	-	900	+15
					0.00	-	900	+55

⊠ Blisters observed after annealing.

DISCUSSION OF RESULTS AND COMPARISON WITH OTHER WORK.

The available diffusion characteristics of helium and the other inert gases are summarised in Table 10. The methods used to obtain these results have already been described in some detail (see Introduction) and fall into three classes:-

- (a) Fission gas release methods (84, 85, 86, 87, 89, 90).
- (b) Transmutation methods (91, 92,) of which the present work on lithium/aluminium alloy is an example.
- (c) "Sandwich" methods involving injection of gas ions and subsequent cold-welding of metal surfaces (9, 18, 19, 91). The present work on gold is a typical example of this method.

The injection of alpha particles into a metal produces the helium atoms in a very thin layer and so far experiments have only been carried out with very high local concentrations of gas and for purposes other than measuring diffusion characteristics. These methods are not listed but the effects observed are of interest. On annealing the gas-containing metal (e.g. Cu (14) or Be (65, 93) ) the helium has been found to accumulate in bubbles, the conclusion being that vacancies migrate towards the gas atoms and not vice versa. This sort of effect would be expected for the large atom members of the inert gas group but it is rather surprising to find helium behaving similarly since the helium atom, being small and already in an interstitial position, might well have been expected to move interstitially, at least at relatively low temperatures (11). The strong evidence that vacancy, and not atom, movement is the primary

mechanism in bubble formation lends weight to the conclusion that the observed diffusion of helium in aluminium in the present case is substitutional in type.

Since the results of (a) necessarily relate to the higher inert gases it is not proposed to deal with them except to mention that the formation of bubbles of gas in fissile materials on annealing is a very well characterised phenomenon (97, 87, 90).

The sandwich method (c) has been extensively used but is probably not as satisfactory as the homogeneous solution (transmutation) technique of (b). Some of the more obvious reasons for this have already been mentioned in the section dealing with gold, but since both methods have been used in the present work, and in the closely related work recently carried out by MURRAY and PINCUS (91, 92), it is of interest to discuss the matter more fully.

Of all the workers using the sandwich method only TOBIN (18, 19) ~~has found it fully satisfactory. Using this technique he found that~~ simple volume diffusion of xenon and krypton takes place in silver. It would not be expected for these gases to diffuse at all easily, both on account of their large sized atoms and the tendency for them to form bubbles, and the observed diffusion may well have been more complex than was at first realised. The energy of activation observed accords with a lattice diffusion mechanism, being too high for micro-crack or grain boundary diffusion, but it is possible that the gas could escape by true lattice diffusion inwards to the line of the cold weld rather than outwards toward the more distant free surfaces. If the weld were

not a perfect one the gas could then find an easy path to the edge of the weld via micro-cracks.

Although these two processes have different activation energies the energy relating to the rate determining step is the only one relevant to the process as a whole. Thus it would be possible to measure an apparently pure volume diffusion effect whereas in point of fact this is only the rate determining step. If this were indeed the case then the diffusion coefficients obtained would have to be re-calculated on the basis of a different diffusion thickness ( $h$ ), and since this must be appreciably less than the original physical thickness used, the diffusion coefficient will be reduced in the manner,  $D_{\text{new}} = D_{\text{old}} \times \left( \frac{h_{\text{old}}}{h_{\text{new}}} \right)^2$ .

The similar work carried out by LE CLAIRE and ROWE is subject to the same possible source of error although the diffusion of argon is more easily visualised than that of xenon or krypton. The diffusion coefficients reported by these authors, however, are appreciably higher than those obtained in the present work for the diffusion of helium in gold. Published data (11) suggests that while helium may possibly diffuse in metals by either an interstitial or vacancy mechanism, only the latter is available to the larger atoms of the inert gas group. Thus, quite apart from the greater ease of formation of a vacancy in gold (.6 e.v. as against 1.1 e.v. in silver), it would be expected that helium would have a greater mobility in gold. It would appear that either the helium was completely trapped in gross bubbles in the gold, or that the results of LE CLAIRE and ROWE are in error due to the mechanism postulated above.

A secondary effect observed by LE CLAIRE and ROWE was the fall-off in the value of "D" if several successive anneals were used. This is significant since bubble formation could be responsible for such an effect. It was not observed by TOBIN (18, 19), however, using the gases xenon and krypton which would be expected to form bubbles more readily than helium.

The work of MURRAY and PINCUS (91) is of great relevance to the present discussion. Using the sandwich method for helium in aluminium values for the diffusion coefficients at 400°C. and 470°C. were obtained. These results are compared with those of the present work in table 8. It was also found (cf. (9)) that the diffusion coefficient decreased in successive anneals. Using the lithium/aluminium technique adopted in the present work they obtained highly inconsistent results, very little variation of helium evolution being observed with temperature. Moreover, the diffusion coefficients given by this technique were much smaller than those obtained using the sandwich method. A later report by the same workers (92) again using the lithium/aluminium method gives values for the diffusion coefficient of  $2.4 \times 10^{-10}$  cm<sup>2</sup>/sec. at 575°C. This value is still lower than that obtained from their experiments with the helium sandwich and they attribute this to too ready an evolution of gas from the sandwich via the cold-weld. This seems a likely explanation since the energy of activation for the observed process was only 0.65 ev. ( $\sim 15$  kcal/mole) and therefore fully consistent with microcrack diffusion.

The lithium content in the transmutation experiments was respectively  $\sim 10$  at. % and  $\sim 0.02$  at. %. It should be noted that the former value is

rather too high a figure to admit of true solubility on the basis of either NOWAK's (72) or VOSSKÜHLER's (68) work and this may account for some of the inconsistency, although too great an amount of lithium might have been expected to increase the amount of gas evolved, not decrease it.

Metallographic examination of the specimens annealed for 95 hours at 575°C. (92) showed evidence of bubble formation, principally at grain-boundaries and sub-boundaries (cf. BARNES (15, 20)). This observation agrees with the results obtained for the discs D.13 and D.16 which indicate that a marked falling-off of the helium evolution begins after ~6 hours annealing at 580°C. Taken together, these observations would indicate that the total amount of helium evolved in 95 hours might be considerably less than that which would have been evolved assuming a linear dependence of  $\frac{c}{c_0}$  on the square root of the time. It would therefore be of interest to know the mathematical treatment used by MURRAY and PINCUS to derive their value of  $2.4 \times 10^{-10}$  cm<sup>2</sup>/sec at 575°C. since this figure differs considerably from the values obtained for D.13 and D.16 at substantially the same temperature. If their result is based on the total quantity of gas evolved in 95 hours then it could be in error due to the accumulation of helium in bubbles. This would tend to give a lower result than that obtained during the present work, where this effect has been allowed for. On the other hand the initial burst of gas observed in the present work may have been sufficient to "overcompensate" for the helium which accumulated in bubbles and this would give too high a result for the diffusion coefficient. This initial high evolution rate is very dependent on the physical state

of the metal and it introduces a very variable factor. It may certainly be said that the phenomena observed in the present work rule out the possibility of calculating values for "D" simply from a knowledge of the total amount of gas evolved in a known time, and if this method was used in (92) then it might well account for some of the deviation from the values obtained during the present work.

The concentrations of helium used in the present work were not identical with those used by MURRAY and PINCUS but it seems unlikely that the difference in the values for the diffusion coefficient could be accounted for in this way. The diffusion coefficient is indeed a concentration dependent quantity but usually the value of "D" varies only slowly if the concentration is small (115), as was the case in both the present work and that of MURRAY and PINCUS.

It should be pointed out that the fusion method of releasing helium from specimens (to determine  $\alpha_0$ ) used by MURRAY and PINCUS is not a reliable one. During the present work it was found to be very difficult to achieve a quantitative release of all the gas. Error caused in this way, however, would not be of sufficient magnitude to explain the difference in the results.

Discussion of the results for aluminium with special reference to the diffusion equation.

The factor " $D_0$ " in the general diffusion equation

$$D = D_0 \exp. \left( - \frac{E}{RT} \right)$$

is given by

$$D_0 = \left\{ \exp. \left( \frac{\Delta S}{R} \right) \right\} \frac{k T}{h} \cdot d^2 \cdot \frac{1}{2.72} \quad (112, 113)$$

where

$\Delta S$  = entropy change on activation.

$k$  = Boltzmann's constant.

$h$  = Planck's constant.

In general the change in entropy on activation is least for those systems in which the component atoms are most dissimilar, and greatest for those systems in which the atoms are identical, e.g. self-diffusion. Thus " $D_0$ " should be large for self-diffusion and small for a system such as the present one which involves very dissimilar metal and inert gas atoms.

Since less work must be done in loosening-up an already disordered lattice the energy of activation should be relatively small for systems involving dissimilar atoms and greatest for those systems in which the atoms are identical.

In general these suppositions are borne out, and the empirical Langmuir - Dushman equation,

$$D = \frac{E}{Nh} \cdot d^2 \cdot \exp. \left( - \frac{E}{RT} \right);$$

where " $d$ " is a distance identifiable with the lattice parameter of the solvent, demands that " $D_0$ " should be large when " $E$ " is large. This equation is obeyed by many diffusion systems especially when " $E$ " is large (114) but is not obeyed in the present work. The theory outlined above clearly requires that the diffusion of helium in aluminium should be described by an equation in which " $E$ " and " $D_0$ " are both small. In practice, however, it was found that

$$D = 42. \exp. \left( - \frac{49.7 \times 10^3}{RT} \right) \text{ cm}^2 / \text{ sec.},$$

both " $D_0$ " and " $E$ " having values rather higher than average.

Although the energy of activation for self-diffusion in aluminium is not known exactly, it seems unlikely that it would exceed the figure of  $49.7 \times 10^3$  cal./mole (2.15 ev.) relating to the diffusion of helium in aluminium. Indeed the data in Table 7 suggest a very much lower figure, and we have the apparent anomaly of a system involving very dissimilar atoms having a large " $D_0$ " and an energy of activation greater than that pertaining to self-diffusion. With the larger inert gases (e.g. krypton and xenon in silver (18, 19) ) the relatively low energy of activation ( $35 \times 10^3$  cal./mole) has been attributed to the fact that the large gas atoms cause considerable disordering of the solvent lattice. In the case of helium the atom is easily accommodated in a lattice position, and, although the metal and gas atoms are very dissimilar, little lattice strain is occasioned by differences in atomic radii. Thus the energy of activation for diffusion of helium in metals may well be much higher than would at first be expected.

C O N C L U S I O N S

CONCLUSIONS.

The methods normally used for the elucidation of the diffusion characteristics "D" and "E" have been shown to be inapplicable, without modification, to the case of helium in aluminium. Although the work carried out on the diffusion of helium in beryllium and meteoritic iron is less conclusive, there is a strong suggestion that similar invalidating factors are at work in these systems.

These factors are:-

A.) Too great an amount of helium evolved in the first few minutes of annealing. The evidence suggests that this is either a grain-size dependent mechanism, or more probably is due to the ready release of helium which is loosely trapped in grain boundaries.

The use of single crystals would eliminate both these factors.

B.) Too rapid a decrease in the rate of evolution of gas after a few hours annealing. This is attributed to the accumulation of the helium into bubbles in the metal. The presence of these bubbles has not been directly demonstrated in the present work but there is considerable direct evidence for bubble formation in other inert gas/metal systems.

When the mechanisms outlined in (A) have ceased to be effective, and before that described in (B) comes into operation, there is a region in which the fraction of gas evolved shows a linear dependence on the square root of the time. This region extends further the lower the temperature and this suggests that, as far as is practicable, low temperatures should be used to determine the diffusion characteristics. The coefficient of diffusion for helium in aluminium derived from observations in this

region has been shown to be "D",

$$\text{where } D = 42. \exp. \left( - \frac{49.7 \times 10^3}{RT} \right) \text{ cm.}^2/\text{sec.}$$

The unexpectedly high energy of activation may be attributable to the ease of accommodation of the helium atoms in the aluminium lattice. The value of "E" suggests that the movement of helium in aluminium is substitutional in type.

The helium "sandwich" method as applied to gold gives values for "D" which are considerably lower than those expected on the basis of other work on inert gas/metal systems using the same technique. The failure to observe evolution of helium in the present case is attributed to incomplete cold-welding of the metal surfaces.

In general, the "sandwich" technique appears to be basically unreliable when applied to gas/metal systems and tends to give misleading results for "D". The fact that observed activation energies may have values consistent with substitutional diffusion does not necessarily eliminate the possibility of micro-crack diffusion being responsible for a large part of the gas evolution.

P A R T   T H R E E

GENERAL.

EXPERIMENTAL NOTES.a. The photo-cell mechanism.

This is shown in detail in fig. 31. The sensitive element is a germanium junction photo-electric cell (Standard Telephones and Cables Ltd., TYPE P50A.) of area 0.5x 2.0m.m.. It is sensitive to light of up to 2.1 microns, the peak response being at 1.75 microns, and the output throughout the visible spectrum is high. The energising beam is produced by a 12v. 24w. tungsten lamp and is focussed by a lens of short focal length. Initially the light beam was provided by much smaller bulbs but owing to the scattering of some of the light by the glass tubing it was found more reliable to utilise the greater power of a larger lamp. A large filament also has the advantage that less precise focussing of the beam onto the sensitive element is required, and the power margin is so large that the lamps may be "under-run" thus minimising the chance of their burning out and causing failure of the column. A disadvantage is the greater heating of the photo-cell, but this is not serious. The cells run satisfactorily up to a temperature of 30° C. and only slight trouble has been experienced from this cause. Overheating is manifested by a refusal of the cell to shut off when the light is obscured.

b. Pirani gauge irregularities.

Whilst behaving quite well once they have stopped drifting, the Pirani gauges used in the present work are subject to a very high initial rate of drift, necessitating a settling down period of about three hours. This drift was formerly assigned (106) to the e.m.f.s. produced by the

various metal/metal couples in the gauges, but while this is undoubtedly true in the period during which the various parts of the instruments are at different temperatures, the drift due to this cause should cease immediately thermal equilibrium is established. Most probably this occurs in the first half-hour or so after immersion, and hence the above explanation can be responsible for only some of the instability.

There is no phase change in the nickel (102) or tungsten (103) which could account for the setting up of thermal e.m.f.s, but in the course of this work it was suspected that at least part of the trouble lay with the use of soft-solder in the gauges. Tin, a major constituent of soft-solder, changes from the white to the grey allotrope at temperatures below  $13.2^{\circ}$  C. (104). The rate of change is slow at just below the transition point but becomes rapid at  $-50^{\circ}$  C., the reaction being autocatalytic (105). The presence of two allotropes in contact gives rise to thermal e.m.f.s and it seems likely that much of the drift is caused in this way.

In an attempt to check this hypothesis, a relatively low-melting cadmium solder was substituted for the soft-solder. It was not found possible, however, to apply sufficient heat to melt the solder without also snapping the fine nickel tape, the use of a naked flame being, of course, impracticable.

The initial zero drift does not affect the final accuracy, but it does limit the ready availability of the gauge.

g. A device for the prevention of the entrainment of air by the mercury of the fractionating column.

This device, which prevents the creep of air from the secondary vacuum system of the fractionating column into the gas being analysed, is shown in fig. 32. The level of the mercury shown in the figure is that which would be occupied during evacuation of the column. During the actual fractionating operations, however, the level is above that of the column base-tube (shown on the left of the figure) and any air brought from the secondary system by the moving mercury is immediately removed via tap T.13.

Photo-cell mechanism.

Fig. 31.

"Make and break" device for circulating  
system.

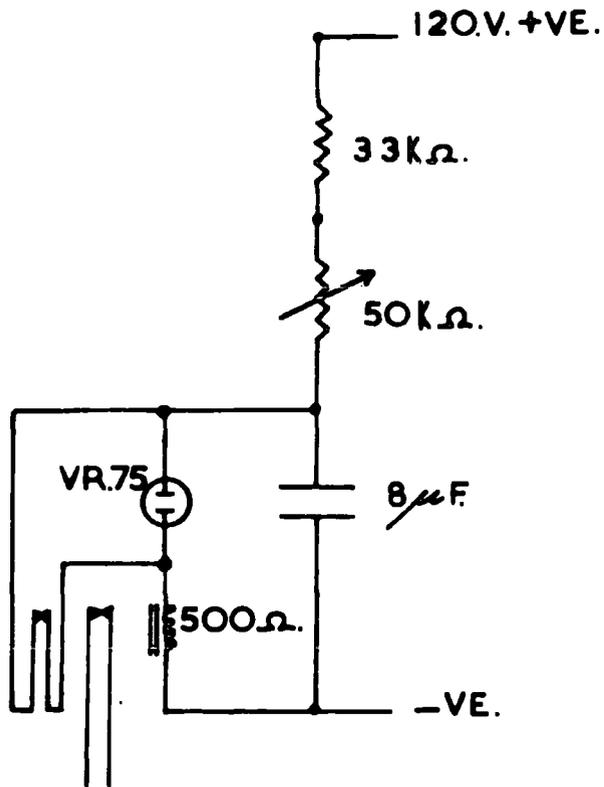
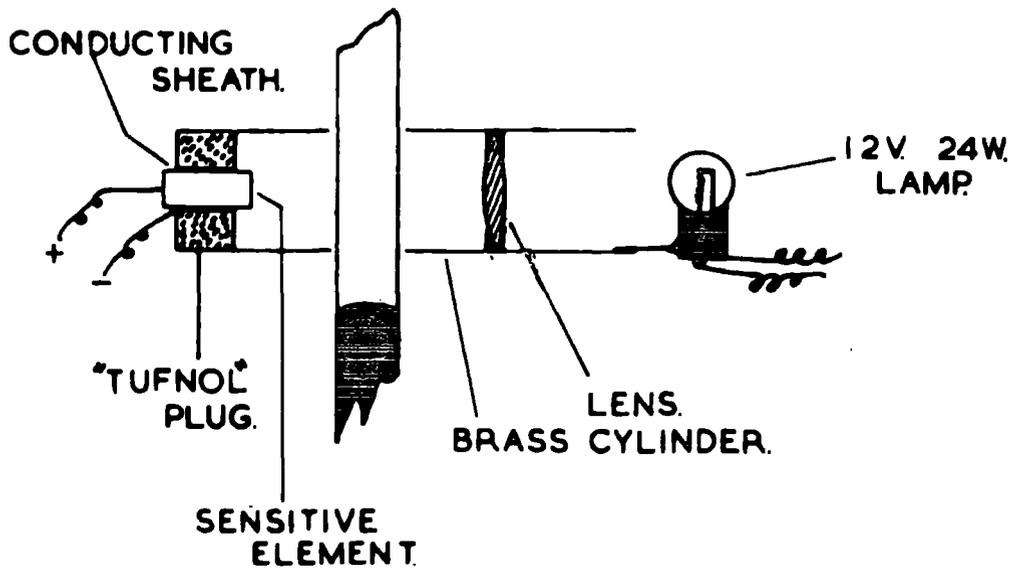
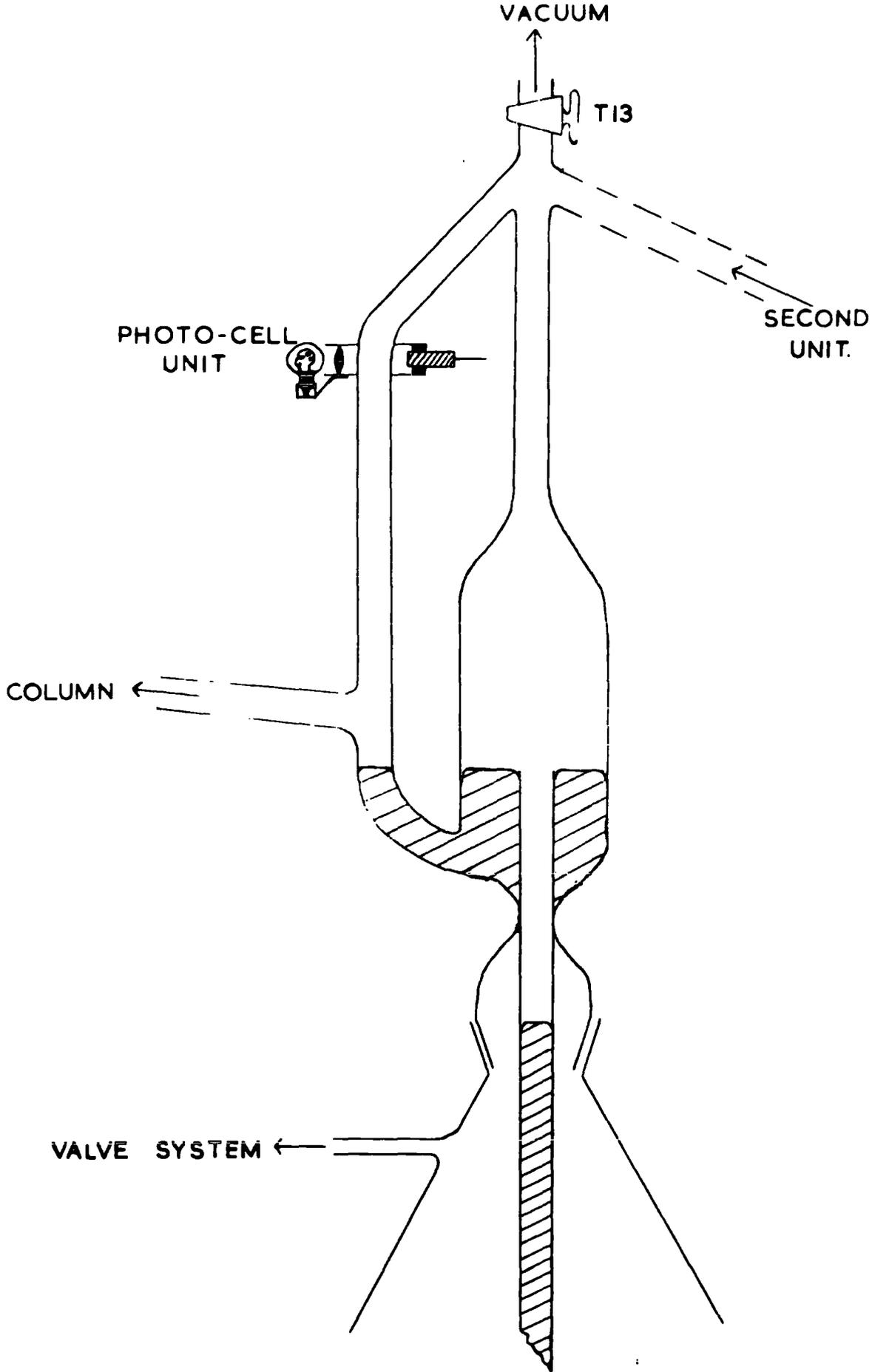


Fig. 32.

Device for preventing the "creep" of air from  
the secondary to the primary vacuum systems.



NOTES ON SOME IDEAS INVESTIGATED BUT NOT ADOPTED.(a) Magnetically operated non-return valve.

As previously mentioned a number of experiments were made with a column using this type of cut-off. The design of the units is shown in fig. 33, an advantage of this type of valve being that no separate row of cut-offs is necessary. The valves consisted of iron rods encased in soda-glass, the glass being ground into a seating just above the volume bulbs. These slugs could be lifted or dropped at the appropriate stages of the mercury cycle by means of the photo-cell operated circuit shown in fig. 33. A further advantage of this particular design is the relatively simple circuit which requires only three photo-cells and three relays.

A "mock-up" of a single unit was constructed and found to operate satisfactorily; a complete column was then built and it was found that, with fifteen units in parallel, the rate of fall of the mercury was so slow that the valves could not trap sufficient mercury to make a gas-tight seal. In order to increase the pump-away speed of the mercury several devices were tried but these resulted in very severe turbulence of the mercury in the column base-tube. Since this threatened to cause damage to the apparatus the idea was abandoned and the design previously described was adopted.

(b) Furnace for the collection of helium evolved over long periods of annealing.

In order to measure the helium evolved over periods of time longer than a few hours it was thought desirable to construct a furnace which

would contain the minimum quantity of heated metal. The design decided upon is shown in fig. 34. Unfortunately it was found impossible to outgas the copper furnace block to anything like the degree necessary for the accurate measurement of the helium evolved from an annealed specimen. The idea was not pursued with any metal other than copper since at this time two stainless steel furnace tubes were made available by A.W.R.E. and these fulfilled most of the desired requirements.

(g) Apparatus for the removal of hydrogen and other gases from the furnace gas mixture.

At one time it was proposed that measurements of the movement of helium in plutonium should be carried out and in order to simplify the apparatus so as to better fulfil the stringent safety precautions necessary when working with this metal an alternative to the fractionation process was sought.

The gases evolved from a well out-gassed stainless-steel tube furnace do not appear to contain either helium or neon, but considerable quantities of hydrogen are evolved and in order to directly measure the helium evolved by a specimen it is essential to absorb or otherwise remove the gases evolved by the walls of the furnace. Most gases may be retained on a charcoal trap at a low temperature, but hydrogen is not only less adsorbed than most gases (107) but the rate of sorption is slow. When designing the apparatus it was borne in mind that the use of oxygen in a system containing heated plutonium is inadmissible, and therefore the hydrogen could not be removed by combustion with this gas. Absorption

methods or methods employing oxide combustion techniques are therefore the only ones permissible, the ordinary technique of a palladium "leak" to remove the hydrogen being impracticable on account of the slow rate of permeation.

Two methods were tried:-

(1) Copper oxide furnace.

The apparatus is shown in fig. 35. This was not ideal for work involving easily oxidisable metals on account of the appreciable dissociation pressure of copper oxide at the working temperature of 350°C. A further disadvantage of this system is the long period required to outgas the oxide and the steel tube. However, the oxide furnace, in conjunction with the charcoal trap cooled to liquid-air temperature, retained a high proportion of the hydrogen and other gases evolved by the tube furnace. An appreciable pressure was registered on the Pirani gauges, however, and it was found that an accuracy of 6% would be the best obtainable for an amount of helium of the order  $10^{-6}$  N.T.P.c.c.s. This was perhaps tolerable for the proposed work on plutonium since simplicity and safety were the dominant considerations, but it was felt that the method described next better fulfilled all the necessary conditions and would enable a much higher precision to be obtained.

(2) Palladium hydrogen absorber.

The apparatus is shown in fig. 36. Palladium black (108) is held in a palladium tube by spirals of platinum wire at each end.

The tube and its contents may be outgassed at a dull red heat and this does not require more than about an hour. To absorb gases other than hydrogen a liquid-air cooled charcoal U-tube is used, the gases travelling from the furnace to the absorber and then through the U-tube to the Pirani gauges.

The temperature at which the tube is operated is critical (109) there being a very sharp decrease in the amount absorbed at a temperature greater than  $125^{\circ}$  C. Owing to the low rate of sorption of hydrogen at low temperatures, the tube was maintained at about  $100^{\circ}$  C., the glass envelope being cooled externally by means of an air blower. With this apparatus it was possible to completely stop hydrogen in the furnace gas from reaching the Pirani gauges.

If a rather higher temperature of operation is not a disadvantage the use of titanium powder has the merit of much greater sorptive capacity (110). The rate of sorption, however, is not appreciable below  $375^{\circ}$  C. (111).

It should be noted that the sensitivity of the measuring apparatus is much reduced by the systems described owing to the increase of the effective dead-space of the Pirani gauges. The gas is no longer compressed into the gauges but distributes itself between these, the furnace, and the hydrogen removal apparatus. A drop in sensitivity by a factor often was observed for system (b), and this restricts the use of such a device to the measurement of relatively large quantities of helium.

By reducing the volume of the apparatus, however, the palladium absorber could be made a very useful tool for this sort of work, particularly if relatively large quantities of helium were to be measured.

Circuit for the operation of experimental  
fractionating column.

Fig. 33.

A single unit of the experimental  
fractionating column.

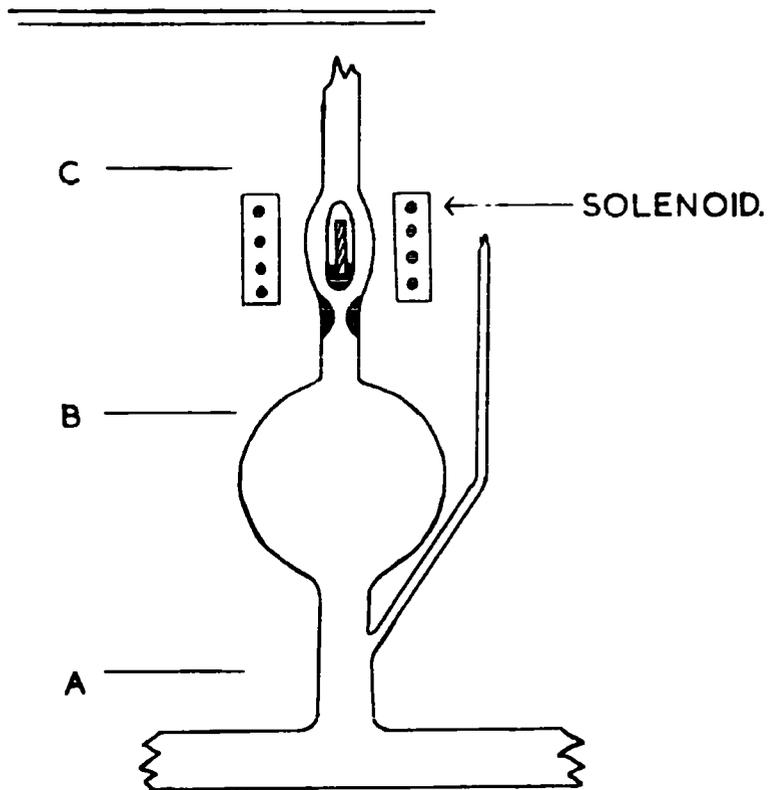
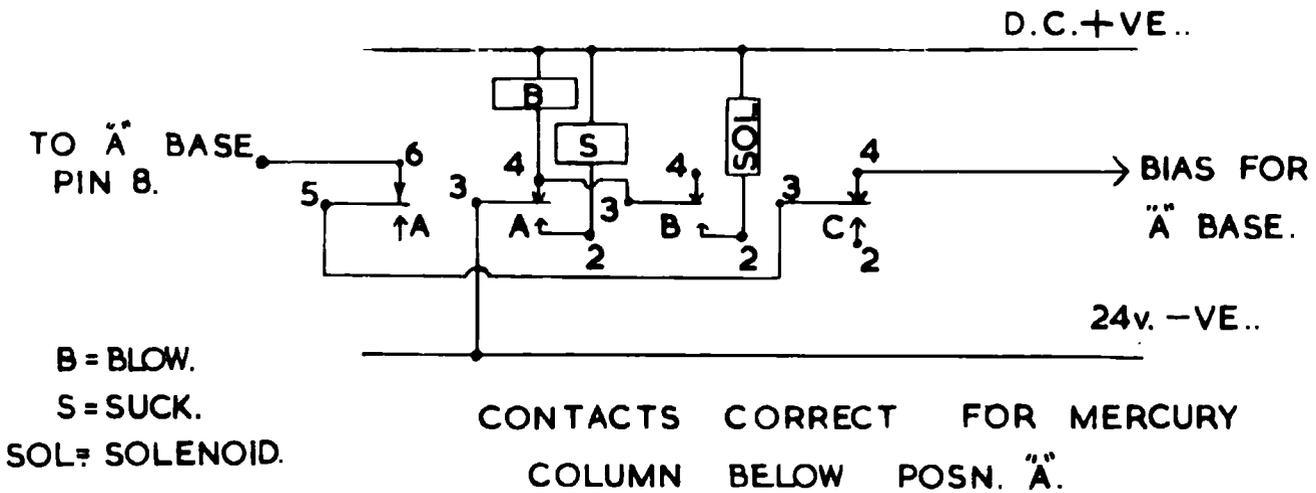


Fig. 34.

Furnace for the collection of the gases evolved  
over long periods.

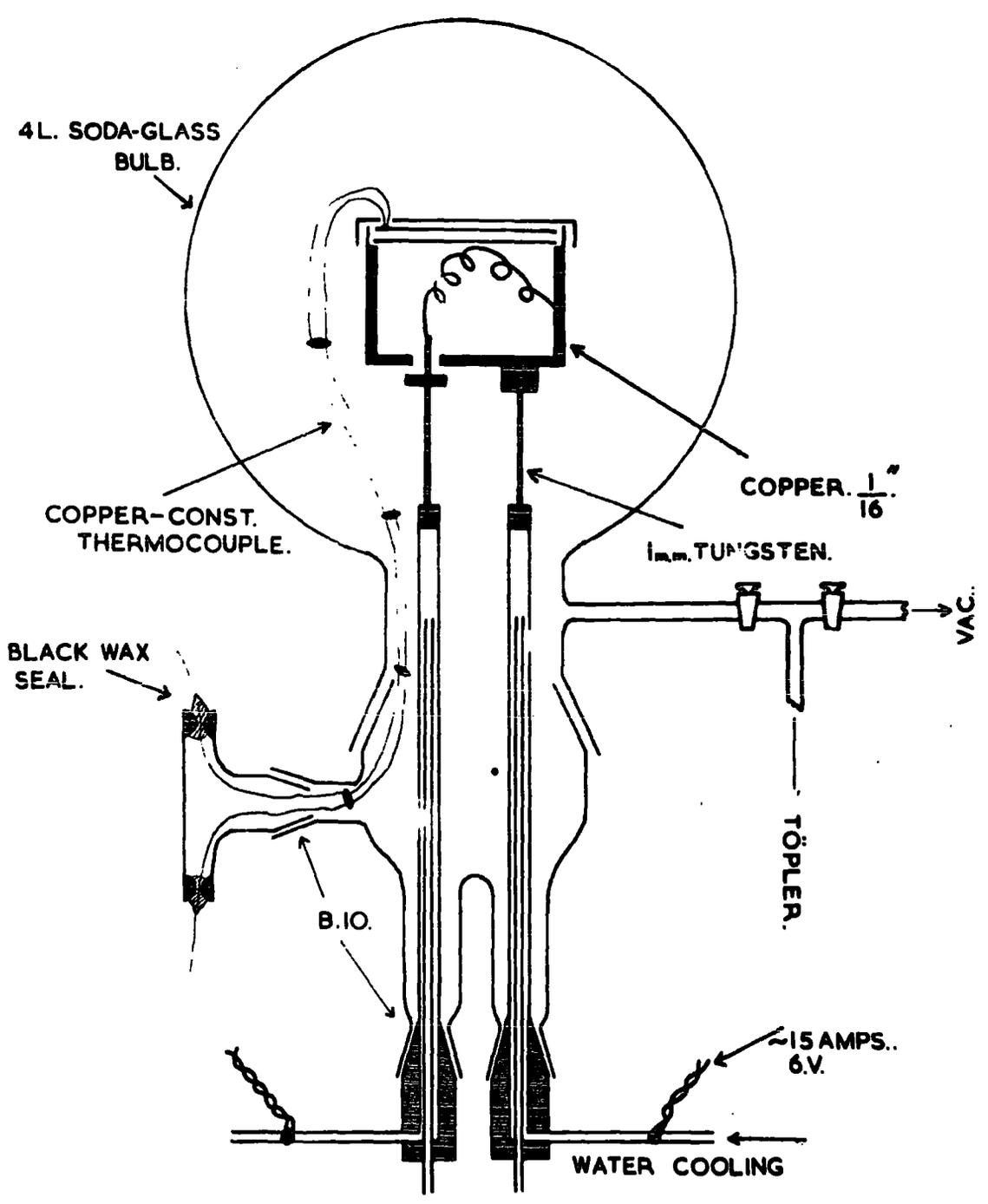


Fig. 35.

Copper oxide furnace.

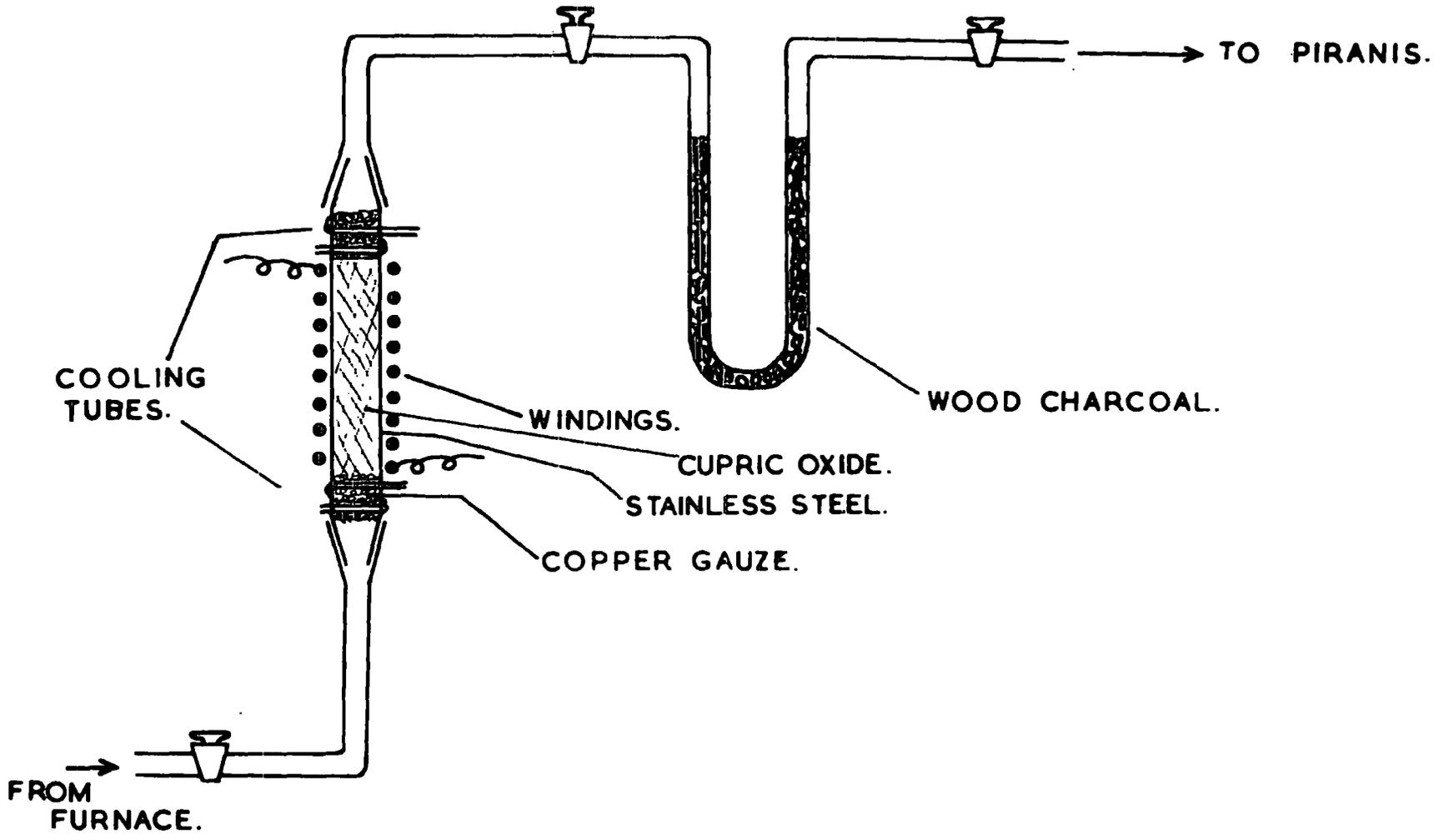
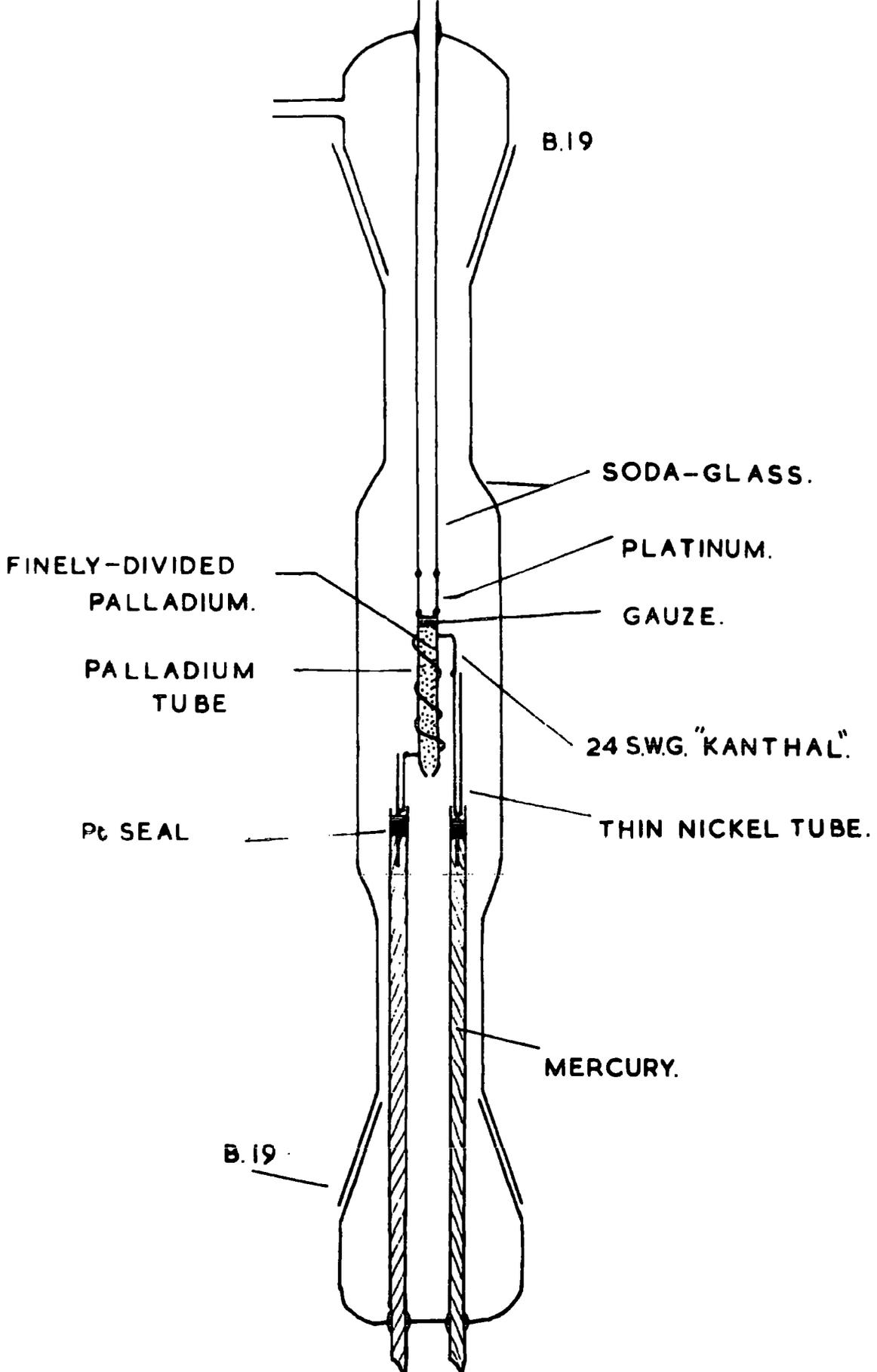
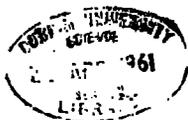


Fig. 36.

Palladium hydrogen-absorber.



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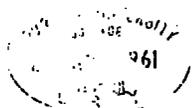
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